Title
Spectroscopic and Computational Analysis of Rare Earth and Actinide Complexes in Unusual Coordination Environments and Oxidation States

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Spectroscopic and Computational Analysis of Rare Earth and Actinide Complexes in Unusual Coordination Environments and Oxidation States

DISSERTATION

submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Megan E. Fieser

Dissertation Committee:
Professor William J. Evans, Chair
Professor Andrew S. Borovik
Professor Filipp Furche

2015
DEDICATION

This dissertation is dedicated to my parents, Ed and Sandy Fieser,
to my brother, Sean Fieser,
and to my best friend and soulmate, Matt Quay.

Thank you all for your love and support.

“If you know you are on the right track, if you have this inner knowledge, then nobody can turn you off … no matter what they say.”
~Barbara McClintock

“We cannot solve problems with the same thinking we used when we created them.”
~Albert Einstein

“Lanthanons-These elements perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us; mocking, mystifying and murmuring strange revelations and possibilities.”
~Sir William Crookes
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Publications

“(C₅Me₅H)¹⁻-based reduction of dinitrogen by the mixed ligand tris(polyalkylcyclopentadienyl) lutetium and yttrium complexes, (C₅Me₅)₃-x(C₅Me₄H)ₓLn” Mueller, T. J.; Fieser, M. E.; Ziller, J. W.; Evans, W. J. Chemical Science 2011, 2, 1992-1996.


“Differentiating Chemically Similar Lewis Acid Sites in Heterobimetallic Complexes: The Rare-Earth Bridged Hydride (C₅Me₅)₂Ln(µ-H₂)Ln’(C₅Me₅)₂ and Tuckover Hydride (C₅Me₅)₂Ln(µ-H) (µ-κ¹:η²-C₅H₂C₅Me₄)Ln’(C₅Me₅) Systems” Fieser, M. E.; Mueller, T. J.; Ziller, J. W.; Evans, W. J. Organometallics 2014, 33, 3882-3890.


“Dinitrogen Reduction, Sulfur Reduction and Isoprene Polymerization via Photochemical Activation of Bis(cyclopentadienyl) Rare Earth Allyl Complexes” Fieser, M. E.; Johnson, C. W.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. *manuscript in preparation*.


“Evaluating Divalent and Trivalent Sm, Tm, and Y Complexes Using X-ray Absorption Near Edge Spectroscopy” Evans, W. J.; Fieser, M. E.; Lezama, J. S.; Kozimor, S. A.; Olson, A. C.; Wagner, G. L. *manuscript in preparation*.


“Lanthanide/Actinide Comparisons of +2 Ions in a Tris(aryloxide)arene Coordination Environment” Fieser, M. E.; La Pierre, H. S.; Halter, D. P.; Heineman, F. W.; Evans, W. J.; Meyer, K. *manuscript in preparation*.

“Reduced Arene Complexes of La$^{2+}$ and Ce$^{2+}$ Metallocenes” Kotyk, C. M.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J. *manuscript in preparation*.

**Presentations**

“Exploring (C$_5$Me$_4$H)$_{1-}$ as a Reductant in Rare Earth Chemistry” Fieser, M. E.; Ziller, J. W.; Evans, W. J. Poster presented at the Western Regional ACS Meeting, Pasadena, CA, November 11, 2011.
“The Dinitrogen Reductive Chemistry of the (C$_5$Me$_4$H)$_{1-}$ Ligand in Tris(Cyclopentadienyl) Rare Earth Complexes” Fieser, M. E.; Ziller, J. W.; Evans, W. J. Oral Presentation at the 243$^{rd}$ ACS Meeting, San Diego, CA, March 27, 2012.


**Awards and Affiliations**

2015  UCI Michael Zach Award for Most Promising Future Faculty Member

2015  American Chemical Society, Division of Inorganic Chemistry Student Travel Award, Denver National Meeting

2015  Regent’s Dissertation Fellowship, University of California, Irvine

2014  Daughters of the American Revolution, William Robert Findley Scholarship

2014  University of California, Irvine, Outstanding Contributions to the Chemistry Department Award

2012  University of California, Irvine, Advanced Level Teaching Assistant Award

2010-present  American Chemical Society, Division of Inorganic Chemistry, member

2008-present  Alpha Chi Sigma, National Professional Chemistry Fraternity, member

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ABSTRACT OF THE DISSERTATION

Spectroscopic and Computational Analysis of Rare Earth and Actinide Complexes in Unusual Coordination Environments and Oxidation States

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Doctor of Philosophy in Chemistry

University of California, Irvine, 2015

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This dissertation describes the use of spectroscopic and computational methods to understand new classes of rare earth and actinide coordination complexes. In Chapters 1 and 2, the use of UV-vis spectroscopy and density functional theory (DFT) to understand a rare form of photochemical activation of rare earth mixed-ligand tris(cyclopentadienyl) complexes, \((\text{C}_5\text{Me}_5)_3-\text{x(C}_5\text{Me}_4\text{H})_\text{x}\text{Ln}\), and metallocene allyl complexes, \((\text{C}_5\text{Me}_5)_2\text{Ln(}\text{C}_3\text{H}_5\) (Ln = Lu, Y) is described. The photochemistry involves a ligand-based reduction in a trivalent rare earth complex that generates a reducing system powerful enough to reduce dinitrogen. Chapter 3 describes the use of Raman spectroscopy to understand bond lengths in reduced dinitrogen rare earth complexes, \([(\text{C}_5\text{Me}_5)_2\text{Ln}](\mu-\eta^2:\eta^2-\text{N}_2)\), and analyze the degree of dinitrogen reduction based on the ancillary ligands. Chapter 4 describes the power of NMR spectroscopy to characterize complicated mixtures of heterobimetallic bridging hydride complexes, \((\text{C}_5\text{Me}_5)_2\text{Ln(}\mu-\text{H})_2\text{Ln}'(\text{C}_5\text{Me}_5)_2\), and tuckover hydride complexes, \((\text{C}_5\text{Me}_5)_2\text{Ln(}\mu-\text{H})(\mu-\eta^1:\eta^5-\text{CH}_2\text{C}_5\text{Me}_4)\text{Ln}'(\text{C}_5\text{Me}_5)\) (Ln, Ln’ = La, Y, Lu). DFT was used to investigate the metal site preferences in these complexes.
Chapters 5 through 10 describe different techniques to understand the first examples of molecular rare earth and actinide tris(cyclopentadienyl) complexes in the formal +2 oxidation state, [K(2.2.2-cryptant)][(CsR5)3Ln] (Ln = Y, lanthanides, Th, U). DFT is used to describe the configuration of these complexes as 4d\(^{1}\) for Y, [Ln\(^{3+}\)]5d\(^{1}\) for 10 lanthanides and [An\(^{3+}\)]6d\(^{1}\) for Th and U (Chapter 5 and 6). UV-vis spectroscopy was used to distinguish between different electron configurations of Ln\(^{2+}\) complexes (Chapter 7). Magnetic susceptibility measurements characterize two Ln\(^{2+}\) complexes to have record high single-ion magnetic moments (Chapter 8). Ligand and metal edge X-ray absorption spectroscopy were used to analyze the oxidation state of the metals (Chapter 9). Reactivity of cyclooctatetraene with Ln\(^{2+}\) complexes is described in Chapter 10. Chapter 11 presents the synthesis of new Ln\(^{3+}\) and Ln\(^{2+}\) complexes, using a tris(aryloxide)arene coordination environment. Chapter 12 describes the use of DFT to predict new coordination environments that could allow the stabilization of the +2 oxidation state for the rare earths and actinides.
Introduction

Redox reactions, the chemical transformations involving either the gain (reduction) or the loss (oxidation) of one or more electrons between reaction partners, constitute one of the two most general types of chemical reactions. Redox chemistry has fundamental importance in both chemical manufacturing, such as the production of sulfuric acid, and biological processes, such as photosynthesis. Redox processes often utilize a redox active metal which changes oxidation state during the reaction. As such, the one of the most fundamental properties of a metal relating to its reactivity is its available oxidation states. The primary goal of this dissertation, is to use spectroscopic and computational methods to study unusual types of redox chemistry as well as unusual oxidation states for the rare earth elements.

Lanthanide Elements. The lanthanide elements are the fifteen elements that range from lanthanum (57) to lutetium (71). Along with yttrium and scandium, these seventeen metals are commonly referred to as the “rare earths” elements. Although termed the rare earths, these elements are relatively abundant and inexpensive in comparison to other metals, as seen in Figure 0.1. In the early 2000’s, however, demand for five rare earths, namely yttrium,
neodymium, europium, dysprosium and terbium, has increased due to their use in clean energy technology. These five elements have been labelled as critical materials.

The lanthanide elements are some of the largest elements in the periodic table, with 9-coordinate ionic radii ranging from 1.216 Å for La$^{3+}$ to 1.032 Å for Lu$^{3+}$. There is a gradual decrease in the ionic radii of approximately 0.01 Å from metal to metal across the lanthanide series, Figure 0.2. The additional nuclear charge along with the poor shielding of the f orbitals account for this decrease in ionic size.

![Figure 0.2. Gradual decrease in ionic size for 9-coordinate trivalent lanthanides and yttrium, (drawn to scale).](image)

For the transition metals, the nd orbitals extend beyond the core electrons of the metals, and these valence orbitals can participate in bonding and reactivity. For the lanthanides, as seen in Figure 0.3, the 4f orbitals do not extend beyond the Xe core of electrons. This lack in orbital extension leads to limited metal-ligand orbital overlap and the chemistry of the lanthanides is primarily ionic with little valence orbital participation. The 5d orbitals are approximately 50,000 cm$^{-1}$ above the 4f orbitals in Ln$^{3+}$ complexes and traditionally are not thought to participate in lanthanide chemistry. This dissertation will show that these higher-lying 5d orbitals are much more important in the bonding and reactivity of the lanthanides than originally thought.
**Figure 0.3.** Probability distribution of the 4f orbitals and Xe core for Nd$^{3+}$ as a function of radial distance.$^4$

**Rare Earth Redox Chemistry.** Unlike transition metals, which have many different available oxidation states, the lanthanides have a limited range of oxidation states with the trivalent oxidation state being most stable for each lanthanide. The molecular divalent ions for Eu, Yb, and Sm were known as early as 1906,$^6$–$^9$ while it wasn’t until around 2000 that molecular complexes of the Tm$^{2+}$, Nd$^{2+}$, and Dy$^{2+}$ ions were identified.$^{10}$–$^{16}$ Due to the stability of the +3 oxidation state, the divalent lanthanides are strong reductants.$^{13}$

For many years, the +2 oxidation state was not known for the rest of the rare earths. Therefore, it was necessary to find other routes to reduction chemistry that did not involve oxidation of a metal center. Several trivalent rare earth complexes were found to display divalent-like reduction chemistry by virtue of redox active ligands that made reduction chemistry possible for the entire lanthanide series, as summarized in Scheme 0.1. Reactivity studies of the
sterically crowded complexes, (C₅Me₅)Ln, demonstrated they could act like one electron reductants.¹⁷⁻²¹ This reduction was attributed to a ligand based reduction and was called sterically induced reduction. Additionally, bimetallic hydride complexes, such as [(C₅Me₅)Ln]₂(H)₂,²² and bimetallic reduced dinitrogen complexes, such as [(C₅Me₅)₂La(THF)] (μ-η²:η²-N₂),²³ were found to be two electron reductants to generate hydrogen and dinitrogen, respectively.

**Scheme 0.1.** Summary of trivalent lanthanide complexes that act as reductants.

Reduction of dinitrogen to (N≡N)²⁻ was known for the reducing divalent ions, such as Sm²⁺, Tm²⁺, Nd²⁺, and Dy²⁺.²⁴⁻²⁶ Dinitrogen reduction was extended to the rest of the lanthanide series when Ln³⁺ precursors were reduced with an alkali metal in the presence of dinitrogen, Scheme 0.2.²⁷⁻³⁵ Although many of the lanthanides did not have a known divalent state, it was

![Scheme 0.1](image-url)
hypothesized that a transient Ln$^{2+}$ ion could be responsible for this surprising dinitrogen reduction chemistry.

**Scheme 0.2.** Reduction of dinitrogen via LnA$_3$/M and LnA$_2$A'/M.

\[
\text{LnA}_3 + \text{M} \rightarrow \text{N}_2 + \text{(THF)}_x \quad \text{LnA}_2A' + \text{M} \rightarrow \text{N}_2 + \text{(THF)}_x
\]

\(\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Lu}\\ A = \text{N(SiMe}_3)_2; \text{C}_5\text{H}_3\text{(SiMe}_3)_2\text{-1,3}; \text{C}_5\text{H}_4\text{SiMe}_3; \text{C}_2\text{H}_3\text{tBu}_2; \text{OC}_6\text{H}_3\text{tBu}_2\text{-2,6}; \text{C}_5\text{Me}_5; \text{C}_5\text{Me}_4\text{H}\\ A' = \text{BPh}_4; \text{H}; \text{I}; \text{M} = \text{Na; K; KC}_8; \text{x} = 0-2
\]

The first evidence of La$^{2+}$ and Ce$^{2+}$ was published by Lappert and coworkers in 2008.$^{36}$ These complexes were isolated through the reduction of tris(cyclopentadienyl) lanthanide complexes, using the [C$_5$H$_3$(SiMe$_3$)$_2$]$^{1-}$ ligand. This method was further extended by our group, using the (C$_5$H$_4$SiMe$_3$)$^{1-}$ ligand to identify Ln$^{2+}$ ions for the remaining seven rare earth elements without previously known divalent states: yttrium, praseodymium, gadolinium, terbium, holmium, erbium, and lutetium.$^{37-39}$ These new “nontraditional” divalent ions did not show the same properties of the “traditional” six Ln$^{2+}$ ions.

**Dissertation Outline.** The research presented in this dissertation aims to use spectroscopic and computational techniques to further understand new classes of rare earth and actinide coordination complexes. In Chapter 1, UV-vis spectroscopy and density functional theory (DFT) are used to identify a rare form of photochemical activation of mixed-ligand tris(cyclopentadienyl) complexes, (C$_5$Me$_3$)$_{3-x}$(C$_5$Me$_4$H)$_x$Ln (Ln = Y, Lu, Dy; x = 1, 2). This photochemical activation was capable of reducing N$_2$ to (N=N)$^{2-}$ and is explained by a ligand-to-metal charge transfer (LMCT), from the unique ($\eta^3$-C$_5$Me$_4$H)$^{1-}$ ligand present in these complexes.
to a $d_{z^2}$ orbital. In Chapter 2, this photochemical activity is extended to $\eta^3$ allyl complexes, in which the $(C_5Me_5)_2Ln(C_3H_5)$ ($Ln = Lu, Y$) complexes were also found to reduce dinitrogen under irradiation. These allyl complexes were also found to polymerize isoprene to low molecular weight polyisoprene and to reduce $S_8$ to $(S)^{2-}$. DFT studies suggest that this photochemical reactivity is also attributed to a LMCT from the $\eta^3$ ligand to a $d_{z^2}$ orbital.

In Chapter 3, the use of Raman spectroscopy to characterize dinitrogen reduction in single crystals of a series of 20 rare earth complexes of reduced dinitrogen is described. While stretching frequency has become the more preferred method of characterizing reduced dioxygen and dinitrogen transition metal complexes, Raman spectroscopy has been rarely studied in lanthanide and actinide chemistry. Trends in the degree of dinitrogen reduction were observed from the Raman data when trends could not be observed from the crystallographic data.

In Chapter 4, NMR spectroscopy was found to be useful in the characterization of complicated mixtures of heterobimetallic bridging hydride complexes, $(C_5Me_5)_2Ln(H)_2Ln'$ $(C_5Me_5)_2$, and tuckover hydride complexes, $(C_5Me_5)_2Ln(\mu-H)(\mu-\eta^1:\eta^5$:CH$_2$C$_5$Me$_4)Ln'(C_5Me_5)$ ($Ln, Ln' = La, Y, Lu$). Single products of heterobimetallic complexes were obtained when the two metals used were different in size and Lewis acidity, while mixtures were obtained when the two metals were similar in size and Lewis acidity. Surprisingly, the smaller metal occupied the more crowded metal site of the tuckover hydride complex instead of the larger metal, and DFT is used to help explain these metal site preferences.

In Chapter 5, DFT is used to understand the first examples of $Y^{2+}$, $Ho^{2+}$, and $Er^{2+}$ in the $[(18\text{-crown-6})K][(C_3H_4SiMe_3)_3Ln]$ ligand coordination environment. The $Y^{2+}$ complex was analyzed as a $4d^1$ complex, relative to its $4d^0$ $Y^{3+}$ precursor. Calculations of the $Ho^{2+}$ and $Er^{2+}$
complexes were found to be similar to that of the Y$^{2+}$ complex, with calculated mixed orbital electron configurations of 4f$^{n}$5d$^{1}$, relative to its 4f$^{n}$ trivalent precursor. This Chapter also presents DFT studies on a series of reduced tris(cyclopentadienyl) yttrium complexes with different cyclopentadienyl substituents, (Cp$^{8}$Y)$^{1-}$, which were found to correlate the trends in s orbital spin density at the yttrium center with the trends in experimental EPR hyperfine coupling constants for the series. These calculations were extended to the actinides in Chapter 6, in which DFT calculations suggested a 6d$^{2}$ electron configuration for the first Th$^{2+}$ ion, {[C$_{5}$H$_{5}$(SiMe$_{3}$)$_{2}$]$_{3}$Th}$^{1-}$, and a 5f$^{3}$6d$^{1}$ electron configuration for the first U$^{2+}$ ion, [(C$_{5}$H$_{4}$SiMe$_{3}$)$_{3}$U]$^{1-}$.

In Chapter 7, the synthesis of [K(2.2.2-cryptand)]([C$_{5}$H$_{4}$SiMe$_{3}$]$_{3}$Ln] (Ln = La, Ce, Nd, Sm, Eu, Dy, Tm, Yb) allowed for the first comparison of all the lanthanides in the same coordination environment in both +2 and +3 oxidation states. X-ray crystallography, UV-vis spectroscopy and DFT studies were used to distinguish between Ln$^{2+}$ ions with a traditional 4f$^{n+1}$ electron configuration and Ln$^{2+}$ ions with a nontraditional 4f$^{n}$5d$^{1}$ configuration. Magnetic susceptibility measurements, discussed in Chapter 8, and X-ray absorption spectroscopy measurements, discussed in Chapter 9, were used to further understand the electronic properties of the lanthanide series in the [K(2.2.2-cryptand)]([C$_{5}$H$_{4}$SiMe$_{3}$]$_{3}$Ln] coordination environment. Both measurements are able to distinguish electronic differences between the Ln$^{2+}$ ions with the traditional and nontraditional electron configurations. In Chapter 10, reactivity of [K(2.2.2-cryptand)]([C$_{5}$H$_{4}$SiMe$_{3}$]$_{3}$Ln] (Ln = La, Ce, Sm) with cyclooctatetraene is pursued to compare with the reactivity observed between cyclooctatetraene and the first examples of Th$^{2+}$ and U$^{2+}$. 
The reduced C₈H₈ products for all three metals were observed to be different from those of the actinide divalent ions.

In Chapter 11, new divalent lanthanide complexes were synthesized with a ligand containing three aryloxides tethered to a mesityl group for Nd, Gd, Dy, and Er. For Gd, Dy, and Er, the isolation of the Ln²⁺ complex was complicated with the co-crystallization of a trivalent decomposition product, while a pure Ln²⁺ complex could be obtained for Nd. In this ligand environment, structural information was not able to be used as a conclusive way to describe the electron configuration for the divalent ions, as was possible for the [K(2.2.2-cryptand)] [(C₅H₄SiMe₃)₃Ln] ligand coordination environment.

In Chapter 12, DFT was used to identify promising ligand environments towards the isolation of divalent lanthanide complexes. These calculations suggested that aromatic rings should be avoided in ligand design for divalent ions. Additionally, studies of bimetallic hydride complexes were useful to design strategies to synthesize the first Ln–Ln bond.

Appendix A and B includes additional experimental results and computational results that went beyond the topics covered in Chapters 1-12.

References


CHAPTER 1

Dinitrogen Reduction via Photochemical Activation of Heteroleptic Tris(cyclopentadienyl) Rare Earth Complexes

Introduction*

The origin of the research presented in this Chapter was the initial observation that small scale solutions of (C₅Me₅)(C₅Me₄H)₂Lu, 1-Lu, and (C₅Me₅)₂(C₅Me₄H)Y, 2-Y, react slowly with N₂ to form [(C₅Me₅)(C₅Me₄H)Lu]₂(µ-η²:η²-N₂), 3, and [(C₅Me₅)₂Y]₂(µ-η²:η²-N₂), 4-Y, respectively,¹ which was puzzling because Lu³⁺ and Y³⁺ ions are not redox-active ions and (C₅Me₄H)⁻ is normally stable under N₂. Since (C₅Me₄H)₂ is the byproduct of these reactions, the half-reactions shown in Scheme 1.1 are the formal explanation of the observed reactivity.

Among the ligand-based reductions known in organolanthanide chemistry,²⁻⁵ the ligand-based (C₅Me₄H)⁻ half-reaction is most reminiscent of the (C₅Me₅)⁻ half-reaction of sterically induced reduction (SIR)⁶⁻⁸ involving sterically crowded (C₅Me₅)₃M complexes (M = rare earth, U) (e.g., eq1.1).⁷ Steric crowding in (C₅Me₅)₃M enforces unusually long metal–ligand distances, making the (C₅Me₅)⁻⁻ ligand a reactive reductant that forms (C₅Me₅) radicals, which dimerize. Although SIR can reduce substrates with reduction potentials as negative as those of cyclooctatetraene (−1.62 to −1.86 V vs SCE), it has never been observed to be powerful enough to reduce N₂.⁷

Scheme 1.1. Reduction of N\textsubscript{2} by 1-Lu and 2-Y and the Formal Half-Reactions.

Sterically induced reduction does not explain the reactions in Scheme 1, since 2-Y does not contain unusually long metal–ligand bond distances and the more crowded analogue of 1-Lu, namely, (η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})(η\textsuperscript{3}-C\textsubscript{5}Me\textsubscript{4}H)Lu, 2-Lu, was not observed to reduce N\textsubscript{2}.\textsuperscript{1} Moreover, if steric crowding were the cause of the N\textsubscript{2} reduction, the larger and more reducing (C\textsubscript{5}Me\textsubscript{5})\textsuperscript{1−} anion would be expected to be the effective reductant, not (C\textsubscript{5}Me\textsubscript{4}H)\textsuperscript{1−}. Since 2-Y exhibited a new type of η\textsuperscript{3}-cyclopentadienyl coordination, it was possible that this unusual structure was the source of the reactivity. The structure of 1-Lu, however, was unknown, and no reaction was observed with 2-Lu, which has an (η\textsuperscript{3}-C\textsubscript{5}Me\textsubscript{4}H)\textsuperscript{1−} ligand.\textsuperscript{1} Hence the 3 week N\textsubscript{2} reductions in Scheme 1.1 were difficult to rationalize on the basis of any known reduction pathway in rare earth chemistry.
Additionally, the only prior examples of trivalent lanthanide complexes reducing dinitrogen have been in the presence of an external reductant in reactions designated as LnA₃/M where A is an anion that allows these reactions to occur and M is an alkali metal. These reactions were a way of mimicking the known N₂ reduction chemistry with highly reactive Ln²⁺ ions, i.e. Sm²⁺,³⁹ Tm²⁺,¹⁰ Dy²⁺,¹¹ and Nd²⁺.¹² As shown in Scheme 1.2, this provided the first reduced dinitrogen complexes of Sc,¹³ Y,¹⁴ and the diamagnetic lanthanides, La¹⁵ and Lu.¹⁴

Scheme 1.2. Reduction of dinitrogen via LnA₃/M and LnA₂A'/M.

\[
\begin{align*}
2 \text{LnA}_3 + 2 \text{M} & \xrightarrow{\text{N}_2} \frac{\text{(THF)}_x}{2 \text{MA}} \\
2 \text{LnA}_2 \text{A}' + 2 \text{M} & \xrightarrow{\text{N}_2} \frac{\text{(THF)}_x}{2 \text{MA}'}
\end{align*}
\]

Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Y, Ho, Er, Tm, Lu, Sc
A = N(SiMe₃)₂, OC₆H₅(CMe₃)₂-2,6, C₅Me₅, C₅H₄SiMe₃, C₅Me₄H, C₅H₂'Bu₃
A' = BPh₄, H, I; M = K, potassium graphite, Na; x = 0-2

This Chapter details the discovery that this N₂ reduction reaction is photochemically induced. The photoactivity was observed while examining a variety of factors that could affect the reactions in Scheme 1.1. These results suggest a new type of reduction chemistry available to the lanthanides.

Although lanthanide complexes are well-known for their outstanding emission properties, particularly with Eu³⁺ in the red and Tb³⁺ in the green, they are rarely involved in photochemical reactions.¹⁶-²⁰ Ln³⁺ ions are poor absorbers because the contracted nature of the 4f orbitals limits vibrance relaxation of the Laporte-forbidden nature of 4f → 4f transitions. Hence, lanthanide-based emission requires sensitizers. Laporte-allowed ligand-to-metal charge transfer (LMCT) and ligand-to ligand charge transfer (LLCT) transitions have been reported for the lanthanides,²⁰
but photochemistry is generally not an option for productive lanthanide-based transformations.\textsuperscript{16-23} Photochemical reactivity with complexes of the other rare-earth ions, Sc\textsuperscript{3+} and Y\textsuperscript{3+}, is also limited since they are d\textsuperscript{0} species.\textsuperscript{16-20} Even among actinide complexes there are relatively few examples of photochemically activated reactions.\textsuperscript{24-27} It was therefore unexpected that the unusual dinitrogen reduction reactions shown in Scheme 1.1 would be photochemically activated as described in this report.

**Experimental**

The syntheses and manipulations described below were conducted under argon or nitrogen with rigorous exclusion of air and water using glovebox, vacuum line and Schlenk techniques. Solvents were dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium potassium alloy, degassed, and vacuum transferred prior to use. KC\textsubscript{5}Me\textsubscript{5},\textsuperscript{28} KC\textsubscript{5}Me\textsubscript{4}H,\textsuperscript{29} (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}(C\textsubscript{5}Me\textsubscript{4}H)Ln (Ln = Lu, 2-Lu; Y, 2-Y),\textsuperscript{30} (C\textsubscript{5}Me\textsubscript{5})(C\textsubscript{5}Me\textsubscript{4}H)\textsubscript{2}Ln (Ln = Lu, 1-Lu; Y, 1-Y),\textsuperscript{1} (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Ln(\textmu-Ph)\textsubscript{2}BPh\textsubscript{2} (Ln = Ce, Pr, Nd, Sm, Dy),\textsuperscript{31,32} and Y(C\textsubscript{5}Me\textsubscript{4}H)\textsubscript{3}\textsuperscript{33} were prepared according to the literature. \textsuperscript{1}H NMR spectra were obtained on a Bruker DRX500 MHz spectrometer with a BBO probe at 25 °C unless otherwise specified. \textsuperscript{13}C NMR spectra were obtained on a Bruker DRX500 MHz spectrometer operating at 126 MHz with a TCI cryoprobe at 25 °C. IR samples were prepared as KBr pellets and the spectra were obtained on a Varian 1000 FT-IR system. Absorption spectra were collected using a Cary 50 Scan UV-visible spectrometer at 25 °C in either hexane or toluene. Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS analyzer.
\[(\text{C}_5\text{Me}_5)(\text{C}_5\text{Me}_4\text{H})\text{Lu}]_2(\mu-\eta^2:\eta^2-\text{N}_2), \ 3. \text{ In a nitrogen-filled glovebox, (C}_5\text{Me}_5)(\text{C}_5\text{Me}_4\text{H})_2\text{Lu}, 1, (55 \text{ mg}, 0.01 \text{ mmol}) \text{ was dissolved in C}_6\text{H}_6 (3\text{mL}) \text{ and transferred to a sealed 50 mL sidearm Schlenk flask equipped with a greaseless stopcock. Over the course of 3 weeks, dark orange crystals formed. These orange crystals were washed with pentane to yield 3, (22. mg, 50\%) confirmed by }^{1}\text{H NMR spectroscopy.}^1

\[(\text{C}_5\text{Me}_5)_2\text{Y}]_2(\mu-\eta^2:\eta^2-\text{N}_2), \ 4-\text{Y. In a nitrogen-filled glovebox, (C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Y}, 2, (74 \text{ mg}, 0.15 \text{ mmol}) \text{ was dissolved in C}_6\text{H}_6 (4 \text{ mL}) \text{ and transferred to a sealed 50 mL sidearm Schlenk flask equipped with a greaseless stopcock. Over the course of 4 weeks, the yellow solution became a deep red solution containing no insoluble material. The solvent was removed under reduced pressure to produce a red-orange tacky solid which was washed with pentane to yield 4 (38 mg, 67\%), confirmed by }^{1}\text{H NMR spectroscopy.}^{34}

\text{Reactivity of (C}_5\text{Me}_5)_3-x(\text{C}_5\text{Me}_4\text{H})_x\text{Ln Complexes in the Presence of KC}_5\text{Me}_4\text{R (R = H, Me). At the suggestion of a referee,}^1 \text{ in a nitrogen-filled glovebox, samples of 0.049–0.058 mol of (C}_5\text{Me}_5)_3-x(\text{C}_5\text{Me}_4\text{H})_x\text{Ln complexes were dissolved in C}_6\text{H}_6 (3 \text{ mL}), mixed with 0.03 mol of KC}_5\text{Me}_4\text{R and transferred to a sealed 50 mL sidearm Schlenk flask equipped with a greaseless stopcock. Over the course of 4 weeks, the following results were obtained with the combinations indicated.}

(\text{C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Lu}, 2-\text{Lu}, (33 \text{ mg}, 0.058 \text{ mmol}) / \text{KC}_5\text{Me}_4\text{H} (5 \text{ mg}, 0.03 \text{ mmol}): \text{ The solution was pale orange indicating formation of small amounts of a reduced dinitrogen complex and the }^{1}\text{H NMR spectrum showed compounds 2-Lu:3 in a 1:11 ratio as well as multiple other resonances that do not correspond to 2-Lu or 3.}

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(C₅Me₅)₂(C₅Me₄H)₂Lu, 1-Lu, (27 mg, 0.049 mmol) / KC₅Me₄H (5 mg, 0.03 mmol): No red crystals formed as observed in the absence of KC₅Me₄H; the solution remained yellow and the ¹H NMR spectrum showed no evidence for 3.

(C₅Me₅)₂(C₅Me₄H)₂Y, 1-Y, (27 mg, 0.058 mmol) / KC₅Me₅ (5 mg, 0.03 mmol): The solution was pale orange indicating formation of small amounts of a reduced dinitrogen complex. The ¹H NMR spectrum showed several sets of (C₅Me₄H)⁻ resonances including resonances for Y(C₅Me₄H)₃ and 4-Y, but no remaining 1-Y.

(C₅Me₅)₂(C₅Me₄H)₂Dy, 2-Dy. Addition of (C₅Me₅)₂Dy(µ-Ph)₂BPh₂ (303 mg, 0.403 mmol) to a stirred slurry of KC₅Me₄H (72 mg, 0.45 mmol) in C₆H₆ (3 mL) caused the mixture to immediately turn light orange. After 18 h, the cloudy orange mixture was centrifuged and the supernatant filtered. Removal of solvent from the orange filtrate under vacuum gave a pale orange solid that was stirred in hexane (15 mL) for 30 min. This mixture was centrifuged and filtered to remove insoluble material and removal of solvent under vacuum gave 2-Dy as a bright orange solid (108 mg, 48%). X-ray quality crystals of 2-Dy were grown from a concentrated hexane solution at −35 °C. IR: 2966m, 2906s, 2859s, 2725w, 2389w, 1483w, 1438m, 1383m, 1328w, 1106w, 1021w, 786s, 701w, 654m, 609m cm⁻¹. Anal. Calcd for C₂₉H₄₃Dy: C, 62.85; H, 7.82. Found: C, 62.19; H, 7.89.

Photolytic Reduction of N₂. All photolysis experiments were conducted in a hood with aluminum foil covered windows with a Hanovia medium pressure, 450-watt, mercury vapor
lamp (PC451050/610741). The 5.5 inch long lamp was clamped to hang inside a 13 inch x 1.5 inch diameter cavity of a double-walled quartz water cooling jacket. Tap water at 24 °C flowed through the jacket at a rate of 6.4 L per minute and kept the temperature in the hood between 25 and 27 °C. Samples were placed adjacent to the outer wall of the cooling jacket in the middle of the hood. NMR scale experiments were done in sealable J-Young NMR tubes equipped with a greaseless stopcock in 1 mL of C₆D₆ with 0.01-0.025 mmol of compounds 1-Lu, 2-Y, and 2-Lu. Bulk scale reactions were done in a 50 mL sealable Schlenk tube. All reactions were prepared in a nitrogen-filled glovebox. Compounds 1-Lu, 2-Y, and 2-Lu are all bright yellow compounds. Under irradiation, the yellow solutions became orange and full conversion to 3, 4-Y, and [(C₅Me₅)₂Lu]₂(μ-η²:η²-N₂) (4-Lu), respectively, was confirmed by ¹H NMR spectroscopy.¹,³⁴

**Reaction of (C₅Me₅)₂La(μ-Ph)₂BPh₂ with K(C₅Me₄H).** In a nitrogen-filled glovebox, KC₅Me₄H (24 mg, 150 mmol) was added to a stirred colorless slurry of (C₅Me₅)₂La(μ-Ph)₂BPh₂ (110 mg, 151 mmol) in benzene (3 mL). After stirring for 15 h, the yellow solution was centrifuged, filtered, and the solvent was removed under reduced pressure to yield a yellow solid. The solid was stirred in hexane (15 mL) for 1 h, centrifuged, filtered and the hexane was removed under reduced pressure to yield a yellow solid (39 mg). Although the ¹H NMR spectrum shows many overlapping peaks in the (C₅Me₅) and (C₅Me₄H) region from 1.5-2.5 ppm, [(C₅Me₅)₂La]₂(μ-O)³⁵ and (C₅Me₄H)₃La³⁶ were identified along with two additional (C₅Me₄H) resonances at 6.13 and 5.21 ppm. Crystals of (C₅Me₄H)₃La, suitable for X-ray crystallography, were grown from a saturated hexanes solution at −35 °C.

**Reaction of (C₅Me₅)₂Ce(μ-Ph)₂BPh₂ with K(C₅Me₄H).** Similar to the analogous reaction with (C₅Me₅)₂La(μ-Ph)₂BPh₂, KC₅Me₄H (22 mg, 140 mmol) was added to a stirred pink
slurry of (C₅Me₅)₂Ce(µ-Ph)₂BPh₂ (101 mg, 138 mmol) in benzene (3 mL). After stirring for 15 h, the cloudy brown solution was centrifuged, filtered, and the solvent was removed under reduced pressure to yield pink and emerald green solids. The solid was stirred in hexane (15 mL) for 1 h, centrifuged, filtered and the hexane was removed under reduced pressure to yield an emerald green solid (37 mg). The ¹H NMR spectrum of the isolated green solid showed many peaks, suggesting a mixture of products was formed. Crystalline material was consistently obtained as clusters of small emerald green crystals, unsuitable for X-ray crystallography.

**Reaction of (C₅Me₅)₂Pr(µ-Ph)₂BPh₂ with K(C₅Me₄H).** Similar to the analogous reaction with (C₅Me₅)₂La(µ-Ph)₂BPh₂, KC₅Me₄H (59 mg, 370 mmol) was added to a stirred bright yellow slurry of (C₅Me₅)₂Pr(µ-Ph)₂BPh₂ (101 mg, 138 mmol) in benzene (3 mL). After stirring for 15 h, the yellow solution was centrifuged, filtered, and the solvent was removed under reduced pressure to yield a yellow solid. The solid was stirred in hexane (15 mL) for 1 h, centrifuged, filtered and the hexane was removed under reduced pressure to yield a yellow solid. The ¹H NMR spectrum of the isolated yellow solid showed many peaks, suggesting a mixture of products was formed. Crystalline material was consistently obtained as clusters of small yellow crystals, unsuitable for X-ray crystallography.

**Reaction of (C₅Me₅)₂Nd(µ-Ph)₂BPh₂ with K(C₅Me₄H).** Similar to the analogous reaction with (C₅Me₅)₂La(µ-Ph)₂BPh₂, KC₅Me₄H (25 mg, mmol) was added to a stirred pale green slurry of (C₅Me₅)₂Nd(µ-Ph)₂BPh₂ (115 mg, mmol) in benzene (3 mL). After stirring for 15 h, the green solution was centrifuged, filtered, and the solvent was removed under reduced pressure to yield a green solid. The solid was stirred in hexane (15 mL) for 1 h, centrifuged, filtered and the hexane was removed under reduced pressure to yield a lime green solid (40 mg). The ¹H
NMR spectrum of the isolated green solid showed many peaks, suggesting a mixture of products was formed. Crystals of \((\text{C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Nd}, \text{2-Nd}\), suitable for X-ray crystallography were grown from a saturated hexanes solution at \(-35\, ^\circ\text{C}\).

**Reaction of \((\text{C}_5\text{Me}_5)_2\text{Sm(}\mu\text{-Ph})_2\text{BPh}_2\) with \(\text{K(C}_5\text{Me}_4\text{H})\).** Similar to the analogous reaction with \((\text{C}_5\text{Me}_5)_2\text{La(}\mu\text{-Ph})_2\text{BPh}_2\), \(\text{KC}_5\text{Me}_4\text{H}\) (36 mg, 220 mmol) was added to a stirred red slurry of \((\text{C}_5\text{Me}_5)_2\text{Sm(}\mu\text{-Ph})_2\text{BPh}_2\) (168 mg, 227 mmol) in benzene (3 mL). After stirring for 15 h, the red solution was centrifuged, filtered, and the solvent was removed under reduced pressure to yield a red solid. The solid was stirred in hexane (15 mL) for 1 h, centrifuged, filtered and the hexane was removed under reduced pressure to yield a red-orange solid (69 mg). The \(^1\text{H}\) NMR spectrum of the isolated red-orange solid showed many peaks, suggesting a mixture of products was formed. Crystalline material was consistently obtained as clusters of small red crystals, unsuitable for X-ray crystallography.

**X-ray Data Collection, Structure Solution and Refinement for 1-Lu.** A yellow crystal of approximate dimensions 0.10 x 0.16 x 0.19 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\(^{37}\) program package was used to determine the unit-cell parameters and for data collection (45 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\(^{38}\) and SADABS\(^{39}\) to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\(^{40}\) program. The diffraction symmetry was \(2/m\) and the systematic absences were consistent with the monoclinic space group \(P2_1/n\) that was later determined to be correct. The structure was solved by direct methods and refined on \(F^2\) by full-matrix least-squares techniques. The analytical scattering factors\(^{41}\) for neutral atoms were used throughout the analysis. Hydrogen atoms were includ-
ed using a riding model. There were two molecules of the formula-unit present (Z = 8). At convergence, wR2 = 0.1053 and Goof = 1.276 for 10128 variables refined against 547 data (0.80Å), R1 = 0.0537 for those 8738 data with I > 2.0σ(I). Details are given in Table 1.1.

Definitions:
\[ wR^2 = \left( \frac{\sum [w(F_o^2 - F_c)^2]}{\sum [w(F_o^2)]} \right)^{1/2} \]
\[ R1 = \frac{\sum |F_o - |F_c||}{\sum |F_o|} \]
\[ Goof = S = \left( \frac{\sum [w(F_o^2 - F_c)^2]}{(n-p)} \right)^{1/2} \]
where n is the number of reflections and p is the total number of parameters refined.

**X-ray Data Collection, Structure Solution and Refinement for 2-Dy.** A yellow crystal of approximate dimensions 0.16 x 0.22 x 0.32 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group \( P\overline{1} \) was assigned and later determined to be correct. The structure was solved using the coordinates of the lutetium analogue and refined on \( F^2 \) by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and \( U_{iso} \)). There were two molecules of the formula-unit present (Z = 4). At con-
vergence, wR2 = 0.0494 and Goof = 1.037 for 885 variables refined against 11992 data (0.74Å),
R1 = 0.0197 for those 10540 data with I > 2.0σ(I). Details are given in Table 1.1.

**X-ray Data Collection, Structure Solution and Refinement for 2-Nd.** An orange/gold
crystal of approximate dimensions 0.064 x 0.119 x 0.327 mm was mounted on a glass fiber and
transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was
used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a
sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to
yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The diffraction symmetry was 2/m and the systematic absences were consistent with
the monoclinic space group P21/n that was later determined to be correct. The structure was
solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analyti-
cal scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms
were located from a difference-Fourier map and refined (x,y,z and Uiso). At convergence, wR2 =
0.0634 and Goof = 1.050 for 443 variables refined against 6425 data (0.73Å), R1 = 0.0242 for
those 4879 data with I > 2.0σ(I). Details are given in Table 1.1.

**Computational Details.** The initial structure optimizations of 1-Lu and 2-Ln (Ln = La,
Y, Lu, Dy), starting from the available crystal data, were performed using the TPSSh hybrid
meta-GGA functional. Split valence basis sets with polarization functions on non-hydrogen
atoms (SV(P)) were used for light atoms and the triple-zeta valence basis sets with two sets of
polarization functions (def2-TZVP) for Y, La and Lu. TPSSh was chosen due to its estab-
lished performance for transition metal compounds, and reductive Ln chemistry. Relativistic
small-core pseudopotentials were employed for Y, La and Lu. Large f-in-core relativistic pseu-
do potentials and the corresponding basis sets by Dolg et al.\textsuperscript{53} were used for Dy. Vibrational frequencies were computed at the TPSSh/SV(P) level, and all ground state structures were confirmed to be minima by the absence of imaginary modes. A further optimization using larger triple-zeta valence basis sets (def2-TZVP\textsuperscript{48}) for all atoms was then performed. The differences in bond lengths between the SV(P) and the TZVP structures were typically 0.05 Å or less. Fine quadrature grids (size m4)\textsuperscript{54} were used throughout. SCF energies and density matrices were converged to $10^{-7}$ a.u. All computations were performed using the TURBOMOLE program package.\textsuperscript{55} All molecular orbital plots were computed with SV(P) basis sets using contour values of 0.05. Theoretical, zero temperature gas-phase UV-visible spectra were generated from time dependent density functional theory (TDDFT) excitation energy calculations.\textsuperscript{56} Normalized Gaussians centered at the molecular excitations, scaled with the computed oscillator strength,\textsuperscript{57} and fixed root mean width chosen to match the experiment were used to simulate the absorption spectra. Excited state geometry optimizations were also performed for 2-Y and 2-Dy using SV(P) basis sets and the PBE0 functional.\textsuperscript{58} Both the first and second excited states were investigated since these excitations lie within the proposed photoactive frequency range.

Excited state geometry optimizations for 2-Y and 2-Dy in the first ($S_1$) and second ($S_2$) singlet states were performed using SV(P) basis sets and the PBE0 functional. Large-core ECPs and appropriate basis sets were used for Dy while small-core ECPs and SV(P) basis sets were used for Y. The norm of the Cartesian gradient for the $S_1$ states was converged to $10^{-4}$ a.u. The $S_2$ states did not converge, however, due to a conical intersection between the $S_1$ and $S_2$ states in both compounds that causes the optimization procedure to oscillate between states near the intersection. Such a result possibly indicates that excitation of either band could lead to photo react-
tivity since the S₂ may relax to the S₁ state after excitation. All calculations on 2-Dy were done by Jefferson E. Bates in Filipp Furche’s group at UC Irvine.

Results/Discussion

Since only NMR scale reactions were pursued for the reactions in Scheme 1.1, it was valuable to determine whether this slow reaction was a useful route to reduced dinitrogen species. Reactions run on a larger scale with 1-Lu show formation of red crystalline 3 within a day, but typically two weeks are needed to obtain yields of 50%. Larger scale reactions of 2-Y also showed formation of 4-Y in yields >50% within weeks. Although these reactions are slow, they produce reduced dinitrogen species in higher yields and greater purity than 30 min reactions using KC₈ as a reductant.

While examining this unique ligand-based reductive reactivity, neither heating nor increased metal complex concentrations decreased the reaction times. Small amounts of KC₅Me₄R (R = H, Me), added to solutions of 1-Ln and 2-Ln (Ln = Lu, Y), were also not found to catalyze the dinitrogen reduction. In fact, these changes led to ligand redistribution products such as (C₅Me₄H)₃Ln that showed no reductive reactivity. Increasing N₂ pressure also had no noticeable effect. To probe the importance of the (η³-C₅Me₄H)₁⁻ ligand in 2-Y, renewed efforts to obtain the solid-state structure of 1-Lu were made, and it was found to contain the unusual trihapto structural feature: (η²-C₅Me₃)(η²-C₅Me₄H)(η³-C₅Me₄H)Lu, Figure 1.1. This supported the idea that the N₂ reduction reactivity was related to this unusual ligand.
Figure 1.1. Thermal ellipsoid plot of \((\eta^5-C_5Me_5)(\eta^5-C_5Me_4H)(\eta^3-C_5Me_4H)Lu, \textbf{1-Lu})\), drawn at the 50% probability level. There are two independent molecules of \textbf{1-Lu} in the asymmetric unit. The second independent molecule and hydrogen atoms have been committed for clarity.

Since the \(N_2\) reductions in Scheme 1.1 involved only closed shell 4d\(^0\) Y\(^{3+}\) and 4f\(^{14}\) Lu\(^{3+}\) complexes, reactions with an open-shell ion were examined to probe the generality of this photochemistry. The 4f\(^9\) Dy\(^{3+}\) ion was chosen because it is similar in size to Y\(^{3+}\) and reduced dinitrogen complexes of dysprosium had previously been modeled by density functional theory (DFT).\(^{50}\) The reaction of \([C_5Me_5)_2Dy][(\mu-Ph)_2BPh_2]\) with 1.1 equiv of KC\(_5\)Me\(_4\)H yielded \((C_5Me_5)_2(C_5Me_4H)Dy, \textbf{2-Dy})\), which was found by X-ray crystallography to contain an \((\eta^3-C_5Me_4H)^{1-}\) ligand and be isomorphous with \textbf{2-Y}, Figure 1.2. Complex \textbf{2-Dy} also reduced \(N_2\) over a period of weeks to form the \((N=N)^{2-}\) complex, \([(C_5Me_5)_2Dy](\mu-\eta^2:\eta^2-N_2), \textbf{4-Dy})\), as identified by X-ray crystallography.
Figure 1.2. Thermal ellipsoid plot of $(\eta^5$-$C_5$Me$_5$)$_2(\eta^3$-$C_5$Me$_4$H)Dy, 2-Dy, drawn at 50% probability level. There are two independent molecules of 2-Dy in the asymmetric unit. The second independent molecule and hydrogen atoms have been omitted for clarity.

After conventional methods of increasing the rare-earth reaction rates were tried, photoactivation was investigated. Surprisingly, irradiation of NMR samples of yellow 1-Lu and 2-Y with a mercury vapor lamp changed the time scale for producing the red dinitrogen complexes 3 and 4-Y from 3 weeks to 2 h, Scheme 1.2. The orange Dy$^{3+}$ complex 2-Dy could also be photochemically activated. Moreover, irradiation of previously unreactive yellow 2-Lu led to the reduced dinitrogen product $[(C_5$Me$_5$)$_2$Lu]_2(\mu-\eta^2$:$\eta^2$-N$_2$), 4-Lu, although this required 5 h.
To explore the origin of this photoreactivity, the UV-vis spectra of the mixed-ligand complexes 1-Lu and 2-Ln (Ln = Lu, Y, Dy) were obtained, and each was found to contain two broad absorptions. These results are in contrast to the UV-vis spectra of the homoleptic tris(polyalkylcyclopentadienyl) complexes (C₅Me₄H)₃Lu, (C₅Me₄H)₃Y, and (C₅Me₅)₃La, each of which contains only one absorption. The spectra of 2-Y and (C₅Me₄H)₃Y are compared in Figure 1.3. Dinitrogen was reduced even when a GG.420 glass filter was used to block light with wavelengths below 420 nm, suggesting that the photochemically active band is the lower-energy band not found in the homoleptic complexes.
Figure 1.3. UV-vis spectra of 2-Y (blue solid line) and (C₅Me₄H)₃Y (red solid line) along with the DFT-simulated spectrum of 2-Y (blue dotted line). The vertical lines represent the computed excitations, with heights determined by the theoretical oscillator strengths.

DFT calculations on 1-Lu and 2-Ln (Ln = Lu, Y, Dy) converged on lowest-energy C₁-symmetric structures with the unusual trihapto coordination of the (C₅Me₄H)₁⁻ ligand observed crystallographically. The highest occupied molecular orbital (HOMO) of these complexes, shown for 2-Y in Figure 1.4a, is a ligand-based orbital localized on the (η³-C₅Me₄H)₁⁻ ligand. This is significantly different from the HOMOs of the homoleptic (C₅Me₄H)₃Y and (C₅Me₅)₃Y complexes, in which the electron density is distributed evenly over all three rings, Figure 1.4b.
Figure 1.4. Molecular orbital plots of the HOMOs of (a) 2-Y, showing electron density on the $(\eta^3$-$C_5\text{Me}_4\text{H})^{1-}$ ligand, and (b) $(C_5\text{Me}_4\text{H})_3\text{Y}$, showing electron density delocalized over all three ligands, using a contour value of 0.05.

Time-dependent DFT calculations were used to simulate the UV-vis absorption spectrum of 2-Y. As shown in Figure 1.3, the shape of the simulated spectrum is a reasonable match for the experimental spectrum. The calculations showed two LMCT transitions at wavelengths greater than 400 nm that make up the broad peak denoted with an asterisk in Figure 1.3. These two LMCT excitations occur at 412 and 437 nm, and each represents the transfer of an electron from an orbital localized on the $(\eta^3$-$C_5\text{Me}_4\text{H})^{1-}$ ligand to the empty 4d$_{z^2}$ orbital on the metal center, the lowest unoccupied molecular orbital (LUMO) of the complex, Figure 1.5. Hence, these calculations provide a rationale for the observed reactivity. The single electron transfer associated with this excitation would form a C$_5$Me$_4$H radical and a “(C$_5$Me$_5$)$_2$Y*” moiety with the yttrium center in an excited 4d$^1$ state. The C$_5$Me$_4$H radical would be expected to dimerize to the observed (C$_5$Me$_4$H)$_2$ product, and “(C$_5$Me$_5$)$_2$Y*” would be expected to be able to reduce dinitrogen on the basis of Y$^{2+}$ reactivity studies.$^{59-61}$ Analogous LMCT excitations to the 5d LUMO at 412
and 434 were predicted for 2-Dy. A summary of the excitations and oscillator strengths is given in Table 1.2.

![Figure 1.5](image)

**Figure 1.5.** DFT-predicted LMCT bands in the visible-light region for complex 2-Y.

Excited-state geometry optimizations\textsuperscript{62,63} were performed for the first two singlet states of 2-Y and 2-Dy. In all cases, the trihapto coordination was broken, and the distance from the metal to the C\textsubscript{5}Me\textsubscript{4}H ligand increased by more than 0.30 Å. The optimized structures of the ground state and first excited state are superimposed in Figure 1.6.
Although cyclopentadienyl ligands are generally considered to be photochemically innocent, transition-metal examples of homolytic cleavage through LMCT are known. Equations 1.2 and 1.3 show examples with d⁰ complexes. The photo lability of (η⁵-C₅Me₄H)₁⁻ complexes has not been previously studied because this coordination mode was not known before the discovery of 1-Lu and 2-Ln (Ln = Lu, Y, Dy).

\[
\begin{align*}
(\eta^5-C_5H_5)_2TiCl_2 & \xrightarrow{\text{hv}} (\eta^5-C_5H_5)TiCl_2 + C_5H_5 & (1.2) \\
(\eta^5-C_5H_5)_2Zr(C_6H_4Me-4) & \xrightarrow{\text{hv}} 4-MeC_6H_4C_6H_4Me-4 + "(\eta^5-C_5H_5)_2Zr" & (1.3)
\end{align*}
\]

Attempts to synthesize the (C₅Me₅)₂(C₅Me₄H)Ln, 2-Ln, for the larger lanthanides (La, Ce, Pr, Nd, Sm) were found to be complicated with ligand rearrangement. In the case of La, [(C₅Me₅)₂La]₂(µ-O)³⁵ and (C₅Me₄H)₃La³⁶ are two identified products from the reaction of (C₅Me₅)₂Ln(µ-Ph)₂BPh₂ with KC₅Me₄H. However, after numerous attempts, crystals of (C₅Me₅)₂(C₅Me₄H)Nd, 2-Nd were finally characterized by X-ray crystallography, Figure 1.7. As
seen in Figure 1.7, all three rings are bound pentahapto to Nd, which is different than the \((\eta^3\text{-C}_5\text{Me}_4\text{H})^\text{1–}\) coordination observed in 1-Lu and 2-Ln (Ln = Lu, Y, Dy). Although this complex didn’t show the \((\eta^3\text{-C}_5\text{Me}_4\text{H})^\text{1–}\) unique binding mode that provided an accessible photochemical reduction pathway for the smaller metals, this allowed for a comparison with \((\text{C}_5\text{Me}_5)_3\text{Nd}\) to determine how the loss of one methyl group changes the steric crowding.

![Figure 1.7. Thermal ellipsoid plot of \((\text{C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Nd}, 2-\text{Nd}, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.](image)

The \((\text{C}_5\text{Me}_5\text{H})^\text{1–}\) ligand in 2-Nd tilts towards the metal with the hydrogen-substituted C(25) closest to the Nd center. This is similar to the structure of \((\text{C}_5\text{Me}_5\text{H})_3\text{Lu}\) and presumably occurs to minimize steric crowding. Along with this tilt, one methyl group [C(10) and C(20)] on each \((\text{C}_5\text{Me}_5)^\text{1–}\) ring is displaced approximately 0.44 and 0.45 Å, respectively, from the best
plane of the cyclopentadienide ring. Although this is not the 0.519 Å displacement found in 
(C₅Me₅)₃Nd, which undergoes sterically induced reduction processes, 0.44 and 0.45 Å are much longer than the normal out-of-plane displacements of 0.09-0.31 Å.⁷¹,⁷² This suggests that this complex is more crowded than most Nd metallocene complexes, but the tilting of the 
(C₅Me₄H)⁻ ring alleviates the crowding relative to (C₅Me₅)₃Nd.

The UV-vis spectra were obtained for the crude mixtures of the reactions to synthesize 2-Ln with the larger lanthanides, Figure 1.8. Although the mixtures all contained a broad absorption between 400 and 500 nm, these absorptions were weak in comparison to 2-Ln with the smaller metals, and solutions of these mixtures did not give detectable reduced dinitrogen

![Figure 1.8. UV-vis spectra of reactions mixtures of (C₅Me₅)₂Ln(μ-Ph)₂BPh₂ (Ln = Ce, Pr, N, and Sm) with K(C₅Me₄H).](image-url)
species within 72 hours of irradiation. This could be due to a lack of the \((\eta^3\text{C}_5\text{Me}_4\text{H})^\text{1–}\) ligand that appears to be important for the observed reactivity.

DFT calculations on **2-La** show the HOMO and HOMO-1 to be spread out across all five ligands as shown in, Figure 1.9. This is reminiscent of the HOMO present in the homoleptic \((\text{C}_5\text{Me}_4\text{H})_3\text{Y}\) complex, Figure 1.4. This suggests that the photochemical properties for **2-La** should be no different than the homoleptic tris(cyclopentadienyl) complexes. Therefore the unique photochemical properties observed for **1-Lu** and **2-Ln** \((\text{Ln} = \text{Y}, \text{Lu}, \text{and Dy})\) do appear to require the \((\eta^3\text{C}_5\text{Me}_4\text{H})^\text{1–}\) ligand.

![Figure 1.9](image)

**Figure 1.9.** Molecular orbital plots of (a) HOMO-1 and (b) HOMO of **2-La**, using a contour value of 0.05.

**Conclusion**

In summary, with the appropriate ligand set and metal choice, photochemical activation of rare-earth complexes can occur, leading to powerful reductive reactivity sufficient to reduce \(\text{N}_2\). In this case, complexes with the unusual \((\eta^3\text{C}_5\text{Me}_4\text{H})^\text{1–}\) ligand have HOMOs with electron
density primarily localized on that ligand. These complexes have low-energy LMCT absorptions that can be photoactivated. DFT studies showed that irradiation at these energies could lead to formation of a C₅Me₄H radical and an excited d¹ metal fragment reactive enough to reduce N₂. These results suggest that UV-vis spectra should be routinely obtained for rare-earth complexes since they could reveal potentially unusual electronic features and new opportunities for photochemistry.
Table 1.1. X-ray Data Collection Parameters for 1-Lu, 2-Dy and 2-Nd.

<table>
<thead>
<tr>
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<th>1-Lu</th>
<th>2-Dy</th>
<th>2-Nd</th>
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<tr>
<td>formula</td>
<td>$\text{C}<em>{28}\text{H}</em>{41}\text{Lu}$</td>
<td>$\text{C}<em>{29}\text{H}</em>{43}\text{Dy}$</td>
<td>$\text{C}<em>{29}\text{H}</em>{43}\text{Nd}$</td>
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*Definitions: wR2 = $\sqrt{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]}$; R1 = $\sum|F_o| - |F_c|/\sum|F_o|$.  


Table 1.2. Computed excitation energies using PBE0 and SV(P) basis sets. 2-Dy (large-core) employed large core ECPs and basis sets for Dy. Ground state SCF energies and one-electron density matrix were converged to $10^{-7}$.

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<td>412 ($S_2$)</td>
<td>0.031</td>
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<tr>
<td>2-Dy (large-core)</td>
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<td>412 ($S_2$)</td>
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<td>361 (26 $\AA$)</td>
<td>0.019</td>
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</table>

References

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Academic Publishers.
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CHAPTER 2

Dinitrogen Reduction, Sulfur Reduction, and Isoprene Polymerization via Photochemical Activation of Trivalent Bis(cyclopentadienyl) Allyl Complexes

Introduction

As described in Chapter 1, the traditional view that rare earth complexes have minimal photochemistry was overturned by the observation that dinitrogen can be reduced to \((\text{N} = \text{N})^{2-}\) by photolysis of the \(\text{Ln}^{3+}\) mixed ligand tris(cyclopentadienyl) rare earth complexes \((\text{C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Ln}, 1-\text{Ln}\) \((\text{Ln} = \text{Y}, \text{Lu}, \text{Dy})\), and \((\text{C}_5\text{Me}_5)(\text{C}_5\text{Me}_4\text{H})_2\text{Lu}\).\(^1\) The products of the two electron reduction of \(\text{N}_2\), \([(\text{C}_5\text{Me}_5)_2\text{Ln}]_2(\mu-\eta^2:\eta^2-\text{N}_2), 2-\text{Ln}\), and \([(\text{C}_5\text{Me}_5)(\text{C}_5\text{Me}_4\text{H})\text{Ln}]_2(\mu-\eta^2:\eta^2-\text{N}_2)\), respectively, are formed in reactions in which \((\text{C}_5\text{Me}_4\text{H})^{1-}\) is oxidized to \((\text{C}_5\text{Me}_4\text{H})_2\), Scheme 2.1. The fact that photochemical activation with lanthanides could lead to the potent reduction of dinitrogen was surprising since \(\text{Ln}^{3+}\) ions are poor absorbers.\(^2-6\)

Scheme 2.1. Reduction of Dinitrogen with \((\text{C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Ln}, 1-\text{Ln}\) \((\text{Ln} = \text{Y}, \text{Lu}, \text{Dy})\) and \((\text{C}_5\text{Me}_5)(\text{C}_5\text{Me}_4\text{H})_2\text{Ln}\) \((\text{Ln} = \text{Lu})\) under Photolytic Conditions and Formal Half Reactions.
Density functional theory analysis of the unusual rare earth photochemistry in Scheme 1 indicated that absorptions involving the unusual ($\eta^3$-C$_5$Me$_4$H)$_{1-}$ ligand were responsible.$^1$ Specifically, two absorptions at 412 and 437 nm that are present in the heteroleptic (C$_5$Me$_5$)$_2$(C$_5$Me$_4$H)Ln complexes, but not in the homoleptic analogs, (C$_5$Me$_5$)$_3$Ln or (C$_5$Me$_4$H)$_3$Ln, appear to be involved. Due to the rare nature of this photochemical activation, it was desirable to test the generality of this photoactivity beyond the three metals shown in Scheme 2.1. Extending the reactions of Y, Dy, and Lu to the larger metals in the lanthanide series was problematic because synthesis of pure (C$_5$Me$_5$)$_2$(C$_5$Me$_4$H)Ln, 1, for the larger lanthanides (La, Ce, Pr, Nd, Sm) was complicated by ligand rearrangement, as discussed in Chapter 1.

Given the trihapto nature of the photoactive ($\eta^3$-C$_5$Me$_4$H)$_{1-}$ ligand, it was of interest to determine if the structurally related allyl complexes, (C$_5$Me$_5$)$_2$Ln($\eta^3$-C$_3$H$_5$), 3, could be similarly photoactivated. If so, this would provide a much more facile synthetic route to the reduced dinitrogen complexes, [(C$_5$Me$_5$)$_2$Ln]$_2$(µ-η$_2$-$\eta^2$-N$_2$), 2, since the allyl complexes are precursors to the heteroleptic (C$_5$Me$_5$)$_{3-x}$(C$_5$Me$_4$H)$_x$Ln$^{7,8}$ complexes as well as the loosely-ligated tetraphenylborate cationic metallocene complexes, [(C$_5$Me$_5$)$_2$Ln][(µ-Ph)$_2$BPh$_2$],$^{9-12}$ which can also be used as precursors to the (N=N)$^{2-}$ complexes.$^{13}$ Initially, this study examined the photochemical properties of 3 for the small metals to compare to the mixed tris(cyclopentadienyl) complexes, 1. Since the (C$_5$Me$_5$)$_2$Ln($\eta^3$-C$_3$H$_5$) allyl complexes can be isolated for most of the lanthanides,$^{12,14,15}$ this could provide the opportunity to assess whether this photochemical process is also available to the larger metals.
This Chapter reports that the allyl complexes of the small metals are photoactive and this reactivity can be used not only to reduce dinitrogen, but also to polymerize isoprene. Photopolymerization of isoprene is rare and generally involves radical initiators. To show the generality of the photoactivity of these common metallocene rare earth allyl complexes, S8 was also found to be reduced by Ln3+ allyl complexes under irradiation. Density functional theory (DFT) is used to explain the photochemical activity of 3-Ln (Ln = Y, Lu). A substituted allyl complex, (C5Me5)2Y(CH2C(Me)CH2), 4-Y, synthesized by Casey W. Johnson, was also found to be photoactive. DFT is also used to compare the electronic properties of 4-Y to 3-Y in this Chapter.

Experimental

The syntheses and manipulations described below were conducted under argon or nitrogen with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium potassium alloy, degassed by three freeze–pump–thaw cycles, and vacuum transferred prior to use. (C5Me5)2Ln(C3H5) (Ln = Y,15 Lu,15 Dy12), 2-Ln, were prepared according to the literature. 1H NMR spectra were obtained on a Bruker DRX500 MHz spectrometer with a BBO probe at 25 °C unless otherwise specified. 13C NMR spectra were obtained on a Bruker DRX500 MHz spectrometer operating at 126 MHz with a TCI cryoprobe at 25 °C. IR samples were prepared as KBr pellets and the spectra were obtained on a Jasco 4700 FT-IR system. Absorption spectra were collected using a Cary 50 Scan
UV-Vis spectrometer at 25 °C in toluene or hexanes. Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS analyzer.

**Photolytic Reaction Conditions.** All photolysis experiments were conducted in a hood with aluminum foil covered windows with a Hanovia medium pressure, 450-watt, mercury vapor lamp (PC451050/610741). The 5.5 inch long lamp was clamped to hang inside a 13 inch x 1.5 inch diameter cavity of a double-walled quartz water cooling jacket. Tap water at 24 °C flowed through the jacket at a rate of 6.4 L per minute and kept the temperature in the hood between 25 and 27 °C. Samples were placed adjacent to the outer wall of the cooling jacket in the middle of the hood.

**Photolysis of (C₅Me₅)₂Lu(C₃H₅), 3-Lu, to Form [(C₅Me₅)₂Lu]₂(μ-η²:η²-N₂), 2-Lu.** In a nitrogen-filled glovebox, 3-Lu (12 mg, 0.025 mmol) was dissolved in C₆D₆ (1 mL) and transferred to a sealable J-Young NMR tube equipped with a greaseless stopcock. Under irradiation for 24 h, the yellow solution became deep red, and ¹H NMR analysis revealed full conversion to 2-Lu.¹³

**Photolysis of (C₅Me₅)₂Y(C₃H₅), 3-Y, to Form [(C₅Me₅)₂Y]₂(μ-η²:η²-N₂), 2-Y.** As described for 3-Lu, a yellow solution of 3-Y (10 mg, 0.02 mmol) became red-orange under irradiation for 24 h, and generated a 1.5:1 mixture of 3-Y and 2-Y.¹³

**Isoprene Reactivity. Large Scale Reactions.** In an argon-filled glovebox, ~50 mg 3-Ln (Ln = Y, Lu) and a magnetic stir bar were added to a sealable 50 mL sidearm Schlenk flask equipped with a greaseless stopcock. The flask was added to the high vacuum line and argon was removed under vacuum. Isoprene (approximately 10 mL) was vacuum transferred into the flask. After irradiation for 12 h, gel had formed on the side of the flask near the light source.
The amount of gel continued to increase over the course of 8 days of irradiation. Excess isoprene was removed under vacuum to leave a thick gel, which was sent to Goodyear Tire Company for characterization.

\[
[(\text{C}_5\text{Me}_5)_2\text{Y}]_2(\mu-\text{S}), \text{ 5-Y}. \quad \text{In an argon-filled glovebox, 3-Y (421 mg, 1.05 mmol) was dissolved in toluene (20 mL). S}_8 (17 mg, 0.066 mmol) was added to the yellow solution, which was then transferred to a sealable 50 mL sidearm Schlenk flask equipped with a greaseless stopcock. During irradiation for 4 h, the stirred bright yellow solution became pale yellow. In an argon-filled glovebox, the solvent was removed under vacuum and the solids were washed with pentane to leave a pale yellow solid, \([(\text{C}_5\text{Me}_5)_2\text{Y}]_2(\mu-\text{S}), \text{ 5-Y}. \) Colorless single crystals of 5-Y, suitable for X-ray diffraction, were grown from toluene at \(-35 \, ^\circ\text{C}\). \text{\textsuperscript{1}H NMR (C}_6\text{D}_6\):} \quad \delta 2.07 (s, 60 H, \text{C}_5\text{Me}_5). \quad \text{\textsuperscript{13}C NMR (C}_6\text{D}_6\):} \quad \delta 11.68 (s, \text{C}_5\text{Me}_5), 119.16 (s, \text{C}_5\text{Me}_5). \quad \text{IR:} \quad 2961\text{s,} \quad 2906\text{s,} \quad 2858\text{s,} \quad 2725\text{w,} \quad 1638\text{w,} \quad 1490\text{w,} \quad 1437\text{m,} \quad 1378\text{m,} \quad 1259\text{w,} \quad 1186\text{w,} \quad 1162\text{w,} \quad 1086\text{m,} \quad 801\text{w cm}^{-1}. \quad \text{Anal. Calcd for C}_{40}\text{H}_{60}\text{SY}_2:} \quad \text{C, 63.99;} \quad \text{H, 8.06. Found:} \quad \text{C, 64.51;} \quad \text{H, 8.50. Eight attempts at elemental analysis on this compound including use of crystals examined by X-ray diffraction did not give better analytical data than this. The other seven attempts were analyzed as follows:} \quad 1) \quad \text{C, 63.14;} \quad \text{H, 8.26;} \quad 2) \quad \text{C, 65.11;} \quad \text{H, 8.79;} \quad 3) \quad \text{C, 65.62;} \quad \text{H, 8.71;} \quad 4) \quad \text{C, 65.01;} \quad \text{H, 8.83;} \quad 5) \quad \text{C, 64.68;} \quad \text{H, 8.10;} \quad 6) \quad \text{C, 66.68;} \quad \text{H, 8.91;} \quad 7) \quad \text{C, 64.72;} \quad \text{H, 8.41.}

\]

\[
[(\text{C}_5\text{Me}_5)_2\text{Lu}]_2(\mu-\text{S}), \text{ 5-Lu}. \quad \text{As described for 5-Y, 3-Lu, (124 mg, 0.255 mmol) was combined with S}_8 \text{ in toluene (10 mL). During irradiation for 5 h, the stirred bright yellow solution became a pale yellow. In an argon-filled glovebox, the solvent was removed under vacuum to leave a pale yellow solid, \([(\text{C}_5\text{Me}_5)_2\text{Lu}]_2(\mu-\text{S}), \text{ 5-Lu}, \text{ (65 mg, 55.5%). Colorless}
\]

44
single crystals of 5-Lu, suitable for X-ray diffraction, were grown from toluene, 5-Lu(tol) and hexane, 5-Lu(hex) at –35 °C.

**X-ray Data Collection, Structure Solution and Refinement for 5-Y(tol).** A colorless crystal of approximate dimensions 0.264 x 0.072 x 0.070 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The systematic absences were consistent with the tetragonal space group P21c which was later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. The molecule was located on a two-fold rotation axis. Hydrogen atoms were included using a riding model. There were high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals, although it was probable that hexane solvent was present. The SQUEEZE routine in the PLATON program package was used to account for the electrons in the solvent accessible voids. At convergence, wR2 = 0.0633 and Goof = 1.051 for 205 variables refined against 4554 data (0.78 Å), R1 = 0.0286 for those 4107 data with I > 2.0σ(I). The absolute structure was assigned by refinement of the Flack parameter. Details are given in Table 2.2.

**X-ray Data Collection, Structure Solution and Refinement for 5-Lu(tol).** A yellow crystal of approximate dimensions 0.124 x 0.134 x 0.398 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was
used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\textsuperscript{27} and SADABS\textsuperscript{28} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{22} program. The systematic absences were consistent with the hexagonal space group $P\overline{4} 2_1 c$ which was later determined to be correct. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors\textsuperscript{23} for neutral atoms were used throughout the analysis. The molecule was located on a two-fold rotation axis. Hydrogen atoms were included using a riding model. There were high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals, although it was probable that hexane or toluene solvent was present. The SQUEEZE routine in the PLATON\textsuperscript{24} program package was used to account for the electrons in the solvent accessible voids. At convergence, wR2 = 0.0334 and Goof = 1.093 for 205 variables refined against 5330 data (0.73 Å), R1 = 0.0141 for those 5208 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.\textsuperscript{25} Details are given in Table 2.2.

**X-ray Data Collection, Structure Solution and Refinement for 5-Lu(hex).** A colorless crystal of approximate dimensions 0.198 x 0.166 x 0.096 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{29} program package and CELL_NOW\textsuperscript{30} were used to determine the unit-cell parameters. Data was collected using a 15 sec/frame scan time for a sphere of diffraction data. The raw frame data was processed using SAINT\textsuperscript{27} and TWINABS\textsuperscript{31} to yield the reflection data file (HKLF5 format)\textsuperscript{31}. Subsequent calculations were carried out using the SHELXTL\textsuperscript{32} program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric
triclinic space group $P\overline{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors$^{23}$ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, $wR^2 = 0.0650$ and $Goof = 1.035$ for 410 variables refined against 9521 data (0.74 Å), $R1 = 0.0269$ for those 8485 with $I > 2.0\sigma(I)$. The structure was refined as a three-component twin, BASF$^{32} = 0.14471$ and 0.02977. Details are given in Table 2.2.

**Computational Details.** The initial structure optimizations of 3-Lu, 3-Y, and 4-Y, starting from the available crystal data,$^{15}$ were performed using the TPSSh$^{33}$ hybrid meta-GGA functional. Split valence basis sets with polarization functions on non-hydrogen atoms (SV(P)) were used for light atoms and the triple-zeta valence basis sets with two sets of polarization functions (def2-TZVP) for Y and Lu.$^{34,35}$ TPSSh was chosen due to its established performance for transition metal compounds, reductive Ln chemistry, and Ln photochemistry.$^{1,36-38}$ Relativistic small-core pseudopotentials$^{39}$ were employed for Y and Lu. Vibrational frequencies were computed at the TPSSh/SV(P) level, and all ground state structures were confirmed to be minima by the absence of imaginary modes.$^{40}$ A further optimization using larger triple-zeta valence basis sets (def2-TZVP$^{35}$) for all atoms was then performed. The differences in bond lengths between the SV(P) and the TZVP structures were typically 0.02 Å or less. Fine quadrature grids (size m4)$^{41}$ were used throughout. SCF energies and density matrices were converged to $10^{-7}$ a.u. All calculations were performed using the Turbomole quantum chemistry software.$^{42}$ All molecular orbital plots were computed with SV(P) basis sets using contour values of 0.06. Theoretical, zero temperature gas-phase UV-visible spectra were generated from
time dependent density functional theory (TDDFT) excitation energy calculations. The excitation energies and oscillator strengths for selected transitions of 3-Lu, 3-Y and 4-Y are given in Table 2.3. Calculations were performed in collaboration with Jefferson E. Bates in the Furche group.

**Results**

**UV-visible Spectroscopy.** The UV-visible absorption spectra of 3-Y and 3-Lu are shown in Figure 2.1. Similar to those found for 1-Y and 1-Lu, these spectra contain two broad absorptions with the lowest energy absorption near the 405 nm emission of the medium pressure mercury vapor lamp, used for irradiation. These spectra are also similar to each other in that the low energy absorption is less intense than the high energy absorption. While the low energy absorption is around the same wavelength for both 3-Y ($\lambda_{\text{max}} = 401$ nm) and 3-Lu ($\lambda_{\text{max}} = 395$ nm).
nm), the high energy absorption is red shifted for 3-Y (λ\text{max} = 357 nm) relative to 3-Lu (λ\text{max} = 341 nm). The absorptions of the methylallyl complex, 4-Y, at 357 nm and 397 nm are similar to 3-Y in energy. However the higher energy absorption is significantly more absorbing for 3-Y than 4-Y, while the lower energy absorption is only slightly more intense for 3-Y than 4-Y.

**Photolysis of (C₅Me₅)₂Ln(η³-C₃H₄R) Complexes Under Dinitrogen.** Photolysis of solutions of 3-Y, 3-Lu, and 4-Y in benzene under dinitrogen produced the (N=N)⁻² complexes, [(C₅Me₅)₂Ln]₂(μ-η²-η²-N₂) (Ln = Y, 2-Y; Lu, 2-Lu), which were identified by ¹H NMR spectroscopy,\(^\text{13}\) eq 2.1. The reaction of 3-Lu was complete after 24 h of irradiation, while the analogous reaction of 3-Y only showed 57% completion in the same time frame, suggesting the rate of formation for 2-Lu is faster than that of 2-Y. Gas chromatography/mass spectrometry (GC/MS) analysis, performed by Casey W. Johnson, of the head space of the photochemical reactions of 3-Y and 4-Y with dinitrogen described byproducts of the reactions to be propene and isobutene, respectively. These results are consistent with formation of allyl and methylallyl radicals upon photolysis that hydrogen abstract from solvent to form propene and isobutene.\(^\text{44,45}\)

\[
\begin{align*}
\text{R} &\text{ Ln} \xrightarrow{\text{hv, N}_2} \text{N} \text{ Ln} \\
\text{R} &= \text{H; Ln} = \text{Y, 3-Y; Lu, 3-Lu} \\
\text{R} &= \text{Me; Ln} = \text{Y, 4-Y}
\end{align*}
\]

**Isoprene as a Substrate.** A blank reaction of 3-Y in neat isoprene showed no reactivity between the allyl complexes and this diene. Photolysis of 3-Y and 3-Lu in neat isoprene generated a highly viscous product. ¹H NMR and ¹³C NMR analysis in CDCl₃, performed by Dr. Maggie Flook at Goodyear Tire and Rubber Company and Casey W. Johnson at UCI,
indicated the presence of polyisoprene in the form of cis-1,4-, trans-1,4-, and 3,4-isomers consistent with the literature. Though signals for the 3,4-isomer were found to be predominant, peak overlap prevented determining the ratio of the isomers formed. No evidence of the 1,2-isomer was observed. Molecular weight analysis of the polyisoprene produced from the reaction of 3-\(\text{Y}\), performed by Dr. Maggie Flook at Goodyear Tire and Rubber Company, indicated the polymers consist of primarily low molecular weight polymers with a Mn of 4217 g/mol, a MW of 5633 g/mol and a polydispersity index (PDI) of 1.3.

**Reduction of Sulfur.** Complexes 3-\(\text{Y}\) and 3-\(\text{Lu}\) were also found to react with elemental sulfur, \(\text{S}_8\), in toluene under irradiation to form the bridging sulfide complexes, [(\(\text{C}_5\text{Me}_5\))\(_2\text{Ln}\)](\(\mu\)\(-\text{S}\)), 5, eq 2.2, Figure 2.2. This appears to be just the third example of \(\text{S}_8\) reduced to (S)\(^2^-\) or (S\(_2\))\(^2^-\).

![Figure 2.2](image)

**Figure 2.2.** Thermal ellipsoid plots of [(\(\text{C}_5\text{Me}_5\))\(_2\text{Lu}\)](\(\mu\)-S), 5-\(\text{Lu}\), crystallized from a) hexane and b) toluene, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.
by a trivalent rare earth complex. Although the isolation of 5 is only approximately 50%, the crude reaction solution, after 4 h irradiation, shows no remaining 3-Ln.

The structural nature of 5 is unusual in that 5-Lu crystallized differently from hexane, than from toluene, even though no solvent co-crystallized in either structure. As shown in Table 2.1, when 5-Lu was crystallized from toluene, the crystals were isomorphous with 5-Y(tol), also crystallized from toluene. These two complexes have similar structures and bond lengths after accounting for the difference in the 8-coordinate ionic radius of Y (1.019 Å) and Lu (0.977 Å). The complexes form dimers with equivalent metal centers and Ln–S distances in a narrow range.

Table 2.1. Selected bond lengths (Å) and bond angles of 5-Y and 5-Lu (crystallized from both hexane and toluene).

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2.5026(2) to 2.5433(3) Å. The Ln-S-Ln angles are also similar: 171.91(6)° for 5-Y(tol) and 173.27(5)° for 5-Lu(tol). When 5-Lu is crystallized from hexane, the 5-Lu(hex) crystals form in a different space group than 5-Lu(tol). This crystal structure has a 166.68(5)° Ln-S-Ln angle and the two metals are not symmetry equivalent.

**Density Functional Theory (DFT) Calculations.** A DFT study on \((C_5Me_5)_2Ln(\eta^3-C_3H_5), 3-Ln \) (Ln = Lu, Y), reveals that the HOMO has electron density located on the allyl ligand while the LUMO is a \(d_z^2\) orbital on the metal center, Figure 2.3. Time dependent DFT (TDDFT) studies were done to calculate an excitation spectrum of 3-Ln, from which excitations around both 360 and 390 nm were predicted for 3-Lu and excitations around 370 and 390 nm were predicted for 3-Y. These excitation energies match the experimental spectra well, however the oscillator strength for the low energy excitation (389 nm) for 3-Lu is not as high as would be expected to match the experimental spectrum. Table 2.3 summarizes the excitation energies and oscillator strengths. Upon closer analysis of the absorptions, the lowest energy absorption for both 3-Y and 3-Lu is the HOMO-LUMO ligand to metal charge transfer (LMCT) from the

![Figure 2.3](image.png)

**Figure 2.3.** Molecular orbital plots of (a) the HOMO and (b) the LUMO for 3-Lu, using a contour value of 0.06.
trihapto allyl ligand to a \( d_{z^2} \) orbital. This is analogous to the first two excitations of 1-Y and 1-Lu which were also predicted to be LMCT transitions from the trihapto ligand to a \( d_{z^2} \) orbital.\(^1\) The next excitations under 300 nm are all predicted to be LMCT from the \((\eta^5\text{-C}_5\text{Me}_5)^{1-}\) ligands to \( d_{z^2} \) orbital which is also analogous to the calculations of 1-Ln.

The calculations show that upon excitation, the bond distance from the metal to one of the terminal allyl carbon atoms is greatly decreased while the bond distance to the other end carbon simultaneously lengthens. Upon trying to reach an energy minimum, the allyl ligand approaches \( \eta^1 \) coordination and the closest carbon moves more than 0.30 Å away from the metal center. This is similar to the \((\text{C}_5\text{Me}_4\text{H})^{1-}\) ligand in \((\text{C}_5\text{Me}_5)_2\text{Y}(\eta^3\text{-C}_5\text{Me}_4\text{H})\) upon excitation. The \( \eta^1 \) structure is not a potential energy minimum, however, but it gives insight into the possible reaction mechanism.

DFT studies on the methylallyl complex, 4-Y, reveal a similar HOMO and LUMO as seen for both 3-Y and 3-Lu, Figure 2.4. The TDDFT predicted similar excitations near 360 and 390 nm as was found for 3-Y. The oscillator strength of the excitation for 4-Y near 390 is slightly higher than that for 3-Y, while the oscillator strength of the excitation for 4-Y near 360 nm is almost half that for 3-Y. This matches the observed differences in the experimental UV-vis spectra.
Figure 2.4. Molecular orbital plots of (a) the HOMO and (b) the LUMO of 4-Y, using a contour value of 0.06.

Discussion

The allyl complexes, (C₅Me₅)₂Y(η³–C₃H₅), 3-Y, (C₅Me₅)₂Lu(η³–C₃H₅), 3-Lu and (C₅Me₅)₂Y(CH₂C(Me)CH₂), 4-Y, are similar to the photochemically active (C₅Me₅)₂Ln(η³–C₅Me₄H) and (C₅Me₅)(C₅Me₄H)Ln(η³–C₅Me₄H) compounds in Scheme 2.1 in terms of their yellow color, their UV-vis spectra, and their overall structures with two (η⁵-C₅Me₅)⁻⁻ rings and one η³-ligand. As such, they were good candidates to undergo the photochemistry observed in Scheme 2.1. As shown in eq 2.1, each of the allyl complexes can be photoactivated to reduce N₂ to (N≡N)⁻⁻. Interestingly, the reaction of the Lu allyl, 3-Lu, with dinitrogen under irradiation was found to go to completion within 24 h, while the analogous reaction of 3-Y only reached 57% completion. The reason for this is unknown. DFT calculations suggest that the source of the photoactivity is a LMCT band in the near 390 nm arising from a transition between the HOMO of the allyl complexes, which is localized on the allyl ligand, and the LUMO, which is
mainly d_{x^2-y^2}. The calculations indicate that this would generate an allyl radical and an excited state Ln^{2+} species “(C_{5}Me_{5})_{2}Ln” (Ln = Y, Lu) which should be be capable of reducing dinitrogen based on data on the recently discovered Y^{2+} complexes.\textsuperscript{52,53} Identification of propene and isobutene by GC/MS of the gases over the photolysis is consistent with formation of the allyl radicals followed by hydrogen abstraction.

Irradiation of 3-\textbf{Y} and 3-\textbf{Lu} in neat isoprene led to formation of low molecular weight polyisoprene. NMR evidence showed that a mixture of cis-1,4-, trans-1,4- and 3,4-polyisoprene had formed with a predominance of the 3,4-isomer. This is consistent with radical polymerization of isoprene as opposed to rare-earth metal based coordination polymerization that can give specific isomers.\textsuperscript{54-61} Although selective polymerization was not observed in this case, photo-polymerization of isoprene is rare.\textsuperscript{16-18}

Complexes 3-\textbf{Y} and 3-\textbf{Lu} also can be photoactivated to reduce S_{8} to form the bridging sulfide complexes, 5-\textbf{Y} and 5-\textbf{Lu}, eq 2.2. While the reduction is not as challenging as that of dinitrogen (S to S^{2−} is only −0.476 V vs. SCE\textsuperscript{62}), this reduction suggests that this photochemical process is not restricted to just the reduction of dinitrogen.

Structural analysis of the sulfide bridged complexes provided another example of the variability of organometallic structures based on crystallization conditions. [(C_{5}Me_{5})_{2}Lu]_{2}(μ-S), 5-\textbf{Lu}, was found to crystallize from hexane with a more linear Lu-S-Lu angle, 173.27(5)°, than the 166.68(5)° angle found in crystals obtained from toluene. Similar situations have recently been reported for (C_{5}Me_{5})_{2}Y(NC_{4}Me_{4})\textsuperscript{63} and [(C_{5}Me_{5})_{2}DyH]_{2}\textsuperscript{64} where different crystallization methods have led to different structures of the same complex. Evidently, in some combinations of ligands and metals, the energy surface is very shallow and several structures are possible. This
emphasizes the dangers of drawing conclusions from a single structural feature in a single crystal structure. For example, it could be argued that the more linear 171.91(6)° angle in 5-Y compared to the 166.68(5)° angle in 5-Lu(hex) was due to enhanced covalency with yttrium since it is a transition metal. However, 5-Lu(tol) has a 173.27(5)° angle that is even closer to linear than that in the yttrium structure.

**Conclusion**

Photochemical activation of lanthanide complexes has been extended to allyl complexes, \((C_5Me_5)_2Ln[CH_2C(R)CH_2]\) \((R = \text{H, Ln = Y, 3-Y; Lu, 3-Lu; R = Me, Ln = Y, 4-Y})\), to reduce dinitrogen to form \([((C_5Me_5)_2Y)_2(\mu-\eta^2;\eta^2-N_2)]\), 2-Y. 3-Ln complexes (Ln = Y, Lu) were also found to polymerize isoprene to low molecular weight polymers and reduce \(S_8\) to \((S)^2^-\) under irradiation. DFT calculations were able to explain this photochemical activity as a ligand to metal charge transfer from the allyl ligand to a metal d orbital. The transition would generate an allyl radical and a rare earth ion in the formal +2 oxidation state, which would likely abstract hydrogen from the solvent and reduce dinitrogen, respectively, as is observed.
Table 2.2. X-ray Data Collection Parameters of 5-Y(tol), 5-Lu(tol) and 5-Lu(hex).

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^aDefinitions: wR2 = \left[\sum w(F_o^2 - F_c^2)^2\right]^{1/2} / \left[\sum w(F_c^2)^2\right]^{1/2}; R1 = \sum |F_o| - |F_c|/\sum |F_o|.
Table 2.3. Computed excitation energies using TPSSH and SV(P) basis sets. Ground state SCF energies and one-electron density matrix were converged to $10^{-7}$.

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References


(20) SAINT Version 7.68a, Bruker AXS, Inc.; Madison, WI 2009.


(47) Unpublished work by Maggie Fluke.


CHAPTER 3

Raman and X-ray Crystallographic Study of N–N Bond Reduction in the Rare Earth Dinitrogen Complexes

Introduction

The first example of a planar side-on bonding between a dinitrogen ligand and two metals was reported in 1988 in a rare earth complex, $\text{[(C}_5\text{Me}_5)\text{Sm]}_2(\mu-\eta^2:\eta^2-\text{N}_2)$, $\text{1-Sm}$.1 This complex was quite perplexing because NMR spectroscopy and the Sm–(C$_5$Me$_5$ ring centroid) distances suggested that two Sm$^{3+}$ centers were on either side of a doubly reduced (N$_2$)$_2^{2-}$ bridging ligand, while the N–N bond length [1.088(12) Å] was even shorter than that of free dinitrogen (1.0975 Å).2 Since $\text{1-Sm}$ is in an equilibrium with the Sm$^{2+}$ complex, (C$_5$Me$_5$)$_2$Sm, as shown in eq 3.1,3 it was challenging to isolate this complex to characterize the degree of dinitrogen reduction in other ways.

\[
\begin{align*}
\text{2 Sm} + \text{N}_2 & \rightleftharpoons \text{Sm} \cdots \text{N} \cdots \text{N} \cdots \text{Sm} \\
& \text{(3.1)}
\end{align*}
\]

It was subsequently found that reactions of LnI$_2$ (Ln = Tm, Dy, Nd) and two equivalents of potassium salts of cyclopentadienyl, amide, and aryloxide ligands in the presence of dinitrogen could lead to similar side-on dinitrogen complexes, Scheme 3.1.4,5 The overall structures of these complexes were analogous to that of $\text{1-Sm}$, in that these were Ln$_2(\mu-\eta^2:\eta^2-\text{N}_2)$ complexes. However the N–N bond distances in these complexes were significantly elongated.
Scheme 3.1. Reduction of dinitrogen with Ln(II) ions in the presence of ancillary ligands.

\[
\text{LnI}_2(\text{THF})_3 + 2 \text{KA} \rightarrow \text{Ln(N}_2\text{A(THF)}_x\text{A})\text{Ln(THF)}_x
\]

Ln = Nd, Dy, Tm
A = N(SiMe$_3$)$_2$; C$_5$H$_3$(SiMe$_3$)$_2$-1,3; C$_5$H$_4$SiMe$_3$; C$_5$H$_4$Bu$_2$; OC$_6$H$_3$Bu$_2$-2,6; C$_5$Me$_5$

x = 0-2

from free dinitrogen, with distances ranging from 1.23-1.31 Å in the double bond range. This suggested that while Ln$^{2+}$ complexes with Tm, Dy and Nd could convincingly reduce dinitrogen, the dinitrogen reaction of the Sm complex was still unclear.

In further studies, dinitrogen reduction chemistry was dramatically extended to all of the rare earths (Sc, Y, lanthanides), even those without known $+2$ oxidation states at the time of the discovery of the reduced dinitrogen complexes. This was achieved by reducing a Ln$^{3+}$ complex with an alkali metal in the presence of dinitrogen, Scheme 2.\textsuperscript{6-14} The resulting dinitrogen complexes were similar to the Tm, Dy and Nd complexes, in that they have N–N bond lengths ranging from 1.23 to 1.29 Å. This method also helped identify the first example of an (N$_2$)$_3$\textsuperscript{−} complex.\textsuperscript{11,14-16}

Several dinitrogen complexes have also been obtained with uranium.\textsuperscript{17-24} Three of these complexes exhibit dinitrogen complexes that do not release dinitrogen under vacuum consistent with reduction. However, the N–N bond lengths range from 1.08 to 1.24 Å.\textsuperscript{20,23,24} Four other isolated dinitrogen complexes of uranium show rapid loss of dinitrogen in solution or under vacuum which is consistent with minimal dinitrogen reduction. These also exhibit a broad range of N–N bond lengths from 1.10 to 1.23 Å.\textsuperscript{17-19,21-23} These N–N bond lengths in the uranium
complexes range from that of free dinitrogen to bond lengths similar to many of the lanthanide dinitrogen complexes discussed above. It is evident that the bond lengths in these uranium complexes do not correlate with the strength of dinitrogen binding.

In spite of the numerous examples of these side-on dinitrogen complexes, the most common method of characterizing the degree of dinitrogen reduction in rare earth and actinide chemistry has been X-ray crystallography. Due to the difficulty of getting accurate X-ray data to obtain a reliable N–N bond lengths for many of these complexes, it was desirable to use another technique to learn more about the degree by which the dinitrogen was reduced. It has been shown in transition metal dioxygen chemistry that librational motions of a diatomic molecule between two metals can give systematic errors in the O–O bond length in the crystal structure.\(^{25,26}\) For example, the Tp′Co(O\(_2\)) [Tp′ = hydridotris(3-tert-butyl-5-methylpyrazolyl)borate] complex has a different O–O bond length when the crystal structure was obtained at 22 °C (1.262(8) Å) than when the crystal structure was obtained at −123 °C (1.355(3) Å).\(^{25,27}\)

Stretching frequency is often considered the preferred alternative method to understanding degrees of reduction for diatomic molecules and has been used often in transition metal chemistry.\(^{25,26,28-33}\) A compilation of the reported crystallographic N–N bond lengths versus the NN stretching frequency of reduced dinitrogen complexes shows that the two values are correlated by Badger’s rule, which does not predict a linear relationship.\(^{26}\) Reduction of N\(_2\) to (N=N)\(^2−\) should give good Raman data since N=N double bond stretching vibrations are often found to give strong and well-defined Raman bands between 1580 and 1400 cm\(^{-1}\). These are forbidden in the IR spectra of compounds with inversion symmetry.\(^{34}\)
Only rarely have Raman stretching frequencies been reported in rare earth and actinide dinitrogen complexes. Arnold, Kaltsoyannis, and co-workers, have explored the usefulness of Raman spectroscopy in characterizing dinitrogen reduction with two uranium dinitrogen complexes, and Raman spectra have been measured for two rare earth dinitrogen complexes. According to the literature, only one rare earth dinitrogen complex has had enough disruption in symmetry for the N–N stretch to be observed by IR spectroscopy. This [(C₅Me₅)(C₅Me₄H)Lu](µ-η²:η²-N₂) complex has an N–N stretching frequency of 1736 cm⁻¹ with an N–N bond distance of 1.275(3) Å. N–N stretching frequencies of 1622 cm⁻¹ and 1425 cm⁻¹ have been reported, using Raman spectroscopy, for [(C₅H₂'B₅)₂Nd](µ-η²:η²-N₂) (N–N distance of 1.23 Å) and {[(Me₃Si)₂N]₂Y(THF)](µ-η²:η²-N₂) (N–N distance of 1.268(3) Å), respectively. Since the stretching frequencies and crystal structure data in these three isolated cases did not follow regular trends, it was interesting to examine more examples to determine if any pattern existed.

This Chapter describes the use of Raman spectroscopy to characterize dinitrogen reduction in single crystals of a series of 21 rare earth complexes of reduced dinitrogen. This study was initiated after the crystallographic characterization of [(C₅Me₅)Lu₂(µ-η²:η²-N₂)], 1-Lu, which constituted another example of a rare earth dinitrogen complex with an extremely short N–N bond distance, 1.111(5) Å. Since Lu²⁺ appears to be more reducing than Tm²⁺, Dy²⁺, and Nd²⁺, the short N–N distance in 1-Lu cannot be rationalized in the same way as in the reaction of the less reducing Sm²⁺ complex discussed above.

In order to compare the Raman spectra as consistently as possible with the X-ray crystal structures, techniques to measure Raman spectra of single crystals at UCI were developed. This
Chapter reports that trends are observable by Raman spectroscopy even when no trend is found by crystallography. This makes Raman spectroscopy a useful tool in understanding these reduced dinitrogen complexes.

**Experimental**

The syntheses and manipulations described below were conducted under argon or dinitrogen with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were spared with UHP grade argon (Airgas) and passed through columns containing Q-5 and molecular sieves before use. \((\text{C}_5\text{Me}_5\text{Ln})_2(\mu-\eta^2:\eta^2-\text{N}_2)\) \((\text{Ln} = \text{Lu, Y, Gd, Tb, Sm})^1\)\(^2\) \((\text{C}_5\text{Me}_4\text{H})(\text{THF})\text{Ln})_2(\mu-\eta^2:\eta^2-\text{N}_2)\) \((\text{Ln} = \text{Gd, Dy})^6,10\) and \{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Ln})_2(\mu-\eta^2:\eta^2-\text{N}_2)\) \((\text{Ln} = \text{Gd, Tb, Dy, Y, Ho, Er, Tm})^5,7,8\) were prepared according to literature methods. \{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{L})\text{Y})_2(\mu-\eta^2:\eta^2-\text{N}_2)\} \((\text{L} = \text{DMAP, Ph}_3\text{PO, PhCN, Me}_3\text{NO, Py})^{38}\) were prepared according to literature by Jordan F. Corbey. \((\text{C}_5\text{H}_4\text{Me})_2(\text{THF})\text{Ln})_2(\mu-\eta^2:\eta^2-\text{N}_2)\) \((\text{Ln} = \text{Y, Dy})\) were prepared by David H. Woen.

**Raman Spectroscopy.** Raman spectra were obtained using a Renishaw inVia confocal Raman Microscope, equipped with a 32 mW laser of wavelength 532 nm (laser power 10% and a 20x objective laser). Crystalline samples were loaded in a 1 cm cuvette equipped with a Teflon stopcock, designed to sit flat under the microscope. Exposure times were adjusted between 10 and 30 seconds to optimize the intensity of the spectrum.

All spectra presented have a minimum of 3 crystals having the same spectrum. For most samples, 10 spectra were obtained for each crystal and averaged to get the best resolution. In the case of several samples that had sensitivity to the laser, spectra were confirmed across a
minimum of 5 crystals, with only one spectrum obtained at each spot (additional spectra at the same spot showed decomposition).

**X-ray Data Collection, Structure Solution and Refinement for 1-Lu(A).** A red crystal of approximate dimensions 0.107 x 0.111 x 0.390 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The diffraction symmetry was 4/mmm and the systematic absences were consistent with the tetragonal space group $P\bar{4} 2_1 c$ that was later determined to be correct. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about a two-fold rotation axis. The lutetium atom was disordered approximately 84% (Lu1), 16% (Lu2). Metric data involving the lutetium atom was referenced to the major component Lu(1). Carbon atoms C(16)-C(20) were disordered and included using multiple components, partial site-occupancy-factors and isotropic thermal parameters. At convergence, $wR^2 = 0.0911$ and Goof = 1.145 for 219 variables refined against 4478 data (0.80Å), $R_1 = 0.0325$ for those 3999 data with $I > 2\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter. Details are given in Table 3.7.

**X-ray Data Collection, Structure Solution and Refinement for 1-Lu(B).** A red crystal of approximate dimensions 0.109 x 0.129 x 0.229 mm was mounted on a glass fiber and
transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The diffraction symmetry was 4/mmm and the systematic absences were consistent with the tetragonal space group P421c which was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about a two-fold rotation axis. Carbon atoms C(16)-C(20) were disordered and included using multiple components with partial site-occupancy-factors and isotropic thermal parameters. At convergence, wR2 = 0.0877 and Goof = 1.080 for 209 variables refined against 4430 data (0.78Å), R1 = 0.0318 for those 4204 data with I > 2.0σ(I). The absolute structure was assigned by refinement of the Flack parameter. Solvent accessible voids were examined with the PLATON program SQUEEZE but found not to be significant. A model based on the application of the SQUEEZE routine did not improve the analysis. Details are given in Table 3.7.

**X-ray Data Collection, Structure Solution and Refinement for 1-Lu(C).** A red crystal of approximate dimensions 0.083 x 0.096 x 0.230 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL.
program. The diffraction symmetry was $4/mmm$ and the systematic absences were consistent with the tetragonal space group $P\bar{4}2_1c$ that was later determined to be correct. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors$^{43}$ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about a two-fold rotation axis. The lutetium atom was disordered approximately 92% (Lu1), 8% (Lu2). Metric data involving the lutetium atom was referenced to the major component Lu(1). Carbon atoms C(16)-C(20) were disordered and included using multiple components, partial site-occupancy-factors and isotropic thermal parameters. At convergence, $wR2 = 0.0660$ and Goof = 1.082 for 218 variables refined against 5242 data (0.73Å), $R1 = 0.0254$ for those 4919 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.$^{44}$ Details are given in Table 3.7.

**X-ray Data Collection, Structure Solution and Refinement for 1-Gd.** A red crystal of approximate dimensions 0.248 x 0.296 x 0.618 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX$^{47}$ program package was used to determine the unit-cell parameters and for data collection (5 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT$^{40}$ and SADABS$^{41}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL$^{42}$ program. The diffraction symmetry was $4/mmm$ and the systematic absences were consistent with the tetragonal space group $P\bar{4}2_1c$ that was later determined to be correct. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors$^{43}$ for neutral atoms were used throughout the analysis. Hydrogen atoms were
included using a riding model. The molecule was located about a two-fold rotation axis. At convergence, \( wR^2 = 0.0424 \) and \( Goof = 1.052 \) for 209 variables refined against 5262 data (0.73Å), \( R1 = 0.0169 \) for those 5068 data with \( I > 2.0\sigma(I) \). The absolute structure was assigned by refinement of the Flack parameter.\(^{44}\) There were high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals although it was probable that benzene or methylcyclohexane solvent was present. The SQUEEZE routine in the PLATON\(^{46,50}\) program package was used to account for the electrons in the solvent accessible voids. Details are given in Table 3.8.

**X-ray Data Collection, Structure Solution and Refinement for 1-Tb.** A purple crystal of approximate dimensions 0.095 x 0.109 x 0.264 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\(^{47}\) program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\(^{40}\) and SADABS\(^{41}\) to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\(^{42}\) program. The diffraction symmetry was \( 4/mmm \) and the systematic absences were consistent with the tetragonal space group \( P\bar{4} 2_1c \) that was later determined to be correct. The structure was solved by direct methods and refined on \( F^2 \) by full-matrix least-squares techniques. The analytical scattering factors\(^{43}\) for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about a two-fold rotation axis. At convergence, \( wR^2 = 0.0377 \) and \( Goof = 1.028 \) for 209 variables refined against 5254 data (0.73Å), \( R1 = 0.0159 \) for those 5092 data with \( I > 2.0\sigma(I) \). The absolute structure was assigned by refinement of the Flack parameter.\(^{44}\) There were high residuals present in the final
difference-Fourier map. It was not possible to determine the nature of the residuals although it was probable that benzene or methylecyclohexane solvent was present. The SQUEEZE routine in the PLATON\textsuperscript{46,50} program package was used to account for the electrons in the solvent accessible voids. Details are given in Table 3.8.

**X-ray Data Collection, Structure Solution and Refinement for 2-Gd.** A green crystal of approximate dimensions $0.237 \times 0.280 \times 0.374$ mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{47} program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\textsuperscript{40} and SADABS\textsuperscript{41} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{42} program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups $Cc$ and $C2/c$. It was later determined that space group $C2/c$ was correct. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors\textsuperscript{43} for neutral atoms were used throughout the analysis. Hydrogen atom H(28) was located from a difference-Fourier map and refined (x,y,z and $U_{iso}$). The remaining hydrogen atoms were included using a riding model. The molecule was located about a two-fold rotation axis. A methyl carbon atom on one tetramethylcyclopentadienyl ligand was disordered over two positions (C(16) / C(19)) and included using multiple components with partial site-occupancy factors. The hydrogen atom associated with the disordered tetramethylcyclopentadienyl ligand was not included in the refinement. There was a molecule of toluene solvent present (two per dimeric formula-unit). The solvent was disordered. Carbon atoms C(24)-C(27) were included as above. At
convergence, wR2 = 0.0449 and Goof = 1.071 for 350 variables refined against 6785 data (0.73 Å), R1 = 0.0190 for those 6008 data with I > 2.0σ(I). Details are given in Table 3.8.

**X-ray Data Collection, Structure Solution and Refinement for 2-Dy.** A green crystal of approximate dimensions 0.137 x 0.176 x 0.307 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package and the CELL_NOW program were used to determine the unit-cell parameters. Data was collected using a 15 sec/frame scan time for a sphere of diffraction data. The raw frame data was processed using SAINT and TWINABS to yield the reflection data file (HKLF 5 format). Subsequent calculations were carried out using the SHELXTL program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space groups Cc and C2/c. It was later determined that space group C2/c was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about a two-fold rotation axis. At convergence, wR2 = 0.0790 and Goof = 1.078 for 235 variables refined against 4928 data (0.75 Å), R1 = 0.0316 for those 4482 with I > 2.0σ(I). The structure was refined as a two-component twin, BASF = 0.1165. Details are given in Table 3.8.

**Results**

**X-ray Crystallography.** X-ray diffraction data was obtained for a crystal of the reported [(CsMe5)2Lu]2(µ-η2:η2-N₂) complex, 1-Lu, Figure 3.1. This crystal had a similar unit cell and the same space group, P1, as 1-Tm. The structure is disordered and the data was modeled with
Figure 3.1. Thermal ellipsoid plot of four crystals of [(C₅Me₅)₂Lu₂(μ-η²:η²-N₂)], 1-Lu, drawn at the 50% probability level. Disordered metal centers in 1-Lu, 1-Lu(A), and 1-Lu(B) (those at 7%, 16%, and 8% occupancy, respectively), disordered cyclopentadienyl methyls in 1-Lu(A), 1-Lu(B), 1-Lu(C) and hydrogen atoms are omitted for clarity.

One set of metal positions present at 93% occupancy and another set at 7% occupancy. The N–N bond length was refined to be 1.111(5) Å, Table 3.1. This is significantly shorter than all other Ln³⁺ reduced dinitrogen complexes, except the short distance in 1-Sm. Since the only known Lu²⁺ complex is not stable at room temperature, it would be unusual if 1-Lu was a complex of neutral N₂ bridging between two Lu²⁺ centers. Additional crystallographic data on 1-Lu was obtained on three different crystals. These were all found to have a similar unit cell and the same space group, \( P\bar{4} 2_1c \), as the structure of 1-Y, Figure 3.1.¹³
Although each of these crystals of 1-Lu contained some sort of disorder in metal atoms and/or cyclopentadienide rings, the N–N distances could be resolved. They are 1.190(16) Å for 1-Lu(A), 1.233(10) Å for 1-Lu(B), and 1.242(11) Å for 1-Lu(C), Table 3.1. For other classes of rare earth dinitrogen compounds, such as \([(\text{C}_5\text{Me}_5\text{H})_2\text{Ln(THF)}](\mu-\eta^2:\eta^2-\text{N}_2))\), 2-Ln (Ln = La, Ce, Nd, Pr, Lu), crystallographic data often contain significant disorder in the ligands that make the N–N bond lengths less reliable to discuss.

As can be seen in Figure 3.1 and Table 3.1, all four structures of 1-Lu have very similar arrangements of the ligands, in which the metal to ligand distances and the (C\text{Me}_5\text{H} \text{ring centroid})-M-(C\text{Me}_5\text{H} \text{ring centroid}) angles do not change much across the four different structures. For all four structures, the (C\text{Me}_5\text{H})\text{l}^- \text{ligands are found in an approximate tetrahedral arrangement around the metal centers as previously seen for other structures of 1-Ln (Ln = Y,}
These data suggest that the differences in N–N bond lengths are not due to differences in the arrangement of the cyclopentadienyl ligands.

It has been found that the temperature at which the crystal structure is obtained can have an effect on the stretch of reduced $\text{O}_2$ complexes. The structures of $1-\text{Lu}$ and $1-\text{Lu(A-C)}$ were obtained at 93(2), 143(2), 88(2), and 143(2) K, respectively. Since the N–N bond lengths increase from $1-\text{Lu}$ to $1-\text{Lu(C)}$, there does not appear to be a trend between N–N bond lengths and the temperature at which the crystal structures were obtained for $1-\text{Lu}$.

Additionally, the structures of $1-\text{Gd}$ and $1-\text{Tb}$ were identified via X-ray crystallography, Figure 3.2, to compare the Raman spectra of $1-\text{Ln}$ (Ln = Y, Sm, Lu) with other metals in the lanthanide series. Structural data suggest an N–N bond length of 1.236(5) Å for $1-\text{Gd}$ and 1.238(4) Å for $1-\text{Tb}$, which fit within the range expected for an $(\text{N}_2)^{2-}$ ligand. These complexes are isomorphous with that of $1-\text{Lu(A-C)}$, having the same tetrahedral arrangement of the cyclopentadienyl ligands around the Ln$_2$N$_2$ center.

![Figure 3.2.](image)

**Figure 3.2.** Thermal ellipsoid plot of $[(\text{C}_5\text{Me}_5)_2\text{Ln}]_2(\mu-\eta^2:\eta^2-\text{N}_2)$, (Ln = Gd, $1-\text{Gd}$; Tb, $1-\text{Tb}$) drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.
Although most of the reported structures of \([(\text{C}_{5}\text{Me}_{4}\text{H})_{2}\text{Ln(THF)})\(_{2}\)(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\), 2-Ln, contained too much disorder to discuss bond lengths, the syntheses of the unreported 2-Gd and 2-Dy were pursued. Fortunately, these examples provided crystallographic data good enough to discuss metrical parameters, Figure 3.3. The N–N distances of 1.247(3) and 1.243(7) Å for 2-Gd and 2-Dy, respectively, are both similar to (N\(_{2}\))\(^{2-}\) complexes previously characterized. The syntheses of \([(\text{C}_{5}\text{H}_{4}\text{Me})_{2}(\text{THF})\text{Ln}]_{2}\(_{2}\)(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\) (Ln = Y, 3-Y; Dy, 3-Dy) were pursued by David H. Woen and were found to have N–N distances of 1.250(2) and 1.250(4) Å, respectively.

**Figure 3.3.** Thermal ellipsoid plot of \([(\text{C}_{5}\text{Me}_{4}\text{H})_{2}\text{Ln(THF)})\(_{2}\)(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\), 2-Ln [Ln = Gd (a), Dy (b)] drawn at the 30% probability level. Two (C\(_{5}\text{Me}_{4}\text{H})\) rings in 2-Gd (bottom) are disordered across two positions in which the rings look more like (C\(_{5}\text{Me}_{5})\) rings. Hydrogen atoms are omitted for clarity.

**Raman Spectroscopy.** Raman spectra were obtained for single crystals of several \([\text{A}_{2}\text{Ln(THF)})_{x}]_{2}(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\) (x = 0, 1) complexes, using a Renishaw Raman microscope. The metals and the ancillary ligands were varied to observe any possible trends in the degree of dinitrogen reduction. Single crystals were used to provide the closest comparison of stretching
frequency versus the N–N bond length in the crystal structure. This also provided an opportunity to analyze the uniformity of a single batch of crystals.

The most extensive analysis of uniformity was made by taking 320 Raman spectra across a grid of a single crystal of \([(C_5Me_4H)_2Gd(THF)](\mu-\eta^2:\eta^2-N_2), \textbf{2-Gd}\). Although the crystal appeared to be flat, a variation in intensity, shown in Figure 3.4, was observed which is related to the laser focus on the surface of the crystal. In all scans, however, the stretching frequency was either 1456 or 1457 cm\(^{-1}\). This suggests that the sample is uniformly the same complex across the crystal. This also suggests that one could focus on one section of a crystal with the microscope and use the spectrum as a representation of the entire crystal.

![Figure 3.4](image)

**Figure 3.4.** Comparison of the intensity of the N–N stretch across 320 Raman spectra of a single crystal of \([(C_5Me_4H)_2Gd(THF)](\mu-\eta^2:\eta^2-N_2), \textbf{2-Gd}\).

In another study of uniformity, it was noticed that pale blue crystals of \([(C_5H_4Me)_2(THF)]_3(\mu-\eta^2:\eta^2-N_2), \textbf{3-Y}\), had darker blue spots on the surface. When focusing on these dark blue spots, a spectra containing many Raman bands were be obtained. The intensity
of these multi-band spectra, changed depending on the size of the dark blue spot. When focusing away from the dark blue spots, a simple spectrum with one N–N stretch at 1454 cm\(^{-1}\) was observed. This suggests that Raman spectroscopy could be used as an additional source of confirming purity of crystalline samples. This would be particularly useful with paramagnetic samples.

The data on the 21 dinitrogen complexes are presented in Tables 3.2-3.6. As shown in Figure 3.5, there is no correlation between the N–N bond lengths and N–N Raman stretching frequencies. Each series of complexes is described individually in the following paragraphs.

![Figure 3.5](image-url)  

**Figure 3.5.** Comparison of N–N bond lengths and N–N Raman stretching frequencies for the complexes described in Tables 3.2-3.6.

\{(\text{Me}_3\text{Si})_2\text{N} \}_2\text{Ln(THF)} \{\mu-\eta^2: \eta^2-\text{N}_2\}, 4-\text{Ln}. The largest series of reduced dinitrogen complexes that was studied was the \{(\text{Me}_3\text{Si})_2\text{N} \}_2\text{Ln(THF)} \{\mu-\eta^2: \eta^2-\text{N}_2\}, 4-\text{Ln}\(^{5,7,8}\) compounds. Since these complexes have been reported for many of the lanthanides, they are valuable for searching for periodic trends. The Raman spectra for 4-\text{Ln} (Ln = Gd, Tb, Dy, Ho, Er and Tm), in
the range of 810-1950 cm\(^{-1}\), contain a single strong, well-defined band near 1400 cm\(^{-1}\), that is attributed to the symmetric N–N stretch. The stretching frequency decreases as the atomic number increases from 1432 cm\(^{-1}\) for 4-Gd to 1413 cm\(^{-1}\) for 4-Tm, as shown in Table 3.2 and Figure 3.6. These values are all within the 1580-1400 cm\(^{-1}\) range found for N=N double bonds. Although the crystal structure data for these compounds show no periodic trends in N-N distances, as shown in Figure 3.7, the Raman data indicate that dinitrogen activation increases as the ionic radius of the metal decreases, as shown in Figure 3.8. This also correlates with increasing Lewis acidity and atomic number.

Table 3.2. Crystal structure N–N bond lengths and N–N Raman stretching frequencies for 4-Ln.

<table>
<thead>
<tr>
<th></th>
<th>N–N bond length (Å)</th>
<th>N–N stretching frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Gd</td>
<td>1.278(4)</td>
<td>1432</td>
</tr>
<tr>
<td>4-Tb</td>
<td>1.271(4)</td>
<td>1428</td>
</tr>
<tr>
<td>4-Dy</td>
<td>1.305(6)</td>
<td>1425</td>
</tr>
<tr>
<td>4-Ho</td>
<td>1.264(4)</td>
<td>1421</td>
</tr>
<tr>
<td>4-Er</td>
<td>1.276(5)</td>
<td>1417</td>
</tr>
<tr>
<td>4-Tm</td>
<td>1.264(7)</td>
<td>1413</td>
</tr>
</tbody>
</table>
Figure 3.6. Normalized Raman spectra of 4-Ln (Ln = Gd, Tb, Dy, Ho, Er, Tm).

Figure 3.7. Plot of the N–N bond lengths of 4-Ln versus the 8-coordinate ionic radii.\textsuperscript{52}
Figure 3.8. Plot of the N–N Raman stretching frequencies of 4-Ln versus atomic number (a) and the 8-coordinate ionic radii (b).

Also included in Figure 3.8b are the Raman data on single crystals of 4-Y at 25 °C. This stretch at 1422 cm$^{-1}$, is similar to the previously reported spectrum of a powder sample at 5-10 °C with a stretch at 1425 cm$^{-1}$. The difference between these stretches is small and is likely due to the different temperatures at which the spectra were obtained. In any case, both values are between those of 4-Dy and 4-Ho, which fits for the trend of ionic radius, since the eight-coordinate ionic radius of yttrium (1.019 Å) is between those of dysprosium (1.027 Å) and holmium (1.019 Å).

\[
\begin{align*}
\text{y} & = -0.0714x^2 - 3.2714x + 1435.2 \\
R^2 & = 0.9991
\end{align*}
\]

[(C$_5$Me$_5$)$_2$Ln]$_2$(µ-η$^2$:η$^2$-N$_2$), 1-Ln. The data for the 1-Ln series is given in Table 3.3 and a plot of the Raman spectra is shown in Figure 3.9. Although the frequencies for 1-Tb, 1-Y, and 1-Lu follow the trend seen with the 4-Ln series, the stretch for 1-Gd is equivalent within experimental error with that of 1-Tb and the stretch of 1-Sm is close to that of a crystal of 1-Lu. Since X-ray crystallography was not done on the crystals of 1-Lu used for Raman spectroscopy, it is not clear which of those discussed above was examined. Although 1-Lu decomposed with exposure to the laser used for Raman spectroscopy, a crystalline sample revealed a reproducible
Raman shift of 1414 cm\(^{-1}\) that is assigned to the N–N stretch, Table 3.3. This is on the low end of the 1580-1400 cm\(^{-1}\) range found for N=N double bonds\(^{34}\) indicating reduction of dinitrogen has occurred. This is inconsistent with crystal structure with the short 1.111(5) Å N-N distance found for one of the 1-Lu crystals described above. This stretching frequency is close to that of 4-Tm, following the trend that complexes with the smaller metals have stronger activation of dinitrogen. The Raman shift for the yttrium analogue, 1-Y, was 1428 cm\(^{-1}\), suggesting the smaller, more Lewis acidic lutetium appears to stabilize a more reduced dinitrogen than yttrium. The Raman shifts for 1-Gd and 1-Tb are 1432 and 1433 cm\(^{-1}\), respectively. These shifts are similar to the similarly-sized yttrium analogue. Overall, the Raman data of 1-Ln follow the trend relative to the ionic radius of the metals, as observed for the 4-Ln complexes. However, this trend is not as regular for these 1-Ln complexes, which may be due to the fact that the Raman shift was only resolvable within ±1 cm\(^{-1}\) across different crystals and numerous spectra.

**Table 3.3.** Crystal structure N–N bond lengths and N–N Raman stretching frequencies for 1-Ln.

<table>
<thead>
<tr>
<th></th>
<th>N—N bond length (Å)</th>
<th>N–N stretching frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Lu</td>
<td>1.111(5)-1.242(11)</td>
<td>1414</td>
</tr>
<tr>
<td>1-Y</td>
<td>1.172(6)</td>
<td>1428</td>
</tr>
<tr>
<td>1-Tb</td>
<td>1.238(4)</td>
<td>1433</td>
</tr>
<tr>
<td>1-Gd</td>
<td>1.236(5)</td>
<td>1432</td>
</tr>
<tr>
<td>1-Sm</td>
<td>1.088(12)</td>
<td>1416</td>
</tr>
</tbody>
</table>
Figure 3.9. Normalized Raman spectra of 1-Ln (Ln = Sm, Gd, Tb, Y). The Raman spectrum for 1-Lu is not shown due to sensitivity to the laser that resulted in a poor baseline.

As described above, characterization of the degree of dinitrogen reduction in 1-Sm has been complicated since it is formed in equilibrium with (C₅Me₅)₂Sm and can not be easily separated. The single crystal Raman spectroscopy was perfectly suited for this issue. Therefore, the Raman spectrum was obtained for crystals of the (C₅Me₅)₂Sm and 1-Sm mixture, in which a strong Raman band was observed at 1416 cm⁻¹. This low stretching frequency is consistent with the NMR spectroscopic data for 1-Sm that suggest the complex contains two Sm³⁺ metals with a bridging (N₂)²⁻ unit. The Raman data do not match the extremely short N–N bond distance observed crystallographically. Since this stretch is lower in energy than that for 1-Gd, 1-Tb, and 1-Y, even though it has a much larger eight-coordinate Sm³⁺ ionic radius of 1.079 Å, it does not follow trends above that correlate ionic radius and stretching frequency. The low stretching frequency is consistent with significant reduction of N₂ in 1-Sm which is not consistent with the ready loss of N₂ in the equilibrium of eq 3.1.
\[(\text{C}_5\text{Me}_4\text{H})_2\text{Ln}(\text{THF})](\mu-\eta^2:\eta^2-\text{N}_2), \text{ 2-Ln}, \text{ and } [\text{(C}_5\text{H}_4\text{Me})_2(\text{THF})\text{Ln}](\mu-\eta^2:\eta^2-\text{N}_2), \text{ 3-Ln.} \] Since the Raman spectra for \[[\text{(C}_5\text{Me}_5\text{)}_2\text{Ln}](\mu-\eta^2:\eta^2-\text{N}_2), \text{ 1-Ln}, \text{ and } \{(\text{MeSi})_2\text{N}\}_2\text{Ln}(\text{THF})\] were quite similar for similar metals even with the different ligand environments, \[\text{[N(SiMe}_3\text{)]}_2\] and \[(\text{C}_5\text{Me}_5\text{)}_2\text{Ln}(\text{THF})\], it was of interest to determine if changes to the anionic ancillary ligands could alter the degree of dinitrogen reduction. Therefore, Raman spectra were explored for \text{2-Ln} and \text{3-Ln}, which use the less crowded and less electron donating donating\(^{53}\) \((\text{C}_5\text{Me}_4\text{H})_2\) and \((\text{C}_5\text{H}_4\text{Me})_2\) ligands, respectively.

As shown in Table 3.4 and Figure 3.10, \text{2-Nd}, \text{2-Gd}, and \text{2-Dy} have Raman bands at 1473, 1457, and 1454 cm\(^{-1}\), respectively, which are higher in energy than those for \text{1-Ln} and \text{2-Ln}. These values again decrease as the ionic radius decreases, analogous to the correlations with \text{1-Ln} and \text{4-Ln}. It is tempting, with these data, to claim that the higher N–N stretching frequencies for \text{2-Ln} are due to the less electron donating nature of the ligands in \text{2-Ln} versus the ligands in \text{1-Ln} and \text{4-Ln}. However, the Raman spectra of the even less electron donating ligands in \text{3-Ln} provided Raman bands near the same same energy as for \text{2-Ln}: 1454 cm\(^{-1}\) for \text{4-Y} and 1453 cm\(^{-1}\) for \text{3-Dy}. The comparison of the anionic ligand effect on the degree of dinitrogen reduction is further shown in Table 3.5.
Table 3.4. Crystal structure N–N bond lengths and N–N Raman stretching frequencies for 3-Ln and 3-Ln.

<table>
<thead>
<tr>
<th></th>
<th>N—N bond length (Å)</th>
<th>N–N stretching frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Nd</td>
<td>disordered</td>
<td>1473</td>
</tr>
<tr>
<td>2-Gd</td>
<td>1.247(3)</td>
<td>1457</td>
</tr>
<tr>
<td>2-Dy</td>
<td>1.243(7)</td>
<td>1454</td>
</tr>
<tr>
<td>3-Y</td>
<td>1.250(2)</td>
<td>1454</td>
</tr>
<tr>
<td>3-Dy</td>
<td>1.250(4)</td>
<td>1453</td>
</tr>
</tbody>
</table>

Figure 3.10. Normalized Raman spectra of [(C₅Me₄H)₂Ln(THF)](μ-η²:η²-N₂), (Ln = Nd, 2-Nd; Gd, 2-Gd; Dy, 2-Dy), and [(C₅H₄Me)₂(THF)Ln]₂ (μ-η²:η²-N₂), (Ln = Y, 3-Y; Dy, 3-Dy).
Table 3.5. Crystal structure N–N bond lengths and N–N Raman stretching frequencies for 1-Ln, 2-Ln, 3-Ln and 4-Ln (Ln = Y, Dy, Gd).

<table>
<thead>
<tr>
<th>[A₂Lu(THF)ₓ]₂(μ-η²:η²-N₂)</th>
<th>N–N stretching frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A, x)</td>
<td>Y</td>
</tr>
<tr>
<td>C₅Mes, 0</td>
<td>1428</td>
</tr>
<tr>
<td>N(SiMe₃)₂, 1</td>
<td>1422/1425</td>
</tr>
<tr>
<td>C₅Me₄H, 1</td>
<td>N/A</td>
</tr>
<tr>
<td>C₅H₄Me, 1</td>
<td>1454</td>
</tr>
</tbody>
</table>

{(Me₃Si)₂N]₂Y(L)}₂(μ-η²:η²-N₂) (L = DMAP, Ph₃PO, PhCN, Me₃NO, Py). The THF bound to the metal in 4-Y was varied in efforts to learn how to make better precursors to improve properties for the single molecule magnet, [K(18-crown-6)(THF)₂]

{(Me₃N)₂(THF)Tb]₂(μ-η²:η²-N₂), which displays hysteresis up to 14 K. New (N₂)²⁻ complexes were isolated with DMAP, Ph₃PO, PhCN, Me₃NO, and Py as the neutral donors. The Raman spectra were obtained for these complexes to determine the effects of neutral donors on the N₂ reduction. Like the similar N–N bond lengths of the six complexes, shown in Table 3.6 and Figure 3.11, the N–N Raman stretching frequencies are all very similar to each other, with values ranging from 1419-1428 cm⁻¹. The one outlier is the complex with Ph₃PO ligand, which displays an N–N stretch at 1410 cm⁻¹. This outlier is not the same outlier found in the crystal data: it is the Me₃NO complex that has the much shorter N–N distance than all the others.
Table 3.6. Crystal structure N–N bond lengths and N–N Raman stretching frequencies for \{[(Me_3Si)_2N]_2Y(L)]_2(\mu-\eta^2:\eta^2-N_2)\) (L = DMAP, Ph_3PO, PhCN, Me_3NO, Py).

<table>
<thead>
<tr>
<th>Neutral Ligand (L)</th>
<th>N–N bond length (Å)</th>
<th>N–N stretching frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>1.268(3)</td>
<td>1422/1425</td>
</tr>
<tr>
<td>Ph_3PO</td>
<td>1.262(2)</td>
<td>1410</td>
</tr>
<tr>
<td>DMAP</td>
<td>1.259(2)</td>
<td>1426</td>
</tr>
<tr>
<td>PhCN</td>
<td>1.258(2)</td>
<td>1426</td>
</tr>
<tr>
<td>Py</td>
<td>1.255(2)</td>
<td>1428</td>
</tr>
<tr>
<td>Me_3NO</td>
<td>1.198(3)</td>
<td>1419</td>
</tr>
</tbody>
</table>

Figure 3.11. Normalized Raman spectra of \{[(Me_3Si)_2N]_2Y(L)]_2(\mu-\eta^2:\eta^2-N_2)\) (L = DMAP, Ph_3PO, PhCN, Me_3NO, Py).
Discussion

X-ray crystallography of four crystals of [(C₅Me₅)₂Lu₂(μ-η²:η²-N₂)], 1-Lu, revealed that all contain different N–N bond lengths, two of which were shorter than the expected bond length for an (N₂)²⁻ species. The possibility that these short bond lengths arose from two Lu²⁺ metal centers with a bridging neutral dinitrogen seemed unlikely since there is only one reported example of Lu²⁺ and it is thermally unstable. Since this is the second complex to contain such a short bridging dinitrogen unit, the use of other spectroscopic methods was desirable to better describe the degree of dinitrogen reduction better.

As can be seen in Figure 3.5, there does not appear to be a correlation between the N–N bond lengths and N–N Raman stretching frequencies. Since there are several crystal structures that exhibit unlikely N–N bond lengths, the Raman spectroscopy appears to be the more preferred method of describing dinitrogen reduction in these complexes.

The Raman spectra of {[(Me₃Si)₂N]₂Ln(THF)}₂(μ-η²:η²-N₂), 4-Ln, (Ln = Gd, Tb, Dy, Ho, Er, Tm) describe a quadratic trend in the N–N Raman stretching frequencies, relative to the ionic radii of the metals, Figure 3.8. The quadratic relationship has been described in other correlations.⁵⁴,⁵⁵ The greatest amount of dinitrogen reduction reflected in the lowest N–N stretching frequencies is found with the smallest, most Lewis acidic metals. While the differences in N–N Raman stretching frequencies between lanthanides with similar radii are quite small (~4 cm⁻¹), the trend across the six metals above is consistent, suggesting this is a reliable trend. This general trend from metal to metal is also observed to some extent for other ligand sets such as [(C₅Me₅)₂Ln]₂(μ-η²:η²-N₂), 1-Ln, [(C₅Me₄H)₂Ln(THF)](μ-η²:η²-N₂), 2-Ln,
and \([(\text{CsH}_4\text{Me})_2(\text{THF})\text{Ln}]_2 (\mu-\eta^2:\eta^2-\text{N}_2), \textbf{3-Ln}, \) but there are exceptions with these complexes that suggest this is more complicated than suggested with the \textbf{4-Ln} complexes.

When comparing differences in dinitrogen reduction for the different anionic ligands, it was determined that the ligand environments of \([(\text{CsMe}_5)_2\text{Ln}]_2(\mu-\eta^2:\eta^2-\text{N}_2), \textbf{1-Ln}, \) and \{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ln(THF)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2), \textbf{4-Ln}, \) are very similar to each other with N–N Raman stretching frequencies near 1425 cm\(^{-1}\), while \([(\text{CsMe}_4\text{H})_2\text{Ln(THF)}](\mu-\eta^2:\eta^2-\text{N}_2), \textbf{2-Ln}, \) and \([(\text{CsH}_4\text{Me})_2(\text{THF})\text{Ln}]_2 (\mu-\eta^2:\eta^2-\text{N}_2), \textbf{3-Ln}, \) are also very similar to each other with N–N Raman stretching frequencies near 1455 cm\(^{-1}\). This could suggest that something other than the electron donating strength of the ligands might be responsible for the dinitrogen reduction observed.

Raman spectroscopy of the two complexes that had structures with unusually short N–N bond lengths, namely \textbf{1-Lu} and \textbf{1-Sm}, displayed sharp Raman bands near what is expected for an (N\(_2\))^2\(^{-}\) species. This supports the formal identification of these complexes as containing two Ln\(^{3+}\) metal centers with an (N\(_2\))^2\(^{-}\) bridging ligand.

Finally, changing the THF in \textbf{4-Y} to other Lewis bases, in \{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Y(L)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2) (\text{L} = \text{DMAP}, \text{Ph}_3\text{PO}, \text{PhCN}, \text{Me}_3\text{NO}, \text{Py}) allowed for the analysis of the effect neutral donors have on the degree of dinitrogen reduction. Raman spectra of these complexes suggested that the neutral donor has little effect on the N–N stretching frequencies. The one outlier appeared to be the Ph\(_3\)PO adduct with a noticeably smaller N–N stretching frequency than for the other adducts, which is interesting since the outlier in terms of N–N bond lengths was the Me\(_3\)NO adduct. The reasons for this are unclear.
Conclusion

Single crystal Raman spectroscopy has been explored for 21 rare earth reduced dinitrogen complexes. The technique has been shown to be consistent and reproducible, making Raman spectroscopy a reliable analytical tool for dinitrogen reduction for the rare earth metals. This tool has been able to clarify the formal assignment of the electron configuration of a bridging dinitrogen for structures with unusually short N–N distances as a reduced \((\text{N}_2)^2^-\). Since this assignment fits best for the structures discussed, it is suggested that Raman spectroscopy should be the preferred method to evaluating dinitrogen reduction in rare earth complexes.
Table 3.7. X-ray Data Collection Parameters of four crystals of 1-Lu.

<table>
<thead>
<tr>
<th></th>
<th>1-Lu</th>
<th>1-Lu(A)</th>
<th>1-Lu(B)</th>
<th>1-Lu(C)</th>
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<tr>
<td>formula</td>
<td>C₄₀H₆₀Lu₂N₂</td>
<td>C₄₀H₆₀Lu₂N₂</td>
<td>C₄₀H₆₀Lu₂N₂</td>
<td>C₄₀H₆₀Lu₂N₂</td>
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<tr>
<td>fw</td>
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<td>918.84</td>
<td>918.84</td>
<td>918.84</td>
</tr>
<tr>
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<td>88(2)</td>
<td>143(2)</td>
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<td>0.71073 Å</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>cryst syst</td>
<td>Triclinic</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>space group</td>
<td>P̅ 1</td>
<td>P̅ 4 2 1c</td>
<td>P̅ 4 2 1c</td>
<td>P̅ 4 2 1c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.6530(6)</td>
<td>14.4028(16)</td>
<td>14.3199(19)</td>
<td>14.317(3)</td>
</tr>
<tr>
<td>b (Å)</td>
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<td>14.4028(16)</td>
<td>14.3199(19)</td>
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<td>90</td>
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<td>β (deg)</td>
<td>78.1059(6)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
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<td>γ (deg)</td>
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<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>Z</td>
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<td>1.519</td>
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<td>4.902</td>
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<td>R1 (I &gt; 2σ(I))</td>
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<td>wR2 (all data)</td>
<td>0.0572</td>
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<td>0.0877</td>
</tr>
</tbody>
</table>

a Definitions: wR² = [∑[w(Fo² - Fc²)²]/∑[w(Fo²)]²]¹/²; R1 = ∑|Fo| - |Fc|/∑|Fo|.
Table 3.8. X-ray Data Collection Parameters of 1-Gd, 1-Tb, 2-Gd, and 2-Dy.

<table>
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<th></th>
<th>1-Gd</th>
<th>1-Tb</th>
<th>2-Gd</th>
<th>2-Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C₄₀H₆₀Gd₂N₂</td>
<td>C₄₀H₆₀Tb₂N₂</td>
<td>C₄₄H₆₈Gd₂N₂O₂ •2(C₇H₈)</td>
<td>C₄₄H₆₈Dy₂N₂O₂</td>
</tr>
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<td>886.74</td>
<td>1155.77</td>
<td>982.00</td>
</tr>
<tr>
<td>temp (K)</td>
<td>88(2)</td>
<td>88(2)</td>
<td>88(2)</td>
<td>133(2)</td>
</tr>
<tr>
<td>Wavelength</td>
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<td>0.71073 Å</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
</tr>
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<td>cryst syst</td>
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<td>Tetragonal</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P₄ 2₁c</td>
<td>P₄ 2₁c</td>
<td>C2/c</td>
<td>C2/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>14.4239(19)</td>
<td>14.4075(15)</td>
<td>15.2453(7)</td>
<td>15.7376(15)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.4239(19)</td>
<td>14.4075(15)</td>
<td>13.9938(6)</td>
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<tr>
<td>c (Å)</td>
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<td>19.627(2)</td>
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<td>Volume (Å³)</td>
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<td>4157.5(7)</td>
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<td>α (deg)</td>
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<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
<td>90</td>
<td>90</td>
<td>104.7734(4)</td>
<td>101.2185(11)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calc} (Mg/m³)</td>
<td>1.434</td>
<td>1.446</td>
<td>1.452</td>
<td>1.569</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>3.240</td>
<td>3.469</td>
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<td>3.603</td>
</tr>
<tr>
<td>R1 (I &gt; 2σ(I))</td>
<td>0.0169</td>
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<td>0.0316</td>
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<td>wR2 (all data)</td>
<td>0.0424</td>
<td>0.0377</td>
<td>0.0449</td>
<td>0.0790</td>
</tr>
</tbody>
</table>

*Definitions: wR2 = \left[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\right]^{1/2}; R1 = \sum|F_o| - |F_c|/\sum|F_o|.*

References

(40) SAINT Version 8.34a, Bruker AXS, Inc.; Madison, WI 2013.
CHAPTER 4

Differentiating Chemically Similar Lewis Acid Sites in Heterobimetallic Complexes: The Rare-Earth Bridged Hydride \((\text{C}_5\text{Me}_5)_2\text{Ln}(\mu-\text{H})_2\text{Ln'}(\text{C}_5\text{Me}_5)_2\) and Tuckover Hydride \((\text{C}_5\text{Me}_5)_2\text{Ln}(\mu-\text{H})(\mu-\eta^1: \eta^5-\text{CH}_2\text{C}_5\text{Me}_4)\text{Ln'}(\text{C}_5\text{Me}_5)\) Systems

Introduction

The chemistry of mixtures of Lewis acidic metals is a critical part of processes of practical importance such as catalysis\(^1-3\) and nuclear waste separation.\(^4\) For example, in Ziegler–Natta catalysis, successful polymerization systems depend on the “right” combination of an early-transition-metal catalyst with an alkylaluminum activator.\(^1-3\) These polymerizations have an inherent competition for ligands between the Lewis acidic Al\(^{3+}\) ion and the Ti\(^{n+}\), Zr\(^{n+}\), or rare-earth-metal ions (Ln\(^{3+}\)) that are present. In nuclear waste separation,\(^4\) the competition for ligands involves Lewis acidic lanthanide and actinide ions. Ions of similar size and charge need to be separated, and subtle differences in hard/soft interactions are often used to differentiate the Ln\(^{3+}\) and An\(^{n+}\) Lewis acids.\(^4-10\)

Despite the importance of these mixed-metal systems, relatively little information is available on the chemical competition of Lewis acids because of the challenges in studying mixtures of metal ions. The chemical similarity of the metal ions and their propensity to exchange and form disordered compounds instead of pure heterobimetallic complexes complicates the analysis of heterobimetallic chemistry.

\(^*\) Portions of this Chapter have been published: Fieser, M. E.; Mueller, T. J.; Ziller, J. W.; Evans, W. J. Organometallics 2014, 33, 3882.
In this Chapter, efforts to use $^1$H NMR spectroscopy to examine heterobimetallic chemistry involving complexes of Lewis acidic rare-earth-metal ions are described. Specifically, attempts were made to determine if systems could be defined in which competition between two similar metals could be studied by determining their relative preferences for one site over another in asymmetric heterobimetallic complexes. This would allow direct comparison of the competition between the metals in a single molecule. Precedent for this approach can be found in previously reported exchange studies of the symmetric heterometallic yttrium/lutetium$^{11,12}$ and homometallic yttrium$^{13}$ alkyl and hydride complexes oriented to explore monomer–dimer equilibria. However, each of these involved bimetallic molecules in which both metal positions were equivalent.

A surprising amount of information can be obtained by $^1$H NMR spectroscopy on complicated mixtures by using complexes of hydride ligands and the diamagnetic rare-earth ions La$^{3+}$, Y$^{3+}$, and Lu$^{3+}$.\textsuperscript{11-13} The $I = 1/2$ 100\% naturally abundant $^{89}$Y nucleus is a key component in this analysis due to the observable coupling to the hydride and methylene ligands. These three metals were chosen since they form similar complexes and make two size pairings: a Y/Lu combination that has metals of similar size (eight-coordinate Y$^{3+}$, 1.019 Å; Lu$^{3+}$, 0.977 Å) and La/Y and La/Lu combinations that have metals of much different sizes (eight-coordinate La$^{3+}$, 1.160 Å).\textsuperscript{14} Two combinations of metals with much different sizes were not required for this study, but the La/Lu combination provides a check on the La/Y chemistry and the yttrium coupling assignments.

Rare-earth metallocene hydrides are useful molecules for this study, since they are well-known to form Cp*$_2$Ln(H)$_2$LnCp*$_2$ (Cp* = C$_5$Me$_5$) bimetallic complexes of the type shown in eq

\[ \text{eq} \]
4.1 (Ln = yttrium, lanthanide).\textsuperscript{11-13,15-21} X-ray crystallographic data on the Sm\textsuperscript{3+} (eight-coordinate radius 1.079 Å)\textsuperscript{14} complex show a symmetrical dimer, 2A, although the hydride ligands were not located.\textsuperscript{15} In contrast, the analogous complex of the smaller Y\textsuperscript{3+} ion has an asymmetric structure in the solid state, 2B, with one formally eight-coordinate and one seven-coordinate metal site: Cp*\textsubscript{2}Y(µ-H)YHCp*\textsubscript{2}.\textsuperscript{17} With the smaller yttrium and the four large pentamethylcyclopentadienyl rings, formation of a doubly bridged structure such as 2A could be sterically disfavored.\textsuperscript{22} NMR studies suggest that the (Cp*\textsubscript{2}LnH)\textsubscript{2} complexes are dynamic in solution.\textsuperscript{18-21} For example, (Cp*\textsubscript{2}YH)\textsubscript{2} has a single broad hydride \textsuperscript{1}H NMR resonance at room temperature\textsuperscript{18} but displays a triplet at 288 K\textsuperscript{18,21} consistent with 2A, despite the observed 2B structure in the solid state.\textsuperscript{17} These dynamic complexes will be designated Cp*\textsubscript{2}Ln(H)\textsubscript{2}LnCp*\textsubscript{2}, with the understanding that they could be accessing structures 2A and 2B, as well as dissociated “Cp*\textsubscript{2}LnH” monometallic intermediates.

The homobimetallic Cp*\textsubscript{2}Ln(H)\textsubscript{2}LnCp*\textsubscript{2} hydrides (2; Ln = Y, lanthanide) are also well-known to engage in C–H bond activation of the methyl groups of (C\textsubscript{5}Me\textsubscript{3})\textsuperscript{−} ligands upon heating to make [CH\textsubscript{2}C\textsubscript{5}Me\textsubscript{4}]\textsuperscript{2−} dianions that can form “tuckover”\textsuperscript{16,18,23-27} bridges between the metals, as shown in eq 4.2. These bimetallic complexes have two different metal sites, one seven-coordinate and one eight-coordinate, and provide a basis for examining subtle differences between similar metals.
In this study, the reactions in both eqs 4.1 and 4.2 have been examined with three pairs of metals: Y/Lu, Y/La, and Lu/La. Density functional theory (DFT) has been used to investigate the underlying metal site preferences in these complexes. The results demonstrate how much information can be obtained experimentally on complicated mixtures of bimetallic complexes of similar metals and reveal the level of density functional theory that must be used to evaluate subtle differences between similar metals.

Experimental

The syntheses and manipulations described below were conducted under nitrogen with rigorous exclusion of air and water using glovebox, vacuum-line, and Schlenk techniques. Solvents were dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium potassium alloy, degassed by three freeze–pump–thaw cycles, and vacuum-transferred prior to use. Hydrated lanthanide trichlorides were desolvated according to the literature. Allylmagnesium chloride was purchased as a 2.0 M solution in THF from Aldrich and used as received. H2 (99.99%) was purchased from Praxair and used as received. KCp*,29 Cp*2Ln(η3-C5H5) [Ln = La, 1-La; Lu, 1-Lu; Y, 1-Y],30 and Cp*2Ln(µ-H)(µ-η1:η3-C5H5-C5Me4)LnCp* (Ln = La, 3-La/La;27 Lu, 3-Lu/Lu;24 Y, 3-Y/Y31) were prepared according to the literature. The Cp*2Ln(H)2LnCp*2 complexes (Ln = La, 2-La/La; Lu, 2-Lu/Lu; Y, 2-Y/Y) were prepared as previously described for Nd.32
spectra were obtained on a Bruker DRX500 MHz spectrometer with a BBO probe at 25 °C unless otherwise noted. $^{13}$C NMR spectra were obtained on a Bruker DRX500 MHz spectrometer with a TCI cryoprobe at 25 °C. IR samples were prepared as KBr pellets, and the spectra were obtained on a Varian 1000 FT-IR system. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS analyzer.

**Cp*$_2$Lu(H)$_2$LaCp*$_2$; 2-Lu/La.** 1-La (181 mg, 0.402 mmol) and 1-Lu (195 mg, 0.401 mmol) were combined and dissolved in pentane (20 mL) and placed in a sealable Schlenk flask fitted with a Teflon stopcock. The flask was attached to a high-vacuum line ($10^{-5}$ Torr), and the solution was degassed by three freeze–pump–thaw cycles. The solution was cooled to 0 °C and H$_2$ (1 atm) was introduced to the flask. After the mixture was stirred for 20 min, the flask was degassed to solvent pressure to remove the propene byproduct and H$_2$ (1 atm) was reintroduced into the flask. This evacuation and reintroduction of H$_2$ was performed three times, after which the flask was brought into a glovebox free from coordinating solvents. The pale yellow slurry was filtered through a medium frit, and the resulting powder was washed with a minimal amount of cold pentane (−35 °C). The solid was dried under reduced pressure to yield a single product, Cp*$_2$Lu(H)$_2$LaCp*$_2$ (2-Lu/La), as a pale yellow powder (217 mg, 63%). $^1$H NMR (C$_6$D$_{12}$): $\delta$ 8.67 (s, 2 H, $\mu$-H), 2.08 (s, 30 H, C$_5$Me$_5$), 1.99 (s, 30 H, C$_5$Me$_5$). $^{13}$C NMR (C$_6$D$_{12}$): $\delta$ 123.2 (s, C$_5$Me$_5$), 115.8 (s, C$_5$Me$_5$), 12.9 (s, C$_5$Me$_5$), 12.2 (s, C$_5$Me$_5$). IR: 2973 s, 2902 s, 2856 s, 2723 m, 1639 w, 1493 m, 1438 s, 1389 m, 1379 s, 1277 s, 1168 m, 1060 w, 1020 m, 925 s, 802 w, 714 m, 649 s, 615 w, 593 m, 575 m cm$^{-1}$. Anal. Calcd for C$_{40}$H$_{62}$LaLu: C, 56.07; H, 7.29. Found: C, 56.22; H, 7.60.
Cp*₂Y(H)₂LaCp*₂, 2-Y/La. Following the procedure as described for 2-Lu/La above, a single product, Cp*₂Y(H)₂LaCp*₂ (2-Y/La), was isolated as a pale yellow powder (321 mg, 64%) from the reaction of equimolar amounts of 1-La (291 mg, 0.646 mmol) and 1-Y (259 mg, 0.647 mmol) with excess H₂ (1 atm) in pentane (20 mL). ¹H NMR (C₆D₁₂): δ 6.79 (d, ¹J_YH = 37 Hz, 2 H, µ-H), 2.06 (s, 30 H, C₅Me₅), 1.98 (s, 30 H, C₅Me₅). ¹³C NMR (C₆D₁₂): δ 122.8 (s, C₅Me₅), 116.6 (s, C₅Me₅), 12.8 (s, C₅Me₅), 12.1 (s, C₅Me₅). IR: 2970 s, 2902 s, 2856 s, 2724 m, 2360 w, 2343 w, 1492 m, 1438 s, 1379 s, 1238 s, 1061 w, 1020 m, 949 s, 802 w, 718 m, 621 s, 605 s, 591 s, 573 s cm⁻¹. Anal. Calcd for C₄₀H₆₂LaY: C, 62.33; H, 8.11. Found: C, 61.92; H, 8.20.

Cp*₂Lu(µ-H)(µ-η¹:η⁵-CH₂C₅Me₄)LaCp*, 3-Lu/La. Pale yellow Cp*₂Lu(H)₂LaCp*₂ (2-Lu/La; 279 mg, 0.326 mmol) was placed in a 2.5 cm × 40 cm tube fitted with a Teflon stopcock and attached to a high-vacuum line (10⁻⁵ Torr). The sample was heated to 130 °C for 48 h, after which a single product, 3-Lu/La, was isolated as a red-orange powder (275 mg, 99%). X-ray-quality crystals of 3-Lu/La were grown from a concentrated C₆D₁₂ solution. ¹H NMR (C₆D₁₂): δ 8.09 (s, 1 H, µ-H), 2.02 (s, 30 H, C₅Me₅), 2.01 (s, 15 H, C₅Me₅), 1.98 (s, 6 H, C₅Me₄CH₂), 1.86 (s, 6 H, C₅Me₄CH₂), 0.35 (s, 2 H, CH₂). ¹H NMR (C₆D₆): δ 8.19 (s, 1 H, µ-H), 2.07 (s, 30 H, C₅Me₅), 2.04 (s, 15 H, C₅Me₅), 2.03 (s, 6 H, C₅Me₄CH₂), 1.95 (s, 6 H, C₅Me₄CH₂), 0.61 (s, 2 H, CH₂). ¹³C NMR (C₆D₆): δ 122.3 (s, C₅Me₅), 120.3 (s, C₅Me₅), 119.0 (s, C₅Me₅), 116.6 (s, C₅Me₅), 116.4 (s, C₅Me₅), 41.7 (s, C₅Me₄CH₂), 13.5 (s, C₅Me₄CH₂), 12.7 (s, C₅Me₅), 12.3 (s, C₅Me₄CH₂), 11.8 (s, C₅Me₅). IR: 2965 m, 2904 s, 2857 s, 2724 w, 1494 w, 1439 m, 1379 m, 1213 m, 1163 m, 1060 w, 1021 w, 1004 w, 929 m, 879 w, 802 w, 625 w, 607 m, 594 m, 570 m cm⁻¹.
**Cp*₂Y(μ-H)(μ-η¹:η²-C₅Me₅)LaCp*, 3-Y/La.** Following the procedure for 3-Lu/La, red-orange 3-Y/La (242 mg, 97%) was isolated from pale yellow Cp*₂Y(H)₂LaCp*₂ (2-Y/La; 249 mg, 0.323 mmol). ¹H NMR (C₆D₁₂): δ 6.52 (d, J_YH = 40 Hz, 1 H, μ-H), 2.01 (s, 15 H, C₅Me₅), 2.00 (s, 30 H, C₅Me₅), 1.98 (s, 6 H, C₅Me₅CH₂), 1.76 (s, 6 H, C₅Me₅CH₂), 0.36 (d, J_YH = 2 Hz, 2 H, CH₂). ¹H NMR (C₆D₆): δ 6.64 (d, J_YH = 40 Hz, 1 H, μ-H), 2.06 (s, 15 H, C₅Me₅), 2.05 (s, 30 H, C₅Me₅), 2.03 (s, 6 H, C₅Me₅CH₂), 1.85 (s, 6 H, C₅Me₅CH₂), 0.60 (d, J_YH = 2 Hz, 2 H, CH₂). ¹³C NMR (C₆D₆): δ 122.2 (s, C₅Me₅), 120.3 (s, C₅Me₅), 119.0 (s, C₅Me₅), 117.0 (s, C₅Me₅), 115.9 (s, C₅Me₅), 41.7 (d, J_YC = 23 Hz, C₅Me₅CH₂), 13.3 (s, C₅Me₅CH₂), 12.6 (s, C₅Me₅), 12.3 (s, C₅Me₅CH₂), 11.8 (s, C₅Me₅). IR: 2963 m, 2904 s, 2857 s, 2724 w, 1496 w, 1438 s, 1379 m, 1158 s, 1061 w, 1021 m, 948 w, 914 s, 860 m, 812 w, 589 s, 570 s cm⁻¹. Anal. Calcd for C₄₀H₆₀LaY: C, 62.50; H, 7.87. Found: C, 62.52; H, 7.72.

**Cp*₂Y(μ-SPh)_2LaCp*(μ-SPh)_2LaCp*(μ-SPh)_2YCp*₂, 4-Y/La.** A solution of PhSSPh (13 mg, 0.060 mmol) in C₆H₆ (3 mL) was added dropwise to a stirred solution of 3-Y/La (32 mg, 0.042 mmol) in C₆H₆ (8 mL). The red solution quickly turned yellow and the mixture was stirred for 2 h. Solvent was removed under reduced pressure to produce a yellow tacky solid. ¹H NMR showed several new C₅Me₅ resonances. X-ray quality crystals of 4-Y/La were grown from a concentrated C₆D₆ solution.

**X-ray Data Collection, Structure Solution and Refinement for 3-Lu/La.** An orange crystal of approximate dimensions 0.063 x 0.074 x 0.236 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2³² program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT³³ and SADABS³⁴ to
yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{35} program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group P1 was assigned and later determined to be correct. The structure was solved by direct methods and refined on F\textsuperscript{2} by full-matrix least-squares techniques.\textsuperscript{36} The analytical scattering factors for neutral atoms were used throughout the analysis. The bridging hydride was located from a difference-Fourier map and refined (x,y,z and U\textsubscript{iso}). All other hydrogen atoms were included using a riding model. Carbon atoms C\textsubscript{11} through C\textsubscript{20} were disordered and were included using multiple components, partial site occupancy-factors, and isotropic thermal parameters. Least-squares analysis yielded wR\textsubscript{2} = 0.1633 and Goof = 1.035 for 397 variables refined against 7409 data (0.80Å), R1 = 0.0595 for those 5788 data with I > 2.0σ(I). Details are given in Table 4.4.

\textbf{X-ray Data Collection, Structure Solution and Refinement for 4-Y/La.} A colorless crystal of approximate dimensions 0.135 x 0.186 x 0.548 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX\textsuperscript{2} program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\textsuperscript{39} and SADABS\textsuperscript{40} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{41} program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group P\textbar1 was assigned and later determined to be correct. The structure was solved by direct methods and refined on F\textsuperscript{2} by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located
about an inversion center. There were two molecules of benzene solvent present. At convergence, \( wR^2 = 0.0649 \) and Goof = 1.054 for 547 variables refined against 11564 data (0.74Å), \( R_1 = 0.0274 \) for those 10317 data with \( I > 2.0\sigma(I) \). Details are given in Table 4.4.

**Computational Details.** Structural optimizations for each pair of metals were performed from the known crystal structures of \( 3\text{-La/La}, 3\text{-Lu/Lu}, 3\text{-Lu/La}, \) and \( 3\text{-Y/Lu:Lu/Y} \). Three pairs of metals (Y/Lu, La/Lu, and La/Y) were examined with the metals in each of the two positions for each of the four structures resulting in 24 total converged structures. Since many of the structures were not isolated, these four crystal structures served as a starting point to find the lowest energy optimization. The initial optimizations for each structure were performed for all metal combinations using the TPSSh\(^{42}\) hybrid meta-GGA functional. Split valence basis sets with polarization functions on non-hydrogen atoms [def2-SV(P)]\(^{43}\) were used for light atoms and triple-zeta valence basis sets with two sets of polarization functions (def2-TZVP)\(^{44}\) as well as relativistic small-core pseudopotentials\(^{41}\) for Y, La and Lu. TPSSh was chosen due to its established performance for transition metal and lanthanide compounds\(^{46-51}\). The four converged structures for each metal combination were very similar, having less than 0.02 Å differences. For each metal combination, the converged structure with the lowest energy was used for further optimizations.

Vibrational frequencies were computed at the TPSSh/def2-SV(P) level, and the lowest energy structures were confirmed to be minima by the absence of imaginary modes. Further optimizations using larger triple-zeta valence basis sets (def2-TZVP)\(^{44}\) for all atoms were then performed using the TPSSh,\(^{42}\) TPSS\(^{52}\) and B3-LYP\(^{53,54}\) functionals. The differences in bond lengths between the def2-SV(P) and the TZVP structures with the TPSSh functional were
typically 0.05 Å or less. Fine quadrature grids (size m4) were used throughout. SCF energies and density matrices were converged to $10^{-7}$ a.u. All computations were performed using the TURBOMOLE program package. The total energies of these converged structures show the same trends in the predicted ground state isomer with the different functionals. For the Lu/Y combination, the lowest energy isomer is predicted to be 3-Lu/Y, analogous to experimental observation of a 2:1 ratio of 3-Lu/Y to 3-Y/Lu. However, the lowest energy isomers predicted for Y/La and Lu/La are opposite to what is observed experimentally, in which 3-La/Y and 3-La/Lu are lower in energy than 3-Y/La and 3-Lu/La, respectively. Given the similarity in the different isomers, non-bonded interactions are likely to play a role in determining the energy differences of these structures, so a dispersion correction was added to the semi-local functionals to account for some of the missing physics.

Grimme’s empirical dispersion correction was added to the converged TPSS and B3-LYP TZVP total energies, resulting in a reordering of the most stable isomers. With the dispersion correction the experimentally isolated isomers, 3-Y/La and 3-Lu/La, were predicted to be the lowest energy structures. However, the calculated stabilization was too large for the Lu/Y combination and indicated a 2 kcal/mol lower energy for the Lu/Y isomer compared to the Y/Lu isomer. This result is inconsistent with the experimental isolation of both isomers, so higher level calculations were performed by Jefferson Bates for additional comparison.

Results

Lutetium/Yttrium Heterobimetallic Hydride Complexes, $\text{Cp}^*\text{Ln(H)}_2\text{Ln'}\text{Cp}^*\text{Ln/Ln'}$ and $\text{Cp}^*\text{Ln(η}^3\text{-C}_3\text{H}_5)$ Pre-cursors. The formation of heterobimetallic rare-earth
metallocene complexes was initially investigated by examining hydrogenolysis of mixtures of the lanthanide allyl complexes Cp*\textsubscript{2}Ln(\eta\textsuperscript{3}-C\textsubscript{3}H\textsubscript{5}), 1, which yield Cp*\textsubscript{2}Ln(H)\textsubscript{2}LnCp*, 2, according to eq 4.1. The reaction of hydrogen with equimolar amounts of Cp*\textsubscript{2}Lu(\eta\textsuperscript{3}-C\textsubscript{3}H\textsubscript{5}), 1-Lu, and Cp*\textsubscript{2}Y(\eta\textsuperscript{3}-C\textsubscript{3}H\textsubscript{5}), 1-Y, yielded a pale yellow powder that contained a mixture of three variations of complex 2: the heterobimetallic Cp*\textsubscript{2}Lu(H)\textsubscript{2}YCp*, 2-Lu/Y, and the previously characterized homobimetallic complexes Cp*\textsubscript{2}Lu(H)\textsubscript{2}LuCp*, 2-Lu/Lu\textsuperscript{20,58} and Cp*\textsubscript{2}Y(H)\textsubscript{2}YCp*, 2-Y/Y\textsuperscript{18}. An 86:10:4 ratio, respectively, was observed on the basis of \textsuperscript{1}H NMR spectroscopy, eq 4.3. Given the similar sizes of yttrium and lutetium, formation of a mixture of all possible combinations was not unexpected. Due to the similar solubilities and reactivities of these complexes, heterobimetallic 2-Lu/Y could not be separated from 2-Lu/Lu and 2-Y/Y.

\[
\text{Cp*}_{2}\text{LuH}_{2}\text{LuCp*}_{2} \quad 2\text{-Lu/Lu} \\
\text{Cp*}_{2}\text{YH}_{2}\text{YCp*}_{2} \quad 2\text{-Y/Y} \quad (4.3)
\]

Although there was overlap of the resonances in the C\textsubscript{5}Me\textsubscript{5} region of the \textsuperscript{1}H NMR spectrum (2.0–2.2 ppm), there are three broad resonances in the room temperature \textsuperscript{1}H NMR spectrum assignable to hydride ligands. Two of these match the literature values for the known homobimetallic complexes 2-Lu/Lu (9.10 ppm\textsuperscript{20,58} and 2-Y/Y (5.45 ppm).\textsuperscript{18} The third resonance at 8.01 ppm (\Delta \nu \textsubscript{1/2} = 72 Hz) was tentatively assigned to the heterobimetallic 2-Lu/Y. Variable-temperature NMR studies confirmed these assignments. In methylcyclohexane-d\textsubscript{14}
(C\textsubscript{7}D\textsubscript{14}) at 253 K, the hydride resonance attributed to 2-Y/Y becomes a triplet\textsuperscript{18} and the hydride resonance attributed to 2-Lu/Lu remained unchanged. The broad hydride resonance attributed to 2-Lu/Y becomes a doublet (7.79 ppm, $^{1}J_{\text{YH}}$ = 26 Hz) due to coupling to one yttrium metal (I = 1/2 for $^{89}$Y).

**Lutetium/Lanthanum and Lutetium/Yttrium Heterobimetallic Hydride Complexes from Cp*\textsubscript{2}Ln(\eta\textsuperscript{3}-C\textsubscript{3}H\textsubscript{5}) Precursors.** In contrast to the reaction in eq 4.3 involving metals of similar size, hydrogenolysis of equimolar amounts of 1-Lu and an allyl complex of the largest lanthanide, Cp*\textsubscript{2}La(\eta\textsuperscript{3}-C\textsubscript{3}H\textsubscript{5}), 1-La, forms a single product formulated as Cp*\textsubscript{2}Lu(H)\textsubscript{2}LaCp*\textsubscript{2}, 2-Lu/La, eq 4.4. This complex displayed a single hydride resonance at 8.67 ppm with no evidence of the homobimetallic hydride complexes 2-Lu/Lu and 2-La/La.\textsuperscript{20,58} The analogous reaction of the allyl complexes 1-La and 1-Y with H\textsubscript{2} also formed a single product with a single hydride resonance at 6.79 ppm split into a doublet ($^{1}J_{\text{YH}}$ = 37 Hz) that was formulated as Cp*\textsubscript{2}Y(H)\textsubscript{2}LaCp*\textsubscript{2}, 2-Y/La, eq 4.4.

\[
\text{Cp*}2\text{Lu(}\eta3\text{-C3H5}) + \text{Y}2 \xrightarrow{\text{H2}} \text{Cp*}2\text{Y(H)2LaCp*2} \]

Crystallographic studies of both 2-Lu/La and 2-Y/La revealed a symmetrical arrangement of [Cp*\textsubscript{2}Ln]\textsuperscript{+} metallocene units like that found in [Cp*\textsubscript{2}SmH]\textsubscript{2},\textsuperscript{15} which is consistent with the formation of Cp*\textsubscript{2}Ln(H)\textsubscript{2}LaCp*\textsubscript{2} (Ln = Lu, 2-Lu/La; Y, 2-Y/La). However, due to the disorder in the positions of the metal atoms and the inability to locate the bridging hydride ligands, no additional information was obtainable from the crystallographic data.
The heterobimetallic product 2-Y/La can also be formed by mixing the homobimetallic hydrides 2-La/La and 2-Y/Y in solution. This reaction gives exclusively the heterobimetallic 2-Y/La and is consistent with the formation of a single heterobimetallic product in each reaction in eq 4.4. In these reactions with metals of disparate size and with this ligand set, the heterobimetallic complexes are evidently preferred to the homobimetallic compounds.

**Lutetium/Yttrium Heterobimetallic Tuckover Hydride Complexes, Cp*₂Ln(μ-H)(μ-η^1:η^5-CH₂C₅Me₄)Ln'Cp* (3-Ln/Ln'), from Homobimetallic and Heterobimetallic Hydride Precursors 2-Ln/Ln and 2-Ln/Ln'**. Since the heterobimetallic yttrium/lutetium hydride complex Cp*₂Lu(H)₂YCp*, 2-Lu/Y, could not be separated from the homobimetallic hydride complexes Cp*₂Lu(H)₂LuCp*₂ (2-Lu/Lu) and Cp*₂Y(H)₂YCp*₂ (2-Y/Y), conversion of 2-Lu/Y, 2-Lu/Lu, and 2-Y/Y to a more manageable mixture was attempted. The C–H bond activation reaction of the hydride complexes to form the tuckover hydride complexes Cp*₂Ln(μ-H)(μ-η^1:η^5-CH₂C₅Me₄)Ln'Cp*, 3, according to eq 4.2 was examined in this regard. The mixture of 2-Lu/Y, 2-Lu/Lu, and 2-Y/Y in the ratio 86:10:4 described above was heated in methylecyclohexane to reflux (101 °C) for 5 min to effect the C–H bond activation, and the crude product mixture was recrystallized from methylecyclohexane.

\(^1\)H NMR spectroscopy of the isolated crystalline material showed resonances for four unique variations of complex 3: Cp*₂Y(μ-H)(μ-η^1:η^5-CH₂C₅Me₄)LuCp*, 3-Y/Lu, Cp*₂Lu(μ-H)(μ-η^1:η^5-CH₂C₅Me₄)Cp*, 3-Lu/Y, Cp*₂Lu(μ-H)(μ-η^1:η^5-CH₂C₅Me₄)LuCp*, 3-Lu/Lu, and Cp*₂Y(μ-H)(μ-η^1:η^5-CH₂C₅Me₄)YCp*, 3-Y/Y, eq 4.5. The fact that four variants of 3 are isolated from the three variants of 2 reflects the fact that the two metal positions in 3 are not equivalent. Hence, the order of the metals in these 3-Ln/Ln' descriptors has significance. The
first metal cited is the formally eight-coordinate metal ligated by two \((\eta^5\text{-Cp}^*)\)^{1–} rings, a hydride, and the alkyl portion of the \((\mu-\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)^{2–}\) ligand. This is also labeled Ln\(^1\) in the NMR discussion below. The second metal in 3-Ln/Ln' is the seven-coordinate metal ligated by one \((\eta^5\text{-Cp}^*)\)^{1–} ring, a hydride, and the cyclopentadienyl portion of the \((\mu-\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)^{2–}\) ligand. It is labeled Ln\(^2\).

Although there was significant overlap of resonances in the C\(_5\)Me\(_5\) region of the \(^1\)H NMR spectrum (1.8–2.1 ppm), the four products in eq 4.5 could be definitively identified by making assignments based upon the bridging hydride region of the spectrum using the coupling from yttrium, Figure 4.1. Specifically, the homobimetallic lutetium complex, 3-Lu/Lu, displays a single resonance for the bridging hydride ligand at 6.77 ppm while the homobimetallic yttrium complex, 3-Y/Y, displays a doublet of doublets for the bridging hydride ligand at 3.69 ppm (\(^1\)J\(_{\text{YH}}\) = 29 and 48 Hz), due to splitting by the two unique yttrium metal centers.\(^{18}\) The 29 Hz coupling can be assigned to Y\(^1\) and the 48 Hz coupling to Y\(^2\) (Figure 4.2) if the bridging hydride has a stronger interaction with Y\(^2\), which is bound to only two other anionic ligands [i.e., two (C\(_5\)R\(_5\))\(^{1–}\)] than to Y\(^1\), which is bound to three other anionic ligands [two (C\(_\text{p}^*\))\(^{1–}\) and one (CH\(_2\))\(^{1–}\)]. This
assignment would also give the stronger coupling to the Y² center that is closest to the bridging hydride in the X-ray crystal structure of 3-Y/Y.¹⁸

Figure 4.1. Selected region of the 1H NMR spectrum of the yttrium/lutetium tuckover hydride mixture, showing resonances and coupling constants (¹J_YH in Hz) for the bridging hydride ligands in: (1) Cp*₂Y(μ-H)(μ-η¹:η⁵-CH₂C₅Me₄)LuCp*, 3-Y/Lu; (2) Cp*₂Lu(μ-H)(μ-η¹:η⁵-CH₂C₅Me₄)YCp*, 3-Lu/Y; (3) Cp*₂Lu(μ-H)(μ-η¹:η⁵-CH₂C₅Me₄)LuCp*, 3-Lu/Lu; (4) Cp*₂Y(μ-H)(μ-η¹:η⁵-CH₂C₅Me₄)YCp*, 3-Y/Y.
Figure 4.2. $^1$H NMR coupling constants ($^1J_{YH}$) for the tuckover complexes $\text{Cp}^*\text{Y}(\mu\text{-H})(\mu-\eta^5:\eta^1:\eta^5-\text{CH}_2\text{C}_5\text{Me}_4)\text{LuCp}^*$, 3-Y/Lu, $\text{Cp}^*\text{Lu}(\mu\text{-H})(\mu-\eta^1:\eta^5-\text{CH}_2\text{C}_5\text{Me}_4)\text{YCP}^*$, 3-Lu/Y, and $\text{Cp}^*\text{Y}(\mu\text{-H})(\mu-\eta^1:\eta^5-\text{CH}_2\text{C}_5\text{Me}_4)\text{YCP}^*$, 3-Y/Y.

Using the assumption of small coupling to a Ln$^1$ center and stronger coupling to Ln$^2$, the doublets observed at 5.42 ppm ($^1J_{YH} = 28$ Hz) and 5.21 ppm ($^1J_{YH} = 47$ Hz) can be assigned to the heterobimetallic complexes, 3-Y/Lu and 3-Lu/Y, respectively. A 17:37:19:27 3-Y/Lu:3-Lu/Y:3-Lu/Lu:3-Y/Y ratio was observed by 1H NMR spectroscopy. This ratio of variations of 3 is similar to the ratio observed from ligand redistribution of the homobimetallic complexes 3-Lu/Lu and 3-Y/Y: namely, 16:32:26:22.

X-ray diffraction data were obtained on crystals that formed from heating the mixture of 2-Y/Lu, 2-Lu/Lu, and 2-Y/Y to determine what, if any, information could be obtained in the solid state about this mixture. The data revealed a single structure of formula $\text{Cp}^*\text{Ln}(\mu\text{-H})(\mu-\eta^1:\eta^5-\text{CH}_2\text{C}_5\text{Me}_4)\text{Ln}^\prime\text{Cp}^*$ with disorder at the metal sites; therefore, it will be designated 3-Y/Lu:Lu/Y.

The structure is similar to that of the homobimetallic tuck-over hydride complexes $\text{Cp}^*\text{Ln}(\mu\text{-H})(\mu-\eta^1:\eta^5-\text{CH}_2\text{C}_5\text{Me}_4)\text{LnCp}^*$ (Ln = La,$^{27}$ Sm,$^{16}$ Y,$^{18}$ Lu,$^{24}$), which have been previously characterized by X-ray crystallography. However, 3-Y/Lu:Lu/Y is not isomorphous.
with any of the homobimetallic La, Sm, Y, or Lu analogues. The structural data on 3-Y/Lu:Lu:Y were modeled with a mixture of each metal, lutetium and yttrium, at each of the two unique metal positions in the crystal structure. A model with site occupancy factors of 40/60 for Lu1/Y1 and 60/40 for Lu2/Y2 best fits the data. The 2.579(3) Å Ln2–C(6) bond distance in 3-Y/Lu:Lu:Y is between the 2.556(5) and 2.628(7) Å Ln–C(6) bond distances in the homobimetallic structures 3-Lu/Lu and 3-Y/Y, respectively, Table 4.1. The structure of 3-Y/Lu:Lu/Y also displays a short contact (2.848(3) Å) between Ln1 and C(26). Similar short contacts are observed in 3-Lu/Lu and 3-Y/Y (2.815(5) and 2.846(7) Å, respectively). The similarities of the Ln2–C(6) and Ln1–C(26) distances in 3-Y/Lu:Lu/Y with those in 3-Lu/Lu and 3-Y/Y are consistent with 3-Y/Lu:Lu/Y containing cocry stallized 3-Y/Lu, 3-Lu/Y, 3-Lu/Lu, and 3-Y/Y, as suggested by 1H NMR spectroscopy above. The 17:37:19:27 3-Y/Lu:3-Lu/Y:3-Lu/Lu:3-Y/Y ratio, observed by 1H NMR spectroscopy, would yield a metal distribution of 36/64 for Lu1/Y1 and 56/44 for Lu2/Y2. These values are similar to the metal disorder assignments in the model for the data.

Table 4.1. Selected Bond Distances (Å) for Cp*₂Ln(μ-H)(μ-η¹:η⁵-Ch₂C₅Me₅)LnCp* (Ln = La, Sm, Y, Lu, Lu/Ya, Lu/La) and Their 8-Coordinate M³⁺ Ionic Shannon Radii (Å).

<table>
<thead>
<tr>
<th></th>
<th>La</th>
<th>Sm</th>
<th>Y</th>
<th>Lu</th>
<th>3-Y/Lu:Lu/Y</th>
<th>3-Lu/La</th>
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<tr>
<td>M³⁺ ionic radius</td>
<td>1.160</td>
<td>1.079</td>
<td>1.019</td>
<td>0.977</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ln–C(6)</td>
<td>2.723(5)</td>
<td>2.628(7)</td>
<td>2.631(7)</td>
<td>2.556(5)</td>
<td>2.579(3)</td>
<td>2.622(12)</td>
</tr>
<tr>
<td>Ln–C(26)</td>
<td>3.614(5)</td>
<td>3.900(7)</td>
<td>2.846(7)</td>
<td>2.815(5)</td>
<td>2.848(3)</td>
<td>3.432(16)</td>
</tr>
</tbody>
</table>
Lu/La and Y/La Heterobimetallic Tuckover Hydride Complexes \( \text{Cp}^* \text{Ln} (\mu-H) (\mu-\eta^1:\eta^5-\text{C}_5\text{Me}_4) \text{Ln'Cp}^* \) (3-Ln/Ln'). In contrast to the rapid conversion of the mixture of lutetium/yttrium hydrides to a mixture of tuckover hydrides, eq 4.5, which occurs within 5 min in refluxing methylcyclohexane, the lutetium/lanthanum hydride complex \( \text{Cp}^* \text{Lu(H)}_2 \text{LaCp}^* \), 2-Lu/La, did not form a tuckover complex under similar reaction conditions. Even at reflux in methylcyclohexane for 24 h, no conversion of 2-Lu/La to a tuckover hydride, 3, was observed. However, 2-Lu/La could be converted to a tuckover hydride product in quantitative yield when it was heated to 130 °C under vacuum (10\(^{-6}\) Torr) for 2 days. \(^1\)H NMR spectroscopy showed only one resonance for a bridging hydride (8.09 ppm) in the product and one resonance for methylene protons (0.35 ppm), indicating that the \((\text{C}_5\text{Me}_4\text{CH})_2^2\) ligand only “tucked over” to one metal. No evidence was observed for the homobimetallic tuckover complexes \( \text{Cp}^* \text{La(\mu-H)} (\mu-\eta^1:\eta^5-\text{C}_5\text{Me}_4) \text{LaCp}^* \), 3-La/La,

\(^{27}\) and \( \text{Cp}^* \text{Lu(\mu-H)} (\mu-\eta^1:\eta^5-\text{C}_5\text{Me}_4) \text{LuCp}^* \), 3-Lu/Lu.

This suggested that the isolated product is a heterobimetallic tuckover complex.

X-ray diffraction data obtained on crystals formed from this reaction revealed the complex \( \text{Cp}^* \text{Lu(\mu-H)} (\mu-\eta^1:\eta^5-\text{C}_5\text{Me}_4) \text{LaCp}^* \), 3-Lu/La, eq 4.6, Figure 4.3. The structure is isomorphous with the Sm homobimetallic tuckover hydride complex \( \text{Cp}^* \text{Sm(\mu-H)} (\mu-\eta^1:\eta^5-\text{C}_5\text{Me}_4) \text{SmCp}^* \), 3-Sm/Sm.

\(^{16}\) The different metal centers occupy specific locations in which the smaller metal, Lu, is found in the eight-coordinate position, while the larger metal, La, is seven-coordinate. On the basis of metal size, the larger metal would have been expected to occupy the eight-coordinate site. The structure of 3-Lu/La shows a 2.622(12) Å Lu–C(6) bond distance, which is between the 2.556(5) and 2.723(5) Å Ln–C(6) bond distances in the homobimetallic structures 3-Lu/Lu and 3-La/La, respectively, Table 4.1. The Ln–C(26) bond
length of 3.432(16) Å is also between the 2.815(5) and 3.614(5) Å bond lengths in 3-Lu/Lu and 3-La/La, respectively.

**Figure 4.3.** Thermal ellipsoid plot of Cp*$_2$Lu(µ-H)(µ-η$^1$:η$^5$-CH$_2$C$_5$Me$_4$)LaCp*, 3-Lu/La, drawn at the 30% probability level. Hydrogen atoms, except H1, and the carbon atoms from a disordered C$_5$Me$_5$ group have been omitted for clarity.

Analogous results were observed upon heating the heterobimetallic yttrium/lanthanum hydride complex Cp*$_2$Y(H)$_2$LaCp*, 2-Y/La. Heating 2-Y/La to 130 °C under high vacuum for 2 days quantitatively forms a product that has a $^1$H NMR spectrum that can be assigned to Cp*$_2$Y(µ-H)(µ-η$^1$:η$^5$-CH$_2$C$_5$Me$_4$)LaCp*, 3-Y/La, eq 4.6. The $^1$H NMR spectrum of 3-Y/La
showed a doublet for the bridging hydride ligand (6.52 ppm, $^1J_{YH} = 40$ Hz). The greater coupling observed in the $^1$H NMR spectrum between yttrium and the bridging hydride ligand in 3-Y/La vs 3-Y/Lu, 40 vs 28 Hz, respectively, can be explained by the Lewis acidity of the metals. The difference in Lewis acidity between yttrium and lanthanum in 3-Y/La is larger than that between yttrium and lutetium in 3-Y/Lu. Hence, in 3-Y/La, yttrium would be expected to have an interaction with the bridging hydride ligand larger than that in 3-Y/Lu.

The $^1$H NMR spectrum of 3-Y/La also contained a doublet for the methylene protons (0.36 ppm, $^2J_{YH} = 2$ Hz). The $^{13}$C NMR spectrum showed a doublet for the “tuckover” methylene carbon (41.7 ppm, $^1J_{YC} = 23$ Hz). This is consistent only with yttrium in the Ln$^1$ position that forms the M–C bond resulting from C–H activation of the pentamethylcyclopentadienyl methyl group. Hence, in 3-Y/La as well as 3-Lu/La, the smaller metal is located in the higher coordinate site.

**DFT Calculations.** Initial density functional theory (DFT) calculations were carried out using TPSS,$^{52}$ TPSSh,$^{42}$ and B3-LYP$^{53,54}$ functionals with triple-zeta basis sets$^{44}$ for 3-Lu/Y and 3-Y/Lu. TPSS indicated that 3-Lu/Y was more stable than 3-Y/Lu by 0.34 kcal/mol, Table 4.2. This small difference, less than the 0.59 kcal/mol value of kT, is consistent with the mixture of products found experimentally and with the 37/17 prevalence for the smaller lutetium at the eight-coordinate metal site. The results obtained using TPSSh and B3LYP for all of the metal combinations were analogous to those using TPSS. All calculations were performed with version 6.5 of TURBOMOLE.$^{56}$

The analogous calculations on 3-Y/La and 3-La/Y and on 3-Lu/La and 3-La/Lu indicated that the structures with the larger metal in the higher coordinate site are more stable.
these cases, the differences were larger: the calculations indicated 3-La/Lu is more stable than 3-Lu/La by 1.63 kcal/mol and 3-La/Y is more stable than 3-Y/La by 0.51 kcal/mol, Table 4.2. The calculations match the result expected simply on the basis of the size of the ions, but these do not match the experimental crystallographic result that shows the larger metal in the smaller coordinate site in each case.

Table 4.2. Calculated Differences in Energy (kcal/mol) between 3-Ln/Ln′ and 3-Ln′/Ln (kcal/mol) for Lu/Y, Y/La, and Lu/La Combinations.\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>Lu/Y</th>
<th>Y/La</th>
<th>Lu/La</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ground state</td>
<td>E\textsubscript{3-Lu/Y} − E\textsubscript{3-Y/Lu}</td>
<td>ground state</td>
</tr>
<tr>
<td>DFT</td>
<td>3-Lu/Y</td>
<td>0.34</td>
<td>3-La/Y</td>
</tr>
<tr>
<td>dispersion corr</td>
<td>3-Lu/Y</td>
<td>2.44</td>
<td>3-Y/La</td>
</tr>
<tr>
<td>RPA</td>
<td>3-Lu/Y</td>
<td>1.03</td>
<td>3-Y/La</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The DFT and dispersion correction results were obtained using TPSS.

However, when Grimme’s empirical dispersion correction\textsuperscript{57} was applied to these calculations for the yttrium/lanthanum and lutetium/lanthanum systems, the results reproduced the experimentally observed structures, Table 4.2. With the dispersion correction, 3-Lu/La was found to be more stable than 3-La/Lu, and 3-Y/La was found to be more stable than 3-La/Y. Although the dispersion correction maintained the experimental findings that 3-Lu/Y is preferred to 3-Y/Lu, the calculated stabilization was too large to suggest a mixture should occur. This dispersion correction was also applied to the B3-LYP calculations, which agreed with the results.
of the TPSS calculations. This indicates that an empirical dispersion correction is not sufficient to model these systems.

Further calculations were performed using the random phase approximation (RPA) with triple-zeta basis sets applied to the initial calculations, Table 4.2. These calculations matched the experimental result for all combinations: in all three combinations of metals, the complexes 3 are more stable when the smaller metal is in the more highly coordinated site. The energy differences for these calculations were also reasonable for a mixture to occur for the Lu/Y combinations. Thus, while standard density functionals and dispersion corrections fail to reproduce the experimental results, RPA correctly predicts the experimental results without empiricism, albeit at somewhat higher computational cost.

**Reactivity.** Preliminary reactions of 3-Y/La with PhSSPh showed the formation of a new heterometallic species, Cp*₂Y(μ-SPh)₂LaCp*(μ-SPh)₂LaCp*(μ-SPh)₂YCp*, 4-Y/La, Scheme 4.1, Figure 4.4. This result is different from the reactivity of the homobimetallic 3-Y/Y

**Scheme 4.1.** Reaction of 3-Y/La with PhSSPh and conceivable half reactions.
Cp*₂Y(μ-SPh)₂YCp*₂, Scheme 4.2. Formation of tetrameric species in rare-earth Cp* chemistry is rare, with only 7 examples known, and this appears to be the first example of a heterometallic tetramer species with Cp* as the main ancillary ligand.

Figure 4.4. Thermal ellipsoid plot of Cp*₂Y(μ-SPh)₂LaCp*₂(μ-SPh)₂LaCp*²S₁S₂S₃, 4-Y/La, drawn at the 50% probability level. Hydrogen atoms, ortho, para and meta carbon atoms of each phenyl ring, and two co-crystallized benzene molecules have been omitted for clarity.

The formation of 4-Y/La via Scheme 4.1 formally involves two-electron reductions of three PhSSPh molecules with only two equivalents of 3-Y/La. Possible half reactions are shown in Scheme 4.1 in comparison to those in Scheme 4.2. One Cp* ligand is lost from each La center, which could be the source of the additional two electrons needed for this product to form. This differs from the reaction with 3-Y/Y. Reductions involving the Cp* ligand, namely sterically induced reduction, usually involve the formation of Cp*₂ as the oxidized byproduct. Since Cp*₂ is not an observed byproduct of this reaction, an alternative route could be possible for the loss of these two Cp* ligands.
Scheme 4.2. Reaction of 3-Y/Y with PhSSPh and conceivable half reactions.

Structural parameters of 4-Y/La are compared to the structural parameters of Cp*₂Ln(µ-SPh)₂LnCp*₂ (Ln = Y, 5-Y/Y; La, 5-La/La) in Table 4.3. The Y–S and Y–(C₅Me₅ centroid) bond lengths of 4-Y/La are similar to those of 5-Y/Y, while the La–S and La–(C₅Me₅ centroid) bond lengths of 4-Y/La are shorter than those of 5-La/La. These shorter lanthanum-based distances could be attributed to the lanthanum center only having one cyclopentadienyl ligand in 4-Y/La vs two cyclopentadienyl ligands in 5-La/La.

Table 4.3. Selected Bond Distances (Å) for Cp*₂Ln(µ-SPh)₂LnCp*₂ (Ln = Y, La) and 4-Y/La.

<table>
<thead>
<tr>
<th></th>
<th>5-Y/Y</th>
<th>5-La/La</th>
<th>4-Y/La</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y–(C₅Me₅ centroid)</td>
<td>2.370</td>
<td>—</td>
<td>2.386</td>
</tr>
<tr>
<td></td>
<td>2.402</td>
<td></td>
<td>2.406</td>
</tr>
<tr>
<td>Y–S</td>
<td>2.8931(6)</td>
<td>—</td>
<td>2.8121(7)</td>
</tr>
<tr>
<td></td>
<td>2.9031(6)</td>
<td></td>
<td>2.8313(6)</td>
</tr>
<tr>
<td>La–(C₅Me₅ centroid)</td>
<td>—</td>
<td>2.525</td>
<td>2.494</td>
</tr>
<tr>
<td></td>
<td>2.560</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La–S</td>
<td>—</td>
<td>3.0076(6)</td>
<td>2.9509(6)</td>
</tr>
<tr>
<td></td>
<td>3.0102(6)</td>
<td></td>
<td>2.9322(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.9889(6)</td>
<td>2.9433(6)</td>
</tr>
</tbody>
</table>
Discussion

The synthesis of the heterobimetallic hydride complex Cp*$_2$Lu(H)$_2$YCp*$_2$, 2-Lu/Y, by hydrogenolysis of allyl precursors of similarly sized lutetium and yttrium, eq 4.3, was complicated by the formation of a mixture of products. While heterobimetallic 2-Lu/Y was observed as the main product (86%), it was in a mixture containing the homobimetallic hydride complexes Cp*$_2$Lu(H)$_2$LuCp*$_2$, 2-Lu/Lu, and Cp*$_2$Y(H)$_2$YCp*$_2$, 2-Y/Y. Separation of 2-Lu/Y from this mixture for further reactivity studies was not possible due to the similar properties of the three compounds. In comparison, studies to examine monomer–dimer equilibria with the heterometallic complexes [(C$_5$Me$_4$SiMe$_2$NCMe$_3$)(THF)Ln(µ-H)]$_2$ and [(C$_5$H$_4$Bu)$_2$Ln(µ-H)]$_2$ (Ln = Lu, Y) and the homometallic yttrium complexes [(C$_5$Me$_4$SiMe$_2$CMe$_2$R)Y(µ-H)] (R = Me, Et) gave statistical 1:2:1 mixtures of the Y$_2$:YLu:Lu$_2$ and MeMe/MeEt/EtEt complexes by $^1$H NMR spectroscopy when the individual complexes were mixed. Attempts to examine the product of mixing 2-Y/Y and 2-Lu/Lu were complicated by C–H bond activation reactions to make 3. Formation of 2-Lu/Y was more straightforward by hydrogenolysis, since the C–H bond activation was suppressed under H$_2$.

The formation of the mixture in eq 4.3 was not unexpected with these similarly sized metals. However, it was surprising that the coupling information provided by I = 1/2 yttrium in the NMR spectra allowed each component and the distribution of the mixture to be identified. This shows that, with the proper system, complicated mixtures of complexes of similar Lewis acids can be definitively analyzed and studied.

In contrast to the results with the two small metals lutetium and yttrium, the synthesis of a single, heterobimetallic hydride complex, Cp*$_2$Lu(H)$_2$LaCp*$_2$, 2-Lu/La, occurred with the
large metal/small metal combination of lanthanum and lutetium, eq 4.4. The analogous lanthanum/yttrium pair behaved similarly to give \( \text{Cp}^*\text{Y(H)}_2\text{LaCp}^* \), \( 2\text{-Y/La} \). Evidently, with the \( (\text{Cp}^*\text{H})_3^- \) ligand set in this hydrogenolysis reaction, a heterobimetallic combination of a large and a small metal is preferred to the homobimetallic alternatives. This is consistent with the fact that mixing the homobimetallic hydride complexes gives exclusively the heterobimetallic product: i.e., the reaction of \( 2\text{-La/La} \) with \( 2\text{-Y/Y} \) forms \( 2\text{-Y/La} \).

In the C–H bond activation reactions that generate tuckover hydride complexes, mixtures of the two small metals lutetium and yttrium again form mixtures of homo- and heterobimetallic complexes, eq 4.5. Hence, heating the mixture of \( 2\text{-Lu/Y} \), \( 2\text{-Lu/Lu} \), and \( 2\text{-Y/Y} \) did not lead to selective formation of a single favored tuckover hydride. In this case, four tuckover hydride products were observed, since the two metal positions are not equivalent: \( \text{Cp}^*\text{Y(µ-H)(µ-η^1:η^5-CH}_2\text{C}_5\text{Me}_4)\text{LuCp}^* \), \( 3\text{-Y/Lu} \), \( \text{Cp}^*\text{2Lu(µ-H)(µ-η^1:η^5-CH}_2\text{C}_5\text{Me}_4)\text{YCp}^* \), \( 3\text{-Lu/Y} \), \( \text{Cp}^*\text{2Lu(µ-H)(µ-η^1:η^5-CH}_2\text{C}_5\text{Me}_4)\text{LuCp}^* \), \( 3\text{-Lu/Lu} \), and \( \text{Cp}^*\text{2Y(µ-H)(µ-η^1:η^5-CH}_2\text{C}_5\text{Me}_4)\text{YCp}^* \), \( 3\text{-Y/Y} \), were observed by NMR spectroscopy.

NMR spectroscopy of this mixed-metal system was again valuable and allowed identification of the two heterobimetallic tuckover hydride variants \( 3\text{-Y/Lu} \) and \( 3\text{-Lu/Y} \). Not only were the shifts of the hydrides far enough apart that they could be discerned, but also the coupling with yttrium was definitive. This system was further remarkable in that both the NMR and X-ray crystallographic analysis suggested similar distributions of Y and Lu between the two distinct positions in the \( \text{Cp}^*\text{2Ln(µ-H)(µ-η^1:η^5-CH}_2\text{C}_5\text{Me}_4)\text{Ln'Cp}^* \), \( 3\text{-Y/Lu:Lu/Y} \), structure. The approximate 2:1 \( 3\text{-Lu/Y:3-Y/Lu} \) ratio was unexpected, since the smaller metal, Lu, is in the
larger eight-coordinate position while the slightly larger metal, Y, is located in the seven-coordinate position.

The NMR data showed that when the 2-Lu/Y, 2-Lu/Lu, and 2-Y/Y hydride reagents in an 86:10:4 ratio, with the heterobimetallic complex most prevalent, were converted to tuckover hydride products, the amount of heterobimetallic products was smaller since a 54:19:27 ratio for (3-Y/Lu + 3-Lu/Y):3-Lu/Lu:3-Y/Y was observed. Since this ratio is similar to the ratio observed from ligand redistribution of the homobimetals 3-Lu/Lu:3-Y/Y, it appears to be the thermodynamic ratio arising from exchange reactions with these labile complexes rather than a reflection of relative reactivity. Hence, in this system it was impossible to tell if the C−H bond activation reaction that converted the dihydrides to tuckover hydrides was favored by yttrium over lutetium.

In contrast to the reactions with similarly sized metals, when one metal was the large lanthanum, there was a preference to form the single heterobimetallic hydride Cp*2Ln(H)2LaCp*2 (Ln = Lu, 2-Lu/La; Y, 2-Y/La). This preference for a single heterobimetallic product carried over to the tuckover hydride series, where the formation of a single heterobimetallic tuckover product, Cp*2Ln(µ-H)(µ-η1:η5-CH2C5Me4)LaCp* (Ln = Lu, 3-Lu/La; Y, 3-Y/La), was observed with both the La/Lu and La/Y combinations, eq 4.6. In the yttrium case, the coupling in the 1H NMR spectra clearly showed formation of 3-Y/La and not the isomer 3-La/Y. This preference, with the alkyl component of the tuckover (CH2C5Me4)2− ligand attached to the smaller, more Lewis acidic metal yttrium, is similar to the preference for lutetium in this position in the mixture of 3-Y/Lu and 3-Lu/Y. The preference for 3-Lu/La and 3-Y/La observed in the solid state is also seen in solution: solutions of 3-Lu/La and 3-Y/La do
not display ligand exchange over 30 days. The formation of these preferred isomers is consistent with C–H bond activation of the (Cp*)\(^{1–}\) rings attached to the larger, less Lewis acidic metal.

The heterobimetallic tuckover hydride complexes 3 proved to be challenging in terms of calculating preferred sites for the different metals. With similarly sized metals, the calculations using just TPSS predicted the experimental result that 3-Y/Lu and 3-Lu/Y were close in energy and should exist as mixtures. However, for the small metal/large metal combinations of yttrium/lanthanum and lutetium/lanthanum, the calculations suggested that the most stable complexes would have the larger metal in the more highly coordinated site. Although the calculated energy differences were small and they matched the prediction from simple ionic radius considerations, they did not match the experimental data. When a dispersion correction was applied to the large/small combinations, the prediction matched the experimental results. However, using dispersion corrections with the small/small combination gave a difference too large to match the observed mixture of products. Only with random phase approximation (RPA) corrections were the calculations able to predict the observed results for all three combinations of metals.

Preliminary reactivity studies suggest that the heterobimetallic complexes, 3-Ln/Ln′, can react differently than the homometallic analogue, 3-Y/Y. 3-Y/La reacts with PhSSPh to form a heterotetrametallic species Cp*\(^2\)Y(µ-SPh)\(^2\)LaCp*(µ-SPh)\(^2\)LaCp*(µ-SPh)\(^2\)YCp*\(^2\), 4-Y/La. This suggests that each equivalent of 3-Y/La can reduce a substrate by three electrons, as opposed to the two electron reduction reported for the reaction of homobimetallic 3-Y/Y with PhSSPh. Reactivity of 3-Ln/Ln′ with other substrates previously studied with 3-Y/Y, such as AgOTf and carbodiimides, would be valuable to assess additional differences in reactivity between the homobimetallic and heterobimetallic tuckover hydride complexes.
Conclusion

The heterobimetallic metallocene hydride and tuckover hydride complexes \( \text{Cp}^* \text{Ln}(\mu-H) \text{Ln}' \text{Cp}^* \), \( 2-\text{Ln/Ln}' \), and \( \text{Cp}^* \text{Ln}(\mu-H)(\mu-\eta^1:\eta^5-\text{CH}_2\text{C}_5\text{Me}_4) \text{Ln}' \text{Cp}^* \), \( 3-\text{Ln/Ln}' \), respectively (\( \text{Ln, Ln}' = \text{La, Y, Lu} \)), demonstrate that it is possible to analyze complicated mixtures of rare-earth metals to determine if structural and reactivity preferences exist on the basis of on radial size and Lewis acidity. In this case, complicated mixtures of three types of \( 2-\text{Ln/Ln}' \) complexes and four variations of \( 3-\text{Ln/Ln}' \) compounds could be definitively identified by \(^1\text{H NMR}\) spectroscopy with the similarly sized metals yttrium and lutetium. Reactivity preferences could not be determined in the \( \text{C—H} \) bond activation conversion of \( 2-\text{Ln/Ln}' \) to \( 3-\text{Ln/Ln}' \) because of the lability of the ligands in this particular system and exchange reactions. However, the analogous chemistry with combinations of metals with different sizes showed a decided preference for the heterometallic complexes \( 2-\text{Lu/La} \) and \( 2-\text{Y/La} \) over the homometallic species and for the specific heterometallic tuckover hydride complexes \( 2-\text{Lu/La} \) and \( 2-\text{Y/La} \), with the larger metal in the lower coordinate site. DFT calculations, using a dispersion correction or RPA, further supported the unexpected experimental findings, in which the smaller metal in \( 3-\text{Ln/Ln}' \) prefers the higher coordinate position. This suggests that, in this case, the Lewis acidic character of the metal is more important than steric factors in determining the preferred location for each metal in the molecule.
Table 4.4. X-ray Data Collection Parameters of 3-Lu/La and 4-Y/La.

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<th>3-Lu/La</th>
<th>4-Y/La</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C₄₀H₆₀LaLu</td>
<td>C₆₀H₁₂₀La₂S₀₂Y₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• 2(C₆H₆)</td>
</tr>
<tr>
<td>fw</td>
<td>854.76</td>
<td>2078.13</td>
</tr>
<tr>
<td>space group</td>
<td>PT</td>
<td>PT</td>
</tr>
<tr>
<td>cryst syst</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
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<td>10.9036(6)</td>
</tr>
<tr>
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</tr>
<tr>
<td>c (Å)</td>
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<td>20.2722(11)</td>
</tr>
<tr>
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<td>2444.2(2)</td>
</tr>
<tr>
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<td>95.5082(7)</td>
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<tr>
<td>β (deg)</td>
<td>102.0384(9)</td>
<td>94.1112(7)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>99.3623(9)</td>
<td>92.9533(7)</td>
</tr>
<tr>
<td>Z</td>
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<td>1</td>
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<tr>
<td>ρcalc (Mg/m³)</td>
<td>1.562</td>
<td>1.412</td>
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<tr>
<td>μ (mm⁻¹)</td>
<td>3.884</td>
<td>2.206</td>
</tr>
<tr>
<td>temp (K)</td>
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<td>133(2)</td>
</tr>
<tr>
<td>R1 (I &gt; 2σ(I))</td>
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<td>0.0274</td>
</tr>
<tr>
<td>wR2 (all data)</td>
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<td>0.0649</td>
</tr>
</tbody>
</table>

*Definitions: wR² = [Σ[w(Fo² - Fc²)²] / Σ[w(Fo²)]]¹/²; R1 = Σ|Fo| - |Fc| / Σ|Fo|.*

References


CHAPTER 5
Computational Analysis of Reduced Tris(cyclopentadienyl) Rare Earth Species

Introduction*

Developments in rare earth reductive chemistry have shown that N$_2$ can be reduced to (N=N)$_2^-$, Scheme 5.1, and (N$_2$)$_3^-$ by combining a Ln$^{3+}$ complex with an alkali metal.$^{1-14}$ These LnA$_3$/M and LnA$_2$A$'/M$ reactions (Ln = Sc, Y, lanthanide; A/A' = monoanionic ligands; M = alkali metal) provided “LnA$_2$”-like reactivity even when no Ln$^{2+}$ complexes of the metal were known to exist either as molecular species in solution or in the solid state. Although this reaction has provided numerous reduced N$_2$ complexes, mechanistic information on the N$_2$ reduction has been elusive.

Scheme 5.1. Reduction of N$_2$ with Trivalent Rare Earth Precursors and Alkali Metal

\[
\begin{align*}
\text{LnA}_3 + M & \xrightarrow{N_2} \text{LnA}_2A' \xrightarrow{N_2} \text{MLnA}_3 \quad (\text{THF})x \\
\text{LnA}_2A' + M & \xrightarrow{N_2} \text{LnA}_2A' \xrightarrow{N_2} \text{MLnA}_3 \quad (\text{THF})x \\
\end{align*}
\]

Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu
A = N(SiMe$_3$)$_2$; C$_5$H$_3$(SiMe$_3$)$_2$-1,3; C$_5$H$_4$SiMe$_3$; C$_5$H$_5$'Bu$_2$;
OC$_6$H$_3$'Bu$_2$-2,6; C$_5$Me$_5$; C$_5$Me$_4$H
A' = BPh$_4$; H; I; M= Na; K; KC$_8$; x = 0-2

One possible pathway involves formation of transient intermediates in the +2 oxidation state, i.e. “LnA$_2$” or the ate-salt “MLnA$_3$,”$^{15-17}$ Scheme 5.2. This possibility is quite reasonable

for Tm, Dy, and Nd since these metals form isolable molecular Ln$^{2+}$ complexes in solution$^{8,13,14,18-24}$ and their solid-state diiodides are best described as Ln$^{2+}$(I$_2$)$_2$.$^{25-28}$ This is also reasonable for Y$^{2+}$, a 4d$^1$ ion that reacts with N$_2$.$^{13,14}$

Lappert and coworkers were able to identify the first unambiguous examples of La$^{2+}$ through the reduction of a tris(cyclopentadienyl) Ln$^{3+}$ precursors, eq 5.1.$^{29}$ Using a slightly different Cp ligand, isolation of the first molecular Y$^{2+}$ complex, [(18-crown-6)K][Cp$''_3$Y] (Cp$'' = C_5H_3(SiMe_3)_2$), suggested it might be possible to access a molecular Ln$^{2+}$ species with

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{La} & \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3
\end{align*}
\]

+ K + chelate

\[
\text{THF, Ar} \quad \text{[K(chelate)][Cp$''_3$La]}
\]

(5.1)

different Cp ligand, isolation of the first molecular Y$^{2+}$ complex, [(18-crown-6)K][Cp$'_3$Y] (Cp$' = C_5H_4SiMe_3$; eq 5.2), 1-Y, suggested it might be possible to access a molecular Ln$^{2+}$ species with

\[
\begin{align*}
\text{SiMe}_3 & \quad \text{SiMe}_3 \\
\text{Ln} & \quad \text{Me}_3\text{Si} \\
\text{SiMe}_3 & \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3
\end{align*}
\]

+ KC$_8$ + 18-crown-6

\[
\text{Et}_2\text{O, Ar} - \text{graphite} \quad \text{[K(OCH$_2$CH$_2$)$_6$]}_2\text{[LnMe}_3\text{Si]}
\]

(5.2)

\[
\begin{align*}
\text{Ln} & = \text{Y, Ho, Er}
\end{align*}
\]
Since size and charge are so important in rare earth chemistry, \( \text{Y}^{3+} \) often behaves like the \( \text{Ln}^{3+} \) ions of the late lanthanides that have similar sizes. This led to the isolation of the first molecular \( \text{Ho}^{2+} \) and \( \text{Er}^{2+} \) complexes, \([(18\text{-crown-6})\text{K}][\text{Cp'Ln}] \) (\( \text{Ln} = \text{Ho, 1-Ho} \); \( \text{Er, 1-Er} \)), eq 5.2. Surprisingly, these complexes contained similar physical properties to \( \text{1-Y} \), which is a 4d\(^1\) species since it is a transition metal and has no available f orbitals. This was quite different to the observed differences between a 4f\(n\) \( \text{Ln}^{3+} \) complex and a 4f\(n+1\) \( \text{Ln}^{2+} \) complex, suggesting \( \text{1-Ho} \) and \( \text{1-Er} \) could also be d\(^1\) species. The first part of this Chapter discusses the results of DFT studies on these new Ln\(^{2+}\) ions.

The second part of this Chapter presents results of DFT studies on other types of tris(cyclopentadienyl) yttrium complexes, \( \text{CpR}_3\text{Y} \), in order to help explain the physical properties of a series of complexes prepared by the Evans group in efforts to obtain more stable Ln\(^{2+}\) complexes than found with \( \text{Cp' ligands} \).\(^{30}\) These other complexes were sought because it would be valuable to use different spectroscopic methods, such as magnetic susceptibility measurements (discussed in Chapter 8), X-ray absorption spectroscopy (discussed in Chapter 9) and X-ray photoelectron spectroscopy, to better understand the electronic properties of these new divalent lanthanide ions. However, physical characterization has been challenging for these new divalent ions, due to their high reactivity.

Yttrium was chosen as the primary metal for this investigation, since EPR spectroscopy can provide good evidence for the presence of \( \text{Y}^{2+} \) due to the 100% naturally abundant \( \text{Y}^{89} \) nucleus that gives a doublet signal for this ion.\(^{13,14}\) The simplest cyclopentadienyl ligand \( \text{C}_5\text{H}_5 \) (Cp) was examined as well as the mono-alkyl substituted ligand \( \text{C}_5\text{H}_4\text{Me} \) (Cp\(^{\text{Me}}\)), the indenyl ligand \( \text{C}_9\text{H}_7 \) (Cp\(^{\text{In}}\)), and the bis(silyl) ligand Cp\(^{\text{''}}\) used by Lappert.\(^{29,31-34}\) Earlier studies by
Lappert and co-workers comparing Cp′₃Ln with Cp′′₃Ln (Cp′ = C₅H₅(CMe₃)₂) suggest that trimethylsilyl-substituted complexes are less difficult to reduce than their alkyl analogs, but steric effects, particularly for the smaller rare earth metals, could also affect stability. The effects of silyl substitution on complexes of cyclopentadienyl ligands have been examined in a number of systems, but it appears that the specific effect is system dependent. This study also includes reductions of mixed ligand tris(cyclopentadienyl) complexes, explored by the Evans group, to determine if a combination of ligands could give enhanced stability. While reduction of many of these Cp₃Y precursors gave rise to a doublet signal in the EPR spectra, suggesting the formation of an Y²⁺ species, none were found to be more stable than 2-Y. Only one Y²⁺ complex, [K(2.2.2-cryptand)][Cp″₂CpMe₂Y] was structurally characterized by single crystal X-ray diffraction.

**Experimental**

**Structures Used for Calculations.** Structures used as starting points for DFT calculations were obtained from available single crystal X-ray diffraction data as follows. In all cases, outer sphere solvents and cations, such as K(2.2.2-cryptand) or K(18-crown-6), were removed from the structures.

Cp′₃Y / (Cp′₃Y)₁⁻. Crystal structure data for Cp′₃Y and [(18-crown-6)K][Cp′₃Ln] were used as starting points. CpMe₃Y / (CpMe₃Y)₁⁻. Bound THF was removed from the structure of CpMe₃Y(THF) as the starting point for CpMe₃Y. The converged Y³⁺ structure was used as a starting point for the Y²⁺ complex, (CpMe₃Y)₁⁻. Cp″₂CpY / (Cp″₂CpY)₁⁻. The anion from the crystal structure, [K(2.2.2-cryptand)][Cp″₂CpY], was used as a starting point for both the Y³⁺
and $Y^{2+}$ complexes.  $\text{Cp}''\text{Cp}^\text{MeY} / (\text{Cp}''\text{Cp}^\text{MeY})^{1-}$. Since there was no available crystal structure data for this mixed ligand system, the anion from the crystal structure, [K(2.2.2-cryptand)][Cp''$_2$CpY],$^{30}$ was used and a methyl group was added to the Cp ligand in the spot that appeared to be the least sterically congested. $\text{Cp}'''\text{Y} / (\text{Cp}'''\text{Y})^{1-}$. The crystal structure of Cp $''$_3La$^{37}$ was used as a starting point for the $Y^{3+}$ complex, in which La was replaced with Y. The converged $Y^{3+}$ structure was used as a starting point for the anionic $Y^{2+}$ complex, (Cp'''$_3$Y)$^{1-}$. $\text{Cp}_3\text{Y} / (\text{Cp}_3\text{Y})^{1-}$. The crystal structure of Cp$_3$Ho$^{38}$ was used as a starting point for the $Y^{3+}$ complex, in which Ho was replaced with Y. The converged $Y^{3+}$ structure was used as a starting point for the anionic $Y^{2+}$ complex, (Cp$_3$Y)$^{1-}$. $\text{[(Me}_3\text{Si)}_2\text{N]}_3\text{Y} / \{[(\text{Me}_3\text{Si})_2\text{N]}_3\text{Y}\}^{1-}$. The crystal structure of [(Me$_3$Si)$_2$N]$_3$Y$^{39}$ was used as a starting point for the $Y^{3+}$ complex, in which one of the disordered metal centers was removed. The converged $Y^{3+}$ structure was used as a starting point for the anionic $Y^{2+}$ complex, {[(Me$_3$Si)$_2$N]}$_3$Y$^{1-}$. $\text{Cp}'_3\text{Y(THF)}$. A preliminary crystal structure of Cp$'_3$Dy(THF)$^{30}$ was used and Dy was replaced with Y. $\text{Cp}^\text{Me}_3\text{Y(THF)}$. Crystal structure data were used as a starting point.  $\text{Cp}'\text{In}_3\text{Ln} / (\text{Cp}'\text{In}_3\text{Ln})^{1-}$ (Ln = La, Y). Two structures were used as starting points for the Ln$^{3+}$ complexes. One structure (A) is a crystal structure of Cp$'\text{In}_3\text{Sm}^{40}$ in which Sm was replaced with either Y or La. The other structure (B) is the crystal structure of Cp$'\text{In}_3\text{Ln(THF)}$ (Ln = La,$^{41}$ Y$^{30}$) in which the bound THF was removed. The converged Ln$^{3+}$ structures were used as a starting point for the anionic Ln$^{2+}$ complexes, (Cp$'\text{In}_3\text{Ln})^{1-}$. $\text{Cp}'\text{In}_3\text{Ln(THF)}$ (Ln = La, Y). The crystal structures of Cp$'\text{In}_3\text{Ln(THF)}$ (Ln = La,$^{41}$ Y$^{30}$) were used as the starting points for the Ln$^{3+}$ complexes.

Computational Details. DFT structural optimizations were performed using the hybrid meta-GGA functional, TPSSh.$^{42}$ The initial gas-phase optimization was carried out using
double-zeta quality split-valence basis sets with polarization functions on non-hydrogen atoms [def2-SV(P)] for all light atoms. Small-core ECPs and triple-zeta valence basis sets with two sets of polarization functions on non-hydrogen atoms, def2-TZVP, were used for Y and La. Analytical force constant calculations were carried out for the SV(P) optimized structures, and these were confirmed to be energy minima by the absence of imaginary vibrational modes.

The solvent effects of THF were then incorporated for the neutral and anionic complexes, Cp′₃Y and (Cp′₃Y)⁻ via further geometry optimizations using the continuum solvation model (COSMO). The dielectric constant of THF (ε = 7.520) was used for the reported COSMO calculations since this was the most polar solvent used. Solvent effects are especially important for stabilizing the Ln²⁺ systems because they screen the additional negative charge. All further calculations of anionic complexes discussed below were completed using COSMO, unless otherwise specified. Any structural data discussed in the text is the result of a final optimization using TZVP basis sets for all light atoms. Changes in Ln⁻-(Cp ring centroid) or Ln⁻N distance were on average less than 0.02 Å from SV(P) to TZVP. Fine quadrature grids (at least size m4) and C₁ symmetry were used throughout.

Time dependent DFT (TDDFT) excitation energy calculations were then carried out in conjunction with COSMO on the solvent optimized SV(P) structures (for Cp′₃Y and (Cp′₃Y)⁻ the hybrid functional PBE0 was used). Normalized Gaussians centered at the computed molecular excitations, scaled with the corresponding theoretical oscillator strength, and fixed root mean width of 0.16 eV are used to compare theoretical with experimental spectra. The excitation energies and oscillator strengths for selected transitions of (Cp′₃Y)⁻, (Cp″₂CpY)⁻ and (Cp″₂CpMeY)⁻ are given in Table 5.4 at the end of the Chapter. The % d and % metal
compositions from a Mulliken population analysis (MPA)\textsuperscript{53} of the molecular orbitals of \((\text{Cp'}^3\text{Y})^{1-}\), \((\text{Cp''}_2\text{CpY})^{1-}\), and \((\text{Cp''}_2\text{CpMeY})^{1-}\) are given in Table 5.5 at the end of the Chapter. All molecular orbitals were plotted with a contour value of 0.05 using self-consistent TPSSh/TZVP orbitals (self-consistent TPSSh/SV(P) orbitals were used for \(\text{Cp'}^3\text{Y}\) and \((\text{Cp'}^3\text{Y})^{1-}\)). Ho and Er calculations were performed by Jefferson E. Bates in Filipp Furche’s group at UC Irvine.

Results

\textbf{Cp'}^3\text{Ln} / (\text{Cp'}^3\text{Ln})^{1-}\). Density functional theory (DFT) calculations were performed on the neutral \(\text{Cp'}^3\text{Ln}\) species, \(\text{2-Ln}\), \((\text{Ln} = \text{Y}, \text{Ho}, \text{Er})\) as well as the anion of \([\text{K}(18\text{-crown-6})][\text{Cp'}^3\text{Ln}], \text{1-Ln}\) \((\text{Ln} = \text{Y}, \text{Ho}, \text{Er}), (\text{Cp'}^3\text{Ln})^{1-}\). Experimental structural data are well matched in the calculated structures, indicating the prediction of a small change in metal–Cp'(Cnt) distances between \(\text{2-Ln}\) and the corresponding anion of \(\text{1-Ln}\). The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of \(\text{2-Y}\) are shown in Figure 5.1a. The HOMO is ligand-based, and the LUMO resembles a \(4d_z^2\) orbital, which is reasonable since Y is a second-row transition metal. Surprisingly, the HOMOs and LUMOs of the lanthanide complexes \(\text{2-Ho}\) and \(\text{2-Er}\), Figure 5.1b, are very similar to those of \(\text{2-Y}\). Hence, the LUMOs of \(\text{2-Ho}\) and \(\text{2-Er}\) resemble \(5d_z^2\) orbitals not \(4f\) orbitals. DFT calculations on the anions of \(\text{1-Ln}\) \((\text{Ln} = \text{Y}, \text{Ho}, \text{Er})\) showed a similar situation: the HOMOs of the \((\text{Cp'}^3\text{Ln})^{1-}\) anions in the Ln\(^{2+}\) complexes, Figure 5.2, are \(d_{z^2}\)-like orbitals, similar to the LUMOs of the neutral Ln\(^{3+}\) complexes.
Figure 5.1. Molecular orbital plots of the HOMOs and LUMOs of the neutral complexes \( \text{Cp}^3\text{Ln} \), 2, for (a) \( \text{Ln} = \text{Y} \) and (b) \( \text{Ln} = \text{Ho} \), using a contour value of 0.05. The MO plots for \( 2-\text{Ho} \) are very similar to those for the Er analogue, \( 2-\text{Er} \).

Figure 5.2. Molecular orbital plots of (a) HOMO and LUMO of \( (\text{Cp}^3\text{Y})^{1-} \) and (b) HOMO and LUMO+1 of \( (\text{Cp}^3\text{Ho})^{1-} \), using a contour value of 0.05. The MO plots for \( (\text{Cp}^3\text{Ho})^{1-} \) are very similar to those for the Er analogue \( (\text{Cp}^3\text{Er})^{1-} \).
Time-dependent DFT (TDDFT) calculations on \((\text{Cp}^3\text{Y})^\text{1−}\) predicted an absorption maximum at 518 nm and a small shoulder at 665 nm, Figure 5.3. These two bands are very close to the experimentally observed maxima for \(\text{1-Y}\) at 530 and 700 nm. Substantial components of these excitations involve transitions from the HOMO to the LUMO, LUMO+2, LUMO+4, and LUMO+5, which Mulliken population analysis (MPA)\(^{53}\) predicted to have 59, 21, 3, 12, and 14% d character, respectively, Tables 5.4 and 5.5. Similarly, for the anions of \(\text{1-Ho}\) and \(\text{1-Er}\), excitations with absorption maxima at 476 and 679 nm (\(\text{1-Ho}\)) and 494 and 663 nm (\(\text{1-Er}\)) were calculated and found to comprise transitions from the HOMO to higher-lying LUMOs that also contain significant d character by MPA. These bands agree well with those experimentally observed at 507 and 650 nm for \(\text{1-Ho}\) and 510 and 650 nm for \(\text{1-Er}\). Both the experimental and theoretical maxima of the absorptions observed for \(\text{1-Ho}/(\text{Cp}^3\text{Ho})\)\(^\text{1−}\) and \(\text{1-Er}/(\text{Cp}^3\text{Er})\)\(^\text{1−}\) are slightly blue-shifted with respect to those for \(\text{1-Y}/(\text{Cp}^3\text{Y})\)\(^\text{1−}\), consistent with stronger splitting for 5d- versus 4d-based orbitals. The extinction coefficients of the absorptions \((\varepsilon = 900–4150 \text{ M}^{-1}\)
cm$^{-1}$) are larger than for pure d $\rightarrow$ d transitions and suggest significant ligand contributions. MPA also indicated that the orbitals involved in the computed transitions have significant ligand character, as is evident in the selected LUMO plots for (Cp'3Ln)$^{1-}$ in Figure 5.2.

**Cp$^{R_3}$Y / (Cp$^{R_3}$Y)$^{1-}$**. DFT calculations were later performed on Cp'$''$2CpY, Cp'$''$3Y, Cp'$''$2CpMeY, Cp3Y, and CpMe3Y, collectively called Cp$^{R_3}$Y, as well as their reduction products, (Cp$^{R_3}$Y)$^{1-}$. For each case, similar to the results found for Cp'3Y, a small change in metal–Cp' (Cnt) distances of approximately 0.03 Å between the Ln$^{3+}$ complex and its corresponding Ln$^{2+}$ complex is predicted, Table 5.1. This is consistent with the experimental findings with both the Cp'$''$3Ln$^{29}$ and Cp'3Ln$^{14}$ systems and suggests that reduction products of these five Cp$^{R_3}$Y complexes could have similar properties to (Cp'3Y)$^{1-}$. In addition, the LUMO of the Y$^{3+}$ species, Cp$^{R_3}$Y, and the HOMO of the Y$^{2+}$ species, (Cp$^{R_3}$Y)$^{1-}$, have mainly $d_{z^2}$ character, Figure 5.2. MPA of each Y$^{2+}$ HOMO predicts the molecular orbitals to be primarily metal-based, with the d character being the most prominent, Table 5.2. The DFT results and the reducibility observed are consistent with the importance of the tris(cyclopentadienyl) coordination environment in providing access to the new +2 ions.
Table 5.1. Calculated average $Y$–Cp(Cnt) Distances (Å) in $\text{Cp}^\text{R}_3\text{Y}$ and $(\text{Cp}^\text{R}_3\text{Y})^{1-}$ using TPSSh and TZVP basis sets.

<table>
<thead>
<tr>
<th></th>
<th>M–Cp(Cnt) (Å)</th>
<th></th>
<th>M–Cp'(Cnt) (Å)</th>
<th>Difference (Å)</th>
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<tbody>
<tr>
<td>$\text{Y}^3+$</td>
<td></td>
<td>$\text{Y}^2+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cp}''\text{2CpY}$</td>
<td>2.427</td>
<td>$(\text{Cp}''\text{2CpY})^{1-}$</td>
<td>2.457</td>
<td>0.030</td>
</tr>
<tr>
<td>$\text{Cp}''\text{3Y}$</td>
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<td>0.031</td>
</tr>
<tr>
<td>$\text{Cp}''\text{2Cp}^\text{Me3Y}$</td>
<td>2.438</td>
<td>$(\text{Cp}''\text{2Cp}^\text{Me3Y})^{1-}$</td>
<td>2.470</td>
<td>0.032</td>
</tr>
<tr>
<td>$\text{Cp}'\text{3Y}$</td>
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<td>$(\text{Cp}'\text{3Y})^{1-}$</td>
<td>2.453</td>
<td>0.032</td>
</tr>
<tr>
<td>$\text{Cp}''\text{2Cp}^\text{Me3Y}$</td>
<td>2.411</td>
<td>$(\text{Cp}''\text{2Cp}^\text{Me3Y})^{1-}$</td>
<td>2.450</td>
<td>0.039</td>
</tr>
</tbody>
</table>

Figure 5.4. Molecular orbital plots of the HOMO of $(\text{Cp}^\text{R}_3\text{Y})^{1-}$ (top) and the LUMO of $\text{Cp}^\text{R}_3\text{Y}$ (bottom) for (a) $\text{Cp}_3\text{Y}$, (b) $\text{Cp}^\text{Me3Y}$, (c) $\text{Cp}''\text{3Y}$, (d) $\text{Cp}''\text{2YCp}$, and (e) $\text{Cp}''\text{2YCp}^\text{Me}$, using a contour value of 0.05.
Table 5.2. Mulliken population analysis (MPA) summary for the HOMO of \((\text{Cp}^3\text{Y})^1\)− computed using TPSSh and TZVP basis sets. The % metal character indicates the total metal contribution to the molecular orbital, the % s character indicates how much of the total orbital comes directly from the metal s orbitals and the % d character indicates how much of the total orbital comes directly from the metal d orbitals. Also included are natural population analyses of the s orbital spin density (# electrons) for each compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>HOMO metal contribution</th>
<th>NPA s orbital spin density</th>
<th>Experimental Hyperfine Coupling (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% metal</td>
<td>% s</td>
<td>% d</td>
</tr>
<tr>
<td>((\text{Cp}''2\text{CpY})^1)−</td>
<td>73</td>
<td>17</td>
<td>56</td>
</tr>
<tr>
<td>((\text{Cp}''3\text{Y})^1)−</td>
<td>73</td>
<td>17</td>
<td>56</td>
</tr>
<tr>
<td>((\text{Cp}''2\text{CpMeY})^1)−</td>
<td>74</td>
<td>17</td>
<td>57</td>
</tr>
<tr>
<td>((\text{Cp}''3\text{Y})^1)−</td>
<td>74</td>
<td>17</td>
<td>57</td>
</tr>
<tr>
<td>((\text{Cp}''3\text{Y})^1)−</td>
<td>84</td>
<td>20</td>
<td>64</td>
</tr>
<tr>
<td>((\text{CpMe}''\text{Y})^1)−</td>
<td>86</td>
<td>25</td>
<td>59</td>
</tr>
<tr>
<td>{[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}}^1)−</td>
<td>107a</td>
<td>51</td>
<td>56</td>
</tr>
</tbody>
</table>

\(^{a}\text{MPA is known to overestimate populations and this is reflected in this value over 100\%. The MPA numbers should only be used in a comparative not absolute sense.}

TDDFT calculations on the anions of the two isolated mixed ligand divalent complexes, \([\text{K}(2.2.2\text{-cryptand})][\text{Cp}''2\text{CpY}]\) and \([\text{K}(2.2.2\text{-cryptand})][\text{Cp}''2\text{CpMeY}]\), predicted spectra that matched the experimental spectra well: both contained a strong absorption near 500 nm and a shoulder near 800 nm, Figure 5.5. The predicted spectra of both mixed ligand complexes are also similar to the calculations of \((\text{Cp}''3\text{Y})^1\)−, in that they appear to be slightly blue-shifted relative to the experimental spectra. The excitations involved in the calculated spectra for both \((\text{Cp}'\)
(Cp′′₂CpY)¹⁻ and (Cp′′₂Cp⁻MeY)¹⁻, Tables 5.4 and 5.5, contain transitions to orbitals that are significantly more metal-based (i.e., d → d and d → p) than the excitations for (Cp′₃Y)¹⁻ that had transitions to orbitals that had significant ligand character. This could account for the smaller extinction coefficients observed experimentally for [K(2.2.2-cryptand)][Cp′′₂CpY] and [K(2.2.2-cryptand)][Cp′′₂Cp⁻MeY].

Figure 5.5. Experimental UV-vis spectrum of (a) [K(2.2.2-cryptand)][Cp′₂CpY] (solid) and calculated spectrum of (Cp′₂CpY)¹⁻ (dotted) and (b) [K(2.2.2-cryptand)][Cp′₂Cp⁻MeY] (solid) and calculated spectrum of (Cp′₂Cp⁻MeY)¹⁻ (dotted).

Hyperfine Coupling Constants in (Cp'R₃Y)¹⁻. DFT calculations were also used to evaluate EPR data obtained on the products of reductions of these five Cp'R₃Y complexes. EPR active signals were observed with characteristic hyperfine coupling to an Y²⁺ metal center for all five complexes. The hyperfine coupling constants in Table 5.2 show a progression of increasing A values for the reduction products of tris(cyclopentadienyl) yttrium complexes ligated with C₅H₅(SiMe₃)₂ (Cp'''), C₅H₄SiMe₃ (Cp′), C₅H₅ (Cp) and C₅H₄Me (Cp⁻Me), respectively. Hence an increase in A is correlated with increasing donating ability of the ligands if it is assumed that Me₃Si is less electron donating than H.³⁶ If the more electron donating ligands lead to more
unpaired electron density on the metal, this would be expected to increase \( A \). The DFT calculations also show a correlation of the hyperfine coupling constants with the percent metal character and the percent s character of the HOMOs in the \((\text{C}p^R_3\text{Y})^{1-}\) complexes, Table 5.2.

\[
[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y} / \{[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}^{1-}\}
\]

Calculations were also performed on \(\text{Y}[\text{N}(\text{SiMe}_3)_2]_3\) and its possible reduction product, \(\{\text{Y}[\text{N}(\text{SiMe}_3)_2]_3\}^{1-}\), for comparison with the hyperfine coupling constant data presented for the \((\text{C}p^R_3\text{Y})^{1-}\) ions above. The first EPR evidence of \(\text{Y}^{2+}\) was obtained on this tris(amide) system, although no crystallographic data were obtained on the putative \(\{\text{Y}[\text{N}(\text{SiMe}_3)_2]_3\}^{1-}\) product.\(^{13}\) The LUMO of \(\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Y}\) and the HOMO of \(\{\text{Y}[\text{N}(\text{SiMe}_3)_2]_3\}^{1-}\) have primarily \(d_{z^2}\) character, i.e. they are similar to those found for \(\text{C}p^R_3\text{Y}\) and \((\text{C}p^R_3\text{Y})^{1-}\), Figure 5.6. Although this would not be expected for a trigonal planar geometry, in which the \(d_{xz}\) and \(d_{yz}\) would be expected to be the lowest-lying \(d\) orbitals, the agostic interactions of the \([\text{N}(\text{SiMe}_3)_2]^{1-}\) ligands proposed to be responsible for the trigonal pyramidal structure\(^{54}\) observed in the solid state structure of \(\text{Y}[\text{N}(\text{SiMe}_3)_2]_3\) appear to alter the \(d\) orbital splitting pattern so that \(d_{z^2}\) is lowest. This is further supported by the identification of the higher-lying \(d_{xz}\) and \(d_{yz}\) orbitals as the LUMO+1 and LUMO+2 of \(\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Y}\), Figure 5.6.

![Figure 5.6](image)

**Figure 5.6.** Molecular orbital plots of the LUMO, LUMO+1 and LUMO+2 of \(\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Y}\) and the HOMO of \(\{[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}^{1-}\), using a contour value of 0.05.
Calculations on the predicted reduction product, \(\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Y}\)^1−, reveal a geometry that is trigonal planar instead of trigonal pyramidal. The HOMO is entirely metal based and it has the highest amount of metal and s character of any of the Y^{2+} species described in Table 5.2. This is consistent with its much higher experimental value of \(A\) (110 G) than all of the \((\text{Cp}^\text{R}_3\text{Y})^1−\) ions. The general trend found for MPA is also observed when looking at the s orbital spin density at the yttrium metal center, using natural population analysis (NPA), Table 5.2. The s orbital spin density is very similar between the \((\text{Cp}^\text{R}_3\text{Y})^1−\), with the s orbital spin density being much larger for \(\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Y}\)^1−.

**THF Solvated Complexes, \text{Cp}^\text{R}_3\text{Y}(\text{THF}).** The calculations above were done on the unsolvated \text{Cp}^\text{R}_3\text{Y} complexes because the crystallographically characterized Y^{2+} complexes, \((\text{Cp}’^\text{Y})^1−\) and \((\text{Cp}’’^\text{Y}\text{Cp})^1−\), are isolated solvate-free. However, calculations were also done on THF adducts of the precursors, \text{Cp}’^\text{Y}(\text{THF}) and \text{Cp}^\text{Me}_3\text{Y}(\text{THF}), since the reductions are performed in THF where the precursors are likely to be the THF adducts, \text{Cp}^\text{R}_3\text{Y}(\text{THF}). Numerous \text{Cp}^\text{R}_3\text{Ln}(\text{THF}) complexes have been crystallographically identified. For both \text{Cp}’^\text{Y}(\text{THF}) and \text{Cp}^\text{Me}_3\text{Y}(\text{THF}), the LUMO is a d_{z^2} orbital which is anti-bonding with respect to the THF. Hence, population of this orbital by reduction could lead to loss of THF. Attempts to perform calculations on the anions, \([\text{Cp}’^\text{Y}(\text{THF})]^1−\) and \([\text{Cp}^\text{Me}_3\text{Y}(\text{THF})]^1−\), resulted in structures in which the \text{Y–O(THF)} bond was so long that it was effectively cleaved. Although ground states for \([\text{Cp}’^\text{Y}(\text{THF})]^1−\) and \([\text{Cp}^\text{Me}_3\text{Y}(\text{THF})]^1−\) could not be identified, this provides a rationale for the isolation of Y^{2+} complexes in unsolvated form.

**The Indenide System, \text{Cp}^\text{In}_3\text{Ln} (\text{Ln} = \text{Y, La}).** In contrast to the \text{Cp}^\text{R}_3\text{Y} complexes described above, calculations on the indenyl complexes, \text{Cp}^\text{In}_3\text{Ln} (\text{Ln} = \text{Y, La}), are more
complicated. Studies on the crystallographically characterized THF adducts, Cp\textsubscript{In}\textsubscript{3}Ln(THF) (Ln = Y\textsuperscript{3+}, La\textsuperscript{4+}), presumably present in the THF solutions during reduction, are different from those of the other Cp\textsubscript{R}\textsubscript{3}Y(THF) complexes. The LUMO of these THF-solvated indenyl complexes, Cp\textsubscript{In}\textsubscript{3}Ln(THF), was not a d\textsubscript{z}\textsuperscript{2} orbital. Instead, it had mainly ligand character localized on the C\textsubscript{6} ring of the indenyl ligands, Figure 5.7, Table 5.3. This suggests reduction of these molecules would put more electron density on the ligands than in the other Cp\textsubscript{R}\textsubscript{3}Y reductions. If the increased electron density on the ligand led to C–H bond activation, this would be consistent with the isolation of \{[(C\textsubscript{9}H\textsubscript{7})\textsubscript{2}Dy(\mu-\eta\textsuperscript{5}:\eta\textsuperscript{1}-C\textsubscript{9}H\textsubscript{6})]\textsubscript{2}\} \{K(2.2.2-cryptand)\}\textsubscript{2}, which contained a (C\textsubscript{9}H\textsubscript{6})\textsuperscript{2−} ligand formed by C–H bond activation in the arene ring.

![Figure 5.7. Molecular orbital plots of the LUMO of Cp\textsubscript{In}\textsubscript{3}Y and Cp\textsubscript{In}\textsubscript{3}Y(THF) (top) and the LUMO of Cp\textsubscript{In}\textsubscript{3}La and Cp\textsubscript{In}\textsubscript{3}La(THF) (bottom), using a contour value of 0.05.](image)
Table 5.3. MPA summary for the LUMO of Cp^{In}_3Ln and Cp^{In}_3Ln(THF) and HOMO of (Cp^{In}_3Ln)^{1-} complexes, computed using TPSSh and TZVP basis sets. The % metal character indicates the total metal contribution to the molecular orbital, the % s character indicates how much of the total orbital comes directly from the metal s orbitals and the % d character indicates how much of the total orbital comes directly from the metal d orbitals.

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Calculations were also performed on two unsolvated Cp^{In}_3Ln (Ln = Y, La) complexes with different indenyl geometries around the metal center, one in which the C₆ rings of the indenyl ligands orient above and below the plane of the three Cp^{In}(Cnt), A, and another in which the C₆ rings of indenyl ligands orient in the plane of the three Cp^{In}(Cnt), B. For the A geometry, the LUMOs for both Y and La are primarily dₓ² orbitals, but these orbitals have significantly more ligand character than any of the other Cp^{R}_3Y complexes, Figure 5.7, Table 5.3. For the B geometry, the LUMOs for both Y and La are also primarily dₓ² orbitals, but the % metal character of these orbitals is much closer to that of the Cp^{R}_3Y complexes. This suggests that it may be possible to form an indenyl Ln^{2+} species in the absence of coordinating solvent if reduction can
occur when the indenyl ligands are properly oriented. Calculations of the reduction products of complexes A and B, \((\text{Cp}^{\text{In}}_3\text{Ln})^{1-}\), do suggest primarily metal-based HOMOs as \(d_{z^2}\) orbitals, Figure 5.8, Table 5.3.

**Figure 5.8.** Molecular orbital plots of the HOMO of \((\text{Cp}^{\text{In}}_3\text{Y})^{1-}\) (top) and the HOMO of \((\text{Cp}^{\text{In}}_3\text{La})^{1-}\) (bottom), using a contour value of 0.05.

**Discussion**

DFT studies of the anion of \([\text{(18-crown-6)K}]\text{[Cp'}_3\text{Y}], 1-\text{Y}, namely \((\text{Cp'}_3\text{Y})^{1-}\), suggest the configuration of \(\text{Y}^{2+}\) in a \((\text{Cp'}_3)^{3-}\) ligand environment is \(4d^1\). This is reasonable since \(\text{Y}\) is a second row transition metal with no available \(f\) orbitals. A small change in metal–Cp’(Cnt) distance between 1-\text{Y} and \text{Cp'}_3\text{Y}, 3-\text{Y}, is observed experimentally and computationally, a quality often observed in changes in oxidation states with transition metals.\(^{73}\) The TDDFT excitation spectrum of \((\text{Cp'}_3\text{Y})^{1-}\) matches the experimental spectrum of 1-\text{Y} well, indicating the most
significant absorptions to be $d \rightarrow d/\text{ligand}$ and $d \rightarrow \text{ligand}$. This helps explain the increased extinction coefficients from the expected values for pure $d \rightarrow d$ absorptions.

Surprisingly, calculations of the anions of 1-Ho and 1-Er also suggest that reduction of the neutral Cp$'_3$Ln complexes will also form a $d^1$ species with configurations of $4f^{10}5d^1$ and $4f^{11}5d^1$, respectively. Small changes in metal–Cp’(Cnt) distance between 1-Ln and 3-Ln are observed for both Ho and Er, and this is also found in the calculated structures. This contrasts with the difference in Ln$^{3+}$ versus Ln$^{2+}$ bond distances for Ln = Eu, Yb, Sm, and Tm, where the Ln$^{2+}$ distances are typically 0.1–0.2 Å longer than those for the Ln$^{3+}$ ion. Bond distances are much less sensitive to the metal oxidation state for transition metals than for lanthanides and this could be an indication that a $5d^1$ population for both 1-Ho and 1-Er can explain this subtle change from Ln$^{3+}$ to Ln$^{2+}$. The TDDFT excitation spectra of (Cp$'_3$Ho)$^{1-}$ and (Cp$'_3$Er)$^{1-}$ provide a reasonable fit to the experimental spectra of 1-Ho and 1-Er, which are found to be quite similar to that of 1-Y. The qualitative agreement of the TDDFT excitation spectra with the experimental spectra, in addition to the ground-state structural results, suggest that the 5d orbitals play a more important role in molecular divalent lanthanide chemistry than previously believed.

A similar set of orbitals was previously calculated for the [Cp$''_3$La]$^{1-}$ anion in the La$^{2+}$ complex [K(18-crown-6)(OEt$_2$)][Cp$''_3$La]. The accessibility of the 5d orbitals in Ln$^{2+}$ ions is supported by atomic spectra, which show that the $4f/5d$ gap is much smaller in Ln$^{2+}$ than in Ln$^{3+}$. Recent calculations on solid-state divalent lanthanide halides, chalcogenides, and pnictides consistently show that the $4f$ and $5d$ orbitals are similar in energy in the +2 oxidation state. For (Cp$'_3$Ho)$^{1-}$ and (Cp$'_3$Er)$^{1-}$, the pseudo-D$_{3h}$ crystal field generated by the three Cp’ ligands may split the $4f$ and $5d$ orbitals in such a way that singly occupying a $5d$ orbital is more
energetically favorable than forming a spin pair in the 4f manifold. Such splitting would favor the stabilization of the 4f$^5$d$^1$ configuration of the metal ion, which is an excited configuration of the free ion.

Previous studies of the bonding and electronic structure of ($\eta^5$-C$_5$H$_5$)$_3$M complexes of transition metals,$^{77,78}$ lanthanides,$^{79,80}$ and actinides$^{78,81,82}$ in which the three (C$_5$H$_5$)$_3^-$ rings provide a pseudo-D$_{3h}$ coordination environment showed that the d$_{z^2}$ orbital is significantly lower in energy than the other d orbitals. Since the d$_{z^2}$ orbital cannot effectively interact with the $\pi$ orbitals of the (C$_5$H$_5$)$_3^{3-}$ ligand set, it is not significantly destabilized, if at all, and remains essentially nonbonding with respect to the ligands. Bursten et al.$^{82}$ previously noted for complexes of this type that if the isolated (n+1)d$_{z^2}$ orbital in such D$_{3h}$ structures is low enough in energy, it could potentially compete with the nf orbitals for metal-localized electrons. If 1-Ho and 1-Er, like 1-Y, have d$^1$ configurations, electronic transitions from a ground-state $a_1'$ (d$_{z^2}$) orbital to higher-lying $e''$ (d$_{xz}$, d$_{yz}$) and $e'$ (d$_{xy}$, d$_{x-y^2}$) orbitals in D$_{3h}$ symmetry (or related nondegenerate orbitals in the actual C$_1$ symmetry) would be expected. As shown in Figure 5.2, the LUMO of (Cp$'$$_3$Y)$_{1-}$ and LUMO+1 of (Cp$'$$_3$Ho)$_{1-}$ and (Cp$'$$_3$Er)$_{1-}$ do show significant d$_{xz}$/d$_{yz}$ character.

Calculations performed on a three additional homoleptic and two additional heteroleptic complexes, Cp$^R$$_3$Y, and their predicted reduction products, (Cp$^R$$_3$Y)$_{1-}$, suggested that altering the substituents does not change the expected structural changes between Y$^{3+}$ and Y$^{2+}$ complexes. Additionally, calculations of the experimentally isolated divalent complexes, [K(2.2.2-cryptand)] [Cp$''$$_2$CpY] and [K(2.2.2-cryptand)][Cp$''$$_2$CpMeY], matched the spectroscopic properties well, suggesting that this computational method is reliable for (Cp$^R$$_3$Y)$_{1-}$ complexes other than (Cp
Similar to the calculations for 3-Y and (Cp’3-Y)1−, LUMOs of CpR3Y reasonably match the HOMOs of (CpR3Y)1− as a d2 orbital, with the Y3+ LUMOs containing slightly more ligand character than the Y2+ HOMOs. In addition, MPA analysis of the Y2+ HOMOs was successful in correlating the percent metal and percent s character of that orbital with the experimentally observed EPR hyperfine coupling constants (A), Table 5.4. NPA analysis of the s orbital spin density at the yttrium metal center also was successful in matching the experimentally observed EPR hyperfine coupling constants. An increase in s character for an orbital would result in an increase of the Fermi contact interaction, which would be expected to show an increase in the value of A.

The LUMO of [(Me3Si)2N]3Y and the HOMO of {[(Me3Si)2N]3Y}1− are similar to those calculated for CpR3Y and (CpR3Y)1−: both are d2 orbitals. Although this would be unexpected for a trigonal planar geometry, in which the d3 and d4 would be expected to be the lowest-lying d orbitals, the agostic interactions with the {[(Me3Si)2N]3}3− ligand geometry, proposed to be responsible for the trigonal pyramidal structure observed in the solid state, appear to alter the d orbital splitting similar to that found for the (Cp3)3− ligand geometry. The HOMO for {[(Me3Si)2N]3Y}1− has a significantly higher % metal and % s character than that found for all (CpR3Y)1− complexes, which helps explain why it has a significantly higher value of A in the EPR spectrum.

Calculations of CpIn3Ln, CpIn3Ln(THF), and predicted reduction products, (CpIn3Ln)1−, (Ln = Y, La) showed results that differ from those of CpR3Y and (CpR3Y)1−. The LUMO of CpIn3Ln(THF) (Ln = Y, La) is different than all others previously discussed, in that the orbital is >80% ligand-based. Hence, reduction might not simply populate the d2 orbital and lead to Ln2+. 
but it could put more electron density on the ligand, making it more reactive. This in turn could lead to the observed metalation as one of the reaction pathways in this complicated reaction. The largest amount of electron density appears on the C₆ ring of the indenide ligand and the observed C–H bond activation occurs in the C₆ ring of the product, \{[(C₉H₇)₂Dy(µ-η⁵:η¹-C₉H₆)]₂\} \{K(2.2.2-cryptand)\}₂. Calculations of two different geometries of unsolvated Cpⁿ⁺₃Ln and (Cpⁿ⁻₃Ln)¹⁻ reveal primarily dₓ² character in the Ln³⁺ LUMO and Ln²⁺ HOMO, with varying amounts of % ligand character depending on the geometry of the indenide ligands. This suggests that isolation of an Ln²⁺ could be possible in the absence of coordinating solvents, like THF, but ligand activation could still be a potential problem.

**Conclusion**

DFT studies on a series of tris(cyclopentadienyl) yttrium complexes in comparison to their proposed or characterized reduction products has identified a class of complexes in the formal +2 oxidation state to have a 4d¹ electron configuration. Calculations of (Cp‴₃Ln)¹⁻ for Ho and Er suggest that these Ln²⁺ ions have a 4fⁿ5d¹ electron configuration, instead of the 4fⁿ⁺¹ configuration found for other literature Ln²⁺ complexes. A trend observed in the EPR hyperfine coupling (A) connects the ligand donation abilities to the % metal and % s character in the HOMO of the reduction product. Additionally, calculations help explain differences in reduction chemistry of Cpⁿ⁺₃Ln complexes, resulting in unexpected C–H activation of the (C₉H₇)¹⁻.
Table 5.4. Electronic excitation summary for (Cp\textsubscript{3}Y\textsuperscript{1−}), (Cp\textsubscript{2}CpY\textsuperscript{1−}), and (Cp\textsubscript{2}Cp\textsubscript{Me}Y\textsuperscript{1−}) computed using TPSSh (or PBE0) and SV(P) basis sets. Only pertinent excitations with oscillator strengths larger than 10\textsuperscript{-3} a.u. are included.

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Table 5.5. Mulliken population analysis summary for anions. The % metal character indicates the total metal contribution to the molecular orbital, the % d character indicates how much of the total orbital comes directly from the metal d orbitals.

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<td>LUMO+4 (148a)</td>
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LUMO+5 (149a) 93 0
LUMO+6 (150a) 26 2
LUMO+7 (151a) 11 6
LUMO+8 (152a) 28 15

References


(61) Liu, T.; Ding, F.; Li, J. Krystallografiya 2004, 49, 867.
(64) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. J. Am. Chem. Soc. 1988, 110, 4983.
(73) For example, \( \text{Cp}_2\text{TiCl}_2 \) (Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622) and \([\text{Cp}_2\text{Ti(\(\mu\)-Cl)}]_2 \) (Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645) have average \( \text{C}(\eta^5\text{-Cp}) \) bond lengths of 2.370 and 2.350 Å, respectively. Similarly, \( \text{Cp}_4\text{Zr} \) (Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 5238) and \( \text{Cp}_3\text{Zr} \) (Lukens, W. L., Jr.; Andersen, R. A. *Organometallics* **1995**, *14*, 3435) both have the same average \( \text{Zr} - \text{C}(\eta^5\text{-Cp}) \) bond length of 2.58 Å.


CHAPTER 6

Computational Analysis of Reduced \((\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}\) and \([\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{Th}\) Species

Introduction*

One of the fundamental characteristics of any metal is the extent to which it loses electrons to form charged species in different formal oxidation states. This ionization can occur in the gas phase to form short-lived species in a wide range of oxidation states, but the number of oxidation states available in solution in molecular metal complexes for productive chemistry is smaller. Chemists have tested the limits of oxidation states of all the elements for over 100 years and the boundaries of oxidation states accessible in solution are well established. The identification of new oxidation states is rare.

Nevertheless, as discussed in Chapter 5, new oxidation states recently have been discovered for the rare earth metals in soluble molecular species by examining reductions of \(\text{Ln}^{3+}\) ions (\(\text{Ln} = \text{yttrium} \) and the lanthanides) with potassium. The first molecular \(\text{Ln}^{2+}\) complexes for \(\text{Ln} = \text{La}, \text{Y}, \text{Ho}, \text{and Er}\) were discovered by reduction of the tris(cyclopentadienyl) complexes, \(\text{Cp'}^3\text{Ln}\) and \(\text{Cp''}^3\text{Ln}\), eq 6.1 \([\text{Cp'} = \text{C}_5\text{H}_4\text{SiMe}_3; \text{Cp''} = \text{C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}]\). Since the rare earth metals have been less studied than other elements, it may be understandable that their full range of oxidation states is just being defined. However, another factor was the experimental difficulty in isolating the \(\text{Y}^{2+}, \text{Ho}^{2+}, \text{and Er}^{2+}\) complexes: the syntheses required short reaction times,

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temperatures below $-35^\circ$C, and argon as an inert atmosphere since the compounds react with dinitrogen. Further studies have shown that 2.2.2-cryptand is a superior encapsulating ligand to stabilize the $K^+$ counterion in these complexes and this has allowed the $+2$ oxidation state to be obtained for $Pr^{2+}$, $Gd^{2+}$, $Tb^{2+}$, and $Lu^{2+}$ in the $[K(2.2.2\text{-cryptand})][Cp^3\text{Ln}]$ complexes, 1. As a result, the $+2$ oxidation state is now known for all the rare earth metals except radioactive promethium.

$$\begin{align*}
\text{Ln} = Y, \text{La, Ce, Ho, Er} & \quad R = \text{SiMe}_3 \quad R' = \text{H or SiMe}_3 \\
\end{align*}$$

It was of interest to determine if this approach to new $M^{2+}$ ions for the rare earth metals would apply to uranium. Although similarities are often cited in the oxidation state chemistry of the rare earth metals and the later actinides from berkelium on, there is no reason to expect that uranium, with its diverse oxidation state chemistry involving $+3$, $+4$, $+5$, and $+6$ ions, would necessarily mimic the rare earths in this regard. In fact, since the search for the existence of a $U^{2+}$ ion in molecular species had been active for over 30 years it might be expected that uranium would not behave analogously.

Attempts to synthesize molecules containing $U^{2+}$ were published as early as 1980. During this time period, species such as “$(C_5\text{Me}_5)_2U$” were discussed as possible transient intermediates in $U^{3+}$ reduction reactions, although it was concluded that “there is no evidence that any uranium(II) species is ever produced”. $U^{2+}$ has also been discussed in complexes
where the oxidation states of the ligands are ambiguous.\textsuperscript{12-20} For example, the [(anion)\textsubscript{2}U\textsubscript{2}](C\textsubscript{6}H\textsubscript{6}) complexes could contain U\textsuperscript{4+} and (C\textsubscript{6}H\textsubscript{6})\textsuperscript{4−}, U\textsuperscript{3+} and (C\textsubscript{6}H\textsubscript{6})\textsuperscript{2−}, or U\textsuperscript{2+} and neutral benzene, C\textsubscript{6}H\textsubscript{6}.\textsuperscript{12,13,20} Since the C\textsubscript{6}H\textsubscript{6} moiety in these complexes is not planar and is not displaced by strong neutral donor ligands, the U\textsuperscript{2+} hypothesis is unlikely. Solid state structures formally containing U\textsuperscript{2+}, e.g., the sulfide US,\textsuperscript{21} have been known since the 1950s, but these have properties consistent with U\textsuperscript{3+} or U\textsuperscript{4+} with delocalized electrons in the solid state lattice.\textsuperscript{22} U\textsuperscript{2+} has also been reported in the gas phase,\textsuperscript{23} as a transient ion formed radiolytically,\textsuperscript{24} and as OUCO in a neon matrix,\textsuperscript{25} but molecular U\textsuperscript{2+} species isolable in solution were unknown.

Synthesis of a Th\textsuperscript{2+} complex seemed even more unlikely for several reasons. Complexes of Th\textsuperscript{3+} are already difficult to obtain. The Th\textsuperscript{4+/Th\textsuperscript{3+}} redox potential is estimated to be between −3.0 and −3.8 V vs. NHE\textsuperscript{26-28} and a Th\textsuperscript{3+/Th\textsuperscript{2+}} redox potential of −4.9 V vs. NHE is in the literature.\textsuperscript{29} Reduction to metallic thorium would be predicted to be favored before formation of a Th\textsuperscript{2+} species.\textsuperscript{29} Many studies have been reported to find oxidation states lower than +4 for thorium,\textsuperscript{30-44} but only five Th\textsuperscript{3+} complexes have ever been structurally characterized.\textsuperscript{36,38,39,43,44}

Nevertheless, the first isolable molecular species containing a U\textsuperscript{2+} ion and a Th\textsuperscript{2+} ion were both obtained from the reduction of Cp’\textsubscript{3}U, \textbf{2}, to form [K(2.2.2-cryptand)][Cp’\textsubscript{3}U], \textbf{3}, and the reduction of Cp’’\textsubscript{3}Th, \textbf{4}, to form [K(2.2.2-cryptand)][Cp’’\textsubscript{3}Th], \textbf{5}, respectively, eq 6.2. In this Chapter, density functional theory (DFT) is used to analyze these new U\textsuperscript{2+} and Th\textsuperscript{2+} complexes. These calculations indicate that the U\textsuperscript{2+} complex, \textbf{3}, has a quintet 5f\textsuperscript{3}6d\textsuperscript{1} electron configuration, while the Th\textsuperscript{2+} complex, \textbf{5}, has a 6d\textsuperscript{2} configuration.
Experimental

**Uranium Computational Details.** Structural optimizations starting from the crystal data of 2\textsuperscript{45} and 3 were carried out using density functional theory (DFT) for several possible electronic occupations to determine the ground state of each complex. Counter cations were removed from the experimental crystal structures before the start of each optimization. Quartet and doublet states corresponding to a $5f^3$ occupation were investigated for 2, while for 3 triplet and quintet states both corresponding to a $5f^36d^1$ occupation were pursued. The hybrid meta-GGA functional of Tao, Perdew, Staroverov, and Scuseria, TPSSh\textsuperscript{46} was used in conjunction with double-zeta quality split-valence basis sets with polarization functions [def2-SV(P)]\textsuperscript{47} for all non-hydrogen, light atoms. Small quasi-relativistic effective core potentials\textsuperscript{48} (ECPs) and triple-zeta quality basis sets (def-TZVP)\textsuperscript{49} were used for U. Vibrational frequencies\textsuperscript{50} were computed for the optimized structures and these were confirmed to be potential energy minima by the absence of imaginary modes.

In order to account for solvation effects, a second structural optimization was carried out using the continuum solvation model (COSMO).\textsuperscript{51} The dielectric constant of THF ($\varepsilon = 7.520$)\textsuperscript{52}
was used for the reported COSMO calculations since this was the most polar solvent used in the synthesis. Solvent effects have been shown to be important for Ln$^{2+}$ systems because they screen the additional negative charge.$^{3,4}$ The changes in bond length between the SV(P) optimized structures and those from a third optimization using TZVP basis sets for light atoms were typically smaller than 0.02 Å. All results were computed in C$_1$ symmetry, and ground state energies were converged to $10^{-7}$ a.u. using fine quadrature grids (at least size m4).$^{53}$ Molecular orbitals were plotted with a contour value of 0.05. All calculations were carried out using the TURBOMOLE version 6.5 program package.$^{54}$

The results of the initial optimizations indicated the quartet structure was lower in energy for Cp’$^3$U, 2, as expected for 5f$^3$ U$^{3+}$, and that the quintet structure was lower in energy for (Cp’$^3$U)$^{1-}$, 3. Additional single-point energy calculations of the triplet-quintet energy gap were then performed on the optimized TPSSH quintet structure for 2 using different density functionals,$^{55-57}$ Table 6.1, to ensure the result is not sensitive to the choice in functional.

**Table 6.1.** Spin state energy differences for (Cp’$^3$U)$^{1-}$, 3, predicted by different functionals. Def2-SV(P) basis sets were used for all light atoms, except TPSS which was paired with def2-SVPD basis sets for light atoms.

<table>
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<tr>
<th>Functional</th>
<th>Energy Splitting (E$<em>{\text{triplet}}$ − E$</em>{\text{quintet}}$) (kcal/mol)</th>
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<td>TPSSH</td>
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</tr>
<tr>
<td>TPSS</td>
<td>4.90</td>
</tr>
<tr>
<td>BHLYP</td>
<td>6.46</td>
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<tr>
<td>B3LYP</td>
<td>6.06</td>
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All of the methods tested predict the quintet to be the ground state with the triplet state approximately 4-7 kcal/mol higher in energy. Mulliken population analysis\textsuperscript{58} (MPA) indicates both states to be $5f^36d^1$ in character, differing primarily in the spin orientation of the $6d^1$ electron. Tests with larger basis sets for light atoms led to small changes in the energy differences, but not to the overall trend.

Time dependent DFT (TDDFT) excitation energy calculations\textsuperscript{59} of the lowest 200 spin-unrestricted excitations of 3 were carried out on the solvent—optimized structures using the recently developed gauge-invariant implementation\textsuperscript{60} of TPSSh and split-valence basis sets. The first 90 excitations for 2 were also computed from self-consistent orbitals, obtained on the optimized structures using TPSS\textsuperscript{61} within the RI-J approximation,\textsuperscript{62-64} in order to compare with the excitations predicted for 3. The change from TPSSh to TPSS did not change the qualitative comparison, but greatly reduced the computational cost of the calculations. Diffuse functions were also added to the basis set (def2-SVPD)\textsuperscript{65} for light atoms, while small core ECPs and TZVP basis sets were used for uranium. To simulate the UV-Vis spectra, a normalized Gaussian scaled by the predicted oscillator strength was centered at each molecular excitation, and a root mean square width of 0.23 eV was chosen to fit experiment.\textsuperscript{66} Representative excitations (in nm) and oscillator strengths in the length gauge (in a.u.) from each band, and dominant single-particle contributions for each transition are reported in Table 6.2 (at the end of the Chapter).

Between 550 and 900 nm, the predicted excitations for 2 and 3 are generally metal-to-metal with strong $d\rightarrow s/p$ and $f\rightarrow s/p$ character. The ligand contribution to these transitions is much smaller than for the shorter wavelength absorptions, and thus the extinction coefficients are smaller. In the 350-550 nm range the excitations are $f/d\rightarrow\pi^*$ in nature and show increased
ligand character with the decrease in wavelength. For 2, the predicted oscillator strengths for excitations in this region of the spectrum are considerably smaller than those of 3, which is expected for transitions originating from the 5f\(^3\) configuration of U\(^{3+}\) where the f orbitals do not effectively mix with the ligand orbitals. The sharp, narrow peak near 300 nm for 3 is predominantly a ligand to metal charge transfer excitation from the Cp’ π orbitals to the singly occupied 5d\(\sigma\) orbital. This peak is entirely absent in the experimental spectrum of 2, but present in the spectra measured and predicted for 3.

For further comparison, the lowest 150 excitations of the triplet state for 3 were also computed, Table 6.2. However, the predicted curve does not match the experimental spectrum in shape or intensity in the 500-900 nm range. This result, in addition to the lower total energy of the quintet state, further validates the assigned 5f\(^3\)6d\(^1\) ground state for U\(^{2+}\) in 3. These calculations were performed in a collaboration with Jefferson E. Bates in the group of Professor Filipp Furche at UC Irvine.

**Thorium Computational Details.** Initial gas-phase structural optimizations were performed starting from the crystal data of [C\(_3\)H\(_3\)(SiMe\(_3\))\(_2\)]\(_3\)Th, 4,\(^{36}\) and [K(2.2.2-cryptand)]\{[C\(_3\)H\(_3\)(SiMe\(_3\))\(_2\)]\(_3\)Th\}, 5, using the hybrid meta-GGA functional, TPSSh.\(^{46}\) Counter cations were removed from the crystal structure of 5 before the start of the optimizations. Double-zeta quality split-valence basis sets with polarization functions, [def2-SV(P)],\(^{47}\) were used for all non-hydrogen, light atoms. Scalar-relativistic effective core potentials (ECPs)\(^{67}\) and triple-zeta valence basis sets, def-TZVP,\(^{68}\) with the two tight g functions removed, were used for Th. Vibrational frequencies\(^{50}\) were computed for the optimized structure of 5 and the structure was confirmed to be a potential energy minimum by the absence of imaginary modes.
In order to account for solvation effects, a second structural optimization was carried out using the continuum solvation model (COSMO). The dielectric constant of THF ($\varepsilon = 7.520$) was used for the reported COSMO calculations since this was the most polar solvent used in the synthesis. Solvent effects have been shown to be important for Ln$^{2+}$ systems because they screen the additional negative charge. The changes in bond length between the SV(P) optimized structures and those from a third optimization using TZVP basis sets for light atoms were typically smaller than 0.02 Å. All results were computed in C1 symmetry and ground state energies were converged to $10^{-7}$ a.u. using fine quadrature grids (at least size m4). Molecular orbitals were plotted with a contour value of 0.05. All calculations were carried out using the TURBOMOLE version 6.5 program package. Calculations of (C$_{5}$H$_{5}$)$_{3}$Th and [(C$_{5}$H$_{5}$)$_{3}$Th]$^{1-}$ were performed by Professor Filipp Furche at UC Irvine.

Time dependent DFT (TDDFT) excitation energy calculations of the lowest 60 spin-unrestricted excitations of 4, and the lowest 60 excitations from self-consistent orbitals for 5 were carried out on the solvent optimized structures using the recently developed gauge-invariant implementation of TPSSh and split-valence basis sets. Diffuse functions were also added to the basis set (def2-SVPD) for light atoms, while small core ECPs and TZVP basis sets were used for thorium. To simulate the UV-Vis spectra, a normalized Gaussian scaled by the predicted oscillator strength was centered at each molecular excitation, and a root mean square width of 0.14 eV was chosen to fit experiment. Representative excitations (in nm) and oscillator strengths in the length gauge (in a.u.) from each band, and dominant single-particle contributions for each transition are reported in Table 6.2.
Transitions were analyzed with a Mulliken population analysis (MPA).\(^{58}\) Between 500 and 800 nm the predicted excitations for 4 and 5 are primarily metal-to-metal with strong d/s→p/f character and minor ligand contributions. Excitations around 750 nm have mostly d/s→f character, while the excitations localized near 600 nm have mostly d/s→p character. Two large groups of excitations are predicted in the 300-400 nm range, which consist of d/s→π* excitations. As the wavelength decreases, the transitions go to orbitals with more ligand character, similar to that seen for the lanthanides and uranium. Predicted excitations for 4 are very similar to those for 5, although the oscillator strengths for the excitations are much weaker than for 5, which is consistent with intensities of the experimental spectra. Between 370 and 900 nm, the predicted excitations are primarily metal-to-metal, with d/s→f character between 700 and 900 nm and d/s→p character between 370 and 500 nm. Below 370 nm, the transitions consist of d/s→π* excitations.

Results/Discussion

**Uranium(II) Calculations.** X-ray diffraction data showed that [K(2.2.2-cryptand)][Cp′\(_3\)U], 3, is isomorphous with the Ln\(^{2+}\) rare earth complexes, [K(2.2.2-cryptand)][Cp′\(_3\)Ln] (Ln = Y, Pr, Gd, Tb, Ho, Er, Lu), 1.\(^4\) The [K(2.2.2-cryptand)]\(^+\) cation in 3 is well separated from the anion and has normal structural parameters.\(^4\) The average U–(Cp′ ring centroid) distance in 3 (2.521 Å) is 0.013 Å longer than that in Cp′\(_3\)U, 1 (2.508 Å).\(^45\) This small difference is similar to the 0.02–0.03 Å difference between the 4f\(^n\) Ln\(^{3+}\) Cp′\(_3\)Ln complexes and the Ln\(^{2+}\) complexes 1 that appear to have 4f\(^n+5d^1\) rather than 4f\(^n+1\) electron configurations.\(^4\) The small difference in distances between 3 and 2 is consistent with 6d character in 3 as these small changes in M–(ring
centroid) distances match the small changes in radial size commonly seen in transition metal complexes,\textsuperscript{69} but contrast with the 0.10-0.20 Å differences generally seen for complexes of 4f\(^{n+1}\) Ln\(^{2+}\) complexes compared to their 4f\(^n\) Ln\(^{3+}\) counterparts.\textsuperscript{70-76}

Density functional theory (DFT)\textsuperscript{54} was used to examine the energies of the possible electron configurations for the U\(^{2+}\) ion in 3. Small core quasi-relativistic effective core potentials and basis sets were used for uranium.\textsuperscript{48,49} The DFT calculations indicate a 5f\(^3\)6d\(^1\) quintet ground state for the (Cp\('\)\textsubscript{3}U)\(^{1-}\) anion. The highest occupied molecular orbital (HOMO) has mainly 6d\(^1\) character and resembles a d\(_{z^2}\) orbital, Figure 6.1. This is similar to the HOMOs of the 4f\(^n\)5d\(^1\)

![Density functional theory calculations.](image)

**Figure 6.1.** Density functional theory calculations. (a) Contour plot of the HOMO of the (Cp\('\)\textsubscript{3}U)\(^{1-}\) anion in 3. Contour value is 0.05. (b) Qualitative 5f and 6d splitting of the different electronic configurations found in gas-phase and molecular U\(^{2+}\) ions.

Ln\(^{2+}\) complexes, 1.\textsuperscript{4} Previous studies of trivalent tris(cyclopentadienyl) actinide complexes\textsuperscript{5,37,39,77,78} have shown the 6d\(_{z^2}\) orbital can be comparable in energy with he 5f orbitals. Calculations also indicate a 5f\(^3\) quartet ground state for 1 and predict a small change of U−(Cp'
ring centroid) distance between the \((\text{Cp}'_3\text{U})^{1-}\) anion and 2 as 0.017 Å, similar to the experimental observation.

Atomic spectral data suggested that ground state assignment for \(\text{U}^{2+}\) is \(5f^4\) with the lowest lying excited state having \(6f^35d^1\) character.\textsuperscript{79,80} Given that the measured d-f splitting is only 210 cm\(^{-1}\) for \(\text{U}^{2+}\) in the gas phase, the appropriate chemical environment might shift the relative ordering of these configurations. In fact, results from Bursten et al.\textsuperscript{5,77,78} indicated that the \(6d_z\) orbital should mix with the \(7s\) orbital, but still remain non-bonding to the Cp ligands, resulting in an overall stabilization with respect to the other d orbitals by the trigonal \((\text{Cp}_3)^{3-}\) ligand field. In their reported MO diagram for \(\text{Cp}_3\text{U}\) this hybrid orbital is below the valence f/π manifold for uranium. The small energy difference in the atom also suggests that the ground state of 3 may have some multi-reference character, and the possibility of a \(5f^4\) state with considerable weight in the true ground-state wavefunction of the complex can not be excluded. Nevertheless, the results discussed above suggest that the \(5f^36d^1\) configuration is dominant.

The UV-vis spectrum of 2 displays low extinction coefficients typical of \(f \rightarrow f/\pi^*\) transitions for the \(5f^3\) \(\text{U}^{3+}\) ion. Here, \(f \rightarrow f/\pi^*\) denotes a mixture of \(f \rightarrow f\) and \(f \rightarrow \pi^*\) transitions with considerable ligand character. Complex 3 on the other hand, absorbs much more strongly in the UV-vis due to transitions of predominantly \(6d \rightarrow 6d/\pi^*\) character, Figure 6.1. This behavior is reminiscent of the \(\text{Ln}^{2+}\) complexes, 1, which exhibit strong \(5d \rightarrow 5d/\pi^*\) transitions in the UV-vis region.\textsuperscript{4} Time dependent DFT calculations of the UV-vis spectra of 2 and \((\text{Cp}_3\text{U})^{1-}\), Figure 6.2, qualitatively match the experimental results. The calculations on \((\text{Cp}_3\text{U})^{1-}\) predict strong absorptions due to \(6d \rightarrow \pi^*/5f\) and \(\pi \rightarrow 6d/5f\) transitions that match the experimentally observed peaks. In contrast, the calculated excitations of 2 lack strong absorptions in the 350–900 nm
range. This is consistent with the 6d\(^1\) character of the ground state of (Cp\(^3\)U)\(^{1-}\) vs the 5f\(^3\) configurations of the U\(^{3+}\) complex 2.

![UV-vis spectrum](image)

**Figure 6.2.** Experimental (solid) and calculated quintet (dotted) UV-vis spectra of (Cp\(^3\)U)\(^{1-}\) in THF at 298 K, with pertinent theoretical excitations shown as vertical lines and theoretical extinction coefficients scaled down by a factor of 1.5.

**Thorium(II) Calculations.** X-ray diffraction data showed that both Cp\(^{"}\)\(^3\)Th, 4, and [K(2.2.2-cryptand)][Cp\(^{"}\)\(^3\)Th], 5, have a trigonal planar arrangement of the three Cp\(^"\) rings around thorium with a sum of (ring centroid)-Th-(ring centroid) angles of 360°. The average Th–(Cp\(^"\) ring centroid) distances of 2.521 Å in 5 are equivalent to the 2.520 Å distances in 4. These negligible differences in the Th–(ring centroid) distances between the Th\(^{3+}\) precursor and the formally Th\(^{2+}\) complex is similar to the small differences between 2 and 3 discussed above for uranium and the small differences between the Cp\(^{3}\)Ln complexes and 1. As described above for
uranium, these small changes in M–(ring centroid) distances match the small changes in radial size commonly seen in transition metal complexes. In the case of 1, this was attributed to a 4f⁶5d¹ configuration. NMR spectroscopy (¹H NMR and ¹³C NMR), EPR, SQUID and Evans method measurements all suggested that the (Cp''₃Th)₁⁻ anion has no magnetic moment.

DFT using the TPSSh functional was used to examine the (Cp''₃Th)₁⁻ anion in 5. Calculations using scalar-relativistic effective core potentials and triple-zeta valence basis sets, def-TZVP, for thorium predicted trigonal planar structures for 4 and (Cp''₃Th)₁⁻ that match the crystallographic data. The calculated Th–(Cp'' ring centroid) lengths of 2.538 Å for 4 and 2.526 Å (Cp''₃Th)₁⁻ are similar to the experimentally determined distances of 2.52 Å. It is interesting to note that the calculations for the Th³⁺ complex show a slightly longer metal ligand distance than for the Th²⁺ complex. The calculations indicate a spin-paired ground state of 6d² for (Cp'₃Th)₁⁻ and a 6d¹ ground state for Cp''₃Th; the latter is consistent with previous analyses of Cp'₃Th, (C₅Me₅)₂[¹PrNC(Me)N¹Pr]Th⁴³ and [K(DME)₂][{C₈H₆(Si¹BuMe₂)₂}₂Th]₄⁸. Gas-phase studies of Th²⁺ indicate a ground state of 5f¹6d¹, but the 6d² configuration is just 63 cm⁻¹ higher and the 5f¹7s¹ is 2527 cm⁻¹ higher than the ground state.⁸⁰ For [(C₅H₅)₂Th]⁻ the triplet 5f¹6d¹ state is computed to be 9–14 kcal/mol higher in energy than the singlet 6d² ground state.

The 6d² singlet ground state can arise in this case due to stabilization of a d₄z orbital by the trigonal ligand environment as found in DFT calculations on (Cp'₃Ln)₁⁻ and (Cp'₃U)₁⁻ complexes, discussed above, and noted earlier in the literature for tris(cyclopentadienyl) metal complexes.⁵,³⁷,³⁹,⁷⁷,⁷⁸,⁸⁴-⁸⁶ Indeed, both the lowest unoccupied molecular orbital (LUMO) of Cp''₃Th and the highest occupied molecular orbital (HOMO) of (Cp''₃Th)₁⁻ have d₄z character, Figure 6.3.
Figure 6.3. Contour plots of (a) the LUMO of Cp''₃Th and (b) the HOMO of the (Cp''₃Th)¹⁻ anion in 5. Contour value is 0.05.

The UV-vis spectrum of 5 in THF contains intense absorptions near 650 nm with extinction coefficients as high as 23000 M⁻¹ cm⁻¹. This value is significantly larger the highest extinction coefficient of 5000 M⁻¹ cm⁻¹ for Cp''₃Th, which is quite similar to the extinction coefficients observed for the 4fⁿ5d¹ Ln²⁺ and 5f³6d¹ U²⁺ complexes, 1 and 3, respectively.⁴,⁸³

Time-dependent density functional theory was used to simulate the UV-vis spectra for Cp''₃Th, Figure 6.4, and (Cp''₃Th)¹⁻, Figure 6.5. The maxima in the calculated spectra are lower in energy than those observed experimentally, but this is often the case with such calculations.⁸⁷ Analysis of the calculated low energy peak for (Cp''₃Th)¹⁻ shows that it arises from metal-to-metal transitions that have d → f and d → p character. The high energy peaks arise from metal-to-ligand charge transfer transitions similar to those found in the spectral analysis of (Cp'Ln)¹⁻²⁻⁴ and (Cp'U)¹⁻⁸³. However, the d → f transitions found for (Cp''₃Th)¹⁻ were not apparent in the analysis of the spectra of (Cp'Ln)¹⁻²⁻⁴ and (Cp'U)¹⁻⁸³. The calculated oscillator strengths of the 6d¹ Th³⁺ complex are very similar to the calculated oscillator strengths of the U²⁺ complex,
assigned with a 5f^36d^1 configuration. The intense increase in extinction coefficients from a 6d^0 to 6d^1 to 6d^2 suggests that the occupancy of the d_z^2 orbital has a significant impact on the absorption properties of these complexes.

Figure 6.4. Experimental (solid) and calculated (dotted) UV-vis spectra of 4 in THF at 298 K, with pertinent theoretical excitations shown as vertical lines and theoretical extinction coefficients scaled down by a factor of 1.5.
Figure 6.5. Experimental (solid) and calculated (dotted) UV-vis spectra of 5 in THF at 298 K, with pertinent theoretical excitations shown as vertical lines and theoretical extinction coefficients scaled down by a factor of 1.4.

Conclusion

In summary, the use of density functional theory (DFT) has been useful in assigning a quintet $5f^36d^1$ ground state for the first isolated molecular $U^{2+}$ complex, [K(2.2.2-cryptand)] [Cp$'_3$U], and a singlet $6d^2$ ground state for the first isolated molecular $Th^{2+}$ complex, [K(2.2.2-cryptand)][Cp$''_3$Th]. Time-dependent DFT was valuable to understand the electronic properties behind the unique new electron configurations.
Table 6.2. Electronic excitation summary for 2 and 3 (S = 1), computed using TPSS and SVPD basis sets for light atoms, and corresponding ECPs/basis sets for the heavy metals as described in the text. TPSSh was used for the S = 2 state of 3, 4 and 5. Only excitations that have the largest oscillator strength (in the length gauge) from each band are reported. The 130 α orbital is the HOMO for 2, while 131 α is the HOMO for S = 2 for 3. The 128 β orbital is unoccupied for 1 and S = 2 of 3, while it is occupied for the S = 1 state of 3.

| Compound | Wavelength (nm) | Oscillator Strength (len) | Dominant Contributions |%
|----------|----------------|---------------------------|------------------------|
| 2        | 1264.6         | 0.004                     | 129 α 131 α            | 39.0
|          | 906.5          | 0.002                     | 129 α 132 α 134 α     | 25.5
|          | 864.1          | 0.001                     | 128 α 134 α 133 α     | 35.2
|          | 436.4          | 0.005                     | 130 α 134 α 133 α     | 21.0
|          | 406.5          | 0.006                     | 130 α 140 α 126 α     | 95.3
|          | 342.0          | 0.026                     | 128 α 150 α 132 α     | 47.2
|          | 300.9          | 0.0006                    | 128 α 135 α 150 α     | 44.7
| 3 (S = 2)| 784.8          | 0.008                     | 128 α 133 α 135 α     | 53.1
|          | 611.0          | 0.009                     | 131 α 136 α 135 α     | 36.4
|          | 489.5          | 0.014                     | 131 α 143 α 130 α     | 26.4


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References


CHAPTER 7

Structural, Spectroscopic, and Theoretical Comparison of Traditional vs Recently Discovered Ln$^{2+}$ Ions in the [K(2.2.2-cryptand)][(C$_5$H$_4$SiMe$_3$)$_3$Ln] Complexes: The Variable Nature of Dy$^{2+}$ and Nd$^{2+}$

Introduction*

For over 50 years, it was thought that only six lanthanide elements would form +2 ions. Eu$^{2+}$, Yb$^{2+}$, and Sm$^{2+}$ were known since the 1920s in solution and in the solid state. Tm$^{2+}$, Dy$^{2+}$, and Nd$^{2+}$ were known only in the solid state until 1997–2001 when the first solution examples were found. The existence of just six Ln$^{2+}$ ions was well justified on the basis of extensive solid state data and calculated redox potentials. Solid state compounds formed under thermodynamic control at high temperature that contained +2 ions by stoichiometry, e.g., LnX$_2$,, were found to be Ln$^{2+}$(X$^{1−}$)$_2$ salts only with Ln = Eu, Yb, Sm, Tm, Dy, and Nd. For the other lanthanides, the solids were best described as Ln$^{3+}$(X$^{1−}$)$_2$(e$^{1−}$) materials with a delocalized electron in a conduction band; i.e., Ln$^{2+}$ did not form under these conditions. A “configuration crossover” was described for the difference between the six “pseudo-alkaline-earth lanthanides,” i.e., Eu, Yb, Sm, Tm, Dy, and Nd, and the other lanthanides.

A similar dichotomy was observed in solution based on calculated generic reduction potentials for conversion of a 4f$^n$ Ln$^{3+}$ ion to a 4f$^{n+1}$ Ln$^{2+}$ ion, Table 7.1. The calculated reduction potentials for the lanthanides beyond the traditional six Ln$^{2+}$ ions known in the solid state were so negative, namely, −2.7 to −3.9 V vs NHE (−3.1 to −4.3 V vs Fc/Fc$^+$), that these

ions would be expected to decompose all common solvents. Indeed, the high reactivity of even Dy$^{2+}$ and Nd$^{2+}$ with solvents suggested that the more reducing ions would be unstable in solution.$^{8-10,13,14,24-29}$

**Table 7.1.** Calculated Ln$^{3+}$/Ln$^{2+}$ Reduction Potentials of Yttrium and the Lanthanides.$^{17,22}$

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<td>Pr</td>
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<td>Sm</td>
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However, as described in Chapter 5, it subsequently was shown that Ln$^{2+}$ ions are accessible for all of the lanthanides except Pm, which was not investigated because of its radioactivity. Complexes of nine new +2 ions, La$^{2+}$, Ce$^{2+}$, Pr$^{2+}$, Gd$^{2+}$, Tb$^{2+}$, Ho$^{2+}$, Er$^{2+}$, Y$^{2+}$, and Lu$^{2+}$, were synthesized via Schemes 7.1 and 7.2.$^{30-33}$ These new complexes had major structural differences compared to complexes of the traditional six +2 ions in that the difference in bond distances between a +2 ion complex and its +3 ion analog was small. Hence, all of the Ln$^{2+}$ complexes in Schemes 7.1 and 7.2 have Ln−(cyclopentadienyl ring centroid) distances that are only 0.020–0.032 Å (~1%) longer than their Ln$^{3+}$ analogs. This contrasted so sharply with the 0.10–0.20 Å (~6%) differences generally seen for complexes of Eu$^{2+}$, Yb$^{2+}$, Sm$^{2+}$, Tm$^{2+}$, Dy$^{2+}$,
and Nd\textsuperscript{2+} compared to their Ln\textsuperscript{3+} counterparts\textsuperscript{9,10,18,34–37} that there was initial skepticism that the new complexes contained +2 ions.

**Scheme 7.1.** Crystallographically Characterized Products of Reduction of Cp''\textsubscript{3}Ln (Ln = La and Ce; Cp'' = C\textsubscript{5}H\textsubscript{3}(SiMe\textsubscript{3})\textsubscript{2}-1,3) by Lappert et al.\textsuperscript{30}

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{Ln} & \quad \text{Me}_3\text{Si} \\
\text{SiMe}_3 & \quad \text{SiMe}_3 \\
\text{SiMe}_3 & \quad \text{SiMe}_3 \\
\text{Ln} = \text{La, Ce} & \quad \text{(1)} \\
\end{align*}
\]

+ K + 18-crown-6 Et\textsubscript{2}O, Ar

\[
\begin{align*}
\text{[K(18-crown-6)(OEt\textsubscript{2})][Cp''\textsubscript{3}La]} & \quad \text{and} \\
\text{[K(18-crown-6)(OEt\textsubscript{2})\textsubscript{2}][Cp''\textsubscript{3}Ce]\text{·}[Cp''\textsubscript{3}Ce]} & \quad \text{(2)} \\
\end{align*}
\]

**Scheme 7.2.** Crystallographically Characterized Products of Reduction of Cp'\textsubscript{3}Ln (Ln = Y, Pr, Gd, Tb, Ho, Er, Lu; Cp' = C\textsubscript{5}H\textsubscript{4}SiMe\textsubscript{3}).\textsuperscript{31–33}

\[
\begin{align*}
\text{SiMe}_3 & \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{Ln} & \quad \text{Me}_3\text{Si} \\
\text{Ln} = \text{Y, Ho, Er} & \quad \text{(1)} \\
\end{align*}
\]

+ KC\textsubscript{8} + 18-crown-6 Et\textsubscript{2}O, Ar

\[
\begin{align*}
\text{[K(2.2.2-cryptand)][Cp''\textsubscript{3}La]} & \quad \text{(2)} \\
\text{[K(2.2.2-cryptand)][Cp''\textsubscript{3}La]} & \quad \text{(2)} \\
\end{align*}
\]
The large differences in bond distances between Ln\(^{2+}\) complexes of the traditional six Ln\(^{2+}\) lanthanides and their Ln\(^{3+}\) analogs are expected, since there are large differences between the radii of 4\(f^n\) Ln\(^{3+}\) and 4\(f^{n+1}\) Ln\(^{2+}\) ions and there is little metal–ligand interaction due to the contracted nature of the 4f orbitals. A typical example is that the average Sm–(C\(_5\)Me\(_5\) centroid) and Sm–O distances in the Sm\(^{2+}\) complex (C\(_5\)Me\(_5\))\(_2\)Sm(THF)\(_2\) (2.599 and 2.633 Å, respectively)\(^{38}\) are 0.176 and 0.173 Å longer than those in the compositionally similar Sm\(^{3+}\) compound [(C\(_5\)Me\(_5\))\(_2\)Sm(THF)\(_2\)][BPh\(_4\)] (2.423 and 2.457 Å).\(^{39}\) Another example pertinent to this study is the 2.486 Å average Sm–(Cp\(^n\) centroid) distance in the Sm\(^{3+}\) complex, Cp\(^n\)_3Sm,\(^{40}\) vs the 2.676 Å analog in [K(18-crown-6)(toluene)]{Cp\(^n\)_3Sm}.\(^{35}\)

The small differences in bond distances in the +2 vs +3 complexes in Schemes 7.1 and 7.2 were similar to the small changes with changing oxidation state observed in transition metal complexes.\(^{41}\) In transition metal complexes, the bonding is not simply a sum of ionic radii because there are covalent interactions between the metal d orbitals and the ligands. Since spectroscopic and theoretical analyses indicated that the Ln\(^{2+}\) ions in Schemes 7.1 and 7.2 had 4\(f^n5d^1\) and not 4\(f^{n+1}\) electron configurations (4\(d^1\) for Y\(^{2+}\)), the small increases in bond distances could be explained by the d character in the configurations of the +2 ions. The accessibility of d\(^1\) configurations for these ions was consistent with the crystal field splitting in the tris(cyclopentadienyl) ligand environment of these compounds.\(^{42-47}\) In this trigonal field, the d\(_{z^2}\) orbital is lowest in energy. Apparently, its energy is low enough with respect to the 4f orbitals that the d\(_{z^2}\) orbital can be populated in the reduction reactions of Schemes 7.1 and 7.2.

Although a correlation existed between 4\(f^n5d^1\) electron configuration and Ln\(^{3+}\)/Ln\(^{2+}\) size differences for the +2 ions in Schemes 7.1 and 7.2 vs the traditional six +2 ions with 4\(f^{n+1}\)
configurations, the size comparisons were not made on the same set of complexes. Accordingly, it was of interest to make the [K(2.2.2-cryptand)][Cp′3Ln] complexes, 2, of the traditional six +2 ions, Eu²⁺, Yb²⁺, Sm²⁺, Tm²⁺, Dy²⁺, and Nd²⁺, for direct comparison with those in Scheme 7.2. To include comparisons with the Ln²⁺ ions found by Lappert, Scheme 7.1, using one uniform ligand set, the Ln = La and Ce versions of 2 were also synthesized. To make the Ln³⁺/Ln²⁺ bond distance comparisons, the Cp′₃Ln complexes, 1, of Eu, Yb, Sm, Tm, and Dy also had to be synthesized and structurally characterized.

These syntheses and crystallographic analyses allow the first comparison of all the lanthanides in the same coordination environment in both +2 and +3 oxidation states. The results are described in this Chapter along with a comparison of UV–vis spectra of the analogous complexes of the traditional six Ln²⁺ ions vs all the other Ln²⁺ ions in the series. The density functional theory (DFT) analysis of the structural and spectroscopic data have proven very valuable in understanding the results and are also reported.

Experimental

The syntheses and manipulations described below were conducted under argon with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were sparged with UHP grade argon (Airgas) and passed through columns containing Q-5 and molecular sieves before use. NMR solvents (Cambridge Isotope Laboratories) were dried over NaK/benzophenone, degassed by three freeze–pump–thaw cycles, and vacuum-transferred before use. Anhydrous LnCl₃ (Ln = La, Ce, Nd, Sm, Dy, Yb), LnI₂(THF)₂ (Ln = Eu, Yb), LnI₃(THF)₃.₅ K₈C₈, AgBPh₄, KC₈, Cp′₃Ln, 1-Ln (Ln = La, Ce, Nd, Sm, Dy, Yb), were
prepared according to literature. 2,2,2-Cryptand, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Acros Organics), was placed under vacuum (10⁻³ Torr) for 12 h before use. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were obtained on a Bruker GN500 or CRYO500 MHz spectrometer at 298 K. For some paramagnetic compounds, ¹H NMR spectra could only be observed when a capillary tube containing pure deuterated solvent was placed in the paramagnetic solution to assist in properly locking and shimming the instrument. IR samples were prepared as KBr pellets, and the spectra were obtained on a Varian 1000 FT-IR spectrometer. Elemental analyses were performed on a PerkinElmer 2400 series II CHNS elemental analyzer. UV−vis spectra were obtained in THF at 298 K using a Varian Cary 50 Scan UV−vis spectrophotometer.

[K(2.2.2-cryptand)][Cp′₃La], 2-La. In an argon-filled glovebox, Cp′₃La, 1-La (208 mg, 0.378 mmol), and 2,2,2-cryptand (142 mg, 0.377 mmol) were combined and dissolved in THF (2 mL). KC₈ (75 mg, 0.55 mmol) was quickly added to the stirred colorless solution. The reaction mixture immediately turned black/violet, and after 1 min of stirring, Et₂O (3 mL) was added and the mixture was filtered to remove a black precipitate, presumably graphite. The dark purple filtrate was cooled to −35 °C in the freezer for 1 h. The solution was layered with additional Et₂O (15 mL) and stored at −35 °C for 24 h to produce a black/purple crystalline solid. The mother liquor was decanted and the solids were rinsed with Et₂O (2 mL) and briefly dried under vacuum to yield 2-La as a black/purple crystalline solid that analyzed as the solvate [K(2.2.2-cryptand)][Cp′₃La]·THF (230 mg, 59%). IR: 3069m, 2946s, 2887s, 2820m, 1925w, 1577w, 1480m, 1447m, 1433m, 1405w, 1354s, 1301m, 1260m, 1237s, 1172s, 1135s, 1105s, 1082s, 1034s, 949s, 932m, 901s, 832s, 745s, 729m, 688w, 673m, 626m cm⁻¹. Anal. Calcd for
C₄₂H₇₅N₂O₆Si₃KLa·C₄H₈O: C, 53.21; H, 8.06; N, 2.70. Found: C, 52.83; H, 8.44; N, 2.74. UV–vis (THF) \( \lambda_{\text{max}} \), nm (\( \varepsilon \), M⁻¹ cm⁻¹): 310 (4400), 433 (3900 shoulder), 502 (5600 shoulder), 554 (6500), 692 (2600 shoulder).

\[ \text{[K}(2.2.2\text{-cryptand})][\text{Cp}'_3\text{Ce}], 2-\text{Ce.} \]  As described for 2-La, bright blue solids of 1-Ce (189 mg, 0.342 mmol) and 2.2.2-cryptand (129 mg, 0.343 mmol) were dissolved in THF (2 mL) to form an amber solution, which was combined with KC₈ (65 mg, 0.48 mmol) to produce 2-Ce as a black/purple crystalline solid that analyzed as the solvate [K(2.2.2-cryptand)][Cp′₃Ce]·THF (188 mg, 53%). Black/purple single crystals of 2-Ce·THF, suitable for X-ray diffraction, were grown from THF/Et₂O at −35 °C. IR: 3070w, 2946s, 2888s, 2821m, 2486w, 1585w, 1480m, 1447m, 1434m, 1405w, 1355s, 1301m, 1260m, 1237s, 1172s, 1135s, 1107s, 1081s, 1035s, 950m, 932m, 901s, 832s, 746s, 730m, 673w, 626m cm⁻¹. Anal. Calcd for C₄₂H₇₅N₂O₆Si₃KCe·C₄H₈O: C, 53.14; H, 8.05; N, 2.69. Found: C, 52.94; H, 8.37; N, 2.73. UV–vis (THF) \( \lambda_{\text{max}} \), nm (\( \varepsilon \), M⁻¹ cm⁻¹): 385 (3800), 462 (4000 shoulder), 538 (4500), 635 (4700).

\[ \text{[K}(2.2.2\text{-cryptand})][\text{Cp}'_3\text{Nd}], 2-\text{Nd.} \]  As described for 2-La, dull green solids of 1-Nd (206 mg, 0.370 mmol) and 2.2.2-cryptand (140 mg, 0.372 mmol) were dissolved in THF (2 mL) to form a light aquamarine-purple solution, which was combined with KC₈ (71 mg, 0.52 mmol) to produce 2-Nd as a black/maroon-purple crystalline solid that analyzed as the solvate [K(2.2.2-cryptand)][Cp′₃Nd]·THF (106 mg, 27%). IR: 3072m, 2946s, 2888s, 2824m, 2362w, 1925s, 1589w, 1480m, 1447m, 1435m, 1354s, 1301m, 1260m, 1236s, 1174s, 1135s, 1107s, 1082s, 1036s, 950s, 932m, 902s, 832s, 747s, 674w, 631m cm⁻¹. Anal. Calcd for C₄₂H₇₅N₂O₆Si₃KNd·C₄H₈O: C, 52.93; H, 8.02; N, 2.68. Found: C, 52.58; H, 8.31; N, 2.71. UV–vis (THF) \( \lambda_{\text{max}} \), nm (\( \varepsilon \), M⁻¹ cm⁻¹): 420 (4700), 483 (4200 shoulder), 654 (2000 shoulder).
[**K(2.2.2-cryptand)][Cp′₃Sm]**, 2-Sm. As described for 2-La, a light orange solution of 1-Sm (191 mg, 0.340 mmol) and 2.2.2-cryptand (128 mg, 0.340 mmol) in THF (2 mL) was combined with KC₆ (50 mg, 0.37 mmol) to produce 2-Sm as a dark purple crystalline solid that analyzed as the solvate [**K(2.2.2-cryptand)][Cp′₃Sm]·THF (171 mg, 48%). IR: 3337w, 3270w, 3068m, 2948s, 2891s, 2824s, 2349w, 2086w, 1570s, 1438s, 1354s, 1302m, 1260s, 1240s, 1183s, 1135s, 1107s, 1082s, 1035s, 950s, 932m, 904s, 832s, 737s, 677m, 628m cm⁻¹. Anal. Calcd for C₄₂H₇₅N₂O₆Si₃KSm·C₄H₈O: C, 52.62; H, 7.97; N, 2.67. Found: C, 52.49; H, 8.34; N, 2.64. UV–vis (THF) λ_max, nm (ε, M⁻¹ cm⁻¹): 360 (700), 402 (500), 509 (600), 566 (400 shoulder), 680 (200).

[**K(2.2.2-cryptand)][Cp′₃Eu]**, 2-Eu. In an argon-filled glovebox, a solution of KCp′ (31 mg, 0.18 mmol) and 2.2.2-cryptand (66 mg, 0.18 mmol) in THF (1 mL) was added to a stirred solution of Cp′₂Eu(THF)₂, 3-Eu (100 mg, 0.175 mmol), in THF (1 mL). An immediate color change from bright red-orange to dark magenta-purple resulted. After 5 min of stirring, the solution was concentrated to ∼0.5 mL under reduced pressure, layered with Et₂O (6 mL), and stored at −35 °C for 2 d to produce dark purple crystals, suitable for X-ray diffraction. The mother liquor was decanted and the crystals were briefly dried under vacuum to yield 2-Eu as a dark purple crystalline solid that analyzed as the solvate [**K(2.2.2-cryptand)][Cp′₃Eu]·THF (150 mg, 82%). IR: 3068m, 2948s, 2892s, 2825m, 1480w, 1447m, 1438m, 1361s, 1354s, 1302m, 1259m, 1239s, 1183m, 1135s, 1105s, 1082s, 1035s, 950s, 932m, 904s, 832s, 746s, 687w, 677w, 639w, 628m cm⁻¹. Anal. Calcd for C₄₂H₇₅N₂O₆Si₃KEu·C₄H₈O: C, 52.54; H, 7.79; N, 2.61. Found: C, 52.43; H, 7.98; N, 2.62. UV–vis (THF) λ_max, nm (ε, M⁻¹ cm⁻¹): 483 (300), 559 (200 shoulder).
**Cp′₃Dy, 1-Dy.** In an argon-filled glovebox, a sealable 100 mL side arm Schlenk flask equipped with a greaseless stopcock was charged with DyCl₃ (492 mg, 1.83 mmol), a magnetic stir bar, and Et₂O (20 mL). A solution of KCp′ (1.00 g, 5.67 mmol) in Et₂O (20 mL) was added to the stirred slurry, and the mixture was stirred at room temperature for 12 h. The solvent was removed under vacuum from the resulting yellow mixture. Hexane (40 mL) was added to the reaction flask. The flask was attached to a Schlenk line, and the mixture was heated to reflux for 6 h. The solvent was removed under vacuum, and the flask was brought into a glovebox free of coordinating solvents. Additional hexane (30 mL) was added, and the resulting yellow suspension was filtered to remove white solids, presumably KCl and KCp′. The solvent was removed from the filtrate under vacuum. The resulting bright yellow solids were extracted with pentane (10 mL), and removal of solvent under vacuum afforded 1-Dy as a microcrystalline bright yellow solid (906 mg, 86%). ³¹H NMR (C₆D₆): δ 141 (br s, C₅H₄SiMe₃, 6H), −216 (br s, C₅H₄SiMe₃, 27H). IR: 3966w, 3914w, 3554w, 3471w, 3067w, 2953m, 2895m, 2717w, 2619w, 2422w, 2385w, 2349w, 2284w, 2233w, 2080w, 1997w, 1932w, 1873w, 1782w, 1753, 1655w, 1555w, 1443m, 1414m, 1400m, 1366m, 1313m, 1243s, 1198m, 1178s, 1063m, 1042s, 904s, 869s, 834s, 796s, 776s, 752s, 685m, 631m cm⁻¹. Anal. Calcd for C₂₄H₃₉Si₃Dy: C, 50.19; H, 6.84. Found: C, 49.79; H, 6.74.

**[K(2.2.2-cryptand)][Cp′₃Dy], 2-Dy.** As described for 2-La, a light yellow solution of 1-Dy (158 mg, 0.275 mmol) and 2.2.2-cryptand (103 mg, 0.274 mmol) in THF (2 mL) was combined with KC₈ (52 mg, 0.38 mmol) to produce 2-Dy as a black/dark maroon-purple crystalline solid that analyzed as the solvate [K(2.2.2-cryptand)][Cp′₃Dy]·THF (124 mg, 43%). IR: 3078w, 2947m, 2888s, 2825m, 2360w, 1480w, 1447w, 1354m, 1301w, 1260m, 1236m,
1176m, 1135m, 1105s, 1082s, 1036s, 950m, 932w, 903s, 831s, 751m, 673w, 626w cm\(^{-1}\). Anal. Calcd for C\(_{42}\)H\(_{75}\)N\(_2\)O\(_6\)Si\(_3\)K\(_4\)·C\(_4\)H\(_8\)O: C, 52.02; H, 7.88; N, 2.64. Found: C, 51.92; H, 8.22; N, 2.63. UV−vis (THF) \(\lambda_{\text{max}}\), nm (\(\varepsilon\), M\(^{-1}\) cm\(^{-1}\)): 483 (3400), 644 (1000 shoulder).

\[\text{[K(2.2.2-cryptand)][Cp}'_3\text{Tm}], 2-Tm.\] As described for 2-La, a light yellow solution of 1-Tm (258 mg, 0.444 mmol) and 2.2.2-cryptand (167 mg, 0.444 mmol) in THF (2 mL) was combined with KC\(_8\) (79 mg, 0.58 mmol) to produce 2-Tm as a black/brown crystalline solid that analyzed as the solvate [K(2.2.2-cryptand)][Cp}'_3\text{Tm}·THF (313 mg, 66%). IR: 3076w, 2948m, 2890s, 2825m, 2764w, 2731w, 2360w, 2341w, 1480w, 1447m, 1382m, 1397w, 1361m, 1354s, 1302m, 1259m, 1240s, 1182m, 1135s, 1105s, 1082s, 1035s, 950m, 932w, 905m, 833s, 748s, 735s, 687w, 677w, 630w, 552w cm\(^{-1}\). Anal. Calcd for C\(_{42}\)H\(_{75}\)N\(_2\)O\(_6\)Si\(_3\)K\(_4\)·C\(_4\)H\(_8\)O: C, 51.71; H, 7.83; N, 2.62. Found: C, 51.32; H, 8.27; N, 2.64. UV−vis (THF) \(\lambda_{\text{max}}\), nm (\(\varepsilon\), M\(^{-1}\) cm\(^{-1}\)): 416 (600), 550 (400), 634 (300 shoulder), 794 (100 shoulder).

\text{Cp}'_3\text{Yb, 1-Yb.}\] As described for 1-Sm, in an argon-filled glovebox, YbCl\(_3\) (751 mg, 2.72 mmol) and KCp' (1.52 g, 8.62 mmol) were combined to produce 1-Yb as a microcrystalline forest green solid (338 mg, 22%). Before the pentane extraction, a significant amount of red solids were observed and identified as [Cp'_2Yb(\mu-Cl)]\(_2\) through X-ray diffraction.\(^{58}\) Dark green single crystals of 1-Yb, suitable for X-ray diffraction, were grown from pentane at −35 °C. \(^1\text{H}\) NMR (C\(_6\)D\(_6\)): \(\delta 44.2\) (s, C\(_5\)H\(_4\)SiMe\(_3\), 27H), 43.8 (s, C\(_5\)H\(_4\)SiMe\(_3\), 6H), −21.5 (br s, C\(_5\)H\(_4\)SiMe\(_3\), 6H). IR: 2954m, 2895w, 2388w, 2236w, 2086w, 1933w, 1760w, 1663w, 1568w, 1527w, 1444m, 1410w, 1365m, 1313w, 1244s, 1198m, 1177s, 1063m, 1044s, 906s, 834s, 778s, 752s, 686m, 631m cm\(^{-1}\). Anal. Calcd for C\(_{24}\)H\(_{39}\)Si\(_3\)Yb: C, 49.29; H, 6.72. Found: C, 48.65; H, 6.69.
As described for 2-Eu, in an argon-filled glovebox, Cp′2Yb(THF)2, 3-Yb (664 mg, 1.12 mmol), 2.2.2-cryptand (423 mg, 1.12 mmol), and KCp′ (200 mg, 1.13 mmol) were combined to produce 2-Yb·THF as emerald green crystals that were suitable for X-ray diffraction (906 mg, 75%). 1H NMR (THF-d8): δ 5.93 (s, C5H4SiMe3, 6H), 5.73 (s, C5H4SiMe3, 6H), 3.51 (s, OCH2CH2O, 12H), 3.48 (t, 3JHH = 4.5 Hz, NCH2CH2O, 12H), 2.50 (t, 3JHH = 4.5 Hz, NCH2CH2O, 12H), 0.14 (s, C5H4SiMe3). 13C NMR (C6D6): δ 117.0 (C5H4SiMe3), 110.7 (C5H4SiMe3), 109.2 (C5H4SiMe3), 71.3 (OCH2CH2O), 68.4 (NCH2CH2O), 54.8 (NCH2CH2O), 1.6 (C5H4SiMe3). IR: 3075w, 2949m, 2890m, 2826m, 1480w, 1438m, 1354s, 1302m, 1240s, 1183m, 1135s, 1081s, 1035s, 945s, 932m, 905s, 832s, 738s, 677m, 638m, 630m, 571m cm⁻¹. Anal. Calcd for C42H75N2O6Si3KYb·C4H8O: C, 51.51; H, 7.80; N, 2.61. Found: C, 51.13; H, 7.81; N, 2.47. UV–vis (THF) λmax, nm (ε, M⁻¹ cm⁻¹): 335 (900 shoulder), 378 (800), 534 (50), 684 (200).

X-ray Data Collection, Structure Solution and Refinement for 2-Ce. A black crystal of approximate dimensions 0.254 x 0.182 x 0.180 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group P21/c that was later determined to be correct. The structure was solved using the coordinates of the yttrium analogue and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout.
the analysis. There was one molecule of THF solvent present. Hydrogen atoms associated with
the solvent molecule were included using a riding model. The remaining hydrogen atoms were
freely refined (x, y, z and Uiso). At convergence, wR2 = 0.0538 and Goof = 1.029 for 841
variables refined against 13436 data (0.73 Å), R1 = 0.0225 for those 11822 data with I > 2.0σ(I).
Details are given in Table 7.3.

**X-ray Data Collection, Structure Solution and Refinement for 1-Yb.** A green crystal
of approximate dimensions 0.150 x 0.226 x 0.441 mm was mounted in a cryoloop and
transferred to a Bruker SMART APEX II diffractometer. The APEX2
program package was
used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a
sphere of diffraction data). The raw frame data was processed using SAINT
and SADABS to
yield the reflection data file. Subsequent calculations were carried out using the SHELXTL
program. The diffraction symmetry was mmm and the systematic absences were consistent with
the orthorhombic space group Pbca that was later determined to be correct. The structure was
solved using the coordinates of the dysprosium analogue and refined on F2 by full-matrix least-
squares techniques. The analytical scattering factors for neutral atoms were used throughout
the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x, y, z and
Uiso). At convergence, wR2 = 0.0510 and Goof = 1.044 for 409 variables refined against 6468
data (0.74 Å), R1 = 0.0211 for those 5635 data with I > 2.0σ(I). Details are given in Table 7.3.

**Results**

**Synthesis of Cp’3Ln (Ln = Sm, Dy, Tm).** The synthesis of the previously unknown
Cp’3Ln complexes, 1 (Ln = Sm, Eu, Dy, Tm, Yb), needed as precursors in this study and for
structural comparison, was attempted following the published syntheses of analogs of the other metals.\(^{31-33,54-57}\) For \(\text{Ln} = \text{Sm}\) and \(\text{Dy}\), the reaction of 3 equiv of \(\text{KCP}'\) with \(\text{LnCl}_3\) generated the desired bright orange \(\text{Cp}'_3\text{Sm}\), \(\text{1-Sm}\), and bright yellow \(\text{Cp}'_3\text{Dy}\), \(\text{1-Dy}\), Scheme 7.3. Since the analogous metal trichloride reaction was not as successful with thulium, bright yellow \(\text{Cp}'_3\text{Tm}\), \(\text{1-Tm}\), was prepared from the iodide precursor, \(\text{TmI}_3(\text{THF})_{3.5}\),\(^{51}\) with 3 equiv of \(\text{KCP}'\), Scheme 7.3. \(\text{1-Sm}\), \(\text{1-Dy}\), and \(\text{1-Tm}\) were characterized by X-ray crystallography, and were found to be isomorphous with the other \(\text{1-Ln}\) complexes.\(^{31-33,54-57}\)

**Scheme 7.3.** Routes for Synthesizing \(\text{Cp}'_3\text{Ln}\) Compounds, 1, from Lanthanide

\[
\begin{align*}
\text{LnCl}_3 & \quad \text{+ 3 KCP}' \quad \text{Et}_2\text{O; hexane} \quad 3 \text{ KCl} \\
\text{Ln} = \text{Sm, Dy} & \quad \text{3 KCl} \\
\end{align*}
\]

For \(\text{Ln} = \text{Eu, Yb}\) and \([\text{K(2.2.2-cryptand)}][\text{Cp}'_3\text{Ln}]\) \((\text{Ln} = \text{Eu, Yb})\). Attempts to make \(\text{Cp}'_3\text{Eu}\), \(\text{1-Eu}\), from \(\text{EuCl}_3\) according to Scheme 7.1 were not successful. This was not unexpected, since it is known that the reaction of 3 equiv of \(\text{NaC}_5\text{Me}_5\) with \(\text{EuCl}_3\) resulted in the isolation of the \(\text{Eu}^{2+}\) complex \((\text{C}_5\text{Me}_5)_2\text{Eu(THF)}_2\) rather than \((\text{C}_5\text{Me}_5)_3\text{Eu}\).\(^{69}\) Similarly, the reaction of \(\text{EuCl}_3\) with 2 equiv of \(\text{KCP}^R\) \([\text{CP}^R = \text{C}_5\text{H}_4\text{CH(SiMe}_3)_2]\) to make \(\text{Cp}^R_2\text{EuCl}\) yielded only the \(\text{Eu}^{2+}\) complex, \(\text{Cp}^R_2\text{Eu(THF)}_2\).\(^{27}\) This preference to form +2 complexes for europium and ytterbium is attributed to stabilization due to the half-filled and completely filled 4f electron configurations, 4f\(^7\) and 4f\(^{14}\), respectively, and the concomitant low reduction potentials, Table 7.1. To circumvent these problems, a reverse approach was used
involving first the synthesis of the +2 complexes, 2, and then subsequent oxidation to form the +3 compounds, 1, needed for structural comparison.

Both EuI₂(THF)₂ and YbI₂(THF)₂ react with 2 equiv of KCp' to produce Cp₂Eu(THF)₂, 3-Eu, and Cp₂Yb(THF)₂, 3-Yb, as bright orange-red and purple crystalline solids, respectively, eq 7.1. Complex 3-Yb had been previously synthesized by Na(Hg) reduction of [Cp₂Yb(μ-Cl)]₂, and its identity was verified by ¹H NMR spectroscopy. Although 3-Eu was too paramagnetic to be observed by NMR, single-crystal X-ray diffraction confirmed its composition and structure. The structure of 3-Eu is isomorphous with 3-Yb, but the low quality data precluded a detailed structural discussion.

To obtain the desired [K(2.2.2-cryptand)][Cp₃Ln] products, 2-Eu and 2-Yb, K(2.2.2-cryptand)Cp' was added to 3-Eu and 3-Yb, eq 7.1. Lappert reported a similar reaction in 1998 involving Cp''₂Sm, KCp'', and 18-crown-6 to make [K(18-crown-6)(toluene)₂][Cp₃Sm] [Cp'' = C₅H₅(SiMe₃)₂]. Purple 2-Eu and emerald 2-Yb were characterized by X-ray crystallography, IR spectroscopy, and elemental analysis. Complex 2-Yb exhibited a ¹H NMR spectrum that was characteristic of a diamagnetic compound, which is consistent with its electron configuration being 4f⁴ and not 4f¹³⁵d¹.

The Eu³⁺ complex, Cp₃Eu, 1-Eu, needed for structural comparison was made by oxidation of [K(2.2.2-cryptand)][Cp₃Eu], 2-Eu, with AgBPh₄. The dark red product was
identified by X-ray crystallography, elemental analysis, and IR spectroscopy, eq 7.2. The Yb$^{3+}$ analog, 1-Yb, was also synthesized by the oxidation of [K(2.2.2-cryptand)][Cp$^\prime$Yb], 2-Yb, with AgBPh$_4$ and identified by X-ray crystallography, Figure 7.1, eq 7.2. The green 1-Yb can also be synthesized by reacting 3 equiv of KCp$^\prime$ with YbCl$_3$, Scheme 7.3, although the latter reaction produced significant amounts of the known byproduct, [Cp$^\prime$Yb(µ-Cl)]$_2$.\textsuperscript{70}

\begin{figure}[h]
\centering
\includegraphics[width=\columnwidth]{image.png}
\caption{Molecular structure of Cp$^\prime$Yb, 1-Yb, with thermal ellipsoids drawn at the 50\% probability level. Hydrogen atoms are omitted for clarity.}
\end{figure}

(eq 7.2)
Synthesis of $\text{[K(2.2.2-cryptand)][Cp'}{}^3\text{Ln}]$, 2 ($\text{Ln} = \text{La, Ce, Nd, Sm, Dy, Tm}$).

Following the procedure previously reported for $\text{Ln} = \text{Pr, Gd, Tb, Y, Ho, Er, and Lu}$, which required short reaction times and fast isolation procedures, the $\text{Cp'}{}^3\text{Ln}$ complexes $\text{1-La, 1-Ce, 1-Nd, 1-Sm, 1-Dy, and 1-Tm}$ were reacted with $\text{KC}_8$ in the presence of 2.2.2-cryptand in THF under argon. These reactions yielded deeply colored crystalline products, all of which were determined by X-ray crystallography to be $\text{[K(2.2.2-cryptand)][Cp'}{}^3\text{Ln]}$, 2, Figure 7.2, eq 7.3.

**Figure 7.2.** Molecular structure of $\text{[K(2.2.2-cryptand)][Cp'}{}^3\text{Ce]}$, 2-Ce, with thermal ellipsoids drawn at the 50% probability level. One set of disordered carbons in a disordered trimethylsilyl group, a disordered cocrystallized THF, and hydrogen atoms are omitted for clarity.
The lanthanum complex, 2-La, displays an isotropic EPR spectrum, Figure 7.3, that is very similar to the La$^{2+}$ spectra reported for the [Cp''$_3$La]$^{1-}$ anion by Lappert et al.$^{30,71}$ The octet pattern is evidence of an unpaired electron coupled to the $I = 7/2$ nuclear spin of $^{138}$La (99.9% natural abundance). The large average coupling constant of 154 G and the $g_{\text{iso}}$ value of 1.994 (similar to the 133.5 G and $g_{\text{av}} = 1.990$ of [Cp''$_3$La]$^{1-}$) are both indicative of a metal-centered radical and consistent with the 5d$^1$ configuration assigned to La$^{2+}$. These EPR data can also be compared to the data on the 6d$^1$ Th$^{3+}$ complexes, [C$_5$H$_3$(SiMe$_3$)$_2$-1,3]$_3$Th,$^{72,73}$ [C$_5$H$_3$(SiMe$_2$/Bu)$_2$-1,3]$_3$Th,$^{72}$ (C$_5$Me$_5$)$_2$[iPrNC(Me)N$i$Pr]Th,$^{74}$ [K(DME)$_2$] [C$_8$H$_6$(Si'BuMe$_2$)$_2$]$_2$Th,$^{75}$ and (C$_5$Me$_4$H)$_3$Th$^{76}$ that have EPR spectra with $g$ values of 1.87–1.92.
**Figure 7.3.** Room temperature X-band EPR spectrum of [K(2.2.2-cryptand)][Cp′3La], 2-La, in THF under argon.

**Structural Comparisons.** Crystallographic information was obtained on the Ln\(^{3+}\) complexes 1 (Sm, Eu, Dy, Tm, and Yb) to complement that already in the literature (La,\(^{54}\) Ce,\(^{55,56}\) Nd\(^{57}\)) so that a direct structural comparison of 1 and 2 could be made for these metals to add to the data already available on the other metals in the series.\(^{33}\) The differences between the Ln−(Cp′ centroid) distances of 1 and 2 for Ln = La and Ce, 0.027 and 0.029 Å, respectively, match the small differences observed between 1 and 2 for the Ln\(^{2+}\) ions in Scheme 7.2 where Ln = Y,\(^{31}\) Ho,\(^{32}\) Er,\(^{32}\) Tb,\(^{33}\) Pr,\(^{33}\) Gd,\(^{33}\) Lu\(^{33}\) (0.027–0.032 Å) and between Scheme 7.1 complexes Cp′′3La and [Cp′′3La]\(^{1−}\) (0.020–0.032 Å).\(^{30}\) These small changes in bond length are typical in transition metal chemistry\(^{41}\) and are consistent with the assignment of a 4f\(^n\)5d\(^1\) configuration rather than a 4f\(^{n+1}\) configuration for the +2 ions of these lanthanide metals. The 5d\(^1\) configuration has previously been assigned\(^{30}\) to La\(^{2+}\) in [Cp′′3Ln]\(^{1−}\), and yttrium necessarily has a 4d\(^1\) configuration.
In contrast to these small differences, the differences in Ln−(Cp’ centroid) distances of 1 and 2 for four of the traditional six divalent lanthanides are larger: 0.156 Å (Eu), 0.143 Å (Yb), 0.147 Å (Sm), and 0.123 Å (Tm) (Table 7.2, listed in the order of increasingly negative Ln\(^{3+}/\)Ln\(^{2+}\) reduction potentials in Table 7.1). These larger values match the 0.10−0.20 Å differences found historically for metal–ligand bonds in Ln\(^{2+}\) complexes of Eu, Yb, Sm, Tm, Dy, and Nd\(^{9,10,18,34−37}\) when compared to their Ln\(^{3+}\) analogs. These four 0.123−0.156 Å differences in Ln−(Cp’ centroid) distances between 1 and 2 are consistent with those expected for a 4f\(^{n+1}\) Ln\(^{2+}\) complex vs a 4f\(^{n}\) Ln\(^{3+}\) species. This consistently large difference is attributed to the special nature of the 4f orbitals and their limited radial extension that minimizes metal ligand interaction and causes these complexes to behave more as complexes of “free ions” rather than d-block complexes. Both the spectroscopy and magnetism of complexes of these traditional Ln\(^{2+}\) ions support this free ion view.\(^{16,17,77−82}\)

Table 7.2. Experimental and Calculated Average Ln−(Cp’ Centroid) Distances (Å) in Cp’3Ln, 1, and [K(2.2.2-cryptand)][Cp’3Ln], 2, for the Traditional Six +2 Ions, Eu, Yb, Sm, Tm, Dy, and Nd, Listed in the Order of Ln\(^{3+}/\)Ln\(^{2+}\) Reduction Potentials (Table 7.1)\(^{17,22}\)

<table>
<thead>
<tr>
<th>compound</th>
<th>experimental</th>
<th>calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ln−(Cp’ centroid)(_{avg})</td>
<td>difference</td>
</tr>
<tr>
<td>1-Eu/2-Eu</td>
<td>2.451/2.607</td>
<td>0.156</td>
</tr>
<tr>
<td>1-Yb/2-Yb</td>
<td>2.365/2.508</td>
<td>0.143</td>
</tr>
<tr>
<td>1-Sm/2-Sm</td>
<td>2.461/2.608</td>
<td>0.147</td>
</tr>
<tr>
<td>1-Tm/2-Tm</td>
<td>2.379/2.502</td>
<td>0.123</td>
</tr>
<tr>
<td>1-Dy/2-Dy</td>
<td>2.407/2.443</td>
<td>0.036</td>
</tr>
<tr>
<td>1-Nd/2-Nd</td>
<td>2.489/2.519</td>
<td>0.030</td>
</tr>
</tbody>
</table>
Although four of the traditional six Ln$^{2+}$ ions in complexes of 2 have large Ln−(Cp$^{'}$ centroid) distances compared to the Ln$^{3+}$ analogs, 1, complexes of Dy$^{2+}$ and Nd$^{2+}$ do not (Table 7.2). The Ln$^{3+}$/Ln$^{2+}$ difference between 1 and 2 for Dy is 0.036 Å and for Nd is 0.030 Å. This puts these two metals in the same category as the metals that are expected to have 4f$^n$5d$^1$ configurations in the +2 oxidation state. Hence, in this comparison of the structures of 1 and 2 for all the lanthanides, the complexes of Ln = Eu, Yb, Sm, and Tm fall into one class and the complexes of Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu fall into the other class.

The data on 1 and 2 for Ln = Dy and Nd contrast with most of the data in the literature to date on Dy$^{2+}$ and Nd$^{2+}$ complexes. In general, Shannon radii for eight-coordinate Dy$^{2+}$ and Nd$^{2+}$ are 0.163 and 0.181 Å larger than those of Dy$^{3+}$ and Nd$^{3+}$, respectively. These numbers are based on solid state structures obtained up to 1976 before molecular examples of Dy$^{2+}$ and Nd$^{2+}$ were known. Molecular examples of these ions also show the same trend. For example, the Ln−I distances in NdI$_2$(THF)$_5^{10}$ are 0.22 Å larger than those in [NdI$_2$(THF)$_5$]$^{1+}$. A Dy$^{3+}$ analog of DyI$_2$(DME)$_3^{9}$ is not available for comparison, but the Dy−I distances are actually longer than expected compared to the analogous isomorphous SmI$_2$(DME)$_3$, which has long Sm−I distances typical of a 4f$^{n+1}$ Sm$^{2+}$ ion.

In the course of this structural analysis, Si−C bond distances were also analyzed for 1 and 2, since it has been suggested that the electron added to 1 to make 2 could go into the ligands and be reflected in longer Si−C(Me) or Si−C(ring) bonds. Full data are given in Table 7.4, but there is no discernible difference between the Si−C distances in 1 and 2 for any of the metals. For example, the average Si−C(Me) distance for 2-Y is 1.872 Å vs 1.868 Å for 1-Y. This is quite similar to the average Si−C(Me) distances of 1.873 Å for 2-Eu and 1.867 Å for 1-Eu.
**UV–Visible Spectroscopy.** The UV–vis spectra of 2-La, 2-Ce, 2-Dy, and 2-Nd are shown in Figure 7.4 along with the spectra for 2-Y, which necessarily contains a 4d\(^1\) ion, and 2-Lu, which is a 5d\(^1\) complex since the f shell of the 4f\(^{14}\) Lu\(^{3+}\) ion is filled. These spectra are very similar to those of 2-Gd, 2-Tb, 2-Ho, and 2-Er complexes previously analyzed to have 4f\(^n\)5d\(^1\) ground states.\(^{32,33}\) Each complex has intense absorptions with extinction coefficients of 3000–4000 M\(^{-1}\) cm\(^{-1}\) in the high energy visible region. The spectra differ greatly from those of the corresponding Ln\(^{3+}\) complexes 1. The +3 complexes have low extinction coefficients, since the 4f–4f transitions are Laporte forbidden, and display narrow line widths, since vibronic broadening is minimal due to the limited radial extension of the 4f orbitals.

The UV–vis spectra of 2-Eu, 2-Yb, 2-Sm, and 2-Tm are dramatically different from those of the other [K(2.2.2-cryptand)][Cp\(^\prime\)\(_3\)Ln] complexes as shown in Figure 7.5. For these four metals, the absorptions have lower extinction coefficients, \(\varepsilon \leq 900\) M\(^{-1}\) cm\(^{-1}\), compared to the other 2-Ln complexes including 2-Dy and 2-Nd, also shown for comparison in Figure 7.5. This difference in absorbance is visually noticeable: solutions of 2-Eu, 2-Yb, 2-Sm, and 2-Tm are less intensely colored than those of the other analogs of 2. The absorptions of the traditional 4f\(^{n+1}\) Ln\(^{2+}\) ions are attributed to Laporte allowed 4f–5d transitions.\(^77\)
Figure 7.4. Stacked plot of experimental UV–vis spectra of [K(2.2.2-cryptand)][Cp′₃Ln], 2, for Ln = La, Ce, Nd, and Dy in comparison to Y and Lu, in THF at 298 K. Maximum extinction coefficients for absorption at wavelengths greater than 350 nm (M⁻¹ cm⁻¹) follow: Y (4500), Lu (4500), La (4400), Ce (4700), Nd (4700), Dy (3400).
Figure 7.5. Experimental UV−vis spectra of [K(2.2.2-cryptand)][Cp’3Ln], 2 (Ln = Nd, Sm, Eu, Dy, Tm, Yb), in THF at 298 K.

Theoretical Analysis. Density functional theory (DFT) calculations were performed on both Cp’3Ln, 1, and [Cp’3Ln]1−, 2, for the six lanthanides that traditionally have +2 oxidation states, Ln = Eu, Yb, Sm, Tm, Dy, and Nd, to compare with the calculations reported earlier on the new divalent ions.32,33

Ln3+. Because of the presence of many low-lying excited states and small HOMO−LUMO gaps, self-consistent field calculations of open-shell lanthanide compounds are notoriously difficult to converge. Nevertheless, calculations on the Ln3+ complexes 1 converged smoothly in each case except for Dy. For Eu, Yb, Sm, Tm, and Nd, the lowest energy structures matched crystallographic data within a few hundredths of an angstrom (Table 7.2) as observed
previously for the other lanthanides.\textsuperscript{32,33} In the case of the 4f\textsuperscript{9} Dy\textsuperscript{3+} ion, convergence thresholds were initially lowered and Fermi smearing of occupation numbers with simulated annealing was used.\textsuperscript{84} Once a reasonable structure was obtained, energy and density thresholds were tightened and the calculation converged to an integer 4f\textsuperscript{9} occupation.

\textbf{Eu\textsuperscript{2+}, Yb\textsuperscript{2+}, Sm\textsuperscript{2+}, and Tm\textsuperscript{2+}.} The computed structures of the anionic complexes 2, [Cp\textsuperscript{3}Ln]\textsuperscript{1−}, for the four metals, Ln = Eu, Yb, Sm, and Tm, agree well with the structural and spectroscopic data presented above. For each of these metals, the calculations predict structures of 2 that match the experimental data (Table 7.2). For these four metals, the differences between the Ln−(Cp\textsuperscript{′} centroid) distances of the calculated structures of 1 and 2 are significantly larger than the 0.023–0.034 Å difference calculated for Ln = Pr, Gd, Tb, Ho, Er, Y, and Lu.\textsuperscript{32,33} Specifically, the DFT calculated Ln\textsuperscript{3+}/Ln\textsuperscript{2+} bond length differences for these four metals in 2 vs 1 are Eu, 0.12 Å; Yb, 0.10 Å; Sm, 0.13 Å; Tm, 0.12 Å. The calculations agree with the larger differences found for these ions experimentally in this paper and in other studies.\textsuperscript{9,10,18,34–37,83}

The calculations on Eu, Yb, Sm, and Tm also reveal a different character of the LUMO of the trivalent 1 and the HOMO of the anion of divalent 2 compared to the other metals. For Ln = Pr, Gd, Tb, Ho, Er, Y, and Lu, both the LUMO of 1 and HOMO of 2 appear to be almost identical d\textsubscript{z2} orbitals.\textsuperscript{32,33} However, for Eu and Yb, the LUMO of 1 and the HOMO of 2 are similar six-lobe 4f-like orbitals. For Sm and Tm, the LUMO of 1 and the HOMO of 2 differ: the LUMO of 1 is a six-lobe 4f orbital, while the HOMO of 2 resembles a 4f orbital with eight lobes, Figure 7.6. The LUMOs of 1 for these four ions have significant ligand character as shown in Figure 7.6 for 1-Tm which has 41% ligand character by Mulliken population analysis.\textsuperscript{85} The
fully optimized structures of the anion of 2-Ln for Ln = Eu, Yb, Sm, and Tm all contain an entirely metal-based HOMO.

**Figure 7.6.** Molecular orbital plots of (a) the 134a orbital (LUMO) of 1-Tm and (b) the 133a orbital (HOMO) of the anion in 2-Tm, using a contour value of 0.05.

The energy difference between 4f<sup>n+1</sup> and 4f<sup>n</sup>5d<sup>1</sup> configurations for Eu, Yb, Sm, and Tm was estimated by the \( \Delta \) self-consistent field method. This resulted in 4f to 5d transfer energies of 51.8 kcal/mol (18,100 cm<sup>−1</sup>) for Eu, 49.6 kcal/mol (17,300 cm<sup>−1</sup>) for Yb,<sup>86</sup> and 29.3 kcal/mol (10,200 cm<sup>−1</sup>) for Tm. These numbers can be compared with the differences between the 4f<sup>n</sup> and 4f<sup>n</sup>5d<sup>1</sup> levels obtained experimentally from atomic spectra of the Ln<sup>2+</sup> ions: Eu, 96.9 kcal/mol (33,900 cm<sup>−1</sup>); Yb, 95.5 kcal/mol (33,400 cm<sup>−1</sup>); Sm, 70.0 kcal/mol (24,500 cm<sup>−1</sup>); Tm, 65.5 kcal/mol (22,900 cm<sup>−1</sup>).<sup>87</sup>

Natural population analysis (NPA) supports the notion that the Ln<sup>2+</sup> complexes, [Cp′<sub>3</sub>Eu]<sup>−</sup>, [Cp′<sub>3</sub>Yb]<sup>−</sup>, [Cp′<sub>3</sub>Sm]<sup>−</sup>, and [Cp′<sub>3</sub>Tm]<sup>−</sup>, each have approximately one electron added to the f orbitals in comparison to the Ln<sup>3+</sup> Cp′<sub>3</sub>Ln complexes, Table 7.5. This suggests 4f<sup>7</sup>, 4f<sup>14</sup>,

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4f$^6$, and 4f$^{13}$ ground states for [Cp$'_3$Eu]$^{1-}$, [Cp$'_3$Yb]$^{1-}$, [Cp$'_3$Sm]$^{1-}$, and [Cp$'_3$Tm]$^{1-}$, respectively. This matches all previous data on +2 ions of these metals including the structurally similar [K(18-crown-6)(toluene)$_2$][Cp$''_3$Sm].$^{35}$ Specifically, Table 7.5 shows that for Eu, Yb, Sm, and Tm, the sum of 4d and 5d electron density does not change much between the Ln$^{3+}$ complex and the Ln$^{2+}$ complex and even decreases, whereas the 4f electron density increases from the +3 ion to the +2 ion. For Nd and Dy, the changes in 4f and 5d population are smaller. This can be attributed to partially mixed 4f/5d ground-state configurations. The situation for La is very different: each ion has very little 4f character, and the 5d population increases.

The UV–vis spectra of 2-Ln were simulated using TDDFT calculations that take into account solvent effects via a continuum solvent model COSMO.$^{88}$ Figure 7.7 shows the experimental and calculated spectra for these Ln$^{2+}$ complexes. Examination of the largest calculated transitions in the spectra of the Eu, Yb, Sm, and Tm complexes corroborates the traditional view that the absorptions arise from 4f–5d transitions.$^{77}$ Several transitions originate from primarily occupied 4f orbitals that lie below the HOMO level to the 5d LUMO.

Nd$^{2+}$. In the case of Ln = Nd, the LUMO of 1-Nd has primarily 4f orbital character, but the HOMO of 2-Nd has $d_{z^2}$ orbital character, Figure 7.8. Although there is no requirement that the LUMO of the +3 ion should match the HOMO of the +2 ion, this Nd result differed from all previous calculations comparing 1 and 2.$^{32,33}$ With all the other metals, the LUMO of 1 and the HOMO of 2 were either both d orbitals or both f orbitals. Close inspection of the HOMO of 2-Nd shows that although it is primarily $d_{z^2}$ in nature, the torus of the orbital appears to divide into four small lobes that suggest partial 4f character. Mulliken analysis$^{85}$ of this orbital suggests that the 90% metal contribution to the orbital comprises 29% d and 60% f.
Figure 7.7. Experimental (solid) and calculated (dotted) UV−vis spectra of [K(2.2.2-cryptand)]
[Cp’₃Ln], 2 (Ln = Eu, Yb, Sm, Tm, Nd), in THF at 298 K, with pertinent theoretical excitations
shown as vertical lines and theoretical extinction coefficients scaled up by a factor to best match
the experimental. Calculated UV−vis spectra for 2-Dy are shown in Figure 7.9.

The difference in Ln−(Cp’ centroid) distances of the calculated structures of 1-Nd and 2-
Nd was 0.020 Å, similar to the experimentally determined value, 0.030 Å. This puts Nd in the
category of the Ln²⁺ complexes with 4fⁿ5d¹ configurations. The calculated Nd UV−vis spectrum
is consistent with this assignment in that the major transitions are metal to ligand and not f to d as in the spectra for Eu, Yb, Sm, and Tm.

**Figure 7.8.** Molecular orbital plots of (a) the 131a orbital (LUMO) of 1-Nd and (b) the 131a orbital (HOMO) of the anion in 2-Nd, using a contour value of 0.05.

**Dy²⁺.** As mentioned above, the calculations for dysprosium were problematic even at the Dy³⁺ level. Calculations on 2-Dy predicted a 4f¹⁰ configuration, i.e., a 4fⁿ⁺¹ configuration like that of Eu, Yb, Sm, and Tm, even though the structural and spectroscopic information suggested that Dy²⁺ is more like the Ln²⁺ complexes with 4fⁿ5d¹ configurations. The LUMO of 1-Dy and the HOMO of 2-Dy match: both are 4f orbitals with six lobes. The vertical excitation energy to the 5d¹ occupation is calculated to be 17.8 kcal/mol. This is smaller than the 29.3−51.8 kcal/mol values calculated for Eu, Yb, and Tm (see above) and is consistent with Dy being a “crossover” element in the 2 series where the 4f and 5d energy levels are so similar that there is difficulty elucidating the ground states. The difference in Ln−(Cp’ centroid) distances of the calculated structures of 1-Dy and 2-Dy was 0.073 Å. This is intermediate between the experimentally
found 0.020–0.032 Å differences of Ln$^{2+}$ complexes with 4f$^n$5d$^1$ configurations and the 0.123–0.156 Å differences of the 4f$^{n+1}$ complexes.

The UV–vis spectra of 2-Dy were also simulated for both the ground state 4f$^{10}$ configuration and a higher lying 4f$^9$5d$^1$ configuration, Figure 7.9. The simulated spectrum for the 4f$^9$5d$^1$ case matches the experimental spectrum much better than that of the 4f$^{10}$ configuration. Hence, although DFT predicts the 4f$^{n+1}$ configuration to be more stable, the spectroscopic data are more consistent with a 4f$^n$5d$^1$ ground state.

![Experimental UV–vis spectrum of [K(2.2.2-cryptand)][Cp$^\prime$3Dy], 2-Dy, in THF at 298 K (solid line) with calculated spectra using a 4f$^{10}$ ground state configuration (dotted) and a higher lying 4f$^9$5d$^1$ state configuration. Theoretical extinction coefficients are scaled up by a factor of 12,000 for the 4f$^{10}$ configuration and 2,700 for the 4f$^9$5d$^1$ configuration.](image)

Figure 7.9. Experimental UV–vis spectrum of [K(2.2.2-cryptand)][Cp$^\prime$3Dy], 2-Dy, in THF at 298 K (solid line) with calculated spectra using a 4f$^{10}$ ground state configuration (dotted) and a higher lying 4f$^9$5d$^1$ state configuration. Theoretical extinction coefficients are scaled up by a factor of 12,000 for the 4f$^{10}$ configuration and 2,700 for the 4f$^9$5d$^1$ configuration.
Discussion

**Synthesis.** The synthesis, isolation, and structural determination of the \( \text{Cp'}_3\text{Ln} \), 1, and \([\text{K}(2.2.2\text{-cryptand})][\text{Cp'}_3\text{Ln}] \), 2, compounds have been accomplished for all nonradioactive lanthanides. This provides the rare opportunity to directly compare analogous complexes of all the lanthanides as well as yttrium in the same coordination environment in both the +3 and +2 oxidation states. Making direct structural and electronic comparisons of the entire rare earth series with a single ligand set is challenging, since the steric requirements for thermally stable and crystalline complexes can often change across the series as the radial size diminishes. Fortunately, this was not a problem with the \((\text{Cp'}_3)^{3-}\) ligand set with the metals in both the +2 and +3 oxidation states.

**Structural Data.** All members of the \( \text{Cp'}_3\text{Ln} \), 1, series are isomorphous; their structures vary only slightly from metal to metal because of the gradually changing radial size of the metal ion. This change in average \( \text{Ln}-(\text{Cp'} \text{ centroid}) \) distance vs atomic number, Figure 7.10, follows a quadratic decay as described previously in the literature.\(^{89,90}\)

Since the average \( \text{Ln}-(\text{Cp'} \text{ centroid}) \) distances in \([\text{K}(2.2.2\text{-cryptand})][\text{Cp'}_3\text{Ln}] \), 2, for La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu are about 0.03 Å longer than those in the corresponding complexes of 1, plotting these distances for these metals in Figure 7.10 gives a curve that is similar to that for the complexes of the +3 ions. Since the differences in \( \text{Ln}-(\text{Cp'} \text{ centroid}) \) bond distances for 1 vs 2 with \( \text{Ln} = \text{Eu}, \text{Yb}, \text{Sm}, \text{and Tm} \), 0.123–0.156 Å, are much larger than the 0.03 Å difference for the other metals, their points lie significantly above the trend lines in Figure 7.10.
Figure 7.10. Plot of average Ln−(Cp’ centroid) distances in Cp’3Ln, 1 (blue diamonds), and in [K(2.2.2-cryptand)][Cp’3Ln], 2 (green squares), for each lanthanide metal.

The structural differences between the complexes of Eu, Yb, Sm, Tm and the complexes of the 10 other lanthanides, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu, as well as Y, can be explained by two different electron configurations for their Ln$^{2+}$ ions. With Eu, Yb, Sm, and Tm, large differences are found because reduction of a 4f$^n$ Ln$^{3+}$ ion generates a 4f$^{n+1}$ Ln$^{2+}$ ion. Since there is little interaction of the 4f orbitals with the ligands, the bond distances are simple sums of ionic radii. Since the ionic radii of 4f$^{n+1}$ Ln$^{2+}$ ions are typically 0.1–0.2 Å larger than the 4f$^n$ Ln$^{3+}$ ions,$^{37}$ the metal–ligand bond distances in the complexes are similarly larger. With La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu, small differences are found because reduction of a 4f$^n$ Ln$^{3+}$ ion generates a 4f$^n$5d$^1$ Ln$^{2+}$ ion for the lanthanides and a 4d$^1$ ion for yttrium. Since the d orbitals can interact with the ligands, the bond distances are not necessarily simple sums of ionic radii. This is typical in transition metal complexes in which many factors contribute to bond distances and simple correlations with oxidation states are not observed.$^{41}$
Spectral Data. The UV–vis spectral data on the complexes, [K(2.2.2-cryptand)] [Cp’3Ln], match the structural results above. The set of four ions, Eu2+, Yb2+, Sm2+, and Tm2+, in 2 display different UV–vis spectra from those of the rest. The spectra for La2+, Ce2+, Pr2+, Nd2+, Gd2+, Tb2+, Dy2+, Ho2+, and Er2+ have overall shapes and intensities similar to those seen for the Y2+ and Lu2+ ions that are necessarily 4d1 and 4f145d1 systems, respectively.31–33 The DFT calculations indicate that they arise from metal to ligand transitions. The spectra for Eu2+, Yb2+, Tm2+, and Sm2+ complexes of 2 have different shapes and are weaker in intensity than the 4f n5d1 complexes. They can be modeled as 4f–5d transitions occurring from a 4f n+1 ground state.77

“Set of Four” vs “Traditional Six” Ln2+ Ions. An unusual feature about the structural and spectroscopic data reported here is that complexes of Dy2+ and Nd2+ ions have properties consistent with 4f n5d1 configurations rather than the traditional 4f n+1 configurations obtained by adding an electron to a 4f n Ln3+ ion. The data in this study suggest that the (Cp’3)3− ligand set can change the ground state from 4f n+1 to 4f n5d1 for these two ions. Hence, the previous classification of +2 lanthanide ions into the traditional six 4f n+1 ions with Ln = Eu, Yb, Sm, Tm, Dy, and Nd and the nontraditional 4f n5d1 ions with Ln = La, Ce, Pr, Gd, Tb, Ho, Er, and Lu and 4d1 Y must be modified in the sense that this dichotomy is apparently dependent on the ligand environment. In some coordination environments, specifically the (Cp’3)3− ligand set, Dy and Nd can adopt the 4f n5d1 electron configuration. With this (Cp’3)3− set of ligands, there are only four traditional 4f n+1 Ln2+ ions.

Solid State Precedent for 4f n5d1 Character in Nd2+ and Dy2+ Complexes. In 1976, a high pressure study of NdI2 indicated that the pseudo-alkaline-earth SrI2 structure of this
compound consistent with the salt, Nd$^{2+}$(I$^{-}$)$_{2}$, changed with pressure to give a structure like the Ln$^{3+}$(I$^{-}$)$_{2}$(e$^{1-}$) structures found for La, Ce, and Pr. This was interpreted as a crossover from a 4f$^{4}$ to a 4f$^{3}$5d$^{1}$ configuration for the Nd$^{2+}$ ion under pressure. This constitutes a solid state precedent for the molecular example of 2-Nd that shows the variable nature of the electron configuration of Nd$^{2+}$ depending on the coordination environment.

Another interesting solid state structure involving Nd was the complex [(C$_{5}$H$_{2}$tBu$_{3}$)$_{2}$Nd(µ-I)K(18-crown-6)]. This Nd$^{2+}$ complex had a solid state structure with the Nd−(ring centroid) distance only 0.05 Å larger than that in (C$_{5}$H$_{2}$tBu$_{3}$)$_{2}$Nd(µ-Cl)AlMe$_{3}$, the closest example cited for comparison. This 0.05 Å distance was the smallest increase of bond distances in a Nd$^{3+}$ complex vs a Nd$^{2+}$ complex observed to date for traditional Ln$^{2+}$ complexes and seemed strange. In light of the structure of 2-Nd, this may suggest that this is related to the variable character of Nd$^{2+}$ electron configurations depending on coordination environment. This difference taken with the somewhat smaller than expected difference of 2-Tm vs 1-Tm, namely, 0.12 Å, may be indications of a continuum of bond distances in Ln$^{2+}$ complexes that have 4f$^{n+1}$ and 4f$^{n}$5d$^{1}$ configurations of similar energy.

When this [(C$_{5}$H$_{2}$tBu$_{3}$)$_{2}$Nd(µ-I)K(18-crown-6)] complex was published, its structural parameters were compared favorably with the Dy$^{2+}$ complexes [(C$_{5}$H$_{2}$tBu$_{3}$)$_{2}$Dy(µ-X)K(18-crown-6)], where X = Br and BH$_{4}$. The metal−(ring centroid) distances for these Dy$^{2+}$ structures compared to their Dy$^{3+}$ analogs were analyzed and it was found that these two pairs also show a very small difference. The difference in Ln−(ring centroid) distance for [(C$_{5}$H$_{2}$tBu$_{3}$)$_{2}$Dy(µ-Br)K(18-crown-6)] vs (C$_{5}$H$_{2}$tBu$_{3}$)$_{2}$DyBr is 0.038 Å, and the difference between [(C$_{5}$H$_{2}$tBu$_{3}$)$_{2}$Dy(µ-BH$_{4}$)K(18-crown-6)] and (C$_{5}$H$_{2}$tBu$_{3}$)$_{2}$Dy(BH$_{4}$) is 0.01 Å. Hence,
the [(C₂H₅Bu₃)₂Dy(µ-X)K(18-crown-6)] complexes also provide precedent for Ln²⁺ complexes whose Ln−(ring centroid) distances are not much larger than those of the Ln³⁺ analogs. It seems possible that these Dy²⁺ complexes could also have 4f⁹5d¹ configurations rather than 4f¹⁰ and constitute more examples that Dy is a crossover metal in this regard.

Solid State Data on Ln²⁺ Ions in Alkaline Earth Halide Matrices. The molecular data reported here can also be compared with spectroscopic and magnetic data on solids in which Ln³⁺ ions were doped into MX₂ hosts (M = Ca, Sr, Ba; X = F, Cl) and irradiated with γ radiation from a ⁶⁰Co source at 77 K. The data were analyzed as arising from Ln²⁺ ions trapped in a crystalline cubic lattice of halide ions.⁷⁷,⁹³–⁹⁶ The spectroscopic data supported 4fⁿ⁺¹ ground states for the Ln²⁺ ions except for Gd²⁺ that “probably has f⁷d for its ground configuration” and Ce²⁺ and Tb²⁺ that were considered “borderline” cases.⁹⁶ For La²⁺, a 5d¹ configuration was considered likely.⁹⁶,⁹⁷ These results are consistent with the fact that La, Ce, Gd, and Tb have the lowest 4fⁿ⁺¹ to 4fⁿ5d¹ promotional energies (see below). Additional spectroscopic and paramagnetic resonance data on Ho²⁺ generated under these conditions were also interpreted in terms of a 4f¹¹ configuration.⁹³,⁹⁴ A later study of Ce²⁺ showed data consistent with a 4f¹⁵d¹ ground state.⁹⁵ Subsequent analysis of the La, Ce, Gd, Tb, Lu, and Y results interpreted the data based on a model of “two electrons trapped by a trivalent-rare-earth fluorine-vacancy nearest neighbor complex.”⁹⁸

These data provide further support that the ligand field environment can affect the ground state electronic configuration of the Ln²⁺ ions. Since the ligand field splitting in a cubic environment lowers two d orbitals rather than a single d orbital as found for d₂ in the trigonal environment of the (Cp³)s⁻ ligand set, the d orbital stabilization may not be sufficient to make d
orbital population energetically competitive with f orbital population. Hence, the trapped Ln\(^{2+}\) ions adopt the traditional 4f\(^{n+1}\) configuration in this cubic coordination environment.

**DFT Calculations.** The DFT calculations support the overall view that the +2 ions of Eu, Yb, Sm, and Tm in the molecular complexes 2 are different from the +2 ions of La, Ce, Pr, Gd, Tb, Ho, Er, Y, and Lu in 2 and that Dy and Nd are intermediate and could align with either group. Calculations on the complexes of the metals, Ln = La, Pr, Gd, Tb, Ho, Er, Y, and Lu, indicate the LUMOs for 1 and the HOMOs for 2 are primarily 5d\(_{\sigma}\) (4d\(_{\sigma}\) for Y). In contrast, for Eu, Yb, Sm, and Tm, the LUMO for 1 and the HOMO for 2 are both 4f orbitals, with significant ligand character only observed in the LUMO for 1. Calculations on the differences in Ln−(Cp′ centroid) distances between 1 and 2 and the UV−vis spectra for these two sets of ions fit their respective ground states.

For the two intermediate cases, Dy and Nd, the calculations indicate a near degeneracy of the 4f\(^{n+1}\) and 4f\(^{n}\)5d\(^{1}\) configurations. For such multi-reference states, the present semi-local DFT methodology cannot be expected to be accurate. In the case of Nd, the f-like LUMO of 1-Nd does not match the d-like HOMO of 2-Nd, but the structural difference between these compounds matches experimental data and is consistent with a 4f\(^{3}\)5d\(^{1}\) ground state. For Dy, the ground state of the minimum energy structure for [Cp\(^{3}\)Dy]\(^{1−}\) does not match the best ground state for estimating the UV−vis spectra. Dy appears to be the element in the 2 series where the two electronic states are closest in energy.

**A Continuum between Models.** The 4f\(^{n+1}\) and 4f\(^{n}\)5d\(^{1}\) models are two extremes of a simple single electron approximation model that does not fully describe the actual electronic state in 2. The HOMO of 2-Nd shown in Figure 7.8 provides a pictorial example of this in that it
has components that look both d-like and f-like. It was noted above that the differences in Ln–
(Cp' centroid) distances between 1 and 2 for the set of four decrease in the order of their Ln\(^{3+}/\)
Ln\(^{2+}\) reduction potentials: Eu, 0.156 Å, −0.35 V; Yb, 0.143 Å, −1.15 V; Sm, 0.149 Å, −1.55 V;
Tm, 0.123 Å, −2.3 V.\(^{17}\) The smaller difference for Tm may reflect an actual electronic state that
involves a blending of both electronic extremes. The fact that Dy and Nd may be “crossover”
elements that can adopt either electronic state depending on the ligand set may explain the small
0.01–0.05 Å differences between the Ln–(Cp\(^{\text{III}}\) centroid) distances of [(C\(_5\)H\(_2\)tBu\(_3\))\(_2\)Nd(µ-I)K(18-
crown-6)]\(^{14}\) and [(C\(_5\)H\(_2\)tBu\(_3\))\(_2\)Dy(µ-X)K(18-crown-6)] (X = Br, BH\(_4\))\(^{13}\) and their Ln\(^{3+}\) analogs.
The Nd\(^{2+}\) and Dy\(^{2+}\) ions in these complexes may have considerable 4f\(^{n+1}\)5d\(^1\) character.

The 4f\(^{n+1}\) to 4f\(^{n}5d\(^1\) promotion energies for free Ln\(^{2+}\) ions\(^{87}\) can provide information about
the relative accessibility of the 5d orbitals from metal to metal. In Figure 7.11, the 4f\(^{n+1}\) to
4f\(^{n}5d\(^1\) promotion energies are plotted against the differences in Ln–(Cp' centroid) distance
between 1 and 2. This is a crude diagram, but it can be used to raise some questions regarding
Ln\(^{2+}\) ions.

The gray dotted line above 20,000 cm\(^{-1}\) suggests there is a threshold energy level that
allows the 4f\(^{n}5d\(^1\) configuration to be the ground state. This presumably relates to the amount of
crystal field stabilization that is accessible from the (Cp'\(_3\))\(^{3−}\) ligand set in 2. When a crystal field
can stabilize a d orbital to this extent, formation of a 4f\(^{n}5d\(^1\) +2 ion should be possible. The plot
also suggests that if a ligand field could provide slightly more d orbital stabilization than found
with the (Cp'\(_3\))\(^{3−}\) ligand set, Tm and Sm might also form 4f\(^{n}5d\(^1\) +2 ions.

This plot also shows the similarities in promotion energies between Ho and Er and Nd
and Dy. The positions of Dy and Nd near the dotted line can explain why they are crossover
elements that can form both $4f^{n+1}$ and $4f^55d^1$ divalent ions. However, the similar energies of Ho and Er might suggest they could also form $4f^{n+1} + 2$ ions if promotion energy were the only factor involved. The fact that $4f^{n+1}$ complexes of Ho$^{2+}$ and Er$^{2+}$ have not been identified in solution suggests that more factors are involved and this is too simplistic a view.

**Figure 7.11.** Plot of the $4f^{n+1}$ to $4f^55d^1$ promotion energies (only an estimated energy is available for Dy) vs the differences in Ln−(Cp′ centroid) distances of 2 and 1. The gray dashed line indicates the barrier in promotion energies to reduce the $4f^n$ Cp′Ln to a $4f^{n+1}$ (blue squares on right) or $4f^55d^1$ (red squares on left) configuration of [Cp′Ln]$^{1−}$.

**Conclusion**

Direct comparison of the +3 and +2 ions of all the lanthanides (except Pm, which was not studied because of its radioactivity) in a single uniform coordination environment is now
possible for the first time with the complexes, Cp′5Ln, 1, and [K(2.2.2-cryptand)][Cp′5Ln], 2, respectively. This allows comparison of the properties of 2 for the traditional six Ln$^{2+}$ ions, Eu$^{2+}$, Yb$^{2+}$, Sm$^{2+}$, Tm$^{2+}$, Dy$^{2+}$, and Nd$^{2+}$, long known in solid state and solution chemistry with the properties of 2 with the new nine ions La$^{2+}$, Ce$^{2+}$, Pr$^{2+}$, Gd$^{2+}$, Tb$^{2+}$, Y$^{2+}$, Ho$^{2+}$, Er$^{2+}$, and Lu$^{2+}$ recently discovered in molecular complexes via Schemes 7.1 and 7.2. The results indicate that the former grouping of the six traditional +2 ions with $4f^{n+1}$ ground states and the new nine +2 ions with $4f^n5d^1$ ground states should be modified. In the (Cp′3)$^{3-}$ coordination environment of 2, Dy$^{2+}$ and Nd$^{2+}$ have properties consistent with $4f^n5d^1$ ground states. In 2, only four of the elements traditionally known to form +2 ions, namely, Eu, Yb, Sm, and Tm, have structural and spectroscopic properties consistent with $4f^{n+1}$ ground states. Hence, at this point three categories of Ln$^{2+}$ ions can be identified: one group that forms traditional $4f^{n+1}$ ions, a second group that forms $4f^n5d^1$ ions, and a third group of metals that can cross over between configurations depending on the coordination environment. In the coordination environment of 2, the first class has four members, Eu, Yb, Sm, and Tm, the second class has nine members, La, Ce, Pr, Gd, Tb, Ho, Y, Er, and Lu, and the third class has two, Dy and Nd. In other coordination environments, the numbers in each class may be different depending on the effect of the ligand field on d orbital availability. It is also possible that other categories are yet to be found.

DFT calculations on 1 and 2 are consistent with this analysis. The properties of the traditional set of four as well as the set of nine are well matched by the calculations. The problematic nature of the calculations on the crossover ions, Dy$^{2+}$ and Nd$^{2+}$, is consistent with the presence of two electronic states that are close in energy for each ion. These metals could adopt either configuration depending on subtle differences in the coordination environment.
The 4f–5d promotion energies of the Ln\(^{2+}\) ions are also consistent with these three sets of Ln\(^{2+}\) ions. The four traditional divalent ions have the highest promotion energies and the new nine ions the lowest. Dy and Nd have promotion energies at the borderline between these two other sets. Since Tm, Er, Ho, Dy, and Nd all have promotion energies at the borderline, further studies of Ln\(^{2+}\) complexes should evaluate data with the possibility that either electron configuration could be present.

More generally, these results show that the ligand set can change the ground electronic state in Ln\(^{2+}\) complexes. This has not been observed with Ln\(^{3+}\) complexes where the limited radial extension of the 4f orbitals leads to minimal interaction with the ligand set and where the 5d orbitals are too high in energy to contribute significantly. For the +2 ions, the 5d orbitals are lower in energy. Apparently, with complexes of the Ln\(^{2+}\) ions, the proper ligand field can lower the energy of the 5d orbitals with respect to the 4f orbitals such that 5d can be part of the ground state. The trigonal environment of the (Cp\(^{'3}\))^\(^{-3}\) ligand set is ideal for this purpose, since a single d orbital is stabilized.

In these special ligand fields, the 4f\(^n\)5d\(^1\) configuration is more accessible than the 4f\(^n+1\) ground state for most of the lanthanides so that reduction of Ln\(^{3+}\) to Ln\(^{2+}\) is possible with potassium. The Ln\(^{3+}\)/Ln\(^{2+}\) redox potentials calculated for 4f\(^n\) Ln\(^{3+}\) to 4f\(^n+1\) Ln\(^{2+}\) reduction, Table 7.1, do not apply in the ligand environments that stabilize the 5d orbitals. It will be interesting to determine the range of ligand environments that will stabilize the 5d orbitals and if the accessibility of the 5d orbitals will allow isolation of complexes of Ln\(^{1+}\).
Table 7.3. X-ray Data Collection Parameters of 2-Ce and 1-Yb.

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<tr>
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<th>2-Ce</th>
<th>1-Yb</th>
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</thead>
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<tr>
<td>formula</td>
<td>C_{46}H_{83}CeKN_{2}O_{7}Si_{3}</td>
<td>C_{24}H_{39}Si_{3}Yb</td>
</tr>
<tr>
<td>fw</td>
<td>1039.63</td>
<td>584.86</td>
</tr>
<tr>
<td>temp (K)</td>
<td>88(2)</td>
<td>138(2)</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>cryst syst</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>space group</td>
<td>P2_1/c</td>
<td>Pbca</td>
</tr>
<tr>
<td>a (Å)</td>
<td>16.0225(7)</td>
<td>8.1548(8)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>24.4424(11)</td>
<td>22.333(2)</td>
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<tr>
<td>c (Å)</td>
<td>13.7664(6)</td>
<td>28.580(3)</td>
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<tr>
<td>Volume (Å³)</td>
<td>5390.8(4)</td>
<td>5205.1(8)</td>
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<td>α (deg)</td>
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<td>90</td>
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<tr>
<td>β (deg)</td>
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<td>90</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Z</td>
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<td>8</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}) (Mg/m³)</td>
<td>1.281</td>
<td>1.493</td>
</tr>
<tr>
<td>µ (mm⁻¹)</td>
<td>1.033</td>
<td>3.739</td>
</tr>
<tr>
<td>R1 (I &gt; 2σ(I))(^a)</td>
<td>0.0225</td>
<td>0.0211</td>
</tr>
<tr>
<td>wR2 (all data)(^a)</td>
<td>0.0538</td>
<td>0.0510</td>
</tr>
</tbody>
</table>

\(^a\)Definitions: wR2 = \(\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\)^\(1/2\); R1 = \(\sum|F_o| - |F_c|/\sum|F_o|\).
Table 7.4. Selected Si–C Bond Distances (Å) in 1 and 2 for Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.\textsuperscript{32,33,54-56}

<table>
<thead>
<tr>
<th></th>
<th>2-La/1-La</th>
<th>2-Ce/1-Ce</th>
<th>2-Pr/1-Pr</th>
<th>2-Nd/1-Nd</th>
<th>2-Sm/1-Sm</th>
<th>2-Eu/1-Eu</th>
<th>2-Gd/1-Gd</th>
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<tr>
<td>Si–C(ring) \text{avg}</td>
<td>1.849/1.858</td>
<td>1.849/1.853</td>
<td>1.848/1.860</td>
<td>1.850/1.854</td>
<td>1.848/1.860</td>
<td>1.844/1.858</td>
<td>1.850/1.860</td>
</tr>
<tr>
<td>Si–C(CH\textsubscript{3}) \text{avg}</td>
<td>1.875/1.871</td>
<td>1.872/1.869</td>
<td>1.871/1.869</td>
<td>1.875/1.866</td>
<td>1.868/1.868</td>
<td>1.873/1.867</td>
<td>1.875/1.864</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>2-Tb/1-Tb</th>
<th>2-Dy/1-Dy</th>
<th>2-Ho/1-Ho</th>
<th>2-Er/1-Er</th>
<th>2-Tm/1-Tm</th>
<th>2-Yb/1-Yb</th>
<th>2-Lu/1-Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si–C(ring) \text{avg}</td>
<td>1.848/1.861</td>
<td>1.852/1.858</td>
<td>1.866/1.859</td>
<td>1.865/1.864</td>
<td>1.844/1.862</td>
<td>1.848/1.859</td>
<td>1.850/1.861</td>
</tr>
<tr>
<td>Si–C(CH\textsubscript{3}) \text{avg}</td>
<td>1.869/1.870</td>
<td>1.873/1.865</td>
<td>1.874/1.868</td>
<td>1.869/1.870</td>
<td>1.873/1.867</td>
<td>1.872/1.866</td>
<td>1.871/1.869</td>
</tr>
</tbody>
</table>

Table 7.5. NPA Comparison between Cp\textsubscript{3}Ln and [Cp\textsubscript{3}Ln]\textsuperscript{1−}. The number of 4f electrons (left) and the number of 4d and 5d electrons combined (right) are compared for the two complexes.

<table>
<thead>
<tr>
<th>Ln</th>
<th>Cp\textsubscript{3}Ln / [Cp\textsubscript{3}Ln]\textsuperscript{1−}</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4f e\textsuperscript{1−}</td>
<td>4d and 5d e\textsuperscript{1−}</td>
</tr>
<tr>
<td>Eu</td>
<td>6.556/6.952</td>
<td>10.989/10.675</td>
</tr>
<tr>
<td>Yb</td>
<td>13.465/13.919</td>
<td>10.989/10.725</td>
</tr>
<tr>
<td>Sm</td>
<td>5.373/5.927</td>
<td>11.111/10.702</td>
</tr>
<tr>
<td>Tm</td>
<td>12.277/12.911</td>
<td>11.110/10.746</td>
</tr>
<tr>
<td>Dy</td>
<td>8.936/8.981</td>
<td>11.062/10.899</td>
</tr>
<tr>
<td>Nd</td>
<td>3.221/3.530</td>
<td>11.188/11.177</td>
</tr>
<tr>
<td>La</td>
<td>0.016/0.018</td>
<td>0.934/1.222</td>
</tr>
</tbody>
</table>
References


(59) APEX2 Version 2012.4-0. Bruker AXS, Inc.; Madison WI 2012.
(60) SAINT Version 7.68a, Bruker AXS, Inc.; Madison WI 2009


(86) For unknown reasons, the calculation on Sm was more difficult and a corresponding value for Sm was not obtained. The calculation for Yb used def2-SVP, while the calculations for Eu and Tm used def2-SVPD basis sets.


CHAPTER 8

Record High Single-Ion Magnetic Moments through 4f<sup>n</sup>5d<sup>1</sup> Electron Configurations in the Divalent Lanthanide Complexes [K(2.2.2-cryptand)]
[(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>Ln]

Introduction

As described in Chapter 7, efforts in f element reduction chemistry have shown that Ln<sup>2+</sup> ions can be isolated in molecular species in solution for all the lanthanides (except radioactive promethium) in complexes of formula [K(2.2.2-cryptand)][Cp′′Ln] and [K(2.2.2-cryptand)][Cp′Ln], most of which are isolated according to eq. 8.1 [Cp′ = C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>; Cp′′ = C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>-1,3].<sup>1-3</sup> Previously, it had been assumed that only Eu, Yb, Sm, Tm, Dy, and Nd could form isolable complexes containing Ln<sup>2+</sup> ions, since the calculated 4f<sup>n</sup> Ln<sup>3+</sup> to 4f<sup>n+1</sup> Ln<sup>2+</sup> reduction potentials for all the other lanthanides, -2.7 to -3.9 V vs NHE,<sup>4</sup> were so negative that these ions would decompose any solvent into which they would dissolve.

\[ \text{Ln} = \text{Y, Lanthanides} \quad R = \text{SiMe}_3 \quad R' = \text{H or SiMe}_3 \]

Structural, spectroscopic, and density functional theory analysis of (Cp′Ln)<sup>-</sup> complexes of the new Ln<sup>2+</sup> ions of La, Ce, Pr, Gd, Tb, Ho, Er and Lu suggested that the +2 ions in these species would have 4f<sup>n</sup>5d<sup>1</sup> not 4f<sup>n+1</sup> electron configurations. Their structures and UV-vis spectra were very similar to those of (Cp′Y)<sup>-</sup>, which necessarily has the 4d<sup>1</sup> configuration. The
structures and spectra of complexes of four of the traditional six Ln$^{2+}$ ions, i.e. complexes of Eu, Yb, Sm, and Tm, were consistent with 4f$^{n+1}$ Ln$^{2+}$ ions. However, the analogous data on (Cp$^{5}$Dy)$^{1-}$ and (Cp$^{5}$Nd)$^{1-}$ indicated that in this ligand environment, Dy$^{2+}$ and Nd$^{2+}$ also adopted 4f$^{n}$5d$^{1}$ electron configurations. Hence, at this point in the development of this area, three types of Ln$^{2+}$ complexes can be delineated: (a) Eu, Yb, Sm and Tm form complexes with traditional 4f$^{n+1}$ electron configurations, (b) La, Ce, Pr, Gd, Tb, Ho, Er, and Lu form complexes with 4f$^{n}$5d$^{1}$ electron configurations, and (c) Dy and Nd can form either 4f$^{n+1}$ or 4f$^{n}$5d$^{1}$ complexes depending on the ligand environment.

An important way to evaluate ground state electron configurations of metal complexes is magnetic moment analysis. Magnetic moments of 4f$^{n}$ Ln$^{3+}$ ions are typically evaluated with a $\mu_J = g[J(J+1)]^{1/2}$ formula which applies when the ground $2S+1L_J$ state is well separated from excited states. This “free ion” analysis is successful due to the limited radial extension of the 4f orbitals which limits orbital quenching effects. The $\mu_J$ formula predicts experimentally observed moments for all the Ln$^{3+}$ ions except 4f$^{5}$ Sm$^{3+}$ and 4f$^{6}$ Eu$^{3+}$, which have other J states close to the ground states. The magnetic moments for complexes of Eu$^{2+}$, Yb$^{2+}$, and Sm$^{2+}$ ions were found to match the moment of the next lanthanide in the series as appropriate for a 4f$^{n+1}$ configuration. Therefore Eu$^{2+}$ complexes have magnetic moments similar to 4f$^{7}$ Gd$^{3+}$ complexes, Yb$^{2+}$ complexes are diamagnetic like 4f$^{14}$ Lu$^{3+}$ complexes, and Sm$^{2+}$ complexes have magnetic moments similar to 4f$^{6}$ Eu$^{3+}$ complexes.

Prediction of the magnetic moments of these unprecedented 4f$^{n}$5d$^{1}$ ions, wherein the d$_{z^2}$ orbital is preferentially occupied in the tris(cyclopentadienyl) ligand field, is not so straightforward. There are several ways in which a magnetic moment could be predicted. One
approach involves summing the spin and orbital angular momentum contributions of all the electrons and using a $\mu_J$ formula. This is problematic with configurations where $n > 7$ since the 4f manifold is greater than half filled and the 5d manifold less than half filled. In this case, it is not clear if $J$ should be $L$-$S$ for less than a half filled configuration or $L$+$S$ for a greater than half filled configuration. In addition, since a $d_{z^2}$ orbital has no orbital angular momentum, adding the orbital contribution of the 5d electron may not be appropriate. It is also not clear how to estimate ferromagnetic vs antiferromagnetic coupling between the 5d$^1$ electron and 4f$^n$ manifold. Since the 4f$^n$5d$^1$ description is itself a crude model of the electron configuration, estimation of magnetic moments on this basis is difficult. If the additional d electron enhances spin and also total angular momentum, $J$, it could lead to a concomitant increase in the overall magnetic moment compared to the trivalent lanthanides, which currently exhibit the highest magnetic moments for any metal ion (e.g. $\mu_J = 10.61 \mu_B$ for Ho$^{3+}$ and 10.63 $\mu_B$ for Dy$^{3+}$).

It was therefore of great interest to obtain magnetic data on these new Ln$^{2+}$ complexes to see if insight into the appropriate model for the electronic state of these ions could be determined. This Chapter discusses the results of static and dynamic magnetic susceptibility measurements on the compounds [K(2.2.2-cryptand)][Cp'3Ln·THF, 1-Ln, and their corresponding trivalent analogues Cp'3Ln, 2-Ln, in collaboration with the group of Professor Jeffrey Long at UC Berkeley.
Experimental

In order to ensure the purest samples possible, materials were crystallized immediately before the samples were put under vacuum in glass ampules and shipped overnight on dry ice to the Long group at UC Berkeley for measurement.

\[ \text{Cp}_3\text{Ln}, \quad \text{2-Ln}, \quad (\text{Ln} = \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}) \] were prepared according to literature. Crystalline solids of \text{2-Ln} were grown from concentrated pentane solutions at \(-35 \degree \text{C}\).

\[ \text{[K(2.2.2-cryptand)]}[\text{Cp}_3\text{Ln} \cdot \text{THF}}, \quad \text{1-Ln}, \quad (\text{Ln} = \text{Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm}) \] were prepared in a method similar to literature. In an argon-filled glovebox, \text{Cp}_3\text{Ln} and 2.2.2-cryptand (1 equiv) were combined and dissolved in a THF/\text{Et}_2\text{O} solution (3 mL). The THF:\text{Et}_2\text{O} ratio was changed relative to the scale of the reaction to ensure a concentrated solution upon formation of \text{1-Ln}. If too much THF was present, it was challenging to obtain crystals from the reaction solution, while if too little THF was present, crystallization occurred before filtration, making it difficult to separate the product from the graphite byproduct. \text{KC}_8 (1.5 equiv) was quickly added to the stirred solution, which immediately turned dark. After 2 min of stirring, the mixture was filtered to remove a black precipitate, presumably graphite. The solution was cooled to \(-35 \degree \text{C}\) in the freezer for 2 h. The solution was layered with additional \text{Et}_2\text{O} (15 mL) and stored at \(-35 \degree \text{C}\) for 12 h to produce crystalline solids. The mother liquor was decanted and the solids were rinsed with \text{Et}_2\text{O} (2 mL) and briefly dried under vacuum to yield crystalline solids of \text{1-Ln}. The samples were dried only briefly under vacuum in order to avoid loss of co-crystallized THF molecules from the crystalline lattice. This was important for determining the molecular weight of the complex and maintaining the highest stability of the
sample. Crystalline solids were formed directly from the reaction solution to avoid decomposition in further handling and recrystallization. Recrystallization of 1-Ln from previously prepared samples often showed co-crystallization of decomposition byproduct [K(2.2.2-cryptand)][Cp'] as colorless crystals.

1-Eu was prepared according to literature. Crystalline solids of 1-Eu were obtained from a concentrated 50:50 THF/Et₂O solution. 1-Yb was not examined because it has previously been shown to be diamagnetic by NMR spectroscopy³ as expected for a 4f¹⁴ ion.

Magnetic susceptibility measurements were performed by Katie Meihaus in Jeff Long’s group at UC Berkeley. Magnetic susceptibility measurements were performed using a Quantum Design MPMS2 SQUID magnetometer. Dc susceptibility data measurements were performed at temperatures ranging from 1.8 to 300 K, using applied fields of 1, 0.5, and 0.1 T (variable temperature) and fields ranging from 0 to 7 T (magnetization measurements, 2, 6, and 10 K). Ac magnetic susceptibility measurements were performed using a 4-Oe switching field. All data were corrected for diamagnetic contributions from the core diamagnetism estimated using Pascal’s constants.²²

Results / Discussion

Dynamic magnetic susceptibility measurements performed on all complexes revealed no slow magnetic relaxation under zero dc field. A gradual decline of χ_MT and μ_eff (μ_eff = √8 · χ_MT) with decreasing temperature was observed for the anisotropic trivalent lanthanide species, resulting from the presence of magnetic anisotropy and depopulation of the crystal field levels of the J ground state. For all of the lanthanides, except 2-Sm and 2-Eu, the room temperature μ_eff
values were lower than that predicted for the free Ln$^{3+}$ ions, Figure 8.1 and Table 8.1, an observation previously made for tris(cyclopentadienyl) complexes.$^{23-27}$ The lower moments can be attributed to crystal field splitting in which not all of the crystal field levels of the J ground state are populated. As seen in Figure 8.1c., Cp‘3Ln of the three smallest metals ($Ln = Er, Tm, Yb$) all have room temperature $\chi_M T$ values that are very close to the predicted free ion values, Table 8.1. This is interesting since the smallest metals are the best Lewis acids and would be expected to have the strongest interactions with the ligands. In the case of 2-Sm and 2-Eu, the $\chi_M T$ values are larger than the predicted free ion value, which is common due to low lying excited states, in which a $\mu_J$ approximation is not appropriate, Table 8.1.$^{7-11}$ In the case of isotropic Gd$^{3+}$ ion, the $\chi_M T$ data for 2-Gd are more or less linear over the entire temperature range from 300 to 1.8 K.

![Figure 8.1](image)

**Figure 8.1.** Plot of the magnetic susceptibility times temperature ($\chi_M T$) versus temperature for Cp‘3Ln, 2-Ln, ($Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb$). Colored circles correspond to experimental data and colored lines represent the theoretical room temperature $\chi_M T$ value for each of the free trivalent lanthanides.
Table 8.1. Experimental and predicted $\chi_M T$ values (emu·K/mol) and $\mu_{\text{eff}}$ values ($\mu_B$) for the Ln$^{3+}$ complexes, Cp'$_3$Ln, 2-Ln, with a 4f$^n$ configuration.

<table>
<thead>
<tr>
<th>2-Ln</th>
<th>$n$</th>
<th>Exp. $\chi_M T$</th>
<th>Theor. $\chi_M T$</th>
<th>Exp. $\mu_{\text{eff}}$</th>
<th>Theor. $\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>La</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ce</td>
<td>1</td>
<td>0.68</td>
<td>0.8</td>
<td>2.33</td>
<td>2.53</td>
</tr>
<tr>
<td>Pr</td>
<td>2</td>
<td>1.32</td>
<td>1.6</td>
<td>3.25</td>
<td>3.58</td>
</tr>
<tr>
<td>Nd</td>
<td>3</td>
<td>1.27</td>
<td>1.64</td>
<td>3.19</td>
<td>3.62</td>
</tr>
<tr>
<td>Sm</td>
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<td>0.27</td>
<td>0.09</td>
<td>1.47</td>
<td>0.85</td>
</tr>
<tr>
<td>Eu</td>
<td>6</td>
<td>3.17</td>
<td>0</td>
<td>5.04</td>
<td>0</td>
</tr>
<tr>
<td>Gd</td>
<td>7</td>
<td>7.58</td>
<td>7.88</td>
<td>7.79</td>
<td>7.94</td>
</tr>
<tr>
<td>Tb</td>
<td>8</td>
<td>9.34</td>
<td>11.82</td>
<td>8.64</td>
<td>9.72</td>
</tr>
<tr>
<td>Dy</td>
<td>9</td>
<td>10.19</td>
<td>14.13</td>
<td>9.03</td>
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</tr>
<tr>
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<td>14.07</td>
<td>9.53</td>
<td>10.61</td>
</tr>
<tr>
<td>Er</td>
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<td>11.35</td>
<td>11.48</td>
<td>9.53</td>
<td>9.58</td>
</tr>
<tr>
<td>Tm</td>
<td>12</td>
<td>6.38</td>
<td>7.15</td>
<td>7.14</td>
<td>7.56</td>
</tr>
<tr>
<td>Yb</td>
<td>13</td>
<td>2.42</td>
<td>2.57</td>
<td>4.40</td>
<td>4.53</td>
</tr>
</tbody>
</table>

For most of the divalent lanthanide complexes, 1-Ln, there is a substantial increase in the room temperature $\chi_M T$ and $\mu_{\text{eff}}$ values, relative to the trivalent analogue, 2-Ln, Table 8.2. Three exceptions of 1-Pr, 1-Nd, and 1-Tm exhibit smaller room temperature $\chi_M T$ and $\mu_{\text{eff}}$ values than predicted even for the trivalent lanthanide ions, Table 8.2.
Table 8.2. Experimental and predicted $\chi_M T$ values (emu·K/mol) and $\mu_{\text{eff}}$ values ($\mu_B$) for the Ln$^{2+}$ complexes, [K(2.2.2-cryptand)][Cp'3Ln]·THF, 1-Ln.

<table>
<thead>
<tr>
<th>1-Ln</th>
<th>$n$</th>
<th>Exp. $\chi_M T$</th>
<th>Theor. $\chi_M T$</th>
<th>Exp. $\mu_{\text{eff}}$</th>
<th>Theor. $\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>4f$^n$5d$^1$</td>
<td>4f$^{n+1}$</td>
<td>4f$^n$5d$^1$</td>
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<tr>
<td>Y</td>
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<td>0.4</td>
<td>0.375</td>
<td>N/A</td>
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</tr>
<tr>
<td>La</td>
<td>0</td>
<td>0.37</td>
<td>0.375</td>
<td>0.8</td>
<td>0.375</td>
</tr>
<tr>
<td>Ce</td>
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<td>1.6</td>
<td>1.18</td>
</tr>
<tr>
<td>Pr</td>
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<td>1.07</td>
<td>0.875</td>
<td>1.64</td>
<td>1.98</td>
</tr>
<tr>
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<td>0.9</td>
<td>2.02</td>
</tr>
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<td>1.66</td>
<td>0</td>
<td>0</td>
<td>0.47</td>
</tr>
<tr>
<td>Eu</td>
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<td>7.60</td>
<td>1.5</td>
<td>7.88</td>
<td>0.375</td>
</tr>
<tr>
<td>Gd</td>
<td>7</td>
<td>9.93</td>
<td>10</td>
<td>11.82</td>
<td>8.26</td>
</tr>
<tr>
<td>Dy</td>
<td>9</td>
<td>16.1</td>
<td>17.01</td>
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<td>14.51</td>
</tr>
<tr>
<td>Ho</td>
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<td>16.9</td>
<td>11.48</td>
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</tr>
<tr>
<td>Er</td>
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<td>12.35</td>
<td>14.06</td>
<td>7.15</td>
<td>11.86</td>
</tr>
<tr>
<td>Tm</td>
<td>12</td>
<td>2.22</td>
<td>9.23</td>
<td>2.57</td>
<td>7.53</td>
</tr>
<tr>
<td>Yb</td>
<td>13</td>
<td>0</td>
<td>3.9</td>
<td>0</td>
<td>2.95</td>
</tr>
</tbody>
</table>

For the three metals in the 1-Ln complexes for which a 4f$^{n+1}$ configuration assignment has been established, as described in Chapter 7, namely the Eu$^{2+}$ (Figure 8.2a), Sm$^{2+}$ (Figure 8.2b), and Tm$^{2+}$ (Figure 8.2c) ions, the ground electronic state may be described by LS-coupling. For these metals, this oxidation state has been well established in the literature.$^7$-$^10$ For example, free Eu$^{2+}$ with a 4f$^7$ configuration ($L = 0$, $S = 7/2$) is predicted to exhibit $\chi_M T = 7.88$ emu·K/mol.
and $\mu_{\text{eff}} = 7.94 \mu_B$, according to eq. 8.2 and 8.3. The experimental room temperature $\chi_MT$ value of 7.60 emu·K/mol and $\mu_{\text{eff}}$ value of 7.80 $\mu_B$ for 1-Eu supports the 4f$^7$ assignment, Table 8.2.

Figure 8.2. Plots of the static magnetic susceptibility times temperature ($\chi_MT$) versus temperature collected for (a) 1-Gd (red circles), 1-Eu (blue circles), and 2-Gd (black circles), (b) 1-Sm (red circles) and 2-Sm (black circles), and (c) 1-Tm (red circles) and 2-Tm (black circles). Dashed and solid lines represent the theoretical $\chi_MT$ values at 300 K.

\[
\chi_MT = g_f J(J+1)/8 \quad (8.2)
\]
\[
\mu_{\text{eff}} = \sqrt{g_f J(J+1)} \quad (8.3)
\]

LS-coupling provides a similarly reasonable description of the room temperature values of $\chi_MT$ and $\mu_{\text{eff}}$ for Tm$^{2+}$ with a 4f$^{13}$ configuration, which agrees quite well with the experimental values for 1-Tm, Table 8.2. However, the LS-coupling does not provide an appropriate prediction for Sm$^{2+}$ with a 4f$^6$ configuration. This is similar to 2-Sm. 1-Sm displays an experimental $\chi_MT$ value of 1.66 emu·K/mol and $\mu_{\text{eff}}$ value of 3.64 $\mu_B$, both of which are greater than the predicted value of 0 emu·K/mol or $\mu_B$. This is suggestive of population of a low-lying J excited state, which has previously been shown for Sm$^{2+}$ complexes.28

For the lanthanides that were found to fall into the 4f$^n$5d$^1$ category for the [K(2.2.2-cryptand)][Cp$'_3$Ln]·THF complexes,2,3 a basic description of their ground states can be achieved.
using LS coupling rules. Since density functional theory (DFT) calculations suggested the d electron is occupied in the \(d_{\text{z}^2}\) orbital as described in Chapters 5 and 7, the analysis can be simplified, since the added d electron with respect to the trivalent electron configuration would contribute no orbital angular momentum. There are two possibilities to consider when accounting for the coupling between the d electron, the f electron and the orbital angular momentum contributed by the f electrons. One scenario involves a stronger spin-spin coupling between the f and d electrons than LS coupling, in which the complexes can be described with an overall spin of \(S = S_{4f} + \frac{1}{2}\). This total spin would then couple with the orbital angular momentum contributed by the f electrons, yielding an overall J that can be used in eq. 8.2 or 8.3 to generate a predicted \(\chi M T\) or \(\mu_{\text{eff}}\) value for a given lanthanide. Another scenario is one in which the LS coupling of the f electrons is stronger than the spin-spin coupling between the f and d orbitals. This would suggest that the d electron interacts with a magnetic field independently of the f electrons. To predict the \(\chi M T\) or \(\mu_{\text{eff}}\) value for this scenario involves the addition of the predicted \(\chi M T\) or \(\mu_{\text{eff}}\) value for the d electron (\(\chi M T = 0.375\) emu·K/mol and \(\mu_{\text{eff}} = 1.73\) \(\mu_B\) for \(S = \frac{1}{2}\)) added to the predicted \(\chi M T\) or \(\mu_{\text{eff}}\) value for 2-Ln, Table 8.1. These two scenarios will be referred to as the coupled and uncoupled schemes, respectively, Table 8.2. A similar analysis was first introduced by Cloke and coworkers in their discussion of the magnetism of zero-valent bis(1,3,5-tri-tert-butylbenzene) lanthanide complexes and this work is the motivation behind the present evaluation.16

To investigate these two possibilities, the simplest ion to look at was the \(4f^75d^1\) Gd\(^{2+}\) ion, which should remain isotropic with the addition of an electron in the \(d_{\text{z}^2}\) orbital to the isotropic \(4f^7\) Gd\(^{3+}\) ion. The static magnetic susceptibility for 1-Gd over the temperature range of 1.8 K to
300 K revealed a nearly temperature independent $\chi_MT$ product, with a room temperature $\chi_MT$ of 9.93 emu·K/mol and $\mu_{eff}$ of 8.91 $\mu_B$, Figure 8.2, Table 8.2. Both of these factors support a 4f$^7$5d$^1$ configuration since a 4f$^8$ configuration would be expected to be closer to the predicted $\chi_MT$ value of 11.82 emu·K/mol and the static magnetic susceptibility data would be expected to show signs of magnetic anisotropy.

To address the nature of the interaction between the f electrons and the d electron, variable-field magnetization measurements were performed at temperatures of 2, 6 and 10 K, Figure 8.3. The data overlay quite well with the theoretical magnetization curves defined by an $S = 4$ Brillouin function, Figure 8.3a, while the sum of the $S = 1/2$ and $S = 7/2$ Brillouin functions, Figure 8.3b, does not provide near as close of an agreement with the experimental data. This suggests that the coupled scenario above provides a more reasonable description of the configuration for 1-Gd.

Two other simple cases to consider are 1-Y and 1-La, both $S = 1/2$. For 1-Y, the unpaired electron will necessarily occupy the 4d shell, and for this ion, as well as for 1-La, experimental evidence suggests that the occupied orbital is d$_{z^2}$ in character. Static magnetic susceptibility data for both 1-Y and 1-La reveal room temperature $\chi_MT$ values of 0.4 and 0.37 emu·K/mol and $\mu_{eff}$ values of 1.79 and 1.72 $\mu_B$, respectively, which are very close to the theoretical value expected for an $S = 1/2$, Table 8.2.
Figure 8.3. Variable temperature $M(H)$ curves for 1-Gd collected from 0 to 7 T. Data points are given by colored spheres and solid lines represent the corresponding Brillouin function for (a) an $S = 4$ system and (b) the sum of $S = \frac{1}{2}$ and $S = \frac{7}{2}$.

The remaining lanthanides can be grouped into two categories, based on the agreement of their experimental $\chi_M T$ and $\mu_{\text{eff}}$ values with those predicted for the $4f^{n}5d^{1}$ configuration. The first category encompasses 1-Ln (Ln = Tb, Dy, Ho, Er), where the room temperature $\chi_M T$ and $\mu_{\text{eff}}$ values surpass the predicted values for the uncoupled $4f^{n}5d^{1}$ configuration and closely approach the coupled scenario, in agreement with the results already discussed above for 1-Gd, Table 8.2. The lack of perfect agreement might be attributed to the strong crystal field of the $(\text{Cp}'^\prime)_1^-$ ligand, which could result in incomplete population of the ground J state at room temperature and/or some quenching of orbital angular momentum; the discrepancy could also indicate this simple model does not sufficiently describe the magnetic properties of these compounds. However, the agreement is still quite good and the results of the model correspond well with prior experimental data. Notable for 1-Dy and 1-Ho, Figure 8.4, the room temperature $\chi_M T$ values are
16.1 and 16.26 emu·K/mol and the \( \mu_{\text{eff}} \) values are 11.35 and 11.41 \( \mu_B \), respectively. These appear to represent the highest moments yet exhibited by any metal ion.

**Figure 8.4.** Plot of the static magnetic susceptibility times temperature (\( \chi_M T \)) versus \( T \) for (a) 1-Dy (purple circles) and 2-Dy (black circles) and (b) 1-Ho (pink circles) and 2-Ho (black circles). Dashed colored lines represent the theoretical \( \chi_M T \) value at 300 K assuming the coupled 4f\(^{n}\)5d\(^1\) configuration for each divalent ion, while solid black lines correspond to the theoretical room temperature \( \chi_M T \) value for the corresponding free trivalent ions.

While the \( \chi_M T \) value of 13.73 emu·K/mol and the \( \mu_{\text{eff}} \) value of 10.48 \( \mu_B \) for 1-Tb exceed that expected for the uncoupled 4f\(^{n}\)5d\(^1\) configuration, Table 8.2, Figure 8.5, the predicted room temperature \( \chi_M T \) values for the 4f\(^9\) and coupled 4f\(^{n}\)5d\(^1\) configuration are 14.13 and 14.42 emu·K/mol, respectively. Thus, the difference between the experimental room temperature \( \chi_M T \) value for 1-Tb and either of these theoretical possibilities is similar in magnitude to the error between experimental and predicted \( \chi_M T \) for some of the trivalent compounds discussed above. This observation is also seen for 1-Er, Figure 8.5. The result again highlights the limitations of such a
simple model to describe the magnetic behavior. However, the $\chi_M T$ data for 1-Tb and 1-Er are certainly in support of prior experimental evidence, suggesting the $4f^n 5d^1$ configuration.$^{2,15}$

![Figure 8.5](image)

**Figure 8.5.** Plot of the static magnetic susceptibility times temperature ($\chi_M T$) versus $T$ for (a) 1-Tb (pink circles) and 2-Tb (black circles) and (b) 1-Er (pink circles) and 2-Er (black circles). Dashed colored lines represent the theoretical $\chi_M T$ value at 300 K assuming the coupled $4f^n 5d^1$ configuration for each divalent ion, while solid black lines correspond to the theoretical room temperature $\chi_M T$ value for the corresponding free trivalent ions.

The remaining lanthanides in 1-Ln (Ln = Nd, Ce, Pr), Figure 8.6, fall into a distinct category, with room temperature $\chi_M T$ values that do not agree well with any of the theoretical categories, Table 8.2. These values are substantially lower than those predicted for the uncoupled $4f^n 5d^1$ configuration, and based on the 1-Gd data above, this possibility may therefore be excluded. The experimental values for all three ions fall between those predicted for a coupled $4f^n 5d^1$ and a $4f^{n+1}$ configuration. Based on just the $\chi_M T$ values alone, it is tempting to consider the possibility of a mixed electronic configuration. In the case of 1-Nd, DFT
calculations did suggest that the HOMO contains both d and f character,\(^3\) perhaps adding some credence to this speculation.

![Figure 8.6](image-url)  

**Figure 8.6.** Plot of the static magnetic susceptibility times temperature \((\chi_M T)\) versus \(T\) for (a) 1-Nd (pink circles) and 2-Nd (black circles), (b) 1-Ce (pink circles) and 2-Ce (black circles), and (c) 1-Pr (pink circles) and 2-Pr (black circles). Dashed colored lines represent the theoretical \(\chi_M T\) value at 300 K assuming the coupled 4f\(^{n+1}\) configuration for each divalent ion, while solid black lines correspond to the theoretical room temperature \(\chi_M T\) value for the corresponding free trivalent ions.

**Conclusion**

In support of recent spectroscopic and computational results on the series of compounds [K(2.2.2-cryptand)][Cp’\(\text{Ln}\)]-THF, 1-Ln, dc magnetic susceptibility data suggest that a 4f\(^{n+1}\) configuration is reasonable for 1-Sm, 1-Eu and 1-Tm. Conversely, for the remaining paramagnetic later lanthanides, as well as 1-Y and 1-La, low temperature magnetization data (2-Gd) and room temperature \(\chi_M T\) and \(\mu_{\text{eff}}\) values reveal that a coupled 4f\(^n5d^1\) configuration is more likely. However, 1-Ce, 1-Pr, and 1-Nd are outliers, exhibiting dc susceptibility data that do not
strongly support any configuration. The room temperature $\chi_MT$ and $\mu_{\text{eff}}$ values reveal the severe limitations of such a simple model and the use of magnetic susceptibility data alone in deciphering electronic structure. The data for these three lanthanides could suggest the interesting possibility of a mixed configuration intermediate between $4f^n5d^1$ and $4f^{n+1}$, though additional experiments such as EPR, photoelectron spectroscopy, XAS (discussed in Chapter 9) and even more refined theory to account for the presence of lanthanide anisotropy are imperative to enabling a more rigorous understanding of these molecules.

Even still, dc susceptibility data reveal exceptionally large room temperature $\chi_MT$ values and magnetic moments for the later lanthanides, stemming from the $4f^n5d^1$ configuration. In particular, 1-Dy and 1-Ho exhibit room temperature magnetic moments that are the highest reported for a single metal ion. Although these complexes so not exhibit slow magnetic relaxation, accessibility of such enormous moments could have intriguing implications in single-molecule magnetism and in the design of new bulk magnet materials. Larger magnetic moments are anticipated to diminish tunneling of the magnetization in molecular materials, currently one of the major drawbacks in the design of single-molecule magnets with enhanced hysteresis temperatures. Bulk magnetic materials are currently limited to early lanthanides such as Nd$^{3+}$ and Sm$^{3+}$, an exclusivity that arises from the nature of the magnetic coupling between the f and transition metal d electrons. For the early lanthanides, the coupling is ferromagnetic, while in the case of the later lanthanides, it is antiferromagnetic; thus, while the anisotropy of the former is smaller, the larger magnetic moments that result from ferromagnetic coupling lead to better permanent magnetic behavior. If such novel divalent lanthanides were accessible in bulk magnetic materials, the electronic configuration and the larger moments in the case of the later
lanthanides could impact both the nature of the magnetic coupling and enhance the overall moment of the material, thus holding promise in the design of new hard permanent magnets with large magnetic energy products.

References

(28) A 4f⁶5d¹ configuration where coupling between the f and d electrons is greater than the spin-orbit coupling would also give rise to a predicted room temperature \( \chi_M T = 0 \) emu·K/mol. In the case of a 4f⁶5d¹ configuration where LS coupling dominates over spin-coupling (vida supra), still the experimental \( \chi_M T \) value exceeds the predicted 0.47 emu·K/mol. See also Chilton, N. F.; Goodwin, C. A. P.; Mills, D. P.; Winpenny, R. E. P. Chem. Commun. 2015, 51, 101.
CHAPTER 9
Evaluating Complexes of the Rare Earth Metals in the Formal Oxidation States of +2 and +3 Using X-ray Absorption Near Edge Spectroscopy

Introduction

As discussed in Chapter 7, the complexes [K(2.2.2-cryptand)][Cp\textsubscript{3}Ln], 1, (Cp' = C\textsubscript{5}H\textsubscript{4}SiMe\textsubscript{3}) have been isolated for the entire lanthanide series (except Pm that was not pursued due to radioactivity), most of which are isolated according to eq 9.1\textsuperscript{1,2} Along with the isolation of Cp\textsubscript{3}Ln, 2, for all of the lanthanides (except Pm), these complexes represent a unique opportunity to study the entire lanthanide series in the same ligand coordination environment in two different oxidation states. Chapter 7 discusses the structural, UV-vis spectroscopic, and theoretical analysis of complex 1 for the lanthanides and yttrium. These data are used to separate the lanthanides into two groups in the ligand coordination environment of 1: one group of metals that have an Ln\textsuperscript{2+} electron configuration of 4f\textsuperscript{n+1} (Ln = Eu, Yb, Sm, Tm), relative to the 4f\textsuperscript{n} configuration for the Ln\textsuperscript{3+} precursor, and one group of metals that have an electron configuration of 4f\textsuperscript{n}5d\textsuperscript{1} (Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu).

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Magnetic susceptibility measurements of complexes 1 and 2 for the lanthanides and yttrium, discussed in Chapter 8, suggest this simplified model may not be adequate in describing the electronic structure of 1. Orbital mixing between the metal and cyclopentadienide orbitals could stabilize the unusual electron configuration in a metal C–C antibonding orbital, in analogy to inverted sandwich complexes that contain partially reduced arenes.\(^3,4\) An additional extreme would involve complete reduction of a ligand, in which complex 1 would contain two \((\text{C}_5\text{H}_4\text{SiMe}_3)^{-}\) ligands and one doubly reduced \((\text{C}_5\text{H}_4\text{SiMe}_3)^{2-}\) ligand. Although lengthening of C–C bonds is not observed in the crystal structures of 1, spectroscopic support would help validate the metal based reduction described above.

This Chapter describes the use of synchrotron based spectroscopic techniques to attempt to further understand the complicated electronic structure in 1. X-ray absorption near edge spectroscopy (XANES) has been used to probe covalency\(^5\text{-}^9\) and electronic states\(^10\text{-}^16\) for the lanthanides and actinides and is increasing in use as accessibility to synchrotron radiation increases. X-ray absorption up to 40 keV involves absorption of a photon that transfers its energy to excite an electron leaving behind a core hole in the atom.\(^17\) In XANES, this excited photoelectron will populate unoccupied bound metal orbitals as well as low-lying continuum states. For lanthanides, this would include the unoccupied 4f orbitals and the 5d, 6s, and 6p orbitals.

In a XANES spectrum, the area of interest is the rising edge of the absorption which corresponds to the energy where the absorption coefficient, \(\mu\), is at half-height of the absorption jump observed upon the ionization of a particular core electron. When the core electron is in the most tightly bound \(n = 1\) shell, this is classified as K-edge. When the core electron is in the \(n = 2\)
shell, this is classified as L-edge, which is further separated by fine structure that corresponds to excitation of an electron from 2s, 2p$_{1/2}$, and 2p$_{3/2}$ orbital levels. The nomenclature is further extended as described in Figure 9.1.

**Figure 9.1.** Illustrative X-ray absorption processes for a metal atom.

The XANES technique is sensitive to the spatial arrangement of neighboring atoms around the absorbing atom as well as the charge distribution around the absorbing atom. Since the structural differences observed between 1 and 2 are small, L$_{II/III}$ and M$_{IV/V}$ edge XANES spectra of the lanthanide atoms in complexes 1 and 2 could show an indication of a change in
oxidation state. This shift in the rising edge has been observed for Ln\(^{2+}\) ions in the class of 4f\(^{n+1}\) configurations, in which a significant shift of about 7.5 eV is found between 4f\(^{n+1}\) Ln\(^{2+}\) and 4f\(^n\) Ln\(^{3+}\) complexes.\(^{10,13}\) Since XANES absorptions follow dipole selection rules, \(L_{\text{II/III}}\) edge spectra are predominately \(p \rightarrow d\) excitations and \(M_{\text{IV/V}}\) edge spectra are predominately \(d \rightarrow f\) excitations. Therefore both the \(L_{\text{II/III}}\) edge spectra and \(M_{\text{IV/V}}\) edge spectra could be valuable in comparing the proposed 4f\(^{n+1}\) and 4f\(^n\)5d\(^1\) Ln\(^{2+}\) complexes, all of which are discussed in this Chapter.

While it is expected that an increase in the energy of the rising edge would occur as the oxidation state of the atom of interest increases, studies in transition metal XANES suggests that this correlation is not so straightforward.\(^{18}\) Since changes in oxidation states often cause a change in geometry and/or bond lengths and this can affect the charge distribution at the absorbing atom, it is difficult to assess the degree to which the metal surroundings and the metal oxidation state affect the edge shift. Calculations have been performed on simple molecular clusters, in which the oxidation state of the metal was changed without allowing the ligand atoms to move.\(^{19}\) In this case, edge shifts were found to be much smaller than when the ligands were allowed to relax. Experimental data were obtained on molecular complexes and compared the Mn K-edge spectra between [LMn(III)(acac)N\(_3\)]BPh\(_4\) and [LMn(V)(acac)N]BPh\(_4\) (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), in which the only change in bond lengths is between the (N)\(^3^-\) and (N\(_3\))\(^1^-\) ligands,\(^{20}\) while the other ligands approximately stay the same. The rising edges for these two complexes are both approximately 6550 eV, even with the change in oxidation state.\(^{18}\) This lack of change in the energy of the rising edge between these complexes is well-matched with theoretical calculations of the spectra. Since transition metal XANES spectra seem
to be difficult to predict, it is unclear whether a shift will be expected for the $4f^n5d^1 \text{Ln}^{2+}$ complexes with respect to the $4f^n \text{Ln}^{3+}$ complexes.

In order to assess whether additional reduction of the ligands or increased orbital mixing between the metal and the ligands are present in 1, carbon K-edge measurements were performed. Carbon K-edge involves $1s \rightarrow 2p$ transitions, in which pre-edge transitions can be observed if there is orbital mixing (covalency) with the lanthanide 4f / 5d orbitals or other ligand based orbitals, Figure 9.2. While ligand K-edge has been studied heavily for M–S and M–Cl bonds, the carbon K-edge (~280 eV) is much lower in energy than that for Cl and S (>2400 eV). Therefore carbon K-edge results are complicated due to weakly penetrating incident

![Diagram of Lanthanide, Ln–C, and Carbon Energy Levels](image)

**Figure 9.2.** Illustrative carbon K-edge pre-edge features.
radiation as well as problems with carbon being a common contaminant. In spite of these challenges, Minasian and coworkers have been able to use this technique to analyze bonding in metallocenes such as \((\text{C}_5\text{H}_5)_2\text{MCl}_2\)\(^{22}\) and \((\text{C}_8\text{H}_8)_2\text{M}^8\) complexes.

The work presented in this Chapter was done in collaboration with Stosh A. Kozimor from Los Alamos National Laboratory and Stefan G. Minasian from Lawrence Berkeley National Laboratory. Attempts to measure reliable metal K-, L\(_{II}\)-, L\(_{III}\)-, M\(_{IV}\)- and M\(_{V}\)-edge and carbon K-edge XAS measurements in order to further understand the electronic properties of 1 and 2 are discussed. Due to the high reactivity of 1, strategies to achieve reliable data are also discussed.

**Experimental**

The syntheses and manipulations described below were conducted under argon with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were sparged with UHP grade argon (Airgas) and passed through columns containing Q-5 and molecular sieves before use. 2.2.2-Cryptand, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Acros Organics), was placed under vacuum (10\(^{-3}\) Torr) for 12 h before use. KC\(_8\) was synthesized according to literature.\(^{23}\)

**Sample Synthesis for Stanford Synchrotron Radiation Lightsource (SSRL)**

**Measurements.** \([\text{K}(2.2.2\text{-cryptand})][\text{Cp}'\text{Ln}], 1, \) and \(\text{Cp}'\text{Ln}, 2, \) (Ln = Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm) were synthesized similar to literature methods,\(^{1,2,24-26}\) identical to that described in Chapter 8 and will not be described again. \((\text{C}_5\text{Me}_5)_2\text{SmTHF}_2,^{27}\) \([(\text{Me}_3\text{Si})_2\text{N}]_2\text{SmTHF}_2,^{28}\) and \([(\text{Me}_3\text{Si})_2\text{N}]_3\text{Sm}^{29}\) were prepared by Douglas R. Kindra according
to literature. Crystalline samples of 1 were made within 5 days of travel and stored at −35 °C until transport. The samples were sealed in glass ampules, packed in dry ice, driven directly to SSRL, and stored at −80 °C.

**Sample Preparation for Measurements at SSRL beam line (BL) 11-2.** Three hours prior to analysis by XAS, the lanthanide samples were transferred into an argon-filled glovebox. The samples were kept cold by preparing them on an aluminum block, which had been plumbed to accommodate flowing helium gas cooled from a dry ice/ethanol bath. Samples were loaded into cold nested aluminum sample holders equipped with Kapton windows. One set of windows was taped on and one set was sealed with indium wire.

First, to determine the best way to prepare the samples to prevent decomposition as much as possible, four different samples of 1-Er were prepared. Crystals of 1-Er were crushed either by mortar and pestle or a Wig-L-Bug and a thin layer was smeared onto the Kapton tape window. An additional sample involved crystals of 1-Er crushed with a Wig-L-Bug and smeared as a thick layer onto the Kapton tape window. Finally, crystals of 1-Er were diluted with boron nitride (BN) and pressed to a pellet in the sample holder. The thickly smeared sample could be characterized with 67% of the spectrum having a similar energy for the rising edge as the BN diluted sample and 33% of the spectrum having a similar energy for the rising edge as the thinly smeared sample. This indicated that the thinly smeared sample likely reacted with the adhesive of the Kapton tape, providing a XANES spectrum of a decomposition product, and the BN diluted sample was the most stable since less of the material touched the adhesive. Therefore, the thick smear likely partially reacted with the adhesive (causing some of the spectrum to match that of the thin smear) and the rest did not (causing some of the spectrum to match that of the BN diluted sample).
All subsequent samples were diluted with boron nitride, which was cooled on the cooling block. A mixture of the analyte and BN were weighed out, such that the edge jump for the absorbing atom was calculated to be at an absorption of 1 in the transmission spectrum (between 3 to 8 mg of sample and 60 mg of BN). The solids were ground together with a Wig-L-Bug and pressed to a pellet in the sample holder.

**X-ray Absorption Spectroscopy (XAS) Lanthanide L_{II/III}-edge and Y K-edge Measurements.** The samples were brought out the glovebox, immediately attached to the cold finger of a liquid N\textsubscript{2} cryostat and quickly evacuated (10^{-8} Torr). The cryostat was attached to the BL 11-2 XAFS rail and cooled with liquid N\textsubscript{2}. The rail was equipped with three ionization chambers through which helium gas was continually flowed. One chamber was positioned before the cryostat, to monitor the incident radiation (I\textsubscript{0}). The second chamber was positioned after the cryostat, such that sample transmission (I\textsubscript{1}) could be evaluated against I\textsubscript{0}, while a third chamber (I\textsubscript{2}) positioned downstream from I\textsubscript{1} so that the XANES of a calibration foil could be measured in-situ during the XAFS experiments against I\textsubscript{1}.

XANES spectra were measured at the SSRL under dedicated operating conditions (3.0 GeV, 5\%, 450 mA) on end station 11-2. This beam line, which was equipped with a 26-pole, 2.0 T wiggler, utilized a liquid nitrogen-cooled double-crystal Si[220] monochromator and employed collimating and focusing mirrors. A single energy was selected from the white beam with a liquid-N\textsubscript{2}-cooled double-crystal monochromator utilizing Si[220] (\(\phi = 0\) for Sm, Nd, Pr, La, Tm and Ce) and Si[220] (\(\phi = 90\) for Y, Gd, Er, Ho) crystals. The calibrations were conducted as follows. The Y K-edges were calibrated to the Y K-edge (17038.4 eV) of an Y foil, the Er L_{III}-edges were calibrated to the Er L_{II}-edge of an Er foil (8364 eV), the Ho and Tm L_{III}-edges were calibrated to the Ho L_{III}-edge (8070.1 eV) of a Ho foil, and the Gd L_{III}-edges were calibrated to
Fe K-edge (7112 eV) of an Fe foil. Pr and Sm L\textsubscript{II}-edges were calibrated to Mn K-edge (6539 eV) of a Mn foil. All spectra were measured in fluorescence and transmission mode, when possible. Sample fluorescence was monitored using the solid-state 100-element detector against the incident radiation ($I_0$). Deadtimes were estimated to be less than 3%.

**Sample Preparation for SSRL BL 11-2 and BL 6-2.** One hour prior to analysis by XAS, the lanthanide samples were transferred into an argon-filled glovebox. The samples were kept cold by preparing them on an aluminum block, which had been plumbed to accommodate flowing helium gas cooled from a dry ice/ethanol bath. Samples were loaded into cold, individually nested, aluminum sample holders equipped with Kapton windows. One of the windows was glued on, and the other was sealed with double sided tape to avoid sample exposure to an adhesive. The holder was pressed between two aluminum pieces and gaskets, brought out of the glovebox, and immediately submerged in liquid N\textsubscript{2}.

**Variable Temperature XAS Measurements at SSRL BL 11-2.** The samples were analyzed in a Heliq cryostat at variable temperatures (100 to 6 K). The samples were attached to the cold finger of a liquid N\textsubscript{2} cryostat and quickly evacuated (10^{-8} Torr). The cryostat was attached to the beam line as discussed above. XAS and EXAFS were measured at the SSRL under similar conditions as described above on end station 11-2.

**XAS Emission Measurements at SSRL BL 6-2.** The cryostat was attached to the BL 6-2 rail and cooled with liquid N\textsubscript{2}. The rail was equipped with two ionization chambers through which helium gas was continually flowed. One chamber was positioned before the cryostat, to monitor the incident radiation ($I_0$). The second chamber was positioned after the cryostat, such that sample transmission ($I_1$) could be evaluated against $I_0$. Ge or Si crystals, chosen specifically for each metal measured as follows: for Sm, Si[440] was used for the L\textsubscript{III}-edge and Si[620] was
used for for the L\textsubscript{II}-edge, for Gd, Si[660] was used for the L\textsubscript{III}-edge and Si[444] was used for for the L\textsubscript{II}-edge, for Tb, Si[551] was used for for the L\textsubscript{II}-edge, for Tm, Ge[660] was used for for the L\textsubscript{II}-edge, and for Dy, Ge[444] was used for the L\textsubscript{III}-edge. The crystals were positioned for the fluorescence of a particular energy range to reflect directly to the detector that sits below the sample holder.

**Sample Synthesis for Measurements at the Advanced Light Source (ALS) BL 11.0.2.**

Cp’\textsubscript{3}Ln, 2, (Ln = Y, Pr, Sm) were prepared according to literature, crystallized from concentrated pentane solutions, sealed in glass ampules, packed in dry ice, and driven to the Lawrence Berkeley National Lab. In an argon-filled glovebox, Ln\textsuperscript{3+} samples were prepared by dissolving 1 mg of 2 in 1 mL hexane and cooling the solution in the freezer. The STXM sample plate was cooled on a cold block and a small drop of the cold hexane solution was placed on the center of the Si\textsubscript{3}N\textsubscript{4} window of the sample plate, using a micropipette. The hexane was allowed to evaporate and an additional Si\textsubscript{3}N\textsubscript{4} window was sealed above the sample with epoxy.

In collaboration with Stefan Minasian, methods to synthesize 1 to deposit directly onto the STXM sample plate were pursued. In an argon-filled glovebox, samples of 2 (0.119 - 0.162 mmol) were reduced with 1.5 equiv KC\textsubscript{8} in 3:4 THF to Et\textsubscript{2}O solutions (4 mL) in the presence of 1 equiv cryptand to form 1. After the reactions were allowed to stir for ~2 minutes, 5 drops of the reaction solution were added to cold Et\textsubscript{2}O (1 mL). The STXM sample plate was cooled on a cold block and a small drop of the cold THF/Et\textsubscript{2}O solution was placed on the center of the Si\textsubscript{3}N\textsubscript{4} window of the sample plate, using a micropipette. The THF/Et\textsubscript{2}O was allowed to evaporate and an additional Si\textsubscript{3}N\textsubscript{4} window was sealed above the sample with epoxy.
XAS Lanthanide M_{IV/V}-Edge and Carbon K-Edge Measurements. Single-energy images, carbon K-edge and Pr and Sm M_{IV/V}-edge XANES spectra were acquired using the STXM instrument at the Advanced Light Source-Molecular Environmental Science (ALS-MES) beamline 11.0.2,\textsuperscript{30} which is operated in topoff mode at 500 mA, in a ∼0.5 atm He-filled chamber. An energy calibration was performed at the carbon K-edge for CO\textsubscript{2} gas (294.95 eV). Spectra at each image pixel or particular region of interest on the sample image were extracted from the “stack”, which is a collection of images recorded at multiple, closely spaced photon energies across the absorption edge.

XAS Measurements. All measurements done at SSRL were performed primarily by Stosh A. Kozimor, while all measurements done at the ALS were performed primarily by Stefan G. Minasian.

Results

Sm L_{II/III}-Edge XANES. The background-subtracted and normalized Sm L_{III}-edge XANES spectra for the trivalent Cp’\textsubscript{3}Sm, 2-Sm, and [(Me\textsubscript{3}Si)\textsubscript{2}N]\textsubscript{3}Sm (top) have been compared with that of the divalent (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Sm(THF)\textsubscript{2}, [(Me\textsubscript{3}Si)\textsubscript{2}N]\textsubscript{2}Sm(THF)\textsubscript{2}, and [K(2.2.2-cryptand)] [Cp’\textsubscript{3}Sm], 1-Sm, (bottom) complexes in Figure 9.3. Overall, the spectrum of trivalent 2-Sm (green solid trace) is quite similar to that of trivalent [(Me\textsubscript{3}Si)\textsubscript{2}N]\textsubscript{3}Sm (orange dashed trace). For instance, a large single feature near 6723 eV superimposed on a step-like absorption threshold dominated both spectra, top of Figure 9.3. The well defined rising edges were characterized by nearly identical inflection points at 6720.1 eV [(Me\textsubscript{3}Si)\textsubscript{2}N]\textsubscript{3}Sm and 6720.8 eV for 2-Sm. While these vales are quite similar, the inflection point for 2-Sm was shifted slightly higher in energy.
(0.7 eV), which could be a consequence of the different ligands.

**Figure 9.3.** The background subtracted and normalized Sm L_{III}-edge X-ray absorption spectroscopy near edge spectroscopy (XANES) measurements for the trivalent [(Me_3Si)_2N]_3Sm (green trace) and Cp’_3Sm, **2-Sm**, (orange dashed trace) (top) and divalent (C_5Me_5)_2Sm(THF)_2 (black trace), [(Me_3Si)_2N]_2Sm(THF)_2 (pink dashed trace), and [K(2.2.2-cryptand)][Cp’_3Sm], **1-Sm**, (aqua dashed trace) (bottom) samarium complexes.

The Sm L_{III}-edge XANES spectra for the divalent **1-Sm** (aqua dashed trace) is quite similar to that of divalent [(Me_3Si)_2N]_2Sm(THF)_2 (black trace) and divalent (C_5Me_5)_2Sm(THF)_2
(pink dashed trace). These spectra all contain a large feature near 6716 eV, which were characterized by inflection points at 6713.1 for \((\text{C}_5\text{Me}_5)_2\text{Sm(THF)}_2\), 6713.1 for \([\text{Me}_3\text{Si}]_2\text{N}]_2\text{Sm(THF)}_2\), and 6713.6 eV for \textbf{1-Sm} (Table 9.1). These energy positions were substantially lower (~7 eV; Table 9.2) than that observed for the first inflection point in the trivalent spectra. Similar differences in trivalent vs divalent inflection points were observed at the Sm L\text{II}-edge, as evident from the XANES analyses of \textbf{2-Sm} in comparison to \((\text{C}_5\text{Me}_5)_2\text{Sm(THF)}_2\) and \textbf{1-Sm}, shown in Figure 9.4.

![Figure 9.4](image)

\textbf{Figure 9.4.} The background subtracted and normalized Sm L\text{II}-edge X-ray absorption spectroscopy near edge spectroscopy (XANES) measurements for the trivalent \text{Cp'}\text{Sm}, \textbf{2-Sm}, (orange dashed trace), divalent [K(2.2.2-cryptand)][\text{Cp'}\text{Sm}], \textbf{1-Sm}, (aqua dashed trace), and divalent (C\text{C}_5\text{Me}_5)_2\text{SmTHF}_2 (black trace) complexes.

In each of the divalent Sm L\text{III/II}-edge XANES spectra, there is also a less pronounced feature at higher energy (near 6723 eV). The energy position for this peak seems to correspond
with the edge-feature observed for trivalent [(Me₃Si)₂N]₂Sm and 2-Sm. It is possible that this feature is indicative of multi-configurational ground state for the divalent samarium species, in analogy to previous studies on Yb²⁺.³¹,³² However, because the magnitude of this feature varied significantly from sample-to-sample and because the variable temperature (6–100 K) Sm L₃/2-edge XANES analyses shown no intensity variations, we attribute this feature to contamination with a trivalent contaminant possibly arising from decomposition of part of the sample. Radiation damage of the divalent analyte was observed, given that peak intensities for the edge attributed to the divalent samarium species decreased and the peak intensities for the edge attributed to the trivalent contaminant increased after repeated measurements on the same spot and prolonged exposure to X-ray radiation. Measurement procedures were adjusted to limit X-ray exposure to the sample and sample preparation was altered to limit the length of time the samples were at room temperature. Samples that were prepared individually immediately prior to measurement often contained less trivalent contaminant than samples that were prepared in an 8-slot container, which left the samples at room temperature longer due to the length of time to prepare 8 samples. These changes allowed for spectra with the least amount of observed trivalent contaminant as shown in Figures 9.3 and 9.4. Most likely, the trivalent contamination observed using these optimized procedures arose during sample preparation or was an unwanted byproduct that could not be effectively removed during the synthetic procedures.

Tm L₃-Edge XANES. The background-subtracted and normalized Tm L₃-edge XANES spectra from the trivalent Cp’₃Tm, 2-Tm, and divalent [K(2.2.2-cryptand)][Cp’₃Tm], 1-Tm, shown in Figure 9.5, are quite similar to those observed from the analogous samarium compounds discussed above. The 2-Tm spectrum contains a large single feature near 8652 eV.
which is approximately 7 eV higher in energy than the analogous feature observed in the \textbf{1-Tm} spectrum (\textasciitilde8645 eV), Tables 9.1 and 9.2. Additionally, a small feature is observed near 8652 eV

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure9.5.png}
\caption{The background subtracted and normalized Tm L\textsubscript{III}-edge XANES measurements for the trivalent \textit{Cp'}\textsubscript{3}Tm, \textbf{2-Tm}, (black trace) and divalent \textit{[K(2.2.2-cryptand)]}[\textit{Cp'}\textsubscript{3}Tm], \textbf{1-Tm}, (pink dashed trace) complexes.}
\end{figure}

that likely arises due to a Tm\textsuperscript{3+} contaminant in the \textbf{1-Tm} sample. L\textsubscript{III}-edge XANES studies of TmE (E = S, Se, Te) complexes, that are known to have mixed-valence behavior, revealed similar features near 8645 eV for Tm\textsuperscript{2+} and 8652 eV for Tm\textsuperscript{3+}.\textsuperscript{33,34} As in the samarium case, radiation damage was observed for the \textbf{1-Tm} sample, with the feature near 8652 eV increasing in intensity after repeated measurements at the same spot of the sample and prolonged exposure to X-ray radiation. The improved sample preparation and measurement procedures used for the Sm samples again provided the best spectra with the least amount of trivalent contaminant. Despite this minor contamination, given the high sensitivity of divalent thulium to air and moisture, these

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results provide confidence and credibility in the ability to manipulate air and moisture sensitive organometallics at the synchrotron facility for XANES analyses and highlights the utility of Tm L_{III}-edge XANES for characterizing Tm 4f^{12} vs 4f^{13} electronic configurations in organometallic thulium compounds.

**Yttrium K-Edge XANES.** The background-subtracted and normalized Y K-edge XANES spectra from the Cp'₃Y, 2-Y, and divalent [K(2.2.2-cryptand)][Cp'₃Y], 1-Y, are shown in Figure 9.6. In comparing the spectra for 2-Y and 1-Y, a similar trend was observed as seen in

![Yttrium K-Edge XANES](image)

**Figure 9.6.** The background subtracted and normalized yttrium K-edge XANES measurements for the trivalent Cp'₃Y, 2-Y, (black trace) and divalent [K(2.2.2-cryptand)][Cp'₃Y], 1-Y, (orange dashed trace) complexes.

the samarium and thulium cases, in that the inflection point of the rising edge for 1-Y was lower in energy than that observed for 2-Y. Despite these similarities there were, however, some differences associated with the yttrium spectra. For instance, the inflection point for the 1-Y rising edge was only 2 eV lower in energy than that of 2-Y, which is substantially less than the 7
eV differences observed between the divalent and trivalent lanthanide compounds discussed above, Tables 9.1 and 9.2. Additionally, unlike in the spectra from the divalent samarium and thulium compounds, the yttrium K-edge XANES analysis of 1-Y showed no evidence of trivalent contamination.

Ln L_{III}-Edge XANES (Ln = La, Gd, Ho Er) and Pr L_{II}-Edge XANES. The background-subtracted and normalized Ln L_{III}-edge XANES spectra from the trivalent Cp'3Ln, 2-Ln, and divalent [K(2.2.2-cryptand)][Cp'3Ln], 1-Ln, complexes (Ln = La, Gd, Ho, and Er) are shown in Figures 9.7 and 9.8, while the background-subtracted and normalized Pr L_{II}-edge XANES spectra from the trivalent Cp'3Pr, 2-Pr, and divalent [K(2.2.2-cryptand)][Cp'3Pr], 1-Pr complexes are shown in Figure 9.9. Surprisingly, comparisons of 2-Ln and 1-Ln were very

![Normalized Intensity vs Energy](image)

Figure 9.7. The background subtracted and normalized Ln L_{III}-edge XANES measurements for (a) the trivalent Cp'3La, 2-La, (red trace) and divalent [K(2.2.2-cryptand)][Cp'3La], 1-La, (gold trace) complexes and (b) the trivalent Cp'3Gd, 2-Gd, (purple trace) and divalent [K(2.2.2-cryptand)][Cp'3Gd], 1-Gd, (bronze trace) complexes. The solid lines represent the inflection points of the rising edges.
Figure 9.8. The background subtracted and normalized Ln L_{III}-edge XANES measurements for (a) the trivalent Cp’₃Ho, 2-Ho, (aqua trace) and divalent [K(2.2.2-cryptand)][Cp’₃Ho], 1-Ho, (bronze trace) complexes and (b) the trivalent Cp’₃Er, 2-Er, (blue trace) and divalent [K(2.2.2-cryptand)][Cp’₃Er], 1-Er, (red trace) complexes. The solid lines represent the inflection points of the rising edges.

Figure 9.9. The background subtracted and normalized Ln L_{II}-edge XANES measurements for the trivalent Cp’₃Pr, 2-Pr, (bronze trace) and divalent [K(2.2.2-cryptand)][Cp’₃Pr], 1-Pr, (green trace) complexes.
different than the results discussed for Sm, Tm, and Y above, in that the differences in inflection points of the rising edges of $\mathbf{1-Ln}$ and $\mathbf{2-Ln}$ was less than 0.5 eV. Like the results above, the inflection point for the rising edge of divalent $\mathbf{1-Ln}$ was lower than that for trivalent $\mathbf{2-Ln}$ in all five cases below.

**Nd L$_{\text{II}}$-Edge XANES and Dy L$_{\text{III}}$-Edge XANES.** As seen in Figure 9.10, the differences in the inflection points of the rising edges of $\mathbf{2-Ln}$ and $\mathbf{1-Ln}$ are very small for both Nd and Dy, similar to that observed in Figures 9.7-9.9. This means that the Nd and Dy complexes $[\text{K}(2.2.2\text{-cryptand})][\text{Cp'}\text{Ln}]$, $\mathbf{1-Ln}$, are similar to complexes with the metals that are assigned a $4f^n5d^1$ configuration in comparison to the $4f^n\text{Cp'}\text{Ln}$, $\mathbf{2-Ln}$.

**Figure 9.10.** The background subtracted and normalized (a) Nd L$_{\text{II}}$-edge XANES measurements for the trivalent $\text{Cp'}\text{Nd}$, $\mathbf{2-Nd}$, (green trace) and divalent $[\text{K}(2.2.2\text{-cryptand})][\text{Cp'}\text{Nd}]$, $\mathbf{1-Nd}$, (pink trace) complexes and (b) Dy L$_{\text{III}}$-edge XANES measurements for the trivalent $\text{Cp'}\text{Dy}$, $\mathbf{2-Dy}$, (red trace) and divalent $[\text{K}(2.2.2\text{-cryptand})][\text{Cp'}\text{Dy}]$, $\mathbf{1-Dy}$, (black trace) complexes. The solid lines represent the inflection points of the rising edges.

**Ln L$_{\text{II/III}}$-Edge Emission Spectra.** Samples of $\mathbf{2-Ln}$ and $\mathbf{1-Ln}$ were exposed to X-ray radiation 100 eV above the L$_{\text{II}}$ or L$_{\text{III}}$-edge previously measured for each complex in order to
create a 2p core hole. Emission spectra were taken to observe dipole-allowed 4d → 2p transitions and to determine if 5d → 2p transitions would also be observable for the Ln$^{2+}$ complexes assigned with a 4f$^n$5d$^1$ configuration. As expected, 4d → 2p transitions were observed for 2-Ln (Ln = Sm, Gd, Tb, Dy, Tm). Unfortunately, samples of 1-Ln decomposed in the focused X-ray beam necessary for the measurements. In the case of the Sm L$_{III}$-edge XANES spectrum of 1-Sm, the higher energy feature pertaining to a Sm$^{3+}$ contaminant increased in intensity quickly and the low energy feature pertaining to Sm$^{2+}$ was no longer present within seconds of X-ray exposure.

Pr and Sm M$_{IV/V}$-Edge and Y, Pr, and Sm Carbon K-Edge XANES. Normal contrast images of 2-Ln (Ln = Pr, Sm) and 1-Ln (Ln = Y, Pr Sm), shown in Figure 9.11, show a high degree of crystallinity. This gives confidence that the materials measured are pure and chemically uniform on the micron scale. The procedure used for carbon K-edge measurements

![Figure 9.11.](image)

Figure 9.11. Normal contrast images for Cpʻ₃Ln, 2-Ln, (Ln = Pr, Sm) and [K(2.2.2-cryptand)]
[Cp'3Ln], **1-Ln**, (Ln = Y, Pr, Sm).

of (C5H5)2MCl2 were used in which a solution containing the analyte dissolved in an appropriate solvent (~1 mg in hexane for **2-Ln** and ~1 mg in THF/Et2O for **1-Ln**) was evaporated on a Si3N4 window in an argon filled glovebox.22 This allowed for thin crystals to be formed, which minimizes saturation effects by providing short pathlengths for X-ray radiation. In order to prevent decomposition, **1-Ln** was synthesized immediately prior to measurement in which the solution was diluted appropriately for evaporation on the Si3N4 window.

The M_{IV/V}-edge XANES spectra show a significant shift between **2-Sm** and **1-Sm** in the inflection points of the rising edges, both for the M_{IV} and M_{V}-edge spectra, Figure 9.12a. As seen for the L_{II/III}-edge spectra, the divalent **1-Sm** spectra are shifted to a lower energy than the trivalent **2-Sm**, an indication previously observed for a change in 4f occupancy.35,36 Similar to that found for the L_{II}-edge measurements of **2-Pr** and **1-Pr**, there is no observed shift in the M_{IV}- or M_{V}-edge spectra for **2-Pr** and **1-Pr**, Figure 9.12b. This is consistent with the 4f occupancy not changing between the Pr^{3+} and Pr^{2+} complexes.

![Figure 9.12](image)

**Figure 9.12.** The background subtracted and normalized Ln M_{IV/V}-edge spectra for (a) Cp'3Sm, **2-Sm**, (gold trace) and [K(2.2.2-cryptand)][Cp'3Sm], **1-Sm**, (orange trace) and (b) Cp'3Pr, **2-Pr**, (blue trace).
Carbon K-edge measurements are compared for the trivalent complexes $2$-$\text{Ln}$ ($\text{Ln} = \text{Y, Pr, Sm}$), Figure 9.13. These spectra are compared to that of the previously analyzed $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$ in which the low energy feature is attributed to M–Cp bonds and the high energy feature is attributed to C–C $\pi^*$ bonds of the Cp ring. The differences in the shift and intensity of the low energy features that are likely attributed to the M–Cp bonds do not appear to follow the trend most common to the lanthanides, i.e. Ln ionic radius size and Lewis acidity. Theory will be important in explaining the data obtained. The carbon K-edge measurements of $2$-$\text{Ln}$ are further compared to measurements of $1$-$\text{Ln}$, Figure 9.14. Three pre-edge features are observed for all three spectra of $1$-$\text{Ln}$, in which the lowest energy feature is likely due to the M–Cp bonds, the next feature is likely due to C–C $\pi^*$ bonds of the Cp ring, and the highest energy feature is attributed to the cryptand, as compared to the carbon K-edge spectrum of free cryptand shown in each spectrum of Figure 9.14. Features associated with THF and the trimethylsilyl groups of the Cp’ rings are not likely resolved. The feature likely associated with the C–C $\pi^*$ bonds of the Cp ring does not appear to shift in energy, suggesting the C–C $\pi^*$ bonds are not populated in the reduction of $2$-$\text{Ln}$. Upon reduction of $2$-$\text{Ln}$, the feature likely associated with the M–Cp bonds shifts to higher energy for $1$-$\text{Ln}$. While the Ln$^{2+}$ complexes often show a shift to lower energies in the perspective of metal edge measurements due to a stabilization of the metal core orbitals, the shift to higher energies in the perspective of carbon K-edge measurements suggests the metal valence orbitals shift to higher energy upon the reduction of Ln$^{3+}$ to Ln$^{2+}$.
Figure 9.13. The background subtracted and normalized carbon K-edge spectra for 2-Pr (aqua trace), 2-Y (pink trace), 2-Sm (green trace), and (C₅H₅)₂ZrCl₂ (black trace).²²

Figure 9.14. The background subtracted and normalized carbon K-edge spectra for 1-Ln (red trace), 2-Ln (blue trace), and cryptand (black dashed trace) for Ln = Y (a), Sm (b), and Pr (c).
Discussion

This Chapter reports the use of many X-ray absorption spectroscopy (XAS) tools, including metal K-, L_{II}-, L_{III}-, M_{IV}-, and M_{V}-edge and carbon K-edge measurements, to probe the electronic structure differences between Cp’3Ln, 2-Ln, and [K(2.2.2-cryptand)][Cp’3Ln], 1-Ln, for most of the lanthanides. Due to the reactive nature of 2-Ln and especially 1-Ln, techniques were adapted throughout the course of these studies in order to ensure the most reliable data.

Metal edge XANES measurements were used to analyze 1-Ln for Sm and Tm, both of which have been characterized as 4f^{n+1} configurations in comparison to the 4f^n 2-Ln. For both metals, significant shifts of ~7 eV were observed in the L_{II/III}-edge spectra, in which the inflection point for the rising edge of divalent 1-Ln was found to be at a lower energy than that of trivalent 2-Ln. This shift has been previously observed for both Sm and Tm and are an indication of a decrease in effective nuclear charge from Ln^{3+} to Ln^{2+}.\textsuperscript{10,33,34} Since L_{II/III}-edge measurements are not a direct probe of the 4f occupancy, M_{IV/V}-edge measurements were obtained for 2-Sm and 1-Sm. These spectra showed a similar low energy shift for 1-Sm with respect to 2-Sm. These data provide a clear indication of the 4f^{n+1} configuration for 1-Sm based on previous studies.\textsuperscript{35,36}

Yttrium K-edge XANES measurements were performed for 2-Y and 1-Y, which also revealed a pronounced difference in the edge position of 1-Y relative to 2-Y. Instead of the 7 eV shift observed for Sm and Tm, a 2 eV shift was observed between 2-Y and 1-Y. Although this is shift is not as much as for the lanthanides, this is a significant shift and is reasonable for a change in oxidation state for the transition metals. Nevertheless, these measurements suggest a decrease
in effective nuclear charge from $Y^{3+}$ to $Y^{2+}$, which could be attributed to the population of a 4d orbital. Additional experiments and theory will be needed to confirm this.

Surprisingly, metal $L_{\text{II/III}}$-edge XANES measurements of $1\text{-Ln}$ for several metals with a proposed $4f^{n+1}$ configuration ($\text{Ln} = \text{La, Pr, Gd, Ho, Er}$) showed no significant shift from that of $2\text{-Ln}$. As discussed in the introduction, it is not always clear whether changes in oxidation states for transition metals will result in a shift in the edge position. However it was expected that these metals would have spectra similar to that of $1\text{-Y}$. The difference observed could be a result of comparing yttrium K-edge spectra to the Ln $L_{\text{II/III}}$-edge spectra which correspond to different transitions, or it could be a result of $1\text{-Y}$ populating a 4d orbital versus $1\text{-Ln}$ populating a 5d orbital. It should be noted that although the shift in edge position between $4f^n \text{Ln}^{3+}$ and $4f^{n+1} \text{Ln}^{2+}$ is consistently near 7 eV, the shift in edge position between $5f^2 \text{U}^{4+}$ and $5f^3 \text{U}^{3+}$ complexes is much smaller, near 3 eV.\textsuperscript{10,11}

Although this small shift observed between $1\text{-Ln}$ ($\text{Ln} = \text{La, Pr, Gd, Ho, Er}$) and $2\text{-Ln}$ was not expected and does not confirm a change in oxidation state at this point, the possibility of population of a 4f orbital for these Ln$^{2+}$ complexes can be ruled out since there is little change from the 4f$^n$ $2\text{-Ln}$. In third row transition metal XANES studies, the ratio of the intensities of the white lines in the $L_{\text{III}}$-edge and $L_{\text{II}}$-edge spectra can be used to assign d orbital occupancy since in the $L_{\text{II}}$- and $L_{\text{III}}$-edge experiments the 5d$3/2$ and 5d$5/2$ contribute to the $L_{\text{III}}$-edge feature, while only 5d$3/2$ contributes to the $L_{\text{II}}$-edge feature.\textsuperscript{37-39} This branching ratio analysis could be useful in determining whether a 5d orbital is being populated in $1\text{-Ln}$. Additionally, $M_{\text{IV/V}}$-edge XANES spectra were collected for $2\text{-Pr}$ and $1\text{-Pr}$, which reveal almost identical spectra. While
this again does not definitively confirm a 4f\(^{2}\)5d\(^{1}\) configuration for Pr\(^{2+}\) in 1-Pr, it suggests that the f-orbital configuration of 4f\(^{2}\) is not changing.

Although, many divalent Nd and Dy complexes have been obtained with assigned 4f\(^{n+1}\) configurations, in the ligand coordination environment of 1-Ln\(^{40-43}\) Nd and Dy appear to have spectroscopic qualities closer to a 4f\(^{n}\)5d\(^{1}\) configuration as discussed in Chapter 7.\(^{2}\) Consistent with this both 1-Nd and 1-Dy had very small changes in their edge positions, relative to their trivalent partners, 2-Nd and 2-Dy, respectively. This further suggests that 1-Nd and 1-Dy do not have an added 4f electron.

While emission spectra were successful in observing 4d → 2p transitions for 2-Ln, the 1-Ln complexes were not found to be stable to the focused X-ray beam used for these measurements. This demonstrates the sensitivity of the complexes measured, and new techniques or more stable complexes will need to be developed for these measurements to be successful.

Finally, carbon K-edge XANES measurements were collected for 2-Ln and 1-Ln (Ln = Y, Pr, Sm). Carbon K-edge spectra of all three trivalent 2-Ln complexes reveal two pre-edge features, similar to those observed for (C\(_{5}\)H\(_{5}\))\(_{2}\)ZrCl\(_{2}\), in which the low energy feature (between 285 and 286 eV) was assigned to M–Cp bonds and the high energy feature (between 287 and 288 eV) was assigned to C–C π* bonds.\(^{22}\) The spectra were easily reproducible, with the high energy feature staying consistent for all three 2-Ln samples, while the low energy feature increased in energy and decreased in intensity slightly from Pr to Y to Sm. This does not fit for a trend commonly observed in the rare earths involving metal ionic radius or Lewis acidity and theory will be needed to help explain this differences. Interestingly, 1-Ln for all three complexes
displayed three pre-edge features with the two lower energy features attributed to the same bonds as described for 2-Ln, while the high energy feature was attributed to cryptand when compared to free cryptand. The feature assigned to C–C π* bonds does not change for any of the samples, suggesting that the ligand antibonding orbitals are not being populated. These results, therefore, support metal-based reduction of the metal center from 2-Ln to 1-Ln. In each case of 2-Ln/1-Ln pairs, the feature likely connected to M–Cp bonds decreases in energy from Ln^{3+} to Ln^{2+}. This suggests that the valence orbitals of the Ln^{2+} complexes are higher in energy than the Ln^{3+} complexes.

Conclusion

X-ray absorption near edge spectroscopy (XANES) for metal edges of Cp³Ln, 2-Ln, and [K(2.2.2-cryptand)][Cp³Ln], 1-Ln, complexes were performed. The results are used to support the assignment of a 4fⁿ⁺¹ electron configuration for Sm²⁺ and Tm²⁺ in 1-Ln relative to the trivalent 4fⁿ 2-Ln. Analysis of the transition metal divalent, 1-Y, reveals data that supports lowering the effective nuclear charge at the Y²⁺ metal center relative to the Y³⁺ metal center in 2-Y. However, the data do not definitively confirm a 4d¹ configuration for Y²⁺. Analysis of 1-Ln for lanthanides with assigned 4fⁿ5d¹ configurations (Ln = La, Pr, Nd, Gd, Dy, Ho, Er) rules out the possibility of a 4fⁿ⁺¹ configuration for these metals, but does not definitively confirm a 4fⁿ5d¹ configuration. Analysis of the ligands through carbon K-edge XANES suggest there is no additional reduction of the ligands, ruling out the possibility of two (Cp')¹⁻ ligand and one (Cp')²⁻ ligand and further supporting metal centered reduction. Additionally, the carbon K-edge XANES spectra indicate a change in the M–Cp bonding between trivalent and divalent metals.
Additional experiments and theory will be valuable towards definitively assigning the configurations of these complicated divalent molecules, 1-Ln.

**Table 9.1.** Comparison of the first inflection points for (C₅Me₅)₂Sm(THF)₂, [(Me₃Si)₂N]₂Sm(THF)₂, [(Me₃Si)₂N]₃Sm, Cp’₃Ln, 2-Ln (Ln = Sm, Tm, Y, La, Gd, Ho, Er, Dy), and [K(2.2.2-cryptand)][Cp’₃Ln], 1-Ln (Ln = Sm, Tm, Y, La, Gd, Ho, Er, Dy). The first inflection points were defined as the first point at which the second derivative of the data equaled zero.

<table>
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<th>Compound</th>
<th>Edge</th>
<th>Inflection Point (eV)</th>
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<tbody>
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<td>(C₅Me₅)₂Sm(THF)₂</td>
<td>Lᵢᵢ</td>
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</tr>
<tr>
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<td>Lᵢ</td>
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</tr>
<tr>
<td>[(Me₃Si)₂N]₂Sm(THF)₂</td>
<td>Lᵢᵢ</td>
<td>6713.1</td>
</tr>
<tr>
<td>[(Me₃Si)₂N]₃Sm</td>
<td>Lᵢᵢ</td>
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<td></td>
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<td>8643.4</td>
</tr>
<tr>
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<td>Lᵢᵢ</td>
<td>8650.2</td>
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</tr>
<tr>
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<td>K</td>
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</tr>
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<td>5486.9</td>
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<td>Lᵢᵢ</td>
<td>7246.6</td>
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Table 9.2. Differences between the first inflection points for Cp₃Ln, 2-Ln (Ln = Sm, Tm, Y, La, Gd, Ho, Er, Dy), and [K(2.2.2-cryptand)][Cp₃Ln], 1-Ln (Ln = Sm, Tm, Y, La, Gd, Ho, Er, Dy). Also included are the inflection point differences between [(Me₃Si)₂N]₂Sm and [(Me₃Si)₂N]₂Sm(THF)₂.

<table>
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<th>Compounds</th>
<th>Edge</th>
<th>Inflection Point Difference (eV)</th>
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<td>7.2</td>
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<td>L₂II</td>
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</tr>
<tr>
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<td>L₃III</td>
<td>8643.4</td>
</tr>
<tr>
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<td>L₃III</td>
<td>8075.3</td>
</tr>
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</table>
References


CHAPTER 10

Comparison of Cyclooctatetraene Reduction with Ln$^{2+}$ vs An$^{2+}$ Ions in the [(C$_5$H$_4$SiMe$_3$)$_3$M]$^{1-}$ and {[C$_5$H$_3$(SiMe$_3$)$_2$]M}$^{1-}$ Complexes

Introduction

As described in Chapter 7, the Ln$^{2+}$ complexes [K(2.2.2-cryptand)][Cp$'$$_3$Ln], 1, (Cp$'$ = C$_5$H$_4$SiMe$_3$) have been isolated for the entire lanthanide series (except Pm that was not pursued due to radioactivity).$^{1,2}$ Spectroscopic characterization, discussed in Chapters 7-9, suggests that in the ligand coordination environment of 1, Eu, Yb, Sm, and Tm have a traditional 4f$^{n+1}$ electron configuration relative to the respective 4f$^n$ Cp$'$$_3$Ln, 2, complex, which is analogous to previously isolated Ln$^{2+}$ complexes of these metals.$^{3-11}$ In contrast, spectroscopic data support a non-traditional 4f$^n$5d$^1$ electron configuration for the Ln$^{2+}$ ions in 1 for La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu and a 4d$^1$ configuration for Y.$^{1,2,12-15}$

Reactivity studies of the 1-Ln (Ln = La, Ce, Dy, Y) complexes have demonstrated that these new Ln$^{2+}$ ions are reductants strong enough to reduce substrates such as naphthalene (−2.60 V vs SCE) to generate a trivalent complex with a (C$_{10}$H$_8$)$^{2-}$ ligand, [K(2.2.2-cryptand)][Cp$'$$_2$Ln($^4$-C$_{10}$H$_8$)], eq 10.1.$^{16}$ In the case of Y and La, a second Ln$^{3+}$ byproduct of [K(2.2.2-cryptand)][Cp$'$$_4$Ln], 3, was identified, accounting for the second electron responsible

![Chemical structure](image_url)
for the two electron reduction of naphthalene. In the case of \textbf{3-La}, all four Cp’ rings were bound pentahapto to the metal, while \textbf{3-Y} displayed three $\eta^5$-Cp’ rings and one $\eta^1$-Cp’ ring. This differences are likely due to the differences in ionic radius between La$^{3+}$ (nine coordinate 1.216 Å) and Y$^{3+}$ (1.075 Å).\textsuperscript{17}

With the isolation of \textbf{1} for the entire series of lanthanides, it was of interest to determine any differences in reactivity between the metals with a 4f$^{n+1}$ configuration and the metals with a 4f$^n$5d$^1$ configuration. While reactivity of \textbf{1} was not observed with dinitrogen, reactivity of \textbf{1} with cyclooctatetraene (C$_8$H$_8$) is observed with Ln = Y, La, Ce, Sm, Tb, and Tm and these reactions produced isolable products for several of the metals. It was desirable to study reactions of the Ln$^{2+}$ complexes with C$_8$H$_8$ because the first molecular examples of Th$^{2+}$, [K(18-crown-6)(THF)$_2$] [Cp’’Th] [Cp’’ = C$_5$H$_3$(SiMe$_3$)$_2$],\textsuperscript{18} and U$^{2+}$, [K(2.2.2-cryptand)][Cp’’U], \textbf{1-U},\textsuperscript{19} are known to react with C$_8$H$_8$ and lanthanide/actinide comparisons could be made. Th$^{2+}$ and U$^{2+}$ differ in their reactivity as shown in eqs 10.2 and 10.3, respectively.

\begin{equation} \text{SiMe}_3 \quad \text{SiMe}_3 \quad \text{Me}_3\text{Si} \quad \text{Me}_3\text{Si} \quad \text{K} \quad \text{O} \quad \text{O} \quad \text{O} \\ \text{SiMe}_3 \quad \text{SiMe}_3 \quad \text{SiMe}_3 \quad \text{SiMe}_3 \quad \text{Me}_3\text{Si} \quad \text{Me}_3\text{Si} \quad \text{O} \quad \text{O} \quad \text{O} \end{equation}

\begin{equation} \text{Me}_3\text{Si} \quad \text{SiMe}_3 \quad \text{Th} \quad \text{SiMe}_3 \quad \text{SiMe}_3 \quad \text{SiMe}_3 \\ -[\text{K}(18-c-6)][\text{Cp’’}] + \text{C}_8\text{H}_8 \end{equation}  

\begin{equation} \text{SiMe}_3 \quad \text{SiMe}_3 \quad \text{Me}_3\text{Si} \quad \text{Me}_3\text{Si} \quad \text{K} \quad \text{O} \quad \text{O} \quad \text{O} \\ \text{SiMe}_3 \quad \text{SiMe}_3 \quad \text{SiMe}_3 \quad \text{SiMe}_3 \quad \text{Me}_3\text{Si} \quad \text{Me}_3\text{Si} \quad \text{O} \quad \text{O} \quad \text{O} \\ \text{Me}_3\text{Si} \quad \text{SiMe}_3 \quad \text{U} \quad \text{SiMe}_3 \quad \text{SiMe}_3 \\ -2\text{[K(2.2.2-cryptand)][Cp’’U]} + \text{C}_8\text{H}_8 \end{equation} \textsuperscript{(10.2)}
While there are numerous reduced C$_8$H$_8$ lanthanide complexes in the literature, most have been formed by salt metathesis with an already reduced (C$_8$H$_8$)$_2$$^{2-}$ starting material, K$_2$(C$_8$H$_8$)$_2$.\textsuperscript{20-25} Alternatively, reactions of C$_8$H$_8$ with Ln$^0$ metals (either by themselves or in the presence of I$_2$) are known, and Sm$^{2+}$ and Tm$^{2+}$ complexes also reduce C$_8$H$_8$.\textsuperscript{24,26-31} Additionally, (C$_5$Me$_5$)Ln(C$_8$H$_8$) complexes have been formed from the reduction of C$_8$H$_8$ with Ln$^{2+}$ complexes, such as (C$_5$Me$_3$)$_2$Sm and Ln$^{3+}$ complexes, such as [(C$_5$Me$_5$)$_2$LnH]$_2$ (Ln = Y, Lu).\textsuperscript{32,33} (C$_8$H$_8$)$_2$$^{2-}$ ligands have also been found to be useful in stabilizing single ion magnets and single molecule magnets.\textsuperscript{25,34-39}

This Chapter describes preliminary work on the reactivity of 1 with C$_8$H$_8$ in attempts to compare the reactivity of different Ln$^{2+}$ ions in the same ligand coordination environments as well as to determine if new reduced C$_8$H$_8$ lanthanide complexes could identified. These studies indicate that the Ln$^{2+}$ ions in 1 react with C$_8$H$_8$ to form reduced C$_8$H$_8$ complexes, as expected, but the reactivity was found to be different from that found for Th$^{2+}$ and U$^{2+}$. The reduced C$_8$H$_8$ products were also different between the traditional and non-traditional Ln$^{2+}$ ions.

**Experimental**

The syntheses and manipulations described below were conducted under argon with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were sparged with UHP grade argon (Airgas) and passed through columns containing Q-5 and molecular sieves before use. NMR solvents (Cambridge Isotope Laboratories) were dried over NaK, degassed by three freeze–pump–thaw cycles, and vacuum-transferred before use. KC$_8$,\textsuperscript{40} Cp$'3$Ln, 2-Ln (Ln = La,\textsuperscript{41} Sm$^3$), and [K(2.2.2-cryptand)][Cp$'3$Ln], 1-Ln (Ln = Ce, Tm)$^2$, were
prepared according to literature. 2,2,2-Cryptand, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Acros Organics), was placed under vacuum (10⁻³ Torr) for 12 h before use. Cyclooctatetraene (Sigma-Aldrich) was placed over molecular sieves and degassed by three freeze-pump-thaw cycles before use. ¹H NMR (500 MHz) spectra were obtained on a Bruker GN500 or CRYO500 MHz spectrometer at 298 K.

[K(2.2.2-cryptand)][Cp′₂(CsH₈)La], 4-La. In an argon-filled glovebox, Cp′₃La, 2-La (68 mg, 0.12 mmol), and 2,2,2-cryptand (46 mg, 0.12 mmol) were combined and dissolved in THF (10 mL). KC₈ (25 mg, 0.18 mmol) was quickly added to the stirred colorless solution. The reaction mixture immediately turned black/violet, and after 5 min of stirring, the mixture was filtered to remove a black precipitate, presumably graphite. CsH₈ (one drop, excess) was immediately added to the stirring dark solution, which immediately turned yellow. After allowing the reaction to stir for 30 min, the solvent was removed under vacuum. The solids were extracted in Et₂O, the solution was filtered away from yellow/green solids, and the solvent was removed under vacuum to leave a pale yellow powder. Pale yellow, almost colorless, single crystals of 4-La, suitable for X-ray diffraction were grown from a concentrated Et₂O solution at −35 °C.

[K(2.2.2-cryptand)][Cp′₂(CsH₈)Ce], 4-Ce, and [K(2.2.2-cryptand)][Cp′₄Ce], 3-Ce. In an argon-filled glovebox, CsH₈ (13 µL, 0.12 mmol) was added to a dark purple stirred solution of [K(2.2.2)][Cp′₃Ce], 1-Ce (124 mg, 0.12 mmol) in THF (10 mL), which quickly turned orange. After allowing the reaction to stir for 4 h, the solvent was removed under vacuum. The light orange solids were extracted in Et₂O, the solution was filtered away from light orange solids, and the solvent was removed under vacuum to leave a pale yellow powder. Orange and pale yellow
single crystals suitable for X-ray diffraction, that analyzed as 4-Ce and 3-Ce, respectively, were
grown from the same concentrated Et₂O solution at −35 °C.

[K(2.2.2-cryptand)][(C₈H₈)₂Sm], 5. As described for 4-La, a light orange solution of 2-
Sm (84 mg, 0.15 mmol) and 2.2.2-cryptand (56 mg, 0.15 mmol) in THF (10 mL) was combined
with KC₈ (30 mg, 0.22 mmol) to produce a dark purple solution. C₈H₈ (one drop, excess) was
immediately added to the stirring dark solution, which quickly turned dark orange. After
allowing the reaction to stir for 30 min, the solvent was removed under vacuum. The solids were
washed with Et₂O, to leave an orange powder. Red single crystals of 5-Sm, suitable for X-ray
diffraction were grown from a concentrated THF solution at −35 °C.

[K(2.2.2-cryptand)][Cp′₄Tm], 3-Tm. As described for 4-Ce/3-Ce, C₈H₈ (8 µL, 0.071
mmol) was added to a dark solution of 1-Tm (76 mg, 0.071 mmol) in THF (10 mL) to produce
peach solids. Colorless crystals of 3-Tm , suitable for X-ray diffraction were grown from a
concentrated Et₂O solution at −35 °C.

X-ray Data Collection, Structure Solution and Refinement for 4-La. A colorless
crystal of approximate dimensions 0.132 x 0.183 x 0.260 mm was mounted on a glass fiber and
transferred to a Bruker SMART APEX II diffractometer. The APEX2⁴² program package was
used to determine the unit-cell parameters and for data collection (10 sec/frame scan time for a
sphere of diffraction data). The raw frame data was processed using SAINT⁴³ and SADABS⁴⁴ to
yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴⁵
program. There were no systematic absences nor any diffraction symmetry other than the Friedel
condition. The centrosymmetric triclinic space group P\(\overline{1}\) was assigned and later determined to
be correct. The structure was solved by direct methods and refined on F² by full-matrix least-
squares techniques. The analytical scattering factors\textsuperscript{46} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0591 and Goof = 1.037 for 493 variables refined against 12127 data (0.73Å), R1 = 0.0274 for those 10674 data with I > 2.0σ(I). There were several high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals although it was probable that tetrahydrofuran and/or diethylether solvent was present. The SQUEEZE routine in the PLATON\textsuperscript{47,48} program package was used to account for the electrons in the solvent accessible voids. Details are given in Table 10.1.

**X-ray Data Collection, Structure Solution and Refinement for 3-Ce.** A yellow crystal of approximate dimensions 0.464 x 0.341 x 0.240 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{42} program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\textsuperscript{43} and SADABS\textsuperscript{44} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{45} program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F\textsuperscript{2} by full-matrix least-squares techniques. The analytical scattering factors\textsuperscript{46} for neutral atoms were used throughout the analysis. H(26A) was located from a difference-Fourier map and refined (x,y,z and U_{iso}). There was one half molecule of diethylether solvent present per formula unit which was disordered about an inversion center and included using multiple components with partial site-occupancy-factors. Hydrogen atoms associated with the disordered solvent were not included in
the refinement. All remaining hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0735 and Goof = 1.048 for 613 variables refined against 14394 data (0.74 Å), R1 = 0.0282 for those 12979 data with I > 2.0σ(I). Details are given in Table 10.1.

**X-ray Data Collection, Structure Solution and Refinement for 5-Sm.** A red crystal of approximate dimensions 0.146 x 0.306 x 0.535 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{42} program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\textsuperscript{43} and SADABS\textsuperscript{44} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{45} program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space groups Cc and C2/c. It was later determined that space group Cc was correct. The structure was solved by direct methods and refined on F\textsuperscript{2} by full-matrix least-squares techniques. The analytical scattering factors\textsuperscript{46} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0329 and Goof = 1.046 for 398 variables refined against 8683 data (0.73Å), R1 = 0.0128 for those 8652 data with I > 2.0σ(I). The structure was refined as a two-component inversion twin. Details are given in Table 10.1.

**X-ray Data Collection, Structure Solution and Refinement for 3-Tm.** A colorless crystal of approximate dimensions 0.208 x 0.238 x 0.315 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{42} program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\textsuperscript{43} and SADABS\textsuperscript{44} to
yield the reflection data file. Subsequent calculations were carried out using the SHELXTL \textsuperscript{45} program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group \( P\overline{1} \) was assigned and later determined to be correct. The structure was solved by direct methods and refined on \( F^2 \) by full-matrix least-squares techniques. The analytical scattering factors\textsuperscript{46} for neutral atoms were used throughout the analysis. Hydrogen atoms H(18A), H(19A) and H(26A) were located from a difference-Fourier map and refined (\( x,y,z \) and riding \( U_{iso} \)). The remaining hydrogen atoms were included using a riding model. At convergence, \( wR^2 = 0.0656 \) and Goof = 1.058 for 599 variables refined against 14284 data (0.73Å), \( R_1 = 0.0270 \) for those 13424 data with \( I > 2.0\sigma(I) \).

Results

**Dinitrogen Reactions.** The general reaction of the reduction of an \( Ln^{3+} \) complex in the presence of dinitrogen, as discussed in Chapters 1 and 3, has led to reduced dinitrogen species for most of the lanthanide metals. A proposed intermediate in the formation of these reduced dinitrogen species is an \( Ln^{2+} \) complex. In order to test this theory, reactivity studies of \( 1-Ln \) (\( Ln = Ce, Pr, Gd, Tb, Dy, Ho \)) with dinitrogen were pursued. However these reactions did not lead to reduced dinitrogen species. Surprisingly, a solution of \( 1-Gd \) in THF was allowed to stir in dinitrogen for 2 hours and the only complex crystallized from the solution was unreacted \( 1-Gd \). This lack of reactivity with dinitrogen was also found for the first identified \( La^{2+} \) complex, [K(18-crown-6)Et\_2O][Cp"_3La].\textsuperscript{14}

**\( C_8H_8 \) Reactions.** The reaction of \( 1-Ce \) with 1 equiv of \( C_8H_8 \) led to the isolation of both [K(2.2.2-cryptand)][Cp'\_4Ce], \ 3-Ce, \ and [K(2.2.2-cryptand)][Cp'\_2Ce(C_8H_8)], \ 4-Ce, \ eq 10.4,
Figure 10.1. A disordered cryptand precludes structural analysis of 4-Ce. Eq 10.4 is analogous to eq 10.1, and the isolation of 3-Ce is consistent with the reduction of $C_8H_8$ by two electrons. Isolation of 4-Ce, analogous to $[K(2.2.2\text{-cryptand})][Cp'_{2}Ln(\eta^4-C_{10}H_{18})]$, suggests that the metal center loses one $(Cp')^{1-}$ ligand, which is then trapped by another 1-Ce complex to form 3-Ce. Both the 3-Ce and 4-Ce products are Ce$^{3+}$, accounting for the two electrons needed to reduce $C_8H_8$ to $(C_8H_8)^{2-}$.

\[
\begin{align*}
2\left( \begin{array}{c}
\text{SiMe}_3 \\
\text{Me}_3\text{Si} \\
\text{Ce} \\
\text{SiMe}_3
\end{array} \right) + C_8H_8 & \rightarrow \left( \begin{array}{c}
\text{SiMe}_3 \\
\text{Me}_3\text{Si} \\
\text{Ce} \\
\text{SiMe}_3
\end{array} \right) - [K(2.2.2\text{-cryptand})][Cp'_{2}Ce] \\
\end{align*}
\]

(a) Preliminary thermal ellipsoid plot of the anion in $[K(2.2.2\text{-cryptand})][Cp'_{2}Ce(COT)]$, 4-Ce, with a disordered K(2.2.2-cryptand) eliminated for clarity, and (b) thermal ellipsoid plot $[K(2.2.2\text{-cryptand})][Cp'_{4}Ce]$, 3-Ce, with a half of an ether molecule omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms were omitted for clarity.
The crystals of 3-Ce are formed in the same space group as [K(2.2.2-cryptand)][Cp′4Y], 3-Y, but are not isomorphous. As seen in Figure 10.1b, the structure of 3-Ce has three ($\eta^5$-Cp′)1− rings and one ($\eta^1$-Cp′)1− ring, like that seen for 3-Y. Since the nine-coordinate ionic radius of Ce$^{3+}$ (1.196 Å) is much closer to that of La$^{3+}$ (1.216 Å) than Y$^{3+}$ (1.075 Å), it is surprising that the structure of 3-Ce would be analogous to 3-Y. This suggests that the ionic radius cut-off to isolate a structure of 3-Ln with four ($\eta^5$-Cp′)1− rings is between that of La and Ce. From the preliminary structural data of 3-Ce, the average Ce–(Cp′ centroid) distance of 2.587 Å is not much longer than that of 1-Ce (2.558 Å)$^2$ and is close to that of the 10-coordinate Cp′3CePy (2.578 Å).

The reaction of 1-La with excess C$_8$H$_8$ showed the formation of a product analogous to 4-Ce, namely [K(2.2.2-cryptand)][Cp′2La(C$_8$H$_8$)], 4-La, Figure 10.2. The $^1$H NMR spectrum of the crude reaction mixture did not show evidence for the formation of 3-La as a byproduct of the reaction. While structural data of 4-La suggest the C$_8$H$_8$ ring is not perfectly planar, this has

![Figure 10.2.](image.png)

*Figure 10.2.* Thermal ellipsoid plot of [K(2.2.2-cryptand)][Cp′2La(C$_8$H$_8$)], 4-La, drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.
been observed for other lanthanum complexes with a single (C\(_8\)H\(_8\))\(^2-\) ligand.\(^{31,49,50}\) The average La–(Cp' centroid) distance of 2.69 Å in 4-La, which is longer than that of [K(2.2.2-cryptand)][Cp'\(_2\)La(\(\eta^4\)-C\(_{10}\)H\(_8\))] (2.601 Å), but shorter than that of 3-La (2.724 Å).\(^{16}\) This is consistent with the (\(\eta^8\)-C\(_8\)H\(_8\))\(^2-\) ligand being more sterically crowding than the (\(\eta^4\)-C\(_{10}\)H\(_8\))\(^2-\) ligand. The La–(C\(_8\)H\(_8\) centroid) distance of 2.163 Å is longer than any known La–(C\(_8\)H\(_8\) centroid) bonds that range from 2.025-2.106 Å, including complexes with bridging C\(_8\)H\(_8\) ligands.\(^{31,49,50}\) Complexes 4-La and 4-Ce represent the first examples of a lanthanide complex with two cyclopentadienyl ligands and a (C\(_8\)H\(_8\))\(^2-\) ligand.

In contrast to the reactions of 1-La and 1-Ce, which have 5d\(^1\) and 4f\(^1\)5d\(^1\) electron configurations, respectively, the reaction of 1-Sm, which has a 4f\(^{n+1}\) configuration, with C\(_8\)H\(_8\) led to the isolation of [K(2.2.2-cryptand)][(C\(_8\)H\(_8\))\(_2\)Sm], 5-Sm, eq 10.5, Figure 10.3. This may constitute preliminary evidence that the reactivity of the complexes of 1-Ln appear to vary depending on the electron configuration of the divalent ion. There are several examples in the literature of the [(C\(_8\)H\(_8\))\(_2\)Sm]\(^{-}\) anion with different cations, and the average Sm–(C\(_8\)H\(_8\) centroid) distance of 1.978 Å and (C\(_8\)H\(_8\) centroid)-Sm-(C\(_8\)H\(_8\) centroid) angle of 179.2° in 5-Sm are similar to the other examples.\(^{25,51-53}\) Formation of 5-Sm requires a total of 4 electrons to reduce the two C\(_8\)H\(_8\) ligands. This stoichiometry requires that three equivalents of other Sm\(^{3+}\) byproducts must
be formed. The byproduct expected based on eq 10.1 and 10.4, namely [K(2.2.2-cryptand)] [Cp’4Sm], 3-Sm, has yet to be identified.

![Figure 10.3](image)

**Figure 10.3.** Thermal ellipsoid plot of [K(2.2.2-cryptand)][(C₈H₈)₂Sm], 5-Sm, drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

1-Tm, another Ln²⁺ complex that has a traditional 4fⁿ⁺¹ electron configuration, also reacts with C₈H₈. Although the reaction occurs quickly, a reduced C₈H₈ complex has yet to be isolated. However, the common Ln³⁺ byproduct from reductions with 1-Ln, [K(2.2.2-cryptand)] [Cp’4Tm], 3-Tm, was isolated, Figure 10.4. Preliminary structural data suggest that 3-Tm has two (η⁵-Cp’)¹⁻ rings and two (η¹-Cp’)¹⁻ rings. The smaller nine-coordinate ionic radius of 1.052 Å for Tm³⁺ than the 1.075 Å ionic radius for Y³⁺ appears to be enough to make an additional ring have an η¹ coordination.¹⁷ The average Tm–(Cp’ centroid) distance of 2.359 Å is shorter than that for Cp’₃Tm (2.379 Å) and 1-Tm (2.502 Å). It is unclear why 3-Tm would form with two (η¹-Cp’)¹⁻ rings instead of Cp’₃Tm and KCp’. There appear to be only four other examples of a rare earth metalloocene with two η¹ alkyl ligands.⁵⁴-⁵⁶
Figure 10.4. Preliminary thermal ellipsoid plot of [K(2.2.2-cryptand)][Cp′Tm], 3-Tm, drawn at
the 50% probability level. Hydrogen atoms were omitted for clarity.

Discussion

Reactivity studies of four different divalent ions in the same ligand coordination, namely
in the complex, [K(2.2.2-cryptand)][Cp′Ln], 1-Ln, with cyclooctatetraene (C\textsubscript{8}H\textsubscript{8}) has led to the
formation of two different reduced C\textsubscript{8}H\textsubscript{8} complexes. 1-La and 1-Ce both react with C\textsubscript{8}H\textsubscript{8} to
form [K(2.2.2-cryptand)][Cp′2Ln(C\textsubscript{8}H\textsubscript{8})], 4-Ln, which are the first examples of lanthanide
reduced C\textsubscript{8}H\textsubscript{8} complexes with three rings around the metal center. The byproduct of the
balanced reaction in eq 10.4, [K(2.2.2-cryptand)][Cp′4Ln], 3-Ln, is identified for the Ce reaction.
3-Ce has three (η\textsuperscript{5}-Cp′)\textsuperscript{1−} rings and one (η\textsuperscript{1}-Cp′)\textsuperscript{1−} ring, similar to that found for 3-Y. Since Ce is
the second largest lanthanide, La is likely to be the only lanthanide capable of having four
(η\textsuperscript{5}-Cp′)\textsuperscript{1−} rings, as found for 3-La.\textsuperscript{16} This reduction reaction of C\textsubscript{8}H\textsubscript{8} with the non-traditional 4f
\textsuperscript{5d} Ln\textsuperscript{2+} ions is similar to the analogous reaction with naphthalene.
In contrast, the reactivity of 1-Sm with C₈H₈ led to the isolation of [K(2.2.2-cryptand)]
[(C₈H₈)₂Sm], 5-Sm. Since 1-Sm contains a divalent ion with a traditional 4fⁿ⁺¹ configuration,
this may indicate that while both the traditional and non-traditional divalent lanthanide ions are
capable of reducing C₈H₈ by two electrons, they do not form the same products. Too few data
are available to consider this a trend.

It is unclear whether this difference in formed products is due to the size of the metals or
due to the reduction reactivity of the different configurations. Since La and Ce are the largest
lanthanides, these metals can handle the ligand coordination in 4-Ln, while it could be too
crowded to be isolated for smaller metals, such as Sm. Reduction of the non-traditional and
traditional divalents of 1-Ln with the smaller lanthanides will be useful in determining this.
Interestingly, both reduction products from the reaction of 1-Ln with C₈H₈, namely 4-Ln and 5-
Ln, are different from those of Th²⁺ and U²⁺, both of which form An⁴⁺ complexes of
(C₈H₈)²⁻.¹⁸,¹⁹

The reaction of 1-Tm with C₈H₈ led to the isolation of 3-Tm, which was found to contain
two (η⁵-Cp')¹⁻ rings and two (η¹-Cp')¹⁻ rings. This complex represents a rare example of a
metallocene with two η¹ alkyl ligands. The complex 3-Ln, has been found to form with three
different ligand coordination environments depending on the ionic radius of the metal center.
Conclusion

Reactivity of [K(2.2.2-cryptand)][Cp′3Ln], 1-Ln (Ln = La, Ce), with C8H8 has led to the isolation of a reduced C8H8 complex, [K(2.2.2-cryptand)][Cp′2Ln(C8H8)], 4-Ln. 4-Ln is found to be the first example of a lanthanide C8H8 complex with three rings around the metal center. In contrast, 1-Sm, reacts with C8H8 in a different manner to form [K(2.2.2-cryptand)][(C8H8)2Sm], 5-Sm. Both 4-Ln and 5-Sm are different than the reaction products of [K(18-crown-6)(THF)2][Cp″3Th] and [K(2.2.2-cryptand)][Cp′3U] with C8H8. Reactivity of 1-Ln of the smaller metals with C8H8 will be useful in determining if this difference in reactivity is due to the differences in ionic radius size between La, Ce, and Sm or the difference in electron configuration of the divalent ion used.
### Table 10.1. X-ray Data Collection Parameters of 4-La, 3-Ce, 5-Sm, and 3-Tm.

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<th>3-Ce</th>
<th>5-Sm</th>
<th>3-Tm</th>
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<td>C$<em>{50}$H$</em>{88}$CeKNa$_2$O$_6$Si$_4$</td>
<td>C$<em>{3d}$H$</em>{55}$KNa$_2$O$_6$Sm</td>
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<td>wR2 (all data)$^a$</td>
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<td>0.0735</td>
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$^a$Definitions: wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}; R1 = \sum|F_o| - |F_c|/\sum|F_o|.$
References


(43) SAINT Version 8.34a, Bruker AXS, Inc.; Madison, WI 2013.


CHAPTER 11

Comparisons of Lanthanide vs Actinide +2 Ions in a Tris(aryloxide)arene Coordination Environment

Introduction

As described in Chapters 5 and 7, the reduction of Cp’3Ln and Cp”3Ln complexes [Cp’ = C5H4SiMe3; Cp” = C5H5(SiMe3)2] with KC8 in the presence of a chelate, such as 18-crown-6 or 2.2.2-cryptand, allowed the first isolation of molecular complexes of nine new Ln2+ ions (Ln = La, Ce, Pr, Gd, Tb, Ho, Er, Y, and Lu), Schemes 11.1 and 11.2.1-4 These complexes displayed structural and spectroscopic differences from the traditional six 4f

n+1 Ln2+ ions (Ln = Eu, Yb, Sm, Tm, Nd, Dy), that were consistent with 4f

n5d1 electron configurations for these new +2 ions in comparison to the 4fn configurations of the Ln3+ precursors.

Scheme 11.1. Crystallographically Characterized Products of Reduction of Cp”3Ln (Ln = La and Ce) by Lappert et al.1
Scheme 11.2. Crystallographically Characterized Products of Reduction of Cp'₃Ln (Ln = Y, Pr, Gd, Tb, Ho, Er, Lu).²⁴

Synthesis of [K(2.2.2-cryptand)][Cp'₃Ln], 2, for the entire lanthanide series (except Pm, which was not studied due to its radioactivity) allowed for the first comparison of the +2 ions and +3 ions, Cp'₃Ln, 1, in the same coordination environment for all of the lanthanides.⁴⁵

Surprisingly, in the (Cp'₃)³⁻ coordination environment, the Dy²⁺ and Nd³⁺ complexes, 2-Dy and 2-Nd, have properties consistent with 4fⁿ5d¹ ground states, instead of the previously identified complexes of these ions which have properties consistent with 4fⁿ⁺¹ ground states. These results suggest that the ligand set can change the electronic ground state in Ln²⁺ complexes, making three categories of Ln²⁺ ions: one group that forms traditional 4fⁿ⁺¹ ions, a second group that forms 4fⁿ5d¹ ions, and a third group of metals that can cross over between 4fⁿ⁺¹ and 4fⁿ5d¹ configurations depending on the coordination environment. Based on the characterized Ln²⁺
complexes currently known, the first class has four members (Eu, Yb, Sm, and Tm), the second
class has eight members (La, Ce, Pr, Gd, Tb, Ho, Er, Lu) and the third class has two members
(Dy and Nd).

As discussed in Chapter 6, reduction of Cp’₃U led to the first crystallographically
characterized U²⁺ complex, [K(2.2.2-cryptand)][Cp’₃U], 2-U, eq 1.⁶ Structural, spectroscopic,
and theoretical analysis of 2-U were consistent with a quintet 5fⁿ6d¹ ground state for U²⁺ in this
coordination environment. This complex displayed properties similar to those of the complexes
of the 4fⁿ5d¹ Ln²⁺ ions.

Shortly afterwards, a second U²⁺ complex was crystallographically characterized, through
the reduction of a tris(aryloxide) arene uranium(III) complex, [(^Ad,MeArO)₃mes]U, 3, eq 11.2.⁷,⁸
Derivatives of 3 have been previously shown to contain two covalent δ bonds with the π*
orbitals of the arene, each partially occupied with a single electron.⁹,¹⁰ Analysis of this new U²⁺
complex, [K(2.2.2-cryptand)]{[(^Ad,MeArO)₃mes]U}, 4, was consistent with an S = 2 5f⁴ ground
state for the metal ion. Shortening of the M-(arene centroid) distance in 4 with respect to 3 was
consistent with stabilization of the low-valent metal center via arene interaction.
The isolation of two U$^{2+}$ complexes with two different assigned ground state configurations in two different coordination environments indicated that uranium should fit into the third class of crossover ions described for the lanthanides above. Since U is a congener of Nd, this has some periodic consistency. These results suggested that it would interesting to determine what ground states were present for Ln$^{2+}$ ions in the [(Ad,MeArO)$_3$mes] ligand environment. If Nd was indeed like U, a 4f$^{n+1}$ configuration could be the ground state for Nd$^{2+}$.

To explore this possibility, the synthesis of new +2 lanthanide ions in the presence of the [(Ad,MeArO)$_3$mes] ligand environment was pursued and is reported in this Chapter.

**Experimental**

The syntheses and manipulations described below were conducted under argon with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were sparged with UHP grade argon (Airgas) and passed through columns containing Q-5 and molecular sieves before use. NMR solvents (Cambridge Isotope Laboratories) were dried over NaK/benzophenone, degassed by three freeze–pump–thaw cycles, and vacuum-transferred before use. Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = La, Nd, Gd, Dy, Er),$^{11}$ KC$_8$,$^{12}$ and H$_3$[(Ad,MeArO)$_3$mes],$^7$ were prepared according to literature methods. 2.2.2-Cryptand, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Acros Organics), was placed under vacuum ($10^{-3}$ Torr) for 12 h.
before use. $^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) spectra were obtained on a Bruker GN500 or CRYO500 MHz spectrometer at 298 K. IR samples were prepared as KBr pellets and the spectra were obtained on a Varian 1000 FT-IR spectrometer. Elemental analyses were performed on a PerkinElmer 2400 series II CHNS elemental analyzer. UV–vis spectra were obtained in THF at 298 K using a Varian Cary 50 Scan UV–vis spectrophotometer. EPR spectra were collected using X-band frequency (9.3-9.8 GHz) on a Bruker EMX spectrometer equipped with an ER041XG microwave bridge and the magnetic field was calibrated with DPPH ($g = 2.0036$).

$\left[(\text{Ad,MeArO})_3\text{mes}\right]\text{La, 3-La.}$ In an argon-filled glovebox, a sealable 100 mL side arm Schlenk flask equipped with a greaseless stopcock was charged with a solution of $\text{H}_3[(\text{Ad,MeArO})_3\text{mes}]$ (402 mg, 0.455 mmol) in benzene (40 mL) and a magnetic stir bar. A solution of $\text{La}[\text{N(SiMe}_3)_2]_3$ (376 mg, 0.460 mmol) in benzene (40 mL) was slowly added to the stirred solution. The flask was attached to a Schlenk line and the mixture was stirred and heated to reflux for 12 h. The flask was brought back into the glovebox, the solution was filtered, and the solvent was removed from the colorless filtrate under vacuum. The resulting colorless solid was washed with hexane. The solids were extracted in benzene (15 mL). Hexane (5 mL) was added to the benzene solution and removal of solvent under vacuum afforded 3-La as a colorless solid. Colorless single crystals of 3-La, suitable for X-ray diffraction, were grown from slow evaporation of a C$_6$D$_6$ solution.

$\left[(\text{Ad,MeArO})_3\text{mes}\right]\text{Nd, 3-Nd.}$ As described for 3-La, a solution of $\text{Nd}[\text{N(SiMe}_3)_2]_3$ (251 mg, 305 mmol) in benzene (40 mL) was slowly added to a stirred solution of $\text{H}_3[(\text{Ad,MeArO})_3\text{mes}]$ (256 mg, 0.290 mmol) in benzene (40 mL) to form a light blue solution. The solvent was
removed from the blue filtrate under vacuum and the flask was brought back into the glovebox. The resulting blue solid was washed with hexane. The solids were extracted in benzene (15 mL). Hexane (5 mL) was added to the benzene solution and removal of solvent under vacuum afforded \(3\text{-Nd}\) as a blue solid (163 mg, 56%). Blue single crystals of \(3\text{-Nd}\), suitable for X-ray diffraction, were grown from slow evaporation of a \(\text{C}_6\text{D}_6\) solution. IR: TO DO. Anal. Calc for \(\text{C}_{63}\text{H}_{75}\text{NdO}_3\): C, 73.86; H, 7.38. Found: C, 74.09; H, 7.35.

**Alternative Synthesis of 3-Nd.** This prep is analogous to that described above for \(3\text{-La}\), only the order of addition of the reagents was switched. A solution of \(\text{H}_3[\text{(^Ad,MeArO)}_3\text{mes}]\) (336 mg, 0.380 mmol) in benzene (20 mL) was slowly added to a stirred solution of \(\text{Nd}[\text{N(SiMe}_3)_2]_3\) (333 mg, 0.414 mmol) in benzene (40 mL). Over the 12 h at reflux, blue solids formed in a blue solution. The mixture was centrifuged and filtered to isolate an insoluble blue solid (253 mg). The solvent was removed from the blue filtrate under vacuum and the flask was brought back into the glovebox. The resulting blue solid was washed with hexane. The solids were extracted in benzene (15 mL) and removal of solvent under vacuum afforded \(3\text{-Nd}\) as a blue solid (113 mg, 29%).

\[\text{[(^{Ad,MeArO)}_3\text{mes}]Gd, 3-Gd.}\] As described for \(3\text{-La}\), a solution of \(\text{Gd}[\text{N(SiMe}_3)_2]_3\) (227 mg, 0.271 mmol) in benzene (30 mL) was slowly added to a stirred solution of \(\text{H}_3[\text{(^Ad,MeArO)}_3\text{mes}]\) (236 mg, 0.267 mmol) in benzene (30 mL). The solvent was removed under vacuum and the flask was brought back into the glovebox. The resulting cream solid was washed with hexane. The solids were extracted in benzene (15 mL) and removal of solvent under vacuum afforded \(3\text{-Gd}\) as an off-white solid (275 mg, 99%).

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[(Ad,MeArO)₃mes]Dy, 3-Dy. As described for 3-La, a solution of Dy[N(SiMe₃)₂]₃ (298 mg, 0.354 mmol) in benzene (20 mL) was slowly added to a stirred solution of H₃[(Ad,MeArO)₃mes] (303 mg, 0.343 mmol) in benzene (30 mL). The solvent was removed under vacuum and the resulting cream solid was washed with hexane. The solids were extracted in benzene (10 mL) and removal of solvent under vacuum afforded 3-Dy as an off-white solid (236 mg, 66%). Anal. Calc for C₆₃H₇₅DyO₃: C, 72.56; H, 7.25. Found: C, 72.28; H, 7.31.

[(Ad,MeArO)₃mes]Er, 3-Er. In an argon-filled glovebox, a solution of Er[N(SiMe₃)₂]₃ (43 mg, 0.051 mmol) in THF (7 mL) was slowly added to a magnetically stirred solution of H₃[(Ad,MeArO)₃mes] (43 mg, 0.049 mmol) in THF (7 mL). The mixture was stirred on a hotplate heated to 70 °C for 1.5 h. The solvent was removed under vacuum and the resulting pink solid was washed with hexane. The solids were extracted in THF (10 mL) and removal of solvent under vacuum afforded 3-Er as an pink gel.

Notes on the Synthesis of [(Ad,MeArO)₃mes]Ln, 3-Ln. It should be noted that the preparation of the [(Ad,MeArO)₃mes]Ln complexes analogous to that reported for [(Ad,MeArO)₃mes]U was complicated with formation of insoluble materials. Identical lanthanide reactions run at the same time resulted in different amounts of insoluble materials. As described above for 3-Nd, benzene soluble 3-Ln was often isolated in a higher yield when a solution of Ln[N(SiMe₃)₂]₃ was slowly added to a solution of H₃[(Ad,MeArO)₃mes], versus when a solution of H₃[(Ad,MeArO)₃mes] was slowly added to a solution of Ln[N(SiMe₃)₂]₃. Small scale reactions were found to be most successful in THF instead of benzene: a THF solution of Ln[N(SiMe₃)₂]₃ was added dropwise to a THF solution of H₃[(Ad,MeArO)₃mes] that was pre-heated to 70 °C. This method could only be done on a small (0.05-0.06 mmol) scale.
[K(2.2.2-cryptand)\][[(\text{Ad,MeArO})_3\text{mes}]\text{Nd}], 4-Nd. In an argon-filled glovebox, [(\text{Ad,MeArO})_3\text{mes}]\text{Nd}, 3-Nd (61 mg, 0.060 mmol), was combined with 2.2.2-cryptand (22 mg, 0.058 mmol) in a vial containing a magnetic stir bar and dissolved in 1:1 THF/C_6H_6 (4 mL). KC_8 (15 mg, 0.11 mmol) was quickly added to the pale blue solution. The reaction immediately turned brown. After 2 min, the solution was filtered to remove a black precipitate that was presumably graphite. The resulting red/orange solution was cooled to $-35 \, ^\circ\text{C}$ in the freezer for 24 h. The solution was layered with additional Et_2O (15 mL) and stored at $-35 \, ^\circ\text{C}$ for 12 h to produce brown/orange crystals of 4-Nd suitable for X-ray diffraction.

[K(2.2.2-cryptand)\][{(\text{Ad,MeArO})_3\text{mes}]\text{Gd}}, 4-Gd/6-Gd. As described for 4-Nd, [(\text{Ad,MeArO})_3\text{mes}]\text{Gd}, 3-Gd, (58 mg, 0.056 mmol) and 2.2.2-cryptand (21 mg, 0.058 mmol) were dissolved in 1:1 THF/C_6H_6 (2 mL) to form an off-white solution, which was combined with KC_8 (20 mg, 0.15 mmol) to produce red crystals suitable for X-ray diffraction. The crystals were characterized as a co-crystallized mixture of [K(2.2.2-cryptand)\][{(\text{Ad,MeArO})_3\text{mes}]\text{Gd}}, 4-Gd, and [K(2.2.2-cryptand)\][{(\text{Ad,MeArO})_3\text{mes}]\text{GdH}}, 6-Gd, in an 65:35 ratio.

[K(2.2.2-cryptand)\][{(\text{Ad,MeArO})_3\text{mes}]\text{Er}}, 4-Er/6-Er. As described for 4-Nd, [(\text{Ad,MeArO})_3\text{mes}]\text{Er}, 3-Er, (49 mg, 0.047 mmol) and 2.2.2-cryptand (18 mg, 0.048 mmol) were dissolved in 1:1 THF/C_6H_6 (2 mL) to form a pink solution, which was combined with KC_8 (18 mg, 0.13 mmol) to produce red crystals suitable for X-ray diffraction. The crystals were characterized as a co-crystallized mixture of [K(2.2.2-cryptand)\][{(\text{Ad,MeArO})_3\text{mes}]\text{Er}}, 4-Er, and [K(2.2.2-cryptand)\][{(\text{Ad,MeArO})_3\text{mes}]\text{ErH}}, 6-Er, in an 55:45 ratio.
[K(2.2.2-cryptand)]{[(Ad,MeArO)₃mes]Dy} and [K(2.2.2-cryptand)]{[(Ad,MeArO)₃mes]DyOH}, 4-Dy/7-Dy. As described for 4-Nd, [(Ad,MeArO)₃mes]Dy, 3-Dy, (90 mg, 0.086 mmol) and 2.2.2-cryptand (32 mg, 0.085 mmol) were dissolved in 3:1 THF/C₆H₆ (3 mL) to form an off-white solution, which was combined with KC₈ (18 mg, 0.132 mmol) to produce red crystals suitable for X-ray diffraction. The crystals were characterized as a co-crystallized mixture of [K(2.2.2-cryptand)]{[(Ad,MeArO)₃mes]Dy}, 4-Dy, and [K(2.2.2-cryptand)]{[(Ad,MeArO)₃mes]DyOH}, 7-Dy, in an 2:3 ratio.

**X-ray Data Collection, Structure Solution and Refinement for 3-La.** A colorless crystal of approximate dimensions 0.175 x 0.162 x 0.060 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group P2₁/c that was later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR₂ = 0.0726 and Goof = 1.039 for 610 variables refined against 11962 data (0.75 Å), R₁ = 0.0315 for those 10110 data with I > 2.0σ(I). Details are given in Table 11.3.

**X-ray Data Collection, Structure Solution and Refinement for 3-Nd.** A blue crystal of approximate dimensions 0.301 x 0.088 x 0.071 mm was mounted on a glass fiber and
transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{18} program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\textsuperscript{14} and SADABS\textsuperscript{19} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{20} program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group \( P2_1/c \) that was later determined to be correct. The structure was solved using the coordinates from 3-La, the La analog. The analytical scattering factors\textsuperscript{17} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0850 and Goof = 1.228 for 610 variables refined against 8875 data (0.83 Å), R1 = 0.0453 for those 7703 data with \( I > 2.0\sigma(I) \). Details are given in Table 11.3.

**X-ray Data Collection, Structure Solution and Refinement for 4-Nd.** A red crystal of approximate dimensions 0.349 x 0.234 x 0.214 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{21} program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\textsuperscript{14} and SADABS\textsuperscript{15} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{16} program. The diffraction symmetry was \( m \bar{3} \) and the systematic absences were consistent with the cubic space group \( P2_13 \) that was later determined to be correct. The structure was solved by direct methods and refined on \( F^2 \) by full-matrix least-squares techniques. The analytical scattering factors\textsuperscript{17} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on a three-fold rotation axis. At convergence, wR2 = 0.1279 and Goof = 1.174 for 285 variables refined against 6739 data (0.73 Å), R1 =
0.0482 for those 6400 data with I > 2.0σ(I). The absolute structure was assigned by refinement of the Flack$^{22}$ parameter. There were several high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals although it was probable that toluene solvent was present. The SQUEEZE routine in the PLATON$^{23}$ program package was used to account for the electrons in the solvent accessible voids. Details are given in Table 11.4.

**X-ray Data Collection, Structure Solution and Refinement for 4-Gd/6-Gd.** A red crystal of approximate dimensions 0.102 x 0.177 x 0.181 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2$^{13}$ program package was used to determine the unit-cell parameters and for data collection (180 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT$^{14}$ and SADABS$^{15}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL$^{20}$ program. The systematic absences were consistent with the cubic space group $P2_13$ that was later determined to be correct. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors$^{17}$ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule and counter-ion were located on three-fold rotation axes. The complex appeared to be a mixed composition of approximately Gd$^{2+}$ (65%) / Gd$^{3+}$ (35%). There was approximately 35% of a hydride ligand present bound to Gd(2). The position of the hydride was evident in the electron density map however it was necessary to fix the Gd-H distance and the hydride thermal parameter during refinement. An ether solvent molecule was disordered about a three-fold rotation axis and included with partial site-occupancy-factors. At convergence, wR2 = 0.0951
and Goof = 1.222 for 301 variables refined against 5062 data (0.81), R1 = 0.0372 for those 4861 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter$^{22}$. Details are given in Table 11.4.

**X-ray Data Collection, Structure Solution and Refinement for 4-Er/6-Er.** A red crystal of approximate dimensions 0.200 x 0.240 x 0.280 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX$^{13}$ program package was used to determine the unit-cell parameters and for data collection (3 sec/frame scan time for 99 frames of diffraction data). The raw frame data was processed using SAINT$^{14}$ and SADABS$^{19}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL$^{20}$ program. The systematic absences were consistent with the cubic space group $P2_13$ that was later determined to be correct. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors$^{17}$ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule and counter-ion were located on three-fold rotation axes. The complex appeared to be a mixed composition of approximately $\text{Er}^{2+}$ (55%) / $\text{Er}^{3+}$ (45%). There was approximately 45% of a hydride ligand present bound to Er(2). The position of the hydride was evident in the electron density map however it was necessary to fix the Er-H distance and the hydride thermal parameter during refinement. An ether solvent molecule was disordered about a three-fold rotation axis and included with partial site-occupancy-factors. At convergence, wR2 = 0.0827 and Goof = 1.114 for 301 variables refined against 5953 data (0.73), R1 = 0.0413 for those 5352 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter$^{22}$. Details are given in Table 11.4.
X-ray Data Collection, Structure Solution and Refinement for 4-Dy/7-Dy. A red crystal of approximate dimensions 0.200 x 0.230 x 0.260 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{13} program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time for 112 frames of data). The raw frame data was processed using SAINT\textsuperscript{14} and SADABS\textsuperscript{19} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{20} program. The systematic absences were consistent with the cubic space group \(P2_1\bar{3}\) that was later determined to be correct. The structure was solved by direct methods and refined on \(F^2\) by full-matrix least-squares techniques. The analytical scattering factors\textsuperscript{17} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule and counter-ion were located on three-fold rotation axes. The complex appeared to be a mixed composition of approximately Dy\(^{2+}\) (40\%) / Dy\(^{3+}\) (60\%). There was approximately 60\% of a hydroxide ligand present. An ether solvent molecule was disordered about a three-fold rotation axis and included with partial site-occupancy-factors. At convergence, \(wR^2 = 0.0956\) and \(Goof = 1.043\) for 303 variables refined against 4155 data (0.83\AA\), \(R_1 = 0.0457\) for those 3582 data with \(I > 2.0\sigma(I)\). The absolute structure was assigned by refinement of the Flack parameter\textsuperscript{22}. Details are given in Table 11.4.

Results

Synthesis of the trivalent precursors, \([(\text{Ad,MeArO})_3\text{mes}]\text{Ln}\) (Ln = La, Nd, Gd, Dy, and Er), \(\text{3-Ln}\), was accomplished through the reaction of \(\text{Ln}[\text{N(SiMe}_3\text{)}_2]\) with the protonated ligand \(\text{H}_3[\text{(Ad,MeArO)}_3\text{mes}]\), eq 11.3. The La and Nd versions, \(\text{3-La}\) and \(\text{3-Nd}\), respectively, were
crystallographically characterized, Figure 11.1. Although isomorphous 3-La and 3-Nd crystallize in a different space group ($P2_1/c$) than the P-1 space group of the uranium analogue, 3-U, all three complexes have similar structural parameters, Table 11.1. The M–O distances for both 3-La and 3-Nd fall in the range of reported lanthanide aryloxide bonds with ranges of 2.187-2.287 Å$^{24-30}$ and 2.169-2.202 Å$^{26-28,31-34}$ for La and Nd, respectively. In contrast, the M–(arene centroid) distances of 2.575 and 2.489 Å for 3-La and 3-Nd, respectively, are significantly shorter than those reported for neutral arene lanthanide complexes, such as the 2.628 Å distance in $\text{La}(\eta^6-C_6\text{Me}_6)(\text{AlCl}_4)_3$$^{35}$ and 2.566 Å length in $\text{Nd}(\eta^6-1,3,5-C_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3$$^{36}$

$$\text{Ln}^3+ + 3\text{H}_3[\text{Ad,MeArO}_3\text{mes}] \rightarrow \text{Ln} = \text{La, Nd, Gd, Dy, Er}$$

(11.3)

![Diagram of molecular structure](image)

**Figure 11.1.** Molecular structure of $[\text{(Ad,MeArO)}_3\text{mes}]\text{Nd, 3-Nd}$, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.
Table 11.1. Selected bond lengths (Å) and angles (°) of 3-U, 3-La and 3-Nd.

<table>
<thead>
<tr>
<th>Compound</th>
<th>3-U</th>
<th>3-La</th>
<th>3-Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–O</td>
<td>2.158(2), 2.169(2), 2.178(2)</td>
<td>2.1996(15), 2.2309(16), 2.2490(16)</td>
<td>2.172(3), 2.188(3), 2.200(2)</td>
</tr>
<tr>
<td>M–C_{arene} avg.</td>
<td>2.749</td>
<td>2.937</td>
<td>2.864</td>
</tr>
<tr>
<td>M_{oop}^a</td>
<td>0.475(2)</td>
<td>0.157</td>
<td>0.268</td>
</tr>
<tr>
<td>M–Cent.</td>
<td>2.35</td>
<td>2.575</td>
<td>2.489</td>
</tr>
<tr>
<td>4O–M–O</td>
<td>114.57(9), 113.91(9), 117.51(9)</td>
<td>119.08(6), 110.08(6), 129.32(6)</td>
<td>119.58(10), 110.95(10), 125.00(10)</td>
</tr>
</tbody>
</table>

^a Distance of M from the plane defined by the three O atoms of the (Ad,MeArO)_{mes} ligand

Both examples of 3-Ln have longer M–(arene centroid) distances than that of 3-U, as well as a shorter displacement from the plane defined by the three O atoms of the (Ad,MeArO)_{mes} ligand (this will be defined as the O3 plane) than that found for 3-U. Regardless of these differences in the proximity of the metal center to the arene, the average C–C bonds of the arene are within error to that of the tert-butyl analogue of the free ligand, H3[^Bu,^BuArO]_{mes}^9 suggesting little to no reduction of the arene.

Comparisons of the structural data of 3-La and 3-Nd reveal that the metal center is closer to the arene and further out of the O3 plane in 3-Nd than in 3-La, by 0.086 Å and 0.111 Å, respectively. The displacement of the metal center from the O3 plane is not a result of the metal atom being too small to fit in the plane, since the smaller Nd (0.983 Å, 6-coordinate) has a larger displacement than La (1.032 Å, 6-coordinate).^37 It is unclear whether the metal center is closer to the arene in 3-Nd than 3-La due to the fact that Nd^3+ has three f electrons, two of which could
participate in similar covalent \( \delta \) bonds with the \( \pi^* \) orbitals of the arene as described above for \( 3\)-U, while La\(^{3+}\) has no f electrons. As expected, the Nd is 0.14 Å further from the arene in \( 3\)-Nd than U is in \( 3\)-U, as a result of the minimal radial extension of the 4f orbitals versus the 5f orbitals.\(^{38}\)

Ln–ligand bond lengths are often described by a simple sum of ionic radii because there is little interaction between the 4f orbitals and ligands. As a consequence, Ln-ligand distances often change regularly from one metal to another in analogous complexes based on the ionic radii. However, \( 3\)-La and \( 3\)-Nd do not follow this trend. The La–O distance is 0.040 Å larger than the Nd-O distance which is similar to the difference in ionic radii of 0.049 Å between 3-coordinate La and Nd.\(^{37}\) However, La–(arene centroid) distance is 0.086 Å larger than that of Nd and the average M–C(arene) distance is 0.073 Å larger. The complexes with arene ligand coordination closest to that of \( 3\)-Ln are the lanthanide \( \eta^6 \)-arene-bridged aryloxide dimers, \( \text{Ln}_2(\mu-\kappa^1:\eta^6-O-2,6'-\text{Pr}_2\text{C}_6\text{H}_3)_6 \), \( 5\)-Ln, Figure 11.2, which have an arene ring of the aryloxide ligand in proximity to the metal center to complete the coordination sphere of the metal center.\(^{25,31}\) In these complexes the difference in La–(arene centroid) distance and average La–C(arene) distances are 0.028 Å larger than those of Nd which is also different from the change in ionic radius, suggesting that M-(arene) distances do not follow the trend described above.
Reduction of 3-Nd with potassium graphite in the presence of 2.2.2-cryptand produced a new example of a Nd$^{2+}$ complex, [K(2.2.2-cryptand)]$\{[(\text{Ad,MeArO})_3\text{mes}]\text{Nd}\}$, 4-Nd, eq 11.4.

Complex 4-Nd was crystallographically characterized, Figure 11.3, and found to be isomorphous with 4-U, Table 11.2. Structural data on 4-Nd show that the metal center is 0.123 Å closer to arene centroid than in 3-Nd. This change is not as large as the change of 0.17 Å difference between 3-U and 4-U, which is likely indicative of the limited radial extension of the 4f orbitals versus the 5f orbitals.\textsuperscript{38} Just like what was found for 4-U, the arene carbon atoms are approximately planar in 4-Nd and the C–C(arene) bond lengths only increase by approximately 0.01 Å, suggesting arene reduction does not occur. As analyzed for uranium, the contraction of the M–(arene centroid) distance between 3-Nd and 4-Nd could suggest a greater covalent and/or ionic interaction with the arene due to a change in charge distribution between the metal center.
Figure 11.3. Molecular structure of $[\text{K}(2.2.2\text{-cryptand})] \{[(\text{Ad,MeArO})_3\text{mes}]\text{Nd}]$, 4-Nd, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 11.2. Selected bond lengths (Å) and angles (°) of 4-U, 4-Nd, 4-Gd/6-Gd, 4-Er/6-Er, and 4-Dy/7-Dy.

<table>
<thead>
<tr>
<th>Compound</th>
<th>4-U</th>
<th>4-Nd</th>
<th>4-Gd/6-Gd</th>
<th>4-Er/6-Er</th>
<th>4-Dy/7-Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–O</td>
<td>2.236(4)</td>
<td>2.237(4)</td>
<td>2.203(3)/2.126(3)</td>
<td>2.172(3)/2.077(3)</td>
<td>2.222(3)/2.125(3)</td>
</tr>
<tr>
<td>M–C\text{arene}</td>
<td>2.597(5), 2.633(5)</td>
<td>2.742(6), 2.788(7)</td>
<td>2.672(5)/3.175</td>
<td>2.602(4)/3.170</td>
<td>2.586(5)/3.101, 2.605(6)/3.127</td>
</tr>
<tr>
<td>M–C\text{arene} avg.</td>
<td>2.615</td>
<td>2.765</td>
<td>2.691/3.196</td>
<td>2.618/3.188</td>
<td>2.596/3.113</td>
</tr>
<tr>
<td>C\text{arene}–C\text{arene}</td>
<td>1.432(7), 1.432(8)</td>
<td>1.429(10), 1.434(10)</td>
<td>1.409(8), 1.431(8)</td>
<td>1.415(6), 1.423(6)</td>
<td>1.414(8), 1.415(8)</td>
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<tr>
<td>M\text{oop}\text{a}</td>
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<td>0.530</td>
<td>0.578/0.001</td>
<td>0.637/0.017</td>
<td>0.652/0.055</td>
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<td>M–Cent.</td>
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<td>2.366</td>
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<tr>
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<td>111.77(7)/119.993(2)</td>
<td>111.77(8)/119.93</td>
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</table>
and arene. Theoretical analysis will be important in helping to assign an electron configuration for Nd in 4-Nd.

Reductions of 3-Gd and 3-Er were performed in a manner analogous to that of eq 11.4. Both reactions produced dark red single crystals, suitable for X-ray diffraction, which appeared to be isomorphous with 4-Nd. However the data were best modeled by a mixture of two complexes: the divalent [K(2.2.2-cryptand)]\{[(\text{Ad},\text{MeArO})_3\text{mes}]\text{Ln}\}, 4-Ln, and the trivalent hydride, [K(2.2.2-cryptand)]\{[(\text{Ad},\text{MeArO})_3\text{mes}]\text{LnH}\}, 6-Ln, in an 65:35 ratio for Gd and 55:45 ratio for Er, eq 11.5, Figure 11.4, Table 11.2.

The metal centers in both 4-Ln and 6-Ln lie on a three-fold axis with the same ligand environment, in which Ln1 represents the metal center for 4-Ln and Ln2 represents the metal center for 6-Ln. The metal center for 4-Gd and 6-Gd each have M–O(\text{Ad},\text{MeArO})_3\text{mes} distances (2.203(3) and 2.126(3) Å, respectively) within the 2.090-2.31 Å range for known gadolinium aryloxide bonds,\textsuperscript{27,30,31} while the M–O(\text{Ad},\text{MeArO})_3\text{mes} distance of 2.172(3) Å for 4-Er is longer and the M–O(\text{Ad},\text{MeArO})_3\text{mes} distance of 2.077(3) Å for 6-Er is shorter than the two known erbium aryloxide bonds of 2.083\textsuperscript{39} and 2.097\textsuperscript{40} Å. The metal center in 6-Gd is almost planar with the O\textsubscript{3} plane, displaying just a 0.002 Å displacement, while the metal center in 6-Er is just slightly displaced by 0.017 Å from the O\textsubscript{3} plane. In contrast, the metal centers in 4-Gd and 4-Er have a large displacement from the O\textsubscript{3} plane (0.579 and 0.637 Å, respectively). There is only one Gd\textsuperscript{3+} complex with a Gd–(arene centroid) distance of 2.505 Å for (\eta^6-C_6\text{H}_5\text{Me})\text{Gd(AlBr}_4)_3\textsuperscript{41} and no examples of an Er complex with an Er–(arene centroid) distance, making comparisons difficult. Nonetheless, M–(arene centroid) distances for the Ln\textsuperscript{2+} complex 4-Ln (2.285 and 2.201 Å for Gd and Er, respectively) are much shorter than the M–(arene centroid) distances for the
Ln$^{3+}$ complex 6-Ln (2.862 and 2.855 Å for Gd and Er, respectively) and are between the M–(arene centroid) distances of 4-U and 4-Nd (2.18 Å and 2.366 Å, respectively).

Figure 11.4. Molecular structure of co-crystallized [K(2.2.2-cryptand)][(Ad,MeArO)$_3$mes]Ln, 4-Ln, and [K(2.2.2-cryptand)][(Ad,MeArO)$_3$mes]LnH, 6-Ln, for Ln = Gd (a), Er (b). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms, except H1, are omitted for clarity.

The crystals of 4-Gd/6-Gd display a single isotropic signal at $g_{iso} = 1.99$ in the X-band EPR spectrum, Figure 11.5. This is similar to the X-band EPR spectrum of [K(2.2.2-cryptand)][Cp’3Gd], 2-Gd, which also shows an isotropic signal at $g_{iso} = 1.99$, which is consistent with metal based $S = \frac{1}{2}$ spin systems.$^4$ These EPR data suggest that in the [(Ad,MeArO)$_3$mes] ligand coordination, Gd$^{2+}$ occupies a 4f$^7$5d$^1$ electron configuration in which the d electron is observed as an $S = \frac{1}{2}$ spin system, and the f electrons are not observed.
Figure 11.5. Experimental X-band EPR spectrum of solutions of 4-Gd/6-Gd in THF at 298 K.

When the 4-Er/6-Er mixture was reacted with CCl₄, chloroform was observed. This provided experimental evidence for the presence of a hydride ligand as observed in the crystal structure. The same reaction performed with 4-Nd showed no formation of chloroform. This is consistent with the fact that no disorder was found in the crystal structure of 4-Nd and no co-crystallized Nd-H byproducts were observed.

Reduction of 3-Dy produced dark red crystals suitable for X-ray diffraction, which were also thought to be isomorphous with 4-Nd. Instead, the data were best modeled as a mixture of the divalent [K(2.2.2-cryptand)][{(Ad,MeArO)₃mes]Dy}], 4-Dy, and the trivalent hydroxide [K(2.2.2-cryptand)][{(Ad,MeArO)₃mes]DyOH}], 7-Dy, in a 2:3 ratio. Like the 4-Ln/6-Ln mixtures, 4-Dy and 7-Dy lie on a threefold axis with the same ligand environment, Figure 11.6, Table 11.2, in which Dy1 represents the metal center for 4-Dy and Dy2 represents the metal center for 7-Dy.
Both of the metal centers in 4-Dy/7-Dy have longer M–O(Ad,MeArO)3mes) distances (2.222(3) and 2.125(3) Å, respectively) than any known dysprosium aryloxide bonds which range from 2.056-2.117 Å. For 7-Dy, this could be a result of the rigidity of the ligand since the smaller dysprosium metal center is within 0.055 Å of the O3 plane. 4-Dy contains a significantly shorter M–(arene centroid) distance of 2.177 Å compared to the shortest reported Dy–(arene centroid) distance of 2.471 Å in (η6-C6H6)Dy(AlH4)3. The 2.177 Å distance is equivalent to the 2.18 Å analog seen in 4-U. However, given the limited radial extension of the 4f orbitals, this is likely to be just a coincidence. For 7-Dy, the M–(arene centroid) distance of 2.773 Å is significantly longer than the longest reported Dy–(arene centroid) distance of 2.595 Å in Dy2(μ-κ1:η6-O-2,6-Pr2C6H3)6, 5-Dy. 7-Dy appears to be the first example of a monometallic lanthanide complex with a terminal hydroxide group.
Discussion

Tris(aryloxide) arene lanthanide(III) complexes analogous to \([\text{\textsuperscript{Ad,Me}ArO)}_{\text{\textsuperscript{3}mes}}\text{U}], \text{3-U}\), have been synthesized and characterized. Surprisingly, the two complexes characterized by X-ray diffraction, \([\text{\textsuperscript{Ad,Me}ArO)}_{\text{\textsuperscript{3}mes}}\text{La}], \text{3-La}, and \([\text{\textsuperscript{Ad,Me}ArO)}_{\text{\textsuperscript{3}mes}}\text{Nd}], \text{3-Nd}, do not follow the trends expected based on changing radial size: e.g. although the La-O distances are larger than the Nd-O distance, Nd is closer to the arene ring than predicted based on ionic radii. This suggests that to fully compare the Ln\textsuperscript{3+} complexes with any Ln\textsuperscript{2+} reduction products, it will be necessary to characterize each \textbf{3-Ln} for Ln = Gd, Dy, and Er since their metrical parameters cannot be reliably predicted based on radial size.

Reduction of \textbf{3-Nd} produced just the fourth molecular example of a Nd\textsuperscript{2+} complex, \([\text{K(2.2.2-cryptand)]}\{[(\text{\textsuperscript{Ad,Me}ArO)}_{\text{\textsuperscript{3}mes}}\text{Nd}]\}, \text{4-Nd}\textsuperscript{5,44,45} The structural properties of \textbf{4-Nd}, in comparison to \textbf{3-Nd}, are very similar the differences observed between \textbf{4-U} and \textbf{3-U}\textsuperscript{8} suggesting that Nd in \textbf{4-Nd} could have a 4f\textsuperscript{4} configuration analogous to the 5f\textsuperscript{4} assignment for \textbf{4-U}. Unfortunately, as discussed in Chapter 8, magnetic moment will not help elucidate this assignment since the predicted magnetic moment for 4f\textsuperscript{4}, 2.68 \(\mu_B\), is the same as that predicted for a 4f\textsuperscript{3}5d\textsuperscript{1} configuration assuming the d electron contributes spin only to the magnetic properties of the 4f\textsuperscript{3} core. Theory will be valuable in this assignment.

The reductions of \textbf{3-Gd} and \textbf{3-Er} are more complicated than the Nd case. Single crystals are best modeled as co-crystallized mixtures of new Ln\textsuperscript{2+} complexes, \([\text{K(2.2.2-cryptand)]}\{[(\text{\textsuperscript{Ad,Me}ArO)}_{\text{\textsuperscript{3}mes}}\text{Ln}]\}, \text{4-Ln}, and Ln\textsuperscript{3+} hydride complexes, \([\text{K(2.2.2-cryptand)]}\{[(\text{\textsuperscript{Ad,Me}ArO)}_{\text{\textsuperscript{3}mes}}\text{LnH}]\}, \text{6-Ln}. Reactivity of this mixture for Er with \text{CCl}_4 produced chloroform, giving experimental evidence for the hydride complex, \textbf{6-Ln}. This complicates the
structural analysis of Ln$^{3+}$ and Ln$^{2+}$ ions in the same coordination environment that has been so valuable in evaluating 4f$^n$5d$^1$ vs 4f$^{n+1}$ electron configurations. It also suggests that the more reactive Ln$^{2+}$ ions in the [(Ad,MeArO)$_3$mes] can participate in C-H bond activation. This has been observed by Nief and Deacon with the Nd$^{2+}$ complex, (C$_5$H$_2$Bu$_3$)$_2$Nd(µ-I)K(18-crown-6), which forms {(C$_5$H$_2$Bu$_3$)[C$_5$H$_2$Bu$_2$C(CH$_3$)$_2$CH$_2$-η$_5$:κ$_1$]Nd(µ-I)K(18-crown-6)}. The 4-Gd/6-Gd crystalline sample displays an isotropic X-band EPR signal, analogous to that seen for 2-Gd, which suggests that 4-Gd likely has a 4f$^7$5d$^1$ configuration for Gd. As described in Chapter 7, based on the promotional energies of the free Ln$^{2+}$ ions in the gas phase, La$^{2+}$ and Gd$^{2+}$ are predicted to have 5d$^1$ and 4f$^7$5d$^1$ configurations, respectively. The only two known Er$^{2+}$ complexes, [K(18-crown-6)][Cp′$_3$Er] and [K(2.2.2-cryptand)][Cp′$_3$Er], are characterized as having 4f$^{11}$5d$^1$ configurations. However, the 4f-5d promotional energy of free Er$^{2+}$ is comparable to Nd$^{2+}$ and Dy$^{2+}$, Er could also be a crossover ion.

Although the two complexes crystallize with the same three-fold axis with the same [(Ad,MeArO)$_3$mes] ligand coordination, the data can be modeled with the metal centers for 4-Ln and 6-Ln distinguishable from each other. Since the M–(arene centroid) distance of 2.285 Å is even shorter for 4-Gd than the 2.366 Å distance in 4-Nd, the short M–(arene centroid) distance in 4-Ln cannot be a distinguishing trait for a 4f$^{n+1}$ configuration.

Reduction of 3-Dy also led to a co-crystallized mixture of complexes, a new Dy$^{2+}$ complex, [K(2.2.2-cryptand)]{[(Ad,MeArO)$_3$mes]Dy}, 4-Dy, and a Dy$^{3+}$ hydroxide complex, [K(2.2.2-cryptand)]{[(Ad,MeArO)$_3$mes]DyOH}, 7-Dy, in a 2:3 ratio. Like that found for the 4-Ln/6-Ln mixture, the metal centers for 4-Dy and 7-Dy can be distinguished from each other in models of the crystal data. The origin of the hydroxide ligand is unknown. Normally, isolation
of hydroxides of electropositive metals is attributed to contamination by water, but the use of the same techniques for 3-Dy, as with the other 3-Ln reductions that did not give hydroxide complexes, raises doubt about adventitious water. Nevertheless, the 4-Dy/7-Dy mixture was crystallographically characterized twice. 4-Dy displays the shortest known M–(arene centroid) distance for any lanthanide. Theory will likely be important in understanding this short distance.

It is also unclear why the reductions of 3-Gd and 3-Er would produce mixtures of Ln$^{2+}$ and Ln$^{3+}$ hydrides, while the reduction of 3-Dy would produce a mixture of Dy$^{2+}$ and a Dy$^{3+}$ hydroxide. If Gd$^{2+}$ and Er$^{2+}$ have a 4f$^n$5d$^1$ coordination in this ligand coordination, while Dy$^{2+}$ has a 4f$^{n+1}$ configuration, this change in configuration could account for the difference in reactivity. This would clearly support the suggestion that the ligand coordination environment is important for the configuration of Ln$^{2+}$ ions.

**Conclusion**

Four new divalent lanthanide complexes, [K(2.2.2-cryptand)]{[(Ad,MeArO)$_3$mes]Ln} have been isolated for Nd, Gd, Dy and Er. Three of these new divalent ions were complicated with the co-crystallization of either [K(2.2.2-cryptand)]{[(Ad,MeArO)$_3$mes]LnH} for Gd and Er or [K(2.2.2-cryptand)]{[(Ad,MeArO)$_3$mes]LnOH} for Dy. EPR data suggest a 4f$^7$5d$^1$ electron configuration for Gd$^{2+}$ in the [(Ad,MeArO)$_3$mes] ligand coordination. Structural data have not been found to be a conclusive measure between the 4f$^{n+1}$ and 4f$^n$5d$^1$ electron configurations for the remaining metals. [K(2.2.2-cryptand)]{[(Ad,MeArO)$_3$mes]Dy} was found to have the shortest known M–(arene centroid) distance for any lanthanide.
Table 11.3. X-ray Data Collection Parameters of 3-La, 3-Nd, and 4-Nd.

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<th>3-Nd</th>
<th>4-Nd</th>
</tr>
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<td>C₆₃H₇₅LaO₃</td>
<td>C₆₃H₇₅NdO₃</td>
<td>C₈₁H₁₁₁KN₂NdO₉</td>
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<td>0.71073 Å</td>
<td>0.71073 Å</td>
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<td>Monoclinic</td>
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<td>P₂₁/c</td>
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<tr>
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### Table 11.4. X-ray Data Collection Parameters of 4-Gd/6-Gd, 4-Er/6-Er and 4-Dy/7-Dy.

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</tbody>
</table>

*aDefinitions: \( wR^2 = \left[ \sum (w(F_o^2 - F_c^2)^2) \right] / \left[ \sum (w(F_o^2) \right]^{1/2}; R1 = \left| \sum F_o \right| - \left| \sum F_c \right| / \left| \sum F_o \right|.*

### References


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CHAPTER 12

Computational Predictions of Divalent Rare Earth Ions

Introduction

Advances in reduction chemistry have led to the isolation of new divalent lanthanide ions with a $4f^n5d^1$ configurations, with respect to a $4f^n Ln^{3+}$ precursors, with both a tris(cyclopentadienyl) ligand environment (discussed in Chapters 5 and 7)\(^1\)\(^-\)\(^3\) and a ligand containing three aryloxide ligands tethered to a mesityl group (discussed in Chapter 11). The isolation of the [K(2.2.2-cryptand)][Cp′₃Ln], 1-Ln, complexes for the entire lanthanide series (except Pm, which was not studied because it is radioactive) allowed for physical characterization of all the lanthanides in the +2 and +3 oxidation states for the same ligand coordination.\(^4\) The structural, spectroscopic, and magnetic studies suggested that (Cp₃)\(^3-\) ligand set was important in making the $d_{z^2}$ orbital available. This is consistent with the crystal field splitting in the tris(cyclopentadienyl) ligand environment.\(^5\)\(^-\)\(^10\)

As described in Chapters 7-9, while physical characterization studies of 1-Ln have allowed the $4f^n5d^1$ configuration to be distinguished from the traditional $4f^{n+1}$ configuration for the divalent lanthanides, the reactive nature of the $4f^n5d^1$ complexes has made it challenging to get a full understanding of the electronic nature of this unusual mixed principal quantum number electron configuration. As described in Chapter 5, attempts to alter the substituents on the cyclopentadienyl ligands were not successful in making more stable complexes of the Ln\(^{2+}\) ions. As described in Chapter 11, although an additional Gd\(^{2+}\) complex has been characterized with a $4f^n5d^1$ configuration in a different ligand coordination, namely a mesityl-tethered tris(aryloxide)
ligand coordination environment, this Ln$^{2+}$ complex is likely more reactive than that of 1-Ln, since it is co-crystallized with a Gd$^{3+}$–H species. Additionally, reduction of [(Me$_3$Si)$_2$N]$_3$Y, as discussed in Chapter 5, allowed the formation of an Y$^{2+}$ species that could be identified by EPR, but an Y$^{2+}$ complex could not be identified by X-ray crystallography with this ligand set.

Isolation of new examples of 4f$^{n}$5d$^1$ divalent lanthanide ions in different ligand coordination environments would provide insight into the ligand properties needed to stabilize such reactive ions. Other ligands could potentially provide more stable examples for physical characterization. Additionally, as described in Chapter 8, examples of 4f$^{n}$5d$^1$ Ln$^{2+}$ ions could contain valuable magnetic properties.

Since the properties necessary for stabilizing these divalent ions are not entirely understood, it not clear which ligand coordination environments should be examined experimentally. It would be valuable to have an easy method to narrow down the possibilities before the experimental work has begun. Density functional theory (DFT), as described in Chapters 5, 6, and 7, has been very useful in giving information about the electronic structure of divalent rare-earth and actinide ions. This Chapter describes the use of DFT to examine several ligand coordination environments that are promising candidates for the synthesis of 4f$^{n}$5d$^1$ divalent lanthanide ions. Also discussed are calculations on bimetallic rare earth complexes that are promising candidates for the formation of a metal-metal bond between two rare-earth metals.

**Experimental**

**Structures Used for Calculations.** Structures used as starting points for DFT calculations were obtained from available single crystal X-ray diffraction data as described
below. In all cases, outer sphere solvents and cations and anions, such as K(2,2,2-cryptand) or K(18-crown-6), were removed from the structures. In each case, calculations were performed with Y and La, by replacing the metal centers in the starting crystal structure data with those metals.

**Structure 1.** The crystal structure of [PhNC(Ph)C(Ph)NPh]$_3$Yb$_{12}$ was used as a starting point. **Structure 2.** The crystal structure of Y[PhC(NSiMe$_3$)$_2$][(2-C$_5$H$_4$N)CH$_2$N(CH$_2$CH$_2$NSiMe$_3$)$_2$]$_{13}$ was used as a starting point. **Structure 3.** The crystal structure of samarium 1,4,7-tris(3,5-di-tert-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (Sm[(^BuAr)$_3$tacn)]$_{14}$ was used as a starting point. **Structure 4.** The crystal structure of La{iPrNC(PPh$_2$iPr)N$iPr}$$_3$$_{15}$ was used as a starting point. **Structure 5.** The crystal structure of Y[2,(2,6-Me$_2$C$_6$H$_3$N=CH)C$_6$H$_3$]$_3$$_{16}$ was used as a starting point. **Structure 6.** The crystal structure of [TpMe$_2$Y(CH$_2$Ph)$_2$(THF)]$_{17}$ (TpMe$_2$ = tri(3,5-dimethylpyrazolyl)borate) was used as a starting point.

Y[2,6-(2,4,6-Me$_3$C$_6$H$_2$)C$_6$H$_3$](C$_5$H$_4$Me)$_3$. The crystal structure of Er[2,6-(2,4,6-Me$_3$C$_6$H$_2$)C$_6$H$_3$](C$_5$H$_4$Me)$_3$$_{18}$ was used as a starting point. La calculations were not pursued for this structure. (C$_5$Mes)(C$_8$H$_8$)Ln, (C$_5$Mes)[C$_8$H$_6$(SiMe$_2$'Bu)-1,4]Ln, and (C$_5$Mes)[C$_8$H$_5$(SiMe$_3$)-1,3,7]Ln. The crystal structures of (C$_5$Mes)(C$_8$H$_8$)Sm$_{19}$ (C$_5$Mes) [C$_8$H$_6$(SiMe$_2$'Bu)$_2$-1,4]Yb$_{20}$ and (C$_5$Mes)[C$_8$H$_5$(SiMe$_3$)$_3$-1,3,7]Yb$_{20}$ were used as starting points. (C$_5$Mes)Ln[µ-η$^8$:η$^8$-C$_8$H$_5$(SiMe$_3$)-1,3,7]K(DME)$_2$. The crystal structure of (C$_5$Mes)Yb[µ-η$^8$:η$^8$-C$_8$H$_5$(SiMe$_3$)$_3$-1,3,7]K(DME)$_2$$_{20}$ was used as a starting point. Ln[HB(3,5-Me$_2$pz)$_3$]$_2$. The crystal structure of Sm[HB(3,5-Me$_2$pz)$_3$]$_2$$_{21}$ was used as a starting point. Ln(BH$_4$)$_2$(THF)$_4$. The crystal structure of [Ce(BH$_4$)$_2$(THF)$_5$][BPh$_4$]$_{22}$ was used as a starting point, in which the BPh$_4$ was
removed and the structure was examined as a neutral divalent complex. An initial optimization showed a significantly elongated M–O(THF) bond for one THF molecule. This THF molecule was removed from the structure and the calculations were further pursued for the Ln(BH$_4$)$_2$(THF)$_4$ structure. \textbf{La[N(SiMe$_2$'Bu)$_2$]$_3$/[La[N(SiMe$_2$'Bu)$_2$]$_3$]$_1$}. The crystal structure of La[N(SiMe$_2$'Bu)$_2$]$_3$ was used as a starting point for the La$^{3+}$ calculations. The converged La$^{3+}$ structure was used as a starting point for the La$^{2+}$ calculations.\textsuperscript{2,3} [C$_5$H$_7$'Bu(SiMe$_2$)$_2$C$_5$H$^i$Pr$_2$]$_2$Y$_2$(µ-H)$_2$. The crystal structure of [C$_5$H$_7$'Bu(SiMe$_2$)$_2$C$_5$H$^i$Pr$_2$]$_2$Y$_2$(µ-H)$_2$\textsuperscript{24} was used as a starting point. [Me$_2$Si(C$_5$H$_4$)$_2$Y]$_2$(µ-H)$_2$. The crystal structure of [Me$_2$Si(C$_5$H$_4$)$_2$Y]$_2$(µ-H)$_2$\textsuperscript{25} was used as a starting point. Calculations with La were not pursued for the two structures hydride structures above. [(C$_5$H$_7$'Bu$_2$-$1,3$)$_2$La(µ-H)]$_2$. The crystal structure of [(C$_5$H$_7$'Bu$_2$-$1,3$)$_2$Sm(µ-H)]$_2$\textsuperscript{26} was used as a starting point. Calculations with Y were not pursued for this structure. 

\textbf{Computational Details.} DFT structural optimizations were performed using the hybrid meta-GGA functional, TPSSh.\textsuperscript{27} This functional was chosen due to its established performance in describing the electronic structure of Ln$^{2+}$ ions.\textsuperscript{2-4,28,29} All calculations were performed using the Turbomole quantum chemistry software.\textsuperscript{30} The initial gas-phase optimization was carried out using double-zeta quality split-valence basis sets with polarization functions on non-hydrogen atoms [def2-SV(P)]\textsuperscript{31} for all light atoms. Small-core ECPs\textsuperscript{32} and triple-zeta valence basis sets with two sets of polarization functions on non-hydrogen atoms, def2-TZVP,\textsuperscript{33} were used for Y and La. Analytical force constant calculations\textsuperscript{34} were carried out for the SV(P) optimized structures and these were confirmed to be energy minima by the absence of imaginary vibrational modes.
The solvent effects of THF were then incorporated for the \{La[N(SiMe_2Bu)_2]_3\}^{1-} complex, via further geometry optimizations using the continuum solvation model (COSMO).\(^{35}\) The dielectric constant of THF (\(\varepsilon = 7.520\))\(^{36}\) was used for the reported COSMO calculations since this was the most polar solvent used. Solvent effects are especially important for stabilizing the \(\text{Ln}^{2+}\) systems because they screen the additional negative charge. The solvent effects were not found to be necessary in calculating the neutral divalent structures. All further calculations of the anionic complex, \([\text{La}\{N(SiMe_2Bu)_2\}_3]^{1-}\), discussed below were completed using COSMO, unless otherwise specified. Any structural data discussed in the text is the result of a final optimization using TZVP basis sets for all light atoms. Changes in \(\text{Ln}^{-}\)-ligand distance were on average less than 0.02 Å from SV(P) to TZVP. Fine quadrature grids (at least size m4)\(^{37}\) and \(C_1\) symmetry were used throughout.

Time dependent DFT (TDDFT) excitation energy calculations\(^{38}\) were then carried out (in conjunction with COSMO for \{La[N(SiMe_2Bu)_2]_3\}^{1-}\) on the optimized SV(P) structures. Normalized Gaussians centered at the computed molecular excitations, scaled with the corresponding theoretical oscillator strength, and fixed root mean width of 0.18 eV are used.\(^{39}\) The excitation energies and oscillator strengths for selected transitions of \((C_5\text{Me}_5)Y[\mu-\eta^8:\eta^8-C_8H_5(SiMe_3)_3-1,3,7]K(DME)_2\), \(Y[HB(3,5-\text{Me}_2pz)_3]_2\), \(Y(\text{BH}_4)_2(\text{THF})_4\), and \{La[N(SiMe_2Bu)_2]_3\}^{1-}\) are given in Table 12.1 at the end of the Chapter. The % d and % metal compositions from a Mulliken population analysis (MPA)\(^{40}\) of the molecular orbitals of \((C_5\text{Me}_5)Y[\mu-\eta^8:\eta^8-C_8H_5(SiMe_3)_3-1,3,7]K(DME)_2\), \(Y[HB(3,5-\text{Me}_2pz)_3]_2\), \(Ln(\text{BH}_4)_2(\text{THF})_4\), and \{La[N(SiMe_2Bu)_2]_3\}^{1-}\) are given in Table 12.2 at the end of the Chapter. All molecular orbitals were plotted with a contour value of 0.05 using self-consistent TPSSh/TZVP orbitals. In most
cases, exceptions are discussed, calculations using La instead of Y gave similar results and will not be discussed.

Results

A series of trivalent rare-earth complexes were studied using DFT calculations in order to determine if reduction of these complexes could lead to the formation of a new Ln$^{2+}$ complex. These calculations were performed with La and Y as the large and small metal test subjects, respectively, for the lanthanide series. While yttrium is not a lanthanide, it exhibits similar properties as the lanthanides and is a good test metal to determine the electronic properties of the smaller lanthanides. Additionally, yttrium is often chosen as the primary metal for investigation of new divalent ions, since EPR spectroscopy can provide good evidence for the presence of Y$^{2+}$ due to the 100% naturally abundant $^{89}$Y nucleus that gives a doublet signal for this ion.$^{1,11}$ In most cases, the La calculation results were very similar to the Y calculation results, so the La results will only be discussed if they are different than that of Y.

Complexes of Nitrogen Donor Atom Ligands. A series of six known complexes of nitrogen donor atom ligands,$^{12-17}$ shown in Figure 12.1, were studied using Y as the metal. Nitrogen donor atom ligands are viable since reduction of [(Me$_3$Si)$_2$N]$_3$Y forms a Y$^{2+}$ complex, (although the Y$^{2+}$ product could not be crystallographically identified).$^{11}$ Initial calculations suggested that the LUMO of all six of the complexes in Figure 12.1 was entirely ligand-based, with the majority of the electron density localized on aromatic rings. While these calculations do not indicate promising structures for new divalent ions, they do suggest that aromatic rings should be avoided in the ligand design for the synthesis of new Ln$^{2+}$ complexes.
Figure 12.1. Chemdraw images of six known rare-earth complexes of nitrogen donor atoms.\textsuperscript{12-17}

Cyclopentadienyl Complexes. Calculations were also performed on two known trivalent cyclopentadienyl complexes: \(\text{Y}[2,6-(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)\text{C}_6\text{H}_3]\)(\text{C}_5\text{H}_4\text{Me})_2, \textbf{2-Y}, and \((\text{C}_5\text{Me}_5)(\text{C}_8\text{H}_8)\text{Y}, \textbf{3-Y}. \) As can be seen in Figures 12.2, the lowest unoccupied molecular orbital (LUMO) of \textbf{2-Y} is a \(d_{z^2}\) orbital, similar to that found for the anion of \textbf{1-Ln}. The bulky dimesityl-substituted phenyl group present in complex 2 could be useful in protecting an \(\text{Ln}^{2+}\) ion, with a mesityl substituent sitting above and below the lobes of the \(d_{z^2}\) orbital. Figure 12.3a shows that the LUMO of \textbf{3-Y} is also a \(d_{z^2}\) orbital, although the size of the lobes along the \(z\) axis are smaller than the ring portion of the orbital in the \(xy\) plane, which is different than that of a typical \(d_{z^2}\) orbital. Since lanthanide (\(\text{C}_8\text{H}_8\))\(^2-\) complexes often have limited solubility,\textsuperscript{41} calculations were done on two substituted analogous of \textbf{3-Y}: \((\text{C}_5\text{Me}_5)[\text{C}_8\text{H}_6(\text{SiMe}_2\text{Bu})_2-1,4]\)Y and \((\text{C}_5\text{Me}_5)[\text{C}_8\text{H}_5(\text{SiMe}_3)_{3-1,3,7}]\)Y. As seen in Figure 12.3, all three structures have the same \(d_{z^2}\)
orbital as the LUMO, suggesting the C₈H₈ ligand could be substituted to help solubility without affecting the electronic properties of the complex.

Figure 12.2. Molecular orbital plot of the LUMO of \( \text{Y}[2,6-(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3](\text{C}_5\text{H}_4\text{Me})_2 \), 2, using a contour value of 0.05.

Figure 12.3. Molecular orbital plot of the LUMO of (C₅Me₅)(C₈H₈)Y, 3 (a), (C₅Me₅)[C₈H₆(SiMe₂Bu)₂-1,4]Y (b), and (C₅Me₅)[C₈H₅(SiMe₃)₃-1,3,7]Y (c), using a contour value of 0.05.
In the reduction of $(C_5H_4SiMe_3)_3Ln$, the use of different chelating agents, either 18-crown-6 or 2.2.2-cryptand, led to very different decomposition rates.$^{1-3}$ This was attributed to the possibility that $K(C_5H_4SiMe_3)$ was a byproduct of decomposition and (18-crown-6)$K(C_5H_4SiMe_3)$ was a better leaving group than $(C_5H_4SiMe_3)^{1-}$ with $[K(2.2.2-crypt)]^{1+}$ in the lattice. While it is unknown whether 2.2.2-cryptand will be important in the reduction of 3, reduced $C_8H_8$ complexes, such as $[(C_8H_8)_2Ln]^{1-}$ have been isolated with both inner sphere and outer sphere potassium ions.$^{42-44}$ Additionally, a reduction product of $(C_5Me_5)\left[C_8H_5(SiMe_3)_3\right]Yb$ was isolated with a K ion interacting with the COT ligand in the $(C_5Me_5)Yb[\mu-\eta^8:\eta^8-C_8H_5(SiMe_3)_3\eta^1,3,7]K(DME)_2$ complex, $4-Yb$.$^{20}$ Calculations were performed on the yttrium analogue, $4-Y$, to determine if a divalent complex would be $d^1$. As can be seen in Figure 12.4a, the highest occupied molecular orbital (HOMO) of $4-Y$ is a $d_{z^2}$ orbital, similar to the LUMO of the trivalent analogue, $(C_5Me_5)\left[C_8H_5(SiMe_3)_3\eta^1,3,7\right]Y$. Mulliken population analysis (MPA)$^{40}$ of the $4-Y$ HOMO predicts a primarily metal-based orbital (84% metal).

Since time dependent DFT (TDDFT) excitation energy calculations have been successfully used to simulate the UV-vis spectra of $1-Ln$, the UV-vis spectrum of $4-Y$ was simulated to predict the experimental UV-vis spectrum. As shown in Figure 12.4b, the predicted UV-vis spectrum of $4-Y$ shows several intense absorptions between 500 and 900 nm that combine to form an intense broad absorption. As shown in Tables 12.1 and 12.2, the most intense absorptions are characterized as primarily metal to ligand charge transfer (MLCT) transitions from the HOMO to the ligands. As seen for $1-Ln$, this would likely have extinction coefficients greater than 1000 M$^{-1}$cm$^{-1}$.  

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Figure 12.4. (a) Molecular orbital plot of the HOMO of \((C_5\text{Me}_5)Y[\mu-\eta^8:\eta^8-\text{C}_8\text{H}_5(\text{SiMe}_3)_3-1,3,7]\text{K(DME)}_2\), 4-Y, using a contour value of 0.05, and (b) calculated UV-vis spectra of 4-Y in THF at 298 K, with pertinent theoretical excitations shown as vertical lines.

Tris(pyrazolyl)borate Complexes. Another possible Y\(^{2+}\) complex was \(Y[\text{HB}(3,5-\text{Me}_2\text{pz})_3]_2\), 5-Y, since there is a known 4f\(^{n+1}\) Sm\(^{2+}\) analogue.\(^{21}\) Additionally, since trivalent Sm precursors with outer sphere anions, such as \{Sm[HB(3,5-\text{Me}_2\text{pz})_3]_2\}{\text{BPh}_4}\,^{45} have been previously isolated, it would be synthetically possible to isolate 5-Y through the reduction of \{Y[HB(3,5-\text{Me}_2\text{pz})_3]_2\}{\text{BPh}_4}\. A neutral 4f\(^{n}\)5d\(^1\) divalent lanthanide complex could potentially be more stable than the salt-like complexes of 1-Ln. Calculations suggest that although the HOMO of 5-Y, shown in Figure 12.5a, looks like a d orbital at the metal center, there is significantly more electron density on the ligands. Indeed, MPA analysis of the HOMO suggests that the orbital is only 38% metal based, which is entirely localized in the 4d orbitals. If this complex could be isolated, the electron density spread on the ligands could be useful in stabilizing the divalent state. The simulated UV-vis of 5-Y, as seen in Figure 12.5b, describes
one very intense absorption at 717 nm, which is attributed to a HOMO to ligand transition. Other weaker transitions are attributed to HOMO to metal/ligand orbitals that often contain more than 50% metal-based orbitals.

![Molecular orbital plot](image)

**Figure 12.5.** (a) Molecular orbital plot of the HOMO of Y[HB(3,5-Me₂pz)₃]₂, 5-Y, using a contour value of 0.05, and (b) calculated UV-vis spectra of 5-Y in THF at 298 K, with pertinent theoretical excitations shown as vertical lines.

**Borohydride Complexes.** Another structure that could be isolated as a neutral divalent species is a complex with two (BH₄)⁻ ligands. There are literature examples of trivalent complexes of the structure [Ln(BH₄)₂(THF)₅][BPh₄],²²,⁴⁶ which could be reduced to form a complex of the formula Ln(BH₄)₂(THF)₅. An energy minimum could not be obtained for the structure of Y(BH₄)₂(THF)₅ as a neutral complex. Instead, in the process of the calculation, one THF molecule moved far enough away from the metal center to no longer have a bond. This THF was removed from the structure and an energy minimum was obtained for Y(BH₄)₂(THF)₄, 6-Y. The HOMO of 6-Y, as seen in Figure 12.6a, is a dₓ² orbital, which is 90% metal-based, according to MPA calculations. This is more metal based than 1-Y (74%), 4-Y (84%) and 5-Y.
(38%), which could affect the stability of the divalent complex. The simulated UV-vis of 6-Y predicts three main absorptions, one of which, near 832 nm, is much stronger than the others. This transition is attributed to an allowed d→p absorption, while the higher energy absorptions are primarily HOMO to ligand transitions.

![Molecular orbital plot and UV-vis spectra](image)

**Figure 12.6.** (a) Molecular orbital plot of the HOMO of Y(BH₄)₂(THF)₄, 6-Y, using a contour value of 0.05, and (b) calculated UV-vis spectra of 6-Y in THF at 298 K, with pertinent theoretical excitations shown as vertical lines.

**Sterically Bulky Amide Ligands.** As discussed in Chapter 5, calculations on a predicted reduction product of Y[N(SiMe₃)₂]₃, namely [Y[N(SiMe₃)₂]₃]¹⁻, suggested the HOMO is a dₓ² orbital, similar to that of 1-Ln. However this orbital was entirely metal-based, unlike calculations of 1-Ln which suggested some ligand contribution. Mills and coworkers reported the use of a more bulky amide ligand [N(SiMe₂'tBu)₂]¹⁻ in order to isolate a trigonal planar La[N(SiMe₂'tBu)₂]₃ complex, 7-La,²³ in the solid state instead of the known pyramidal structure found for Y[N(SiMe₃)₂]₃ and other tris(amide) lanthanide complexes.⁴⁷,⁴⁸ Calculations of the trivalent 7-La match the experimental crystal structure well, with only slight elongation (~0.03 Å) of the La–N bond lengths in the calculated structure. Although the d orbital splitting of a
trigonal planar ligand coordination does not suggest a single low-lying \textit{d} orbital, the calculated ground state for \textbf{7-La} suggested a LUMO that was a \textit{d}_{z^2} orbital, similar to that found from the calculations of Y[N(SiMe$_3$)$_2$]$_3$. $^1$H NMR of complex \textbf{7-La} revealed strong agostic interactions,$^{23}$ which could effectively alter the \textit{d} orbital splitting. As seen in Figure 12.7, all five \textit{d} orbitals can be found in the low lying unoccupied orbitals, in which they are found to split in the same order expected for the (Cp$_3$)$^{3-}$ ligand coordination.$^{5-10}$

![Molecular orbital plot](image)

\textbf{Figure 12.7.} Molecular orbital plot of the LUMO, LUMO+1, LUMO+2, LUMO+4 and LUMO+5 of La[N(SiMe$_2$Bu)$_2$]$_3$, \textbf{7-La}, using a contour value of 0.05.

Calculations of the anion of the potential reduction product, \{La[N(SiMe$_2$Bu)$_2$]$_3$\}$^{1-}$, \textbf{8-La}, were also performed. As shown in Figure 12.8a, like the LUMO of \textbf{7-La}, the HOMO of \textbf{8-}
La is a d$_{z^2}$ orbital, which is predicted to be 85% metal-based. The predicted change in La–N bond lengths is approximately 0.1 Å, which is much larger than the 0.03 Å changes in Ln–(Cp centroid) distances observed between (C$_5$H$_4$SiMe$_3$)$_3$Ln to 1-Ln.$^{1-4}$ The predicted UV-vis of 8-La suggests one intense absorption near 609 nm, which is attributed to an allowed d→p transition. The low energy transitions are mostly d→p and d→d transitions, while the high energy transitions are metal to ligand transitions. Although reduction of 7-La produces a dark green solution,$^{49}$ often an indication of the formation of a divalent complex, the reduction product has yet to be isolated. If the La–N bond lengths really do change by 0.1 Å, this significant change in bond lengths could increase the reactivity of this complex.

Figure 12.8. (a) Molecular orbital plot of the HOMO of {La[N(SiMe$_2$Bu)$_2$)$_3$}$^{1-}$, 8-La, using a contour value of 0.05, and (b) calculated UV-vis spectra of 8-La in THF at 298 K, with pertinent theoretical excitations shown as vertical lines.

**Bimetallic Hydride Complexes.** Finally, calculations on three bimetallic hydride complexes were performed since it was hypothesized that the small hydride ligands would be the best ligands to allow a close metal–metal distance. If reduction of these hydride species could
populate a d orbital on each metal, it might be possible to form the first rare earth metal–metal bond. Calculations were performed on known hydride complexes with double ansa ligands, \([\text{C}_5\text{H}_2\text{Bu(SiMe}_2\text{)}_2\text{C}_5\text{H}_2\text{Pr}_2\text{]_2Y}_2(\mu-H)_2, 9-\text{Y},^{24}\) ansa ligands, \([\text{Me}_2\text{Si(C}_5\text{H}_4\text{)}_2\text{Y]_2(\mu-H)_2, 10-\text{Y},^{25}\) and terminal cyclopentadienyl ligands, \([(\text{C}_5\text{H}_3\text{Bu}_2\text{-1,3})_2\text{La}(\mu-H)]_2, 11-\text{La}.^{26}\) Perhaps not surprising, the double ansa ligands are the most rigid and result in the shortest calculated metal–metal distance of 3.512 Å for 9-Y, while 10-Y has the second shortest distance of 3.568 Å, and 11-La has the longest distance of 3.994 Å. As shown in Figure 12.9, the LUMOs of all three complexes suggest reduction occurs to populate the metal d orbitals primarily, with 10-Y having some electron density on the ligands. Interestingly, the LUMO of 9-Y, in comparison to 10-Y and 11-La, is the only orbital that shows orbital overlap between the d orbitals on both metals. While the d orbitals in 10-Y and 11-La have the correct symmetry to have a metal–metal bond, the larger distances between metals is likely to allow significantly less orbital overlap than that of 9-Y.

![Figure 12.9. Molecular orbital plots of the LUMO of (a) [C\text{\textgreek{y}}\text{H}_2\text{Bu(SiMe}_2\text{)}_2\text{C}_5\text{H}_2\text{Pr}_2\text{]_2Y}_2(\mu-H)_2, (b) [\text{Me}_2\text{Si(C}_5\text{H}_4\text{)}_2\text{Y]_2(\mu-H)_2, and (c) [(\text{C}_5\text{H}_3\text{Bu}_2\text{-1,3})_2\text{La}(\mu-H)]_2, using a contour value of 0.05.](image)
The hydride ligands could not be selectively shown separately from all other hydrogens in the molecule, which were removed for clarity.

**Discussion**

DFT calculations have been used to evaluate possible targets for the formation of new classes of Ln\(^{2+}\) complexes with 4f\(^{n}\)5d\(^{1}\) electron configurations. The calculations predict metal-based LUMOS for several types of complexes that are promising candidates for reduction. The calculations also show, in some cases, that reduction will occur mainly on the ligand and these types of complexes should not be given high priority as targets. In particular, the calculations suggest that aromatic rings should be avoided in the ligands chosen for the isolation of divalent ions. These results suggest that the use of DFT to narrow down candidates for divalent ions could be useful to do before starting experimental work.

The calculations identified five ligand coordination environments that are promising to form new examples of 4f\(^{n}\)5d\(^{1}\) divalent lanthanide ions. Reduction of Y[2,6-(2,4,6-Me\(_3\)C\(_6\)H\(_2\)C\(_6\)H\(_3\)](C\(_3\)H\(_4\)Me)\(_2\), \(2\text{-Y}\), (C\(_5\)Me\(_5\))(C\(_8\)H\(_8\))Y, \(3\text{-Y}\), and La\{N(SiMe\(_2\)Bu)\(_2\)\}_3, \(7\text{-La}\), are predicted to form salt-like divalent complexes with outer sphere potassium ions. Calculations of the (C\(_5\)Me\(_5\))Y[\(\mu-\eta^8:\eta^8\)-C\(_8\)H\(_5\)(SiMe\(_3\)\)_3-1,3,7]K(DME)_2 structure, \(4\text{-Y}\), suggest that reduction of \(3\text{-Y}\), as well as any substituted COT analogue, could also lead to an inner sphere potassium ion divalent complex. (C\(_5\)Me\(_5\))(C\(_8\)H\(_8\))Ln complexes have been shown to exhibit single ion magnet behavior, and therefore it would be interesting to determine whether single molecule magnet behavior is maintained upon reduction.\(^{50}\) As discussed in Chapter 8, 4f\(^{n}\)5d\(^{1}\) divalent lanthanide complexes could show interesting magnetic properties due to their higher magnetic moments,
relative to the trivalent lanthanide ions, so the magnetic properties of [(C₅Me₅)(C₈H₈)Ln]⁻ could be very interesting to study. Additionally, calculations of {La[N(SiMe₂Bu)₂]₃}⁻, 8-La, suggest that reduction of 7-La will generate a divalent ion, with several allowed transitions in the simulated UV-vis spectrum. This supports the preliminary experimental results in which a dark solution is formed upon reduction of 7-La.⁴⁹ This is likely a divalent ion. The long calculated La–N distances for 8-La could be the reason why a reduction product has not yet been crystallographically characterized.

Calculations of two neutral divalent ions, Y[HB(3,5-Me₂pz)₃]₂, 5-Y, and Y(BH₄)₂(THF)₄, 6-Y, support a 4d¹ Y²⁺ configuration. There are known trivalent precursors of both 5-Y and 6-Y with an outer sphere (BPh₄)¹⁻ counteranions which could generate the divalent ions above and a KBPh₄ byproduct that has good lattice energy.

Calculations of three bimetallic hydride complexes suggest that reduction of these complexes are predicted to populate d orbitals with the appropriate symmetry to form metal–metal bonds. Additionally, the calculations suggest that the cyclopentadienyl ligands should be chosen to place the metals as close together as possible. The double ansa ligands in [C₅H₂'Bu(SiMe₂)₂C₅H'Pr₂]₂Y₂(μ-H)₂ allowed the shortest metal–metal distance of the molecules studied and the reduction product had the only calculated LUMO with orbital overlap between d orbitals on the metals.

The results of this study demonstrate the valuable data that can be obtained from a short initial calculation (often less than 24 hours) to eliminate lengthy experimental work that is not likely to produce the desired results. While the results of the calculations do not indicate the overall stability of the predicted divalent complexes, the goals of these calculations are to simply
focus experimental work towards the ligand environments that have the highest likelihood of generating \( \text{Ln}^{2+} \) complexes.

**Conclusion**

Calculations of several classes of many rare earth complexes have led to the identification of several promising ligand coordination environments that could be useful in stabilizing new \( \text{Ln}^{2+} \) complexes. These calculations have suggested that aromatic rings present in the ligands will often be reduced before the metal center, which helps direct ligand design away from these substituents. Additionally, calculations of bimetallic hydride complexes have led to the prediction of possible metal–metal bond formation between two rare earth metals.

**Table 12.1.** Electronic excitation summary for \((\text{C}_{5}\text{Me}_5)\text{Y[}\mu-\eta^8:\eta^8-\text{C}_8\text{H}_5(\text{SiMe}_3)_3-1,3,7]\text{K(DME)}_2, \quad 4\text{-Y}, \quad \text{Y[HB(3,5-Me}_2\text{pz})_3]_2, \quad 5\text{-Y}, \quad \text{Ln(BH}_4)_2(\text{THF})_4, \quad 6\text{-Y}, \quad \text{and [La}\{\text{N(SiMe}_2\text{Bu})_2\}_3\}^1, \quad 8\text{-La}, \quad \text{computed using TPSSh and SV(P) basis sets. Only pertinent excitations with oscillator strengths larger than } 3\times10^{-3} \text{ a.u. are included.}
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References


(49) Goodwin, C. A. P.; Mills, D. P.; Evans, W. J. **2015**, unpublished results.

Appendix A

Synthesis and Reactivity of Rare Earth Cyclopentadienyl Complexes in Unusual Coordination Environments and Oxidation States

The first section of this Appendix describe reactivity studies of the mixed ligand tris(cyclopentadienyl) complexes, \((\text{C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Ln} \ (\text{Ln} = \text{Y}, \text{Lu})\), with 1-adamantyl azide and \(\text{CO}_2\). The second section describes the synthesis and photochemical activity of a new example of a complex with an \((\eta^3\text{-C}_5\text{Me}_4\text{H})^{1-}\) ligand, \((\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\eta^5\text{-C}_5\text{Me}_4\text{H})(\eta^3\text{-C}_5\text{Me}_4\text{H})\text{Lu}\). The third section describes the reduction chemistry of \([\text{C}_5\text{H}_4\text{SiMe}_3]_2\text{Ln}(\mu\text{-Cl})_2\) (\(\text{Ln} = \text{Sm, Tm}\)), and the isolation of the \([\text{C}_5\text{H}_4\text{SiMe}_3]_3\text{Y}^{1-}\) anion with a different \([\text{Na}(2.2.2\text{-cryptand})]^{1+}\) cation. The fourth section describes the attempts towards crystallographic characterization of \((\text{C}_5\text{Me}_5)_2\text{Ce}(\text{C}_3\text{H}_5)\).

General Experimental Details

The syntheses and manipulations described below were conducted under argon with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were sparged with UHP grade argon (Airgas) and passed through columns containing Q-5 and molecular sieves before use. NMR solvents (Cambridge Isotope Laboratories) were dried over NaK/benzophenone, degassed by three freeze–pump–thaw cycles, and vacuum-transferred before use. Anhydrous \(\text{LnCl}_3\) (\(\text{Ln} = \text{Y, Ce, Sm, Tm, Lu}\)), \(1\) \(\text{KC}_8\), \(2\) \(\text{K(C}_5\text{Me}_4\text{SiMe}_3)\), \(3\) \(\text{K(C}_5\text{H}_4\text{SiMe}_3)\), \(4\) \((\text{C}_5\text{Me}_4\text{H})_2\text{Lu}(\mu\text{-Ph})_2\text{BPh}_2\), \(5\) \((\text{C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Ln} \ (\text{Ln} = \text{Lu}; \text{Y})\), \(6\) \((\text{C}_5\text{Me}_5)_2\text{Ce}(\text{C}_3\text{H}_5)\), \(7\) \([\text{C}_5\text{H}_4\text{SiMe}_3]_2\text{Sm}(\mu\text{-Cl})_2\), \(8\) and \((\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Y}\) were prepared according to literature. \(2.2.2\text{-Cryptand, 4,7,13,16,21,24-hexaoxa-1,10- diazabicyclo[8.8.8]hexacosane (Acros}\)
Organics), 1-adamantyl azide (Aldrich) was placed under vacuum (10^{-3} Torr) for 12 h before use. 18-crown-6 (Aldrich) was sublimed before use. CO_2 (99.98%) was purchased from AirGas and used as received. ^1H NMR (500 MHz) spectra were obtained on a Bruker GN500 or CRYO500 MHz spectrometer at 298 K. All photolysis experiments were conducted in a hood with aluminum foil covered windows with a Hanovia medium pressure, 450-watt, mercury vapor lamp (PC451050/610741).

**Reactivity Studies of Mixed Ligand (C_5Me_5)_2(C_5Me_4H)Ln Complexes with a Unique (η^3-C_5Me_4H)_1^- Ligand**

As described in Chapter 1, dinitrogen was observed to be reduced to (N=N)_2^- by photolysis of the Ln^{3+} mixed ligand tris(cyclopentadienyl) rare earth complexes (C_5Me_5)_2(C_5Me_4H)Ln, 1-Ln (Ln = Y, Lu, Dy), and (C_5Me_5)(C_5Me_4H)_2Lu. In order to further explore this photochemical activity, reactivity of 1-Ln with other substrates examined. 1-Ln was found to react cleanly with 1-adamantyl azide and CO_2 before irradiation.

The (C_5Me_5)_2(C_5Me_4H)Ln (Ln = Y, 1-Y; Lu, 1-Lu) complexes react with 1-adamantyl azide to form a new products. ^1H NMR spectra of the reaction products with both metals reveal two inequivalent (C_5Me_5)_1^- resonances, suggesting an asymmetric environment for the two (C_5Me_5)_1^- ligands. There is no evidence for any remaining (C_5Me_4H)_1^- bound to a metal center. While [(C_5Me_5)_2Y(μ-N_3)]_3 is known, it is insoluble in the solvents used in this study. It is unclear what the product is.
The \((\text{C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Ln}\) \((\text{Ln} = \text{Y}, \text{1-Y}; \text{Lu}, \text{1-Lu})\) complexes also react with \text{CO}_2 to form a new complexes. Based on the \(^1\text{H}\) NMR spectra for both reactions, complexes are formed in which there are two equivalent \((\text{C}_5\text{Me}_5)^{1-}\) ligands and all four methyl groups on the \((\text{C}_5\text{Me}_4\text{H})^{1-}\) have unique resonances. This suggests \text{CO}_2 insertion into a \text{Ln}–(\text{C}_5\text{Me}_4\text{H}) bond to form a complex of the general formula, \((\text{C}_5\text{Me}_5)_2\text{Ln}[\kappa^2\text{O}_2\text{O'}\text{O}_2\text{C}_5\text{Me}_4\text{H}]\).

**Specific Experimental Details**

**Reactivity of \text{1-Lu} with \text{1-adamantyl azide}**. In a nitrogen-filled glovebox, \((\text{C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Lu}, \text{1-Lu}\) (11 mg, 0.019 mmol), was dissolved in \text{C}_6\text{D}_6 (1 mL). 1-adamantyl azide (5 mg, 0.028 mmol) was added to the bright yellow solution, which quickly turned pale yellow. The solution was added to an NMR tube and the spectrum was taken. \(^1\text{H}\) NMR shows the formation of a new product with two \((\text{C}_5\text{Me}_5)\) resonances: \(^1\text{H}\) NMR \((\text{C}_6\text{D}_6)\): \(\delta\) 2.02 (s, 30 H, \text{C}_5\text{Me}_5), 1.90 (s, 30 H, \text{C}_5\text{Me}_5). There is no evidence for a \((\text{C}_5\text{Me}_4\text{H})\) ligand bound to a metal.

**Reactivity of \text{1-Y} with \text{1-adamantyl azide}**. As describe for \text{1-Lu}, \((\text{C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Y}, \text{1-Y}\) (12 mg, 0.025 mmol) was combined with 1-adamantyl azide (8 mg, 0.045 mmol) in \text{C}_6\text{D}_6 (1 mL). \(^1\text{H}\) NMR shows the formation of a new product with two \((\text{C}_5\text{Me}_5)\) resonances: \(^1\text{H}\) NMR \((\text{C}_6\text{D}_6)\): \(\delta\) 2.00 (s, 30 H, \text{C}_5\text{Me}_5), 1.88 (s, 30 H, \text{C}_5\text{Me}_5). There is no evidence for a \((\text{C}_5\text{Me}_4\text{H})\) ligand bound to a metal.

**Reactivity of \text{1-Lu} with \text{CO}_2**. In a nitrogen-filled glovebox, \((\text{C}_5\text{Me}_5)_2(\text{C}_5\text{Me}_4\text{H})\text{Lu}, \text{1-Lu}\) (41 mg, 0.072 mmol), was dissolved in toluene (6 mL) and added to a 50 mL sidearm Schlenk flask equipped with a greaseless stopcock. The flask was added to a high vacuum line, and the solution was degassed by three freeze–pump–thaw cycles. \text{CO}_2 (1 atm) was introduced...
to the stirring yellow solution, which quickly turned colorless. The reaction was allowed to stir 10 min and the solution was degassed by three freeze–pump–thaw cycles and returned to the glovebox. Solvent was removed under vacuum and the resulting colorless solids were washed with hexane. \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 6.23 (s, 1 H, C\(_5\)Me\(_4\)H), 2.10 (d, 3 H, C\(_5\)Me\(_4\)H), 1.90 (s, 30 H, C\(_5\)Me\(_5\)), 1.82 (d, 3 H, C\(_5\)Me\(_4\)H), 1.69 (d, 3 H, C\(_5\)Me\(_4\)H), 1.58 (d, 3 H, C\(_5\)Me\(_4\)H).

**Reactivity of 1-Y with CO\(_2\).** As described for 1-Lu, \((C_5Me_5)_2(C_5Me_4H)\)Y, 1-Y (39 mg, 0.081 mmol) was combined with CO\(_2\) (1 atm) in toluene to yield colorless solids (34 mg). \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 6.22 (s, 1 H, C\(_5\)Me\(_4\)H), 2.11 (s, 3 H, C\(_5\)Me\(_4\)H), 1.91 (s, 30 H, C\(_5\)Me\(_5\)), 1.81 (s, 3 H, C\(_5\)Me\(_4\)H), 1.68 (s, 3 H, C\(_5\)Me\(_4\)H), 1.58 (s, 3 H, C\(_5\)Me\(_4\)H).

**Synthesis and Photochemical Reactivity of Another Example of a Rare Earth Complex with a Unique (\(\eta^3\)-C\(_5\)Me\(_4\)H)\(^{1−}\) Ligand**

The complex \((\eta^5-C_5Me_5)(\eta^5-C_5Me_4H)(\eta^3-C_5Me_4H)Lu, 2,^{10}\) discussed in Chapter 1, was crystallographically characterized to contain the unusual \((\eta^3-C_5Me_4H)\(^{1−}\) ligand which appears to be important for productive photochemistry in these rare earth cyclopentadienyl complexes. The synthesis of a variant of 2 was pursued using the \((C_5Me_4SiMe_3)\(^{1−}\) ligand, which has been known to participate in C–H bond activation, instead of the \((C_5Me_5)\(^{1−}\) ligand. This was pursued by reacting [(C\(_5\)Me\(_4\)H)\(_2\)Lu][(\(\mu\)-Ph)\(_2\)BPh\(_2\)] with 1.1 equiv of KC\(_5\)Me\(_4\)SiMe\(_3\): this yields (C\(_5\)Me\(_4\)SiMe\(_3\))(C\(_5\)Me\(_4\)H)\(_2\)Lu as yellow crystals, 3. As shown in Figure A.1, the structure of 3 looks similar to 2, in that one of the (C\(_5\)Me\(_4\)H)\(^{1−}\) ligands is trihapto, while the other is pentahapto. The reactivity of this compound was probed by irradiation under an N\(_2\) atmosphere, through
which it formed a red solution that quickly turned yellow. The $^1$H NMR spectrum of this yellow product is consistent with a 1:1 ratio of the $(C_5Me_4SiMe_3)^{1-}$ and $(C_5Me_4H)^{1-}$ ligands bound to the metal center. When placing this product under irradiation, the solution turns red and quickly returns to yellow when the light is removed. Attempts to maintain the red solution long enough for characterization have been unsuccessful.

**Figure A.1.** Preliminary thermal ellipsoid plot of $(\eta^5-C_5Me_4SiMe_3)(\eta^5-C_5Me_4H)(\eta^3-C_5Me_4H)Lu$, 3, drawn at the 50% probability level. There are two independent molecules of 3 in the asymmetric unit. The second independent molecule of 3 and hydrogen atoms are omitted for clarity.

**Specific Experimental Details**

$(C_5Me_4SiMe_3)(C_5Me_4H)_2Lu$, 3. In a nitrogen-filled glovebox, $[(C_5Me_4H)_2Lu][(\mu-Ph)_2BPh_2]$ (184 mg, 0.250 mmol) was dissolved in $C_6H_6$ (25 mL). A slurry of $KC_5Me_4SiMe_3$ in
C₆H₆ (1 mL) was added to the stirring solution. The reaction mixture immediately turned bright yellow. After 2 h, the cloudy yellow mixture was centrifuged and the supernatant filtered. Removal of solvent from the yellow filtrate under vacuum gave a bright yellow solid that was stirred in hexane (15 mL) for 20 min. This mixture was centrifuged and filtered to remove insoluble material and removal of solvent under vacuum gave 3 as a bright yellow solid. X-ray quality crystals of 12 were grown from a concentrated hexane solution at –35 °C. ¹H NMR (C₆D₆): δ 5.49 (s, 2H, C₅Me₄H), 2.25 (s, 6H, C₅Me₄SiMe₃), 2.06 (s, 12H, C₅Me₄H), 1.80 (s, 12H, C₅Me₄H), 1.77 (s, 6H, C₅Me₄SiMe₃), 0.23 (s, 9H, C₅Me₄SiMe₃).

Irradiation of (C₅Me₄SiMe₃)(C₅Me₄H)₂Lu, 3. In a nitrogen-filled glovebox 3 (12 mg, 0.020 mmol) was dissolved in C₆D₆ (1 mL). After irradiation for 12 h, the reaction showed conversion to a product with the following NMR spectrum. ¹H NMR (C₆D₆): δ 5.64 (s, ¹H, C₅Me₄H), 2.17 (s, 6H), 2.11 (s, 6H), 2.02 (s, 6H), 1.88 (s, 6H), 0.49 (s, 9H, C₅Me₄SiMe₃).

Reduction Chemistry of [(C₅H₄SiMe₃)₂Ln(µ-Cl)]₂ (Ln = Sm, Tm), and (C₅H₄SiMe₃)₃Y

In search for other ligand coordination environments that would allow formation of new examples of Ln²⁺ ions, the reduction chemistry of [(C₅H₄SiMe₃)₂Ln(µ-Cl)]₂ (Ln = Sm, Tm), 4-Ln was studied. Since the Tm analogue was not known, it was synthesized and crystallographically characterized, Figure A.2. Dark solutions were formed upon the reduction of 4-Sm and 4-Tm with KC₈, in the presence of 18-crown-6, a common indication of the formation of an Ln²⁺ ion. The dark color persists for over 2 weeks at –35 °C, although no
products have been crystallographically characterized. These reactions were performed in the presence of THF. More isolable products could possibly be isolated from toluene, away from THF, as found by Nief and coworkers in the synthesis of $[(C_5H_2Bu_3)_2Dy(\mu-I)K([18]crown-6)]$.

Figure A.2. Thermal ellipsoid plot of $[(C_5H_4SiMe_3)_2Tm(\mu-Cl)]_2$, 4-Tm, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Reduction of $(C_5H_4SiMe_3)_3Y$ with potassium ($-2.931$ vs SCE) or potassium graphite, in the presence of a chelating agent such as 18-crown-6 or 2.2.2-cryptand, led to the isolation of the first two $Y^{2+}$ complexes. It was questioned whether a weaker reductant, such as sodium ($-2.71$ vs SCE), would be capable of reducing $(C_5H_4SiMe_3)_3Y$. $(C_5H_4SiMe_3)_3Y$ reacts quickly with Na in the presence of 2.2.2-cryptand to form $[Na(2.2.2$-cryptand)]$[(C_5H_4SiMe_3)_3Y]$, 5, as
dark purple crystalline solids, eq A.1. Preliminary structural data of 5, Figure A.3, suggest a similar arrangement of the cyclopentadienyl ligands around the yttrium as found for [K(2.2.2-cryptand)][(C₅H₄SiMe₃)₃Y].¹⁴ Due to the smaller ionic radius, the Na⁺ ion is not symmetrically bound to the cryptand compared to a K⁺ ion, which has been previously observed in the literature.¹⁵ The Na1–N1 distance of 3.1250(18) Å is significantly longer than the Na1–N2 distance of 2.7093(18) Å. The average Y–(C₅H₄SiMe₃ centroid) distance of 2.429 Å is equivalent to the 2.436 Å distance for [K(2.2.2-cryptand)][(C₅H₄SiMe₃)₃Y].¹⁴

\[
\begin{align*}
\text{SiMe}_3 &\quad + \text{Na} &\quad + \text{2.2.2-cryptand} &\quad \text{THF, Ar, RT} \\
\text{Me}_3\text{Si} &\quad \text{Y} &\quad \text{SiMe}_3
\end{align*}
\]

(A.1)

Figure A.3. Thermal ellipsoid plot of [Na(2.2.2-cryptand)][(C₅H₄SiMe₃)₃Y], 5-Y, drawn at the 50% probability level. Hydrogen atoms and a disordered ether molecule are omitted for clarity.
Specific Experimental Details

\[[\text{C}_5\text{H}_4\text{SiMe}_3]_2\text{Tm}(\mu-\text{Cl})\]_2, 4-Tm. Similar to the literature prep of the lutetium analogue, 4-Lu, in an argon-filled glovebox, a sealable 100 mL sidearm Schlenk flask equipped with a greaseless stopcock was charged with TmCl₃ (439 mg, 1.59 mmol), a magnetic stir bar, and Et₂O (20 mL). A solution of KCp’ (550 mg, 3.1 mmol) in Et₂O (20 mL) was added to the stirred slurry, and the mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum from the resulting pale green mixture. Hexane (40 mL) was added to the reaction flask. The flask was attached to a Schlenk line, and the mixture was heated to reflux for 6 h. The solvent was removed under vacuum, and the flask was brought into a glovebox free of coordinating solvents. Additional hexane (30 mL) was added, and the resulting pale green suspension was filtered to remove white solids, presumably KCl and excess K(C₅H₄SiMe₃). Removal of solvent under vacuum afforded 4-Tm as a microcrystalline pale green microcrystalline solid (425 mg, 32%). Pale green single crystals of 4-Tm, suitable for X-ray diffraction, were grown from hexane at −35 °C.

Reduction of 4-Tm. In an argon-filled glovebox, \[[\text{C}_5\text{H}_4\text{SiMe}_3]_2\text{Tm}(\mu-\text{Cl})\]_2, 4-Tm (81 mg, 0.085 mmol), and 18-crown-6 (45 mg, 0.17 mmol) were combined and dissolved in THF (2 mL). KC₈ (29 mg, 0.21 mmol) was quickly added to the stirred colorless solution. The reaction mixture immediately turned black/brown, and after 1 min of stirring, Et₂O (1 mL) was added and the mixture was filtered to remove a black precipitate, presumably graphite. The dark brown filtrate was cooled to −35 °C in the freezer for 1 h. The solution was layered with additional Et₂O (15 mL) and stored at −35 °C for 2 weeks. Although the dark color persisted for 2 weeks at −35 °C, crystals were not observed to form.
Reduction of 4-Sm. As described for the reduction of 4-Tm, a light orange solution of 
\[[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Sm}(\mu-\text{Cl})]_2, \ 4-\text{Sm} \ (58 \ mg, 0.062 \ mmol), \text{ and } 18\text{-crown-6} \ (33 \ mg, 0.12 \ mmol) \ \text{in} \ THF \ (2 \ mL) \ \text{was combined with} \ KC_8 \ (25 \ mg, 0.18 \ mmol) \ \text{to produce a dark purple solution.} \]
This dark color persisted for at least 2 weeks, but crystals were not observed to form.

\[[\text{Na}(2.2.2\text{-cryptand})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Y}}, \ 5-\text{Y}. \ \text{In an argon-filled glovebox,} \ \ (\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Y} \ (81 \ mg, 0.16 \ mmol) \ \text{and} \ 2.2.2\text{-cryptand} \ (63 \ mg, 0.17 \ mmol) \ \text{were combined and dissolved in a} \ 2:1 \ \text{THF/Et}_2\text{O solution} \ (2 \ mL). \ \text{Na (excess) was dropped into the stirring the pale yellow solution.} \ \text{The reaction mixture quickly turned dark purple, and after 4 min stirring, the mixture was filtered. The dark purple filtrate was cooled to \(-35 \degree \ C) \ \text{in the freezer for 1 h. The solution was layered with additional Et}_2\text{O} \ (15 \ mL) \ \text{and stored at \(-35 \degree \ C) \ to afford black single crystals of} \ 5-\text{Y}, \ \text{suitable for X-ray diffraction.}\]

X-ray Data Collection, Structure Solution and Refinement for 4-Tm. A colorless crystal of approximate dimensions 0.204 x 0.257 x 0.413 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{16} program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\textsuperscript{17} and SADABS\textsuperscript{18} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{19} program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group P\(\overline{1}\) was assigned and later determined to be correct. The structure was solved by direct methods and refined on \(F^2\) by full-matrix least-squares techniques. The analytical scattering factors\textsuperscript{20} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located
about an inversion center. At convergence, wR2 = 0.0292 and Goof = 1.096 for 187 variables refined against 4720 data (0.73Å), R1 = 0.0117 for those 4660 data with I > 2.0σ(I).

**X-ray Data Collection, Structure Solution and Refinement for 5-Y.** A red crystal of approximate dimensions 0.220 x 0.263 x 0.389 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{21} program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\textsuperscript{17} and SADABS\textsuperscript{22} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{19} program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group \(P2_1/n\) that was later determined to be correct. The structure was solved by direct methods and refined on \(F^2\) by full-matrix least-squares techniques. The analytical scattering factors\textsuperscript{20} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There was one molecule of diethylether solvent present. The solvent was disordered and atoms O(7), C(44) and C(45) were included using multiple components with partial-site-occupancy factors. At convergence, wR2 = 0.0908 and Goof = 1.026 for 537 variables refined against 13334 data (0.75Å), R1 = 0.0363 for those 10654 data with I > 2.0σ(I).
Table A.1. X-ray Data Collection Parameters of 4-Tm and 5-Y.

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<tr>
<td>c (Å)</td>
<td>12.3926(6)</td>
<td>25.488(6)</td>
</tr>
<tr>
<td>Volume (Å(^3))</td>
<td>950.16(7)</td>
<td>5434(2)</td>
</tr>
<tr>
<td>( \alpha ) (deg)</td>
<td>70.4290(5)</td>
<td>90</td>
</tr>
<tr>
<td>( \beta ) (deg)</td>
<td>76.6074(5)</td>
<td>99.778(3)</td>
</tr>
<tr>
<td>( \gamma ) (deg)</td>
<td>88.7221(5)</td>
<td>90</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>( \rho_{\text{calc}} ) (Mg/m(^3))</td>
<td>1.674</td>
<td>1.191</td>
</tr>
<tr>
<td>( \mu ) (mm(^{-1}))</td>
<td>4.925</td>
<td>1.192</td>
</tr>
<tr>
<td>R1 (I &gt; 2( \sigma )(I))(^a)</td>
<td>0.0117</td>
<td>0.0363</td>
</tr>
<tr>
<td>wR2 (all data)(^a)</td>
<td>0.0292</td>
<td>0.0908</td>
</tr>
</tbody>
</table>

\(^{a}\)Definitions: wR2 = [\( \sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)\] ]^{1/2}; R1 = \( \sum ||F_o|| - ||F_c||/\sum |F_o|\).
Synthesis and Crystallographic Characterization of a Cerium Allyl Complex

As described in Chapter 2, the $\eta^3$ allyl complexes, $(\text{C}_5\text{Me}_5)_2\text{Ln}(\text{C}_3\text{H}_5)$, (Ln = Y, Lu) 6-Ln, have shown photochemical reactivity. Since these complexes have been reported for many of the metals in the lanthanide series, it was of interest to determine whether 6-Ln would also be photochemically active for the larger lanthanides. However, 6-Ln has not been crystallographically characterized for any metals larger than samarium. According to the literature, the THF solvated complex, $(\text{C}_5\text{Me}_5)_2\text{Ce}(\text{C}_3\text{H}_5)(\text{THF})$ is yellow, while 6-Ce is bright green.  

Synthesis of 6-Ce was performed according to the literature prep.  

Surprisingly, bright green crystals, grown from a concentrated hexane solution at $-35 \, ^\circ\text{C}$, were crystallographically characterized as the THF solvated complex, $(\text{C}_5\text{Me}_5)_2\text{Ce}(\text{C}_3\text{H}_5)(\text{THF})$, Figure A.4a. This shows

![Figure A.4](image)

Figure A.4. Preliminary thermal ellipsoid plots of (a) $(\text{C}_5\text{Me}_5)_2\text{Ce}(\text{C}_3\text{H}_5)(\text{THF})$, 6-Ce(THF) and (b) $[(\text{C}_5\text{Me}_5)_2\text{Ce}(\mu-\text{Cl})]_3$, 7-Ce, drawn at the 50% probability level. Hydrogen atoms and a disordered ether molecule are omitted for clarity.
the value of X-ray crystallography, especially with the paramagnetic lanthanides. Additionally, bright orange crystals were isolated from the green crystals and crystallographically characterized as \([\{(C_5Me_5)_2Ce(\mu-Cl)\}_3, \textbf{7-Ce}.\) This trimer is isomorphous with the previously characterized Sm analogue, \textbf{7-Sm}.\(^{23}\) Although \((C_5Me_5)_2LnCl_2K(THF)_2\) is used in the formation of \textbf{6-Ln}, this trimer must be a minor byproduct. This complex is soluble in hexane, making it difficult to separate from the desired allyl complex.

References

Appendix B

Computational Analysis of Lanthanide, Thorium and Bismuth Complexes

General Computational Details

Structural optimizations were carried out using density functional theory (DFT) for each complex discussed. As described in relevant sections of this Appendix, different electronic states were sometimes calculated in order to determine the ground state of a particular complex. Starting structural data used for each calculation are discussed in each individual section of this Appendix. Countercations, if present, were removed from the experimental crystal structures before the start of each optimization. The hybrid meta-GGA functional of Tao, Perdew, Staroverov, and Scuseria, TPSSh, was used in conjunction with double-zeta quality split-valence basis sets with polarization functions [def2-SV(P)] for all non-hydrogen, light atoms. TPSSh was chosen due to its established performance for lanthanide, actinide and bismuth compounds.

Small quasi-relativistic effective core potentials (ECPs) and triple-zeta quality basis sets (def2-TZVP) were used for La, Y, Lu and Bi. Scalar-relativistic effective core potentials (ECPs) and triple-zeta valence basis sets, def-TZVP, with the two tight g functions removed, were used for Th. Vibrational frequencies were computed for the optimized structures and were confirmed to be potential energy minima by the absence of imaginary modes.

In order to account for solvation effects, a second structural optimization was carried out using the continuum solvation model (COSMO) for all charged complexes. The dielectric constant of THF (ε = 7.520) was used for the reported COSMO calculations since this was the most polar solvent used in the synthesis. Solvent effects have been shown to be important for
Ln$^{2+}$ systems because they screen the additional negative charge.$^{3-7}$ The changes in bond length between the SV(P) optimized structures and those from a third optimization using TZVP basis sets for light atoms were typically smaller than 0.02 Å. All results were computed in $C_1$ symmetry, and ground state energies were converged to $10^{-7}$ a.u. using fine quadrature grids (at least size $m^4$).$^{16}$ Molecular orbitals were plotted with a contour value of 0.05, unless otherwise specified. All calculations were performed using the Turbomole quantum chemistry software.$^{17}$ Mulliken population analysis$^{18}$ (MPA) and natural population analysis (NPA)$^{19}$ were additionally used to further understand the electronic properties of many complexes, as discussed in each section.

Time dependent DFT (TDDFT) excitation energy calculations$^{20}$ of the lowest excitations from self-consistent orbitals or from spin-unrestricted excitations were computed. For the charged complexes, the solvent-optimized structures were used for these TDDFT calculations, while for the neutral complexes, the SV(P) optimizations were used. Diffuse functions were also added to the basis set (def2-SVPD)$^{21}$ for light atoms, while the metal centers used the ECPs and TZVP basis sets as described above. To simulate the UV-Vis spectra, a normalized Gaussian scaled by the predicted oscillator strength was centered at each molecular excitation, and a root mean square width of 0.11-0.23 eV was chosen to fit the experimental spectra.$^{22}$ Representative excitations (in nm) and oscillator strengths in the length gauge (in a.u.) from each band, and dominant single-particle contributions for each transition are reported in each individual section. Transitions were analyzed with MPA, and are reported in each section.$^{18}$
Computational Analysis of Bismuth Bonds with Unique Dianionic Ligands*

Introduction

Studies of the chemistry of bismuth stabilized by the NCN phenyl pincer ligand, 2,6-(Me₂NCH₂)₂C₆H₃, Ar',23-29 have revealed that a new type of ligand, a dianionic oxyaryl species, (C₆H₅Bu₂-3,5-O-4)²⁻, can be created when sterically bulky aryloxide ligands react with Ar’BiCl₂, eq B.1.⁸ NMR and IR spectroscopy, crystallographic studies, and DFT calculations indicated that complex 1 is a Bi³⁺ complex with an oxyaryl dianionic ligand that has ring C–C and C–O distances consistent with considerable quinoidal character. Reactivity studies of complex 1, performed by Douglas R. Kindra in the Evans Lab, revealed that complex 1 reacts with CO₂ and COS to provide the first examples of insertion of these small molecule substrates into a Bi–C bond, eq B.2. These reactions generate two new dianionic ligands with quinoidal characteristics. Complexes 2 and 3 each have their two polydentate ligands oriented at right angles. This provides a large amount of space around the metal as is typical for bismuth.⁸,23-29 Complex 1 also has its two ligand planes at 90°, but the orientation differs from that in 2 and 3. If the Ar’ ligand is in the yz plane in all three compounds, the dianionic ligands of 2 and 3 are in

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* Portions of this Appendix have been published: Kindra, D. R.; Casely, I. J.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J. J. Am. Chem. Soc. 2013, 135, 7777.
the xy plane, whereas the dianionic ligand in 1 is in the xz plane. Described in this Appendix section are the results of DFT calculations performed to compare the electronic structures of complexes 2 and 3 with other related bismuth complexes, such as the protonated analogue of 2, \{Ar′Bi[O₂C(C₆H₄′Bu₂-3,5-OH-4)-κ²O,O′]}[BPh₄], 4.

**Results/Discussion**

DFT calculations on 2, 4, and 5 reveal structural minima that agree very well with the crystallographic data. In the case of 3, however, the converged calculated structure, Figure B.1a, did not show the upward bend seen in the crystal structure, Figure B.1c. This structural variation may be due to crystal packing since this bend is not observed in the crystal structure, Figure B.1b, or calculated structural minimum for complex 2. In both 2 and 3, the new dianionic ligands were found to have delocalized bonding with quinoidal character that was not present in the protonated version of 2, namely, 4. An analogous difference was observed in the calculations on 1 and 5.\(^8\)
Figure B.1. (a) DFT calculated converged structure of 3, and thermal ellipsoid plots of 2 (b) and 3 (c) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The highest occupied molecular orbitals (HOMOs) of 2 and 3 are compared with that of 1 in Figure B.2. All three HOMOs are similar in the oxy parts of the ligands shown at the top of the figure. The HOMOs of 2 and 3 differ from 1 in the bottom part of the figure. In both 2 and 3,

Figure B.2. From left to right, HOMO of compounds 1, 2, and 3. All orbitals are drawn with a contour value of 0.05.
the HOMO has considerable C=C character between the ipso carbon and the carboxyl or thiocarboxyl carbon. This extends the quinoidal character of the ligands as seen in Scheme B.1.

**Scheme B.1.** Quinoidal Resonance Structures of the Dianionic Ligands of Compounds 2 and 3, Respectively, Showing Double Bond Character.

This multiple bonding with the ipso carbon is not found in the HOMO of 1 nor in any other orbitals of 1: there is only a small interaction between the ipso carbon and bismuth. Hence there is a higher negative charge on the ipso carbon in 1 that correlates with its reactivity with CO$_2$ and COS.

Natural population analyses (NPA)$^{19}$ on 2 and 3 were compared with that of 1 and indicate that insertion of CO$_2$ and COS does not significantly affect the electron density on the formally dianionic ligands. In 1, the oxyaryl ligand has an NPA value of 0.7 electrons, and the analogous numbers for 2 and 3 are 1.0 and 0.8 electrons, respectively. NPA calculations on the ipso carbon of the dianionic ligand showed 4.515 electrons on C13 of 1 compared to 4.224 and 4.183 electrons for C14 of the oxyarylcarboxy and oxyarylthiocarboxy dianionic ligands of 2 and 3, respectively. The higher electron density on C13 in 1 is spread out to the carboxyl and thiocarboxyl groups in 2 and 3 so that C14 in those compounds has lower electron density. The
electron density on C13 in 1 is also higher than the 4.435 and 4.347 values on the analogous carbons in the protonated conventional aryl complex, 5, and BiPh3, respectively. This difference can be used to rationalize the CO2 and COS insertion reactivity observed for 1 and not for 5 and BiPh3.

**Conclusion**

DFT calculations are useful in comparing complex 1 with its CO2 and COS insertion products, complexes 2 and 3, respectively. These comparisons found that the dianionic nature of the ligand is maintained after CO2 or COS insertion. These calculations were also useful in attributing the unique reactivity of complex 1 with CO2 and COS to the additional electron density of the ipso carbon of the dianionic ligand, relative to the protonated analogue 5 and BiPh3, which do not show CO2 or COS insertion.

**Specific Computational Details**

The structures used in these calculations were from the crystallographic data of complexes 2, 3, 4, the protonated version of 1, [Ar′Bi(C6H5Bu2-3,5-OH-4)][BPh4], 5, and BPh3.8
Calculations on Bis(cyclopentadienyl) Ln(II) Complexes of Reduced Benzene Ligands

Introduction

As described in Chapter 10, evaluation of the reductive chemistry of new Ln$^{2+}$ complexes, [K(2.2.2-cryptand)][Cp$^\prime_3$Ln] (Cp$^\prime$ = C$_5$H$_4$SiMe$_3$),$^{4,7}$ has led to isolation of reduction products with naphthalene and biphenyl (−2.50 V and −2.69 V vs SCE$^{30}$),$^{31}$ as well as 1,3,5,7-cyclooctatetraene (−1.62 and −1.86 vs SCE$^{32}$). These Ln$^{2+}$ complexes did not have the reducing capacity to reduce benzene (−3.43 vs SCE$^{30}$). However, efforts by Christopher M. Kotyk, allowed for the isolation of the first examples of what appears to be a dianionic (C$_6$H$_6$)$^{2−}$ ligand bridging between two Ln$^{2+}$ metal centers in [K(2.2.2-cryptand)]$_2$[(Cp$^\prime_2$Ln)$_2$(μ-$η^6$:η$^6$-C$_6$H$_6$)], 6-Ln (Ln = La, Ce), as shown in eq B.3.

\[ 6\text{-La} \text{ displays } ^1\text{H NMR resonances in the diamagnetic region and an EPR silent spectrum. The complex shows intense broad absorptions in the visible region with extinction coefficients reaching } \sim 8000 \text{ M}^{-1} \text{ cm}^{-1} \text{ in the high-energy visible region. The spectrum is similar in shape to the La}^{2+} \text{ complex, [K(2.2.2-cryptand)][Cp$\prime_3$La], but the extinction coefficients are much higher. Crystal structure data of 6-La suggest reduction of benzene, due to long C–C bonds of the C$_6$ unit and a non-planar C$_6$ ring.} \]
There are several possible explanations for the experimental observations described above. One extreme could involve two Ln$^{2+}$ ions and a (C$_6$H$_6$)$_2^{-}$ dianion, while another could involve two Ln$^{3+}$ ions and a (C$_6$H$_6$)$_4^{-}$ tetranion. Described in this section of Appendix B are the results of DFT calculations used to examine the energies of the possible electron configurations of 6-La.

Results/Discussion

Calculations on the dianion of 6-La found an energy minimum corresponding to a diamagnetic singlet ground state that had metrical parameters that matched the crystal data better than any other electronic configuration. Although this was the best match, the La–C(C$_6$H$_6$) bond lengths in the calculated minimum were 0.05 Å longer than those in the crystal structure. Single-point energy calculations indicate the triplet and quintet states are 30 kcal/mol ($10,500 \text{ cm}^{-1}$) and 62 kcal/mol ($21,800 \text{ cm}^{-1}$) higher than the singlet ground state, respectively. When a geometry optimization of the quintet state was performed, the result was a structure different than the experimentally determined structure in that each metal was only interacting with three carbons of the bridging (C$_6$H$_6$) ligand and the two metals were not interacting with the same carbons as each other, suggesting that this state is not a viable description of 6-La.

The two highest occupied molecular orbitals (HOMO and HOMO$-1$) of the singlet state show significant mixing between the metal orbitals and the $\pi$-bonds of the C$_6$H$_6$ ring, Figure B.3. Mulliken population analyses (MPA)$^{18}$ of the HOMO suggest that 61% of the orbital is localized on $\pi^*$ orbitals of the C$_6$H$_6$ ring with 39% involved with the two metals centers. For HOMO-1,
the orbital is 64% on the ring and 36% on the two metals. This is less than that for the HOMO of the Ln\(^{2+}\) ions in (Cp\(^{'3}\)Ln)\(^{1-}\), which is often >70% metal based depending on the lanthanide.

**Figure B.3.** Molecular orbital plots of (a) the 183a orbital (HOMO) and (b) the 182a orbital (HOMO−1) of the dianion in 6-La, using a contour value of 0.05.

**Table B.1.** MPA and NPA analysis of the dianion in 6-La. The % metal character indicates the total metal contribution to the molecular orbital for each metal and the % d character indicates how much of the total orbital comes directly from the metal d orbitals.

<table>
<thead>
<tr>
<th>Metal Center</th>
<th>182a (HOMO−1) MPA</th>
<th>183a (HOMO) MPA</th>
<th>NPA total density (5d orbital)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% metal</td>
<td>% d</td>
<td>% metal</td>
</tr>
<tr>
<td>La1</td>
<td>18</td>
<td>13</td>
<td>20</td>
</tr>
<tr>
<td>La2</td>
<td>18</td>
<td>13</td>
<td>19</td>
</tr>
</tbody>
</table>

Natural population analysis (NPA)\(^{19}\) of the dianion in 6-La suggests that both La centers have approximately 1.4 5d electrons, which is more than the 1.2 electrons and 0.9 electrons found for (Cp\(^{'3}\)La)\(^{1-}\) and Cp\(^{'3}\)La, respectively, Table B.1. Since there is more electron density on

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each La center than even that for the La\textsuperscript{2+} complex, [K(2.2.2-cryptand)][Cp\textprime\textprime_3La], these calculations indicate that the description involving two Ln\textsuperscript{2+} ions and a (C\textsubscript{6}H\textsubscript{6})\textsuperscript{2−} dianion is the most accurate of the two extreme structures considered above.

Time dependent DFT (TDDFT) calculations were performed to simulate the UV-vis spectrum of \textbf{6-La}. The simulated spectrum of the singlet state gave the best match to the experimental spectrum as shown in Figure B.4. The predicted UV-vis contains three broad absorptions, one of which matches the low energy absorption in the experimental spectrum, while the other two combined fit under the high energy absorption in the experimental spectrum. The excitations between 300 and 1000 nm are comprised of excitations from the HOMO and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_b4.png}
\caption{Experimental (solid) and calculated (dotted) UV-vis spectra of \textbf{6-La} in THF at 298 K, with pertinent theoretical excitations shown as vertical lines and theoretical extinction coefficients scaled down by a factor of 4.7.}
\end{figure}
HOMO−1 orbitals shown in Figure B.3. The lowest energy transitions (< 440 nm) involve transitions to primarily metal-based orbitals with s and/or d character, while the highest energy transitions (> 440 nm) involve transitions to primarily ligand based orbitals.

Conclusion

DFT calculations have been useful to describe orbital mixing between the 5d orbitals and the π* orbitals of the bridging C₆H₆ ring. The calculations suggest that the extreme electronic description involving two Ln²⁺ ions and a (C₆H₆)²⁻ dianion is the closest assignment to give this complex.

Specific Computational Details

The structure used in these calculations was from the crystallographic data of 6-La. The results of the third optimization described above, using COSMO and TZVP basis sets for all atoms, indicated the singlet structure was lower in energy for 6-La. This calculation also matched the crystal structure reasonably, although a La–C(C₆H₆) bond length elongation of 0.04-0.07 Å was observed in comparison to the crystal structure. Calculations of the quintet state were not consistent between the SV(P) optimized structure and optimization using TZVP basis sets for light atoms, neither of which matched the crystal structure. Additional single-point energy calculations of the singlet-triplet and singlet-quintet energy gaps were then performed on the optimized TPSSh singlet structure for 6-La. The triplet state was found to be 30 kcal/mol (10,500 cm⁻¹) higher and the quintet state was found to be 62 kcal/mol (21,800 cm⁻¹) higher than the singlet ground state.
Representative excitations (in nm) and oscillator strengths in the length gauge (in a.u.) from each band, and dominant single-particle contributions for each transition are reported in Table B.2. Transitions were analyzed with MPA, and are reported in Table B.3. 18

**Table B.2.** Electronic excitation summary for the dianion of 6-La, computed using the TPSSh functional and SV(P) basis sets. Only pertinent excitations with oscillator strengths larger than $10^{-3}$ a.u. are included.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength (nm)</th>
<th>Oscillator Strength (len)</th>
<th>Dominant Contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-La</td>
<td>694.01</td>
<td>0.014</td>
<td>183a, 185a, 63.1</td>
</tr>
<tr>
<td></td>
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<td>182a, 184a, 33.7</td>
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<td></td>
<td>616.87</td>
<td>0.082</td>
<td>183a, 186a, 49.7</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>182a, 184a, 30.3</td>
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<td></td>
<td></td>
<td>183a, 185a, 19.5</td>
</tr>
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<td>534.17</td>
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<td>182a, 186a, 93.0</td>
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<td>527.82</td>
<td>0.493</td>
<td>183a, 186a, 46.7</td>
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<td>182a, 184a, 32.0</td>
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<td>183a, 185a, 12.5</td>
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<td>482.05</td>
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<td>182a, 187a, 82.7</td>
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<td>183a, 190a, 14.5</td>
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<td>456.99</td>
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<td>436.29</td>
<td>0.042</td>
<td>183a, 192a, 79.9</td>
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<td>183a, 191a, 10.4</td>
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<td>426.46</td>
<td>0.085</td>
<td>183a, 191a, 85.5</td>
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<td></td>
<td>423.89</td>
<td>0.071</td>
<td>182a, 189a, 84.8</td>
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<tr>
<td>422.72</td>
<td>0.022</td>
<td>182a</td>
<td>190a</td>
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<tr>
<td>418.88</td>
<td>0.033</td>
<td>183a</td>
<td>193a</td>
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<td>406.70</td>
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<td>192a</td>
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<td>399.90</td>
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<td>182a</td>
<td>191a</td>
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<td>390.91</td>
<td>0.032</td>
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<td>193a</td>
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<td>195a</td>
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<td>183a</td>
<td>197a</td>
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<td>203a</td>
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<td>201a</td>
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<td>0.009</td>
<td>182a</td>
<td>202a</td>
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<td>307.92</td>
<td>0.026</td>
<td>183a</td>
<td>206a</td>
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<tr>
<td>302.03</td>
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<td>209a</td>
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</tbody>
</table>

375
Table B.3. Mulliken population analysis summary for the dianion in 6-La. The % metal character indicates the total metal contribution (from both La centers combined) to the molecular orbital, the % d character indicates how much of the total orbital comes directly from the metal d orbitals.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Orbital</th>
<th>% Metal Character</th>
<th>% d Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-La</td>
<td>HOMO−1 (182a)</td>
<td>37</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>HOMO (183a)</td>
<td>42</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>LUMO (184a)</td>
<td>60</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>LUMO+1 (185a)</td>
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<td>18</td>
</tr>
<tr>
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Computational Analysis of Bimetallic Thorium Hydride Complexes

Introduction

As discussed in Chapter 6, the isolation of the first molecular examples of U$^{2+}$, [K(2.2.2-cryptand)][Cp$'_{3}$U], 7, and Th$^{2+}$ complex, [K(18-crown-6)(THF)$_{2}$][Cp$''_{3}$Th] (Cp$''$ = C$_{5}$H$_{5}$(SiMe$_{3}$)$_{2}$), 8, has been accomplished using a Cp$_{3}$An ligand coordination environment. Reactivity of 7 with hydrogen led to the reduction of hydrogen to form a U$^{3+}$–H complex, as shown in eq B.4.

\[
\begin{align*}
2 \begin{array}{c}
\text{K} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
& \quad \begin{array}{c}
\text{Me}_{3}\text{Si} \\
\text{SiMe}_{3}
\end{array}
\rightleftharpoons \begin{array}{c}
\text{K} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\begin{array}{c}
\text{SiMe}_{3} \\
\text{SiMe}_{3}
\end{array} \\
\text{H}_{2} (1 \text{ atm}) \\
\text{THF, 0 }^\circ\text{C}
\end{align*}
\]

(B.4)

Interestingly, reactivity studies of 8 with hydrogen, pursued by Ryan R. Langeslay, formed a different reduced hydrogen species, [K(18-crown-6)(THF)$_{2}$][Cp$''_{2}$Th(H)(µ-H)$_{3}$ThCp$''_{2}$], 9, eq B.5. This complex was interesting in that it appears to have both a Th$^{3+}$ and Th$^{4+}$ center. Since this is just the sixth example of a Th$^{3+}$ complex, it was of interest to understand the electronic structure of 9, as well as determine whether reduction of 9 could produce the first example of a Th$^{3+}$/Th$^{3+}$ bimetallic species. The results of DFT calculations to understand the physical properties observed for 9 are discussed in this Appendix section.
Results/Discussion

DFT calculations on the anion of 9 reveal a structural minimum that agrees very well with the crystallographic data. The HOMO and LUMO, Figure B.5, are both metal based d orbitals, localized on the Th metal center without a terminal hydride, which will be described as Th2. The Th metal center with the terminal hydride will be labelled as Th1. NPA calculations of the anion in 9 describe 0.69 d orbital and 0.86 overall spin densities at the Th2 metal center, while the NPA calculations describe no spin density at the Th1 metal center. This matches the formal assignment of Th1 being Th\(^{4+}\) and Th2 being Th\(^{3+}\).

Figure B.5. Molecular orbital plots of (a) the 263a orbital (HOMO) and (b) the 263b orbital (LUMO) of the anion in 9, using a contour value of 0.05. The metal center on the left is Th2 and the metal center on the right is Th1. The hydride ligands could not be selectively shown separately from all other hydrogens in the molecule, which were removed for clarity.

Although addition of solvent effects, using COSMO, did not change the structural parameters of [Cp'"\(_2\)Th(H)(\(\mu\)-H)\(_3\)ThCp'"\(_2\)]\(^{1-}\), it did stabilize the complex by 24 kcal/mol. TDDFT calculations were performed to simulate the UV-vis spectrum of the anion in 9. The overall

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shape of the experimental spectrum is well matched in the simulated spectrum, Figure B.6, however the energies of the excitations are predicted to be lower in energy than what is observed experimentally. This observation was also seen in the simulated spectrum of 8, as discussed in Chapter 6, and is often seen in these calculations.\textsuperscript{6,33} The two broad, low energy absorptions are primarily metal-to-metal transitions, often having d→f character, while the higher energy absorptions are a combination of metal to metal and metal to ligand transitions. This is very similar to the analysis of the simulated UV-vis spectrum of 8.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_b6.png}
\caption{Experimental (solid) and calculated (dotted) UV-vis spectra of 9 in THF at 298 K, with pertinent theoretical excitations shown as vertical lines and theoretical extinction coefficients scaled down by a factor of 1.5.}
\end{figure}

Calculations on the possible reduction product of 9, [Cp''\textsubscript{2}Th(H)(μ-H)\textsubscript{3}ThCp''\textsubscript{2}]\textsuperscript{2-}, were also performed. Although it was anticipated that reduction of 9 would reduce the Th\textsuperscript{4+} metal
center, Th1, to make a Th$^{3+}$/Th$^{3+}$ bimetallic, the LUMO of the anion of 9 suggested that reduction of the Th$^{3+}$ metal center, Th2, was more likely. Indeed, the structural minimum for the singlet state was found to be the ground state with a triplet state being approximately 2100 cm$^{-1}$ or 6 kcal/mol higher in energy than the singlet state. The HOMO of the singlet state is a doubly occupied orbital localized on the Th2 metal center, Figure B.7a. NPA$^{19}$ calculations support the description of the singlet ground state as a Th$^{2+}$/Th$^{4+}$ bimetallic complex with no evidence for a Th–Th bond.

**Figure B.7.** Molecular orbital plots of (a) the doubly occupied 263a orbital (HOMO) of the singlet state and (b) the singly occupied 264a (HOMO) and 263a (HOMO-1) orbitals of the triplet state of the dianion, [Cp''$_2$Th(H)(μ-H)$_3$ThCp''$_2$]$_2$$^2^-$, using a contour value of 0.05. The metal center on the left is Th2 and the metal center on the right is Th1. The hydride ligands could not be selectively shown separately from all other hydrogens in the molecule, which were removed for clarity.

Calculations of the higher-lying triplet state reveal two singly occupied molecular orbitals (SOMOs), the higher orbital (HOMO) being spread across both metals and the ligands, while the lower orbital is localized on the Th2 metal center, Figure B.7b. NPA calculations show increased
spin density on both Th1 and Th2, providing further support that the triplet state cannot be
described as a simple Th$^{3+}$/Th$^{3+}$ bimetallic species.

**Conclusion**

This section of Appendix B uses DFT to help describe the electronic properties of a
mixed valent thorium hydride complex, [K(18-crown-6)(THF)$_2$][Cp'$''_2$H($\mu$-H)$_3$ThCp'$''_2$], 9.
The calculations match the assignment of a Th$^{4+}$ with a terminal hydride and a Th$^{3+}$ without a
terminal hydride. Additionally, the reduction product of 9 is predicted to be a Th$^{2+}$/Th$^{4+}$ dimer
with a singlet ground state with no evidence for a Th–Th bond.

**Specific Computational Details**

The structure used in these calculations was the anion, [Cp'$''_2$H($\mu$-H)$_3$ThCp'$''_2$]$^{-1}$, from
the crystallographic data of 9. This anion was used as the starting point for calculations of the
dianion, [Cp'$''_2$H($\mu$-H)$_3$ThCp'$''_2$]$^{2-}$, in both the singlet and triplet states, to analyze the possible
reduction products of 9.

Representative excitations (in nm) and oscillator strengths in the length gauge (in a.u.)
from each band, and dominant single-particle contributions for each transition are reported in
table B.4. Transitions were analyzed with MPA, and are reported in Table B.5.$^{18}$
Table B.4. Electronic excitation summary for the anion of 9, $[\text{Cp}''_2\text{Th(H)}(\mu-\text{H})_3\text{ThCp}''_2]^{1-}$, computed using the TPSSh functional and SV(P) basis sets. Only pertinent excitations with oscillator strengths larger than $5\times10^{-3}$ a.u. are included.

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<th>Wavelength (nm)</th>
<th>Oscillator Strength (len)</th>
<th>Dominant Contributions</th>
<th>% comp</th>
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<td>$[\text{Cp}''_2\text{Th(H)}(\mu-\text{H})_3\text{ThCp}''_2]^{1-}$</td>
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Table B.5. Mulliken population analysis summary for the anion in 9. The % metal character indicates the total metal contribution (from both Th centers combined) to the molecular orbital, the % d and %f character indicates how much of the total orbital comes directly from the metal d and f orbitals, respectively.

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Calculations of a Bridging (C₄Ph₄)⁴⁻ Complex

Introduction

Single molecule magnets are molecules that exhibit slow magnetic relaxation after removal of an applied field.³⁴,³⁵ While these molecules can exhibit magnetic hysteresis, relaxation processes limit the magnetic properties to extremely low temperatures. Due to the increased anisotropy and magnetic moment of the lanthanides, relative to the transition metals, lanthanide single molecule magnets have been shown to have the high blocking temperatures, such as an (N₂)³⁻ complex, [K(18-crown-6)(THF)₂][{(Me₃Si)₂N]₂(THF)Tb}₂(µ-η²:η²-N₂)] , with a record high blocking temperature of 14 K.³⁶ The presence of a radical on the bridging ligand between lanthanide centers appeared to allow coupling between the metal centers and therefore enhance the magnetic properties of the complex.

Additional examples of single molecule magnets were subsequently found that had radical bridged organic ligands between two lanthanide centers.³⁵ This section of the appendix describes the use of DFT to determine whether oxidation or reduction of the bimetallic lutetium complex, [CpLu(DME)]₂(C₄Ph₄), ¹⁰,³⁷ prepared Bochkarev and co-workers in 1995, would be predicted to form a new radical bridged species.

Results/Discussion

DFT calculations on ¹⁰ reveals a structural minimum that agrees very well with the crystallographic data. The HOMO and LUMO are both localized on the bridging (C₄Ph₄)⁴⁻ unit, Figure B.8. The HOMO is mostly on the C₄ unit suggesting oxidation of ¹⁰ with an oxidant, such as AgBPh₄, could lead to the isolation of a {[CpLu(DME)]₂(C₄Ph₄)}⁺ complex with a
(C₄Ph₄)³⁻ radical unit between two metal centers. The LUMO is localized more on the phenyl groups of the (C₄Ph₄)⁴⁻ ligand, which suggests that while reduction of 10 would be expected to reduce the bridging ligand, the radical may not interact with the two lanthanide centers enough to enhance coupling for magnetism purposes.

Figure B.8. Molecular orbital plots of 10 (a) the 222a orbital (HOMO) and (b) 223a (LUMO), using a contour value of 0.05.

Conclusion

DFT was used to predict that oxidation of 10 could be a promising route to a new complex with a radical bridged between two lanthanide centers. If this new complex was then made with a paramagnetic lanthanide such as terbium or dysprosium, it could be interesting for magnetic properties.

Specific Computational Details

The structure used in these calculations was from the crystallographic data of [CpLu(DME)]₂(C₄Ph₄).³⁷
References


