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Expanding Synthetic Aspects of Redox and Mechanical Organometallic Chemistry of Rare Earth Complexes

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Expanding Synthetic Aspects of Redox and Mechanical Organometallic Chemistry of Rare Earth Complexes

DISSERTATION

submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Christopher M. Kotyk

Dissertation Committee:
Professor William J. Evans, Chair
Professor Alan F. Heyduk
Professor Elizabeth R. Jarvo

2015
Dedication

For Juliet, Priscilla, John, Nick and Mary.

"Everything in black and white, everything clear-cut and well-defined.

But life, it is not like that, Mademoiselle. There are things that are not yet,

but which cast their shadow before."

Hercule Poirot
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(C₅Me₅)₃Y
(C₅Me₅)₃La
(C₅Me₅)₃Ce
(C₅Me₅)₃Pr
(C₅Me₅)₃Nd
(C₅Me₅)₃Sm
Y[N(SiMe₃)₂]₃
U[N(SiMe₃)₂]₃
(C₅Me₅)₂La[(OC)₂C₅Me₅-κ²-O,O']
(C₅Me₅)₂Ce[(OC)₂C₅Me₅-κ²-O,O']
(C₅Me₅)₂Pr[(OC)₂C₅Me₅-κ²-O,O']
(C₅Me₅)₂Nd[(OC)₂C₅Me₅-κ²-O,O']
(C₅Me₅)₂Sm[(OC)₂C₅Me₅-κ²-O,O']
Y(NCy₂)₃(THF)
Y(NPh₂)₃(THF)₂
[Li(THF)][Y(NiPr₂)₄]
Y(CH₂SiMe₃)(THF)₂
Y(NiPr₂)₃(THF)₂
Y(DMI)₃(THF)₂
[Cp₂Y{µ-O₂C[3-(Me₃Si)C₅H₄]-κ²O,O'}]₂
(C₅Me₅)₂Sm(C₆H₅)(THF)
Cp₂YPh(THF)
Cp₂DyPh(THF)
Acknowledgments

I would like to thank my graduate advisor, Professor William J. Evans. I first met Bill after he spoke at my Conduct of Research course during my first year at UC Irvine when I was still unsure as to what kind of chemistry I wanted to pursue as a graduate student. During Bill's brief lecture it struck me that not only were the discoveries being made in his lab fascinating, but also that the work he was doing related to a section of the periodic table that I realized I knew nothing about. After getting to know Bill and his graduate students, and familiarizing myself with their work, I found an inclusive home on the second floor of Reines Hall as well as a group of mentors and colleagues that shared a passion for discovery and penchant for questioning basic fundamental assumptions about chemistry. I owe much of my success to Bill deciding to give a first-year organic chemist a chance.

I would also like to thank my committee members, Professors Alan Heyduk and Elizabeth Jarvo, for offering their guidance, challenging me, and taking the time to provide an outside perspective on my research. The discussions we had after my advancement exam were a critical part of the spark that inspired me to attempt one of my most exciting projects. Alan and Liz taught me a lot about the importance of seeing data and interpreting chemical systems from different angles and for that they have my sincere gratitude.

I also owe a great deal of thanks to Dr. Joe Ziller and his assistant Jordan Corbey for their patience and expertise in collecting and solving structural data by X-ray crystallography. Regardless of compound or metal center, Joe routinely strives to obtain the best crystal data possible, which for rare earth complexes often means extended windows for data collection and many hours decrypting complicated data. My work would not have been possible without their perseverance and attention to detail.
I would also like to thank my friends and colleagues in the group, with whom I have been privileged to share my time for the last few years. A special thanks is in order for my labmates Dr. Matthew MacDonald and Dr. Megan Fieser. During my time in the Evans Group, I witnessed as new oxidation states of f elements were discovered and added to the periodic table by only a handful of graduate students and professors, and at the epicenter were Matt and Megan who painstakingly fought and championed these discoveries under the intense scrutiny of the wider chemical community. It has been my distinct privilege to be mentored by Matt and Megan, in the fundamentals of our chemistry and rigorously air-free scientific work, and to have the opportunity to play a small role in understanding the chemical nature of new oxidation states for f elements.

Finally, I would like to thank my family and friends from home for their care, support, and patience, especially over such a great distance. And for my wife, Juliet, and the rest my graduate friends, I am honored to have gone on this adventure at UC Irvine with you all and look forward to our continued exploration of the undiscovered.
Curriculum Vitae

Christopher M. Kotyk

Education

**University of California, Irvine** Irvine, CA

**Gettysburg College** Gettysburg, PA

Teaching Experience

**Organic Chemistry: Lecturer** Irvine, CA
- Lead an accelerated 5-week organic chemistry course of 100 undergraduates. (8/2014 – 9/2014)
- Prepared three 2-hour lectures per week and distributed lecture notes through course website.
- Created syllabus and lecture materials and co-wrote exams with teaching assistant.
- Wrote and administered homework assignments, graded with teaching assistant.

**Organic Chemistry Laboratory: Head Teaching Assistant** Irvine, CA
- Oversaw organization of over 50 laboratory sections for over 1100 undergraduate students and over 25 graduate teaching assistants per quarter. (1/2014 – 6/2015)
- Regularly coordinated with stockroom manager to prepare and refine experiment details.
- Managed online teaching tools including Sapling Learning, Turnitin, Piazza and assisted in the incorporation of an electronic lab notebook to reduce paper production.
- Kept experiments up-to-date by regularly improving laboratory handouts.
- Prepared multiple versions of the laboratory practical every quarter testing the students' knowledge of organic chemistry theory and the students' ability to perform common laboratory techniques and manipulations correctly and efficiently.
- Wrote detailed keys and rubrics to aid teaching assistants in grading reports and practicals.
- Prepared and managed an online gradebook for teaching assistants.
- Wrote comprehensive experiment notes to aid teaching assistants teaching for the first time.
- Performed large-scale synthesis of organic starting materials.
Graduate Organometallic Chemistry: Teaching Assistant  Irvine, CA
• Assisted lecture and discussion for class of 27 graduate students. (9/2013 – 12/2013)
• Graded assignments and held office hours to assist graduate level course.

Organic Chemistry: Teaching Assistant  Irvine, CA
• Planned and led weekly discussion sections for undergraduate students. (9/2012 – 6/2013)
• Prepared and graded discussion handouts and homework assignments.
• Graded exams for large classes of up to 400 undergraduate students.

Inorganic Chemistry Laboratory: Teaching Assistant  Irvine, CA
• Instructed 7-hour laboratory section of 12 undergraduate students. (1/2013 – 3/2013)
• Trained undergraduate students in air-free synthesis under inert atmosphere including regular use of glovebox and Schlenk techniques. (3/2012 – 6/2012)
• Utilized sublimation for purification and air-free IR spectroscopy for analysis.
• Assisted in safety training exercises for proper gas cylinder use, the handling of flammable and pyrophoric materials, and liquid nitrogen safety.
• Advised students in advanced scientific writing, graded in-depth lab reports.

Associate Chemist / Lab Manager: QinetiQ North America  Waltham, MA
• Trained undergraduate interns from Northeastern University in laboratory safety and chemical synthesis in a professional industrial environment. (6/2008 – 5/2011)
• Regularly led discussions with undergraduates on organic and inorganic chemistry theory.
• Oversaw and assisted students with polymer and metal organic framework syntheses.
Research Experience

**Organometallic Chemistry: Graduate Student Researcher** Irvine, CA  
Advisor: William J. Evans.  

- Investigated reactivity of new divalent lanthanide complexes with aromatic hydrocarbons.
- Isolated examples or rare, non-bridging reduced naphthalenide and biphenyldiene complexes.
- Discovered bimetallic divalent lanthanide complexes containing bridging reduced benzene.
- Used electrochemistry to examine lanthanide complexes for trends in reduction potential.
- Initiated investigation into solvent-free mechanical synthesis of rare earth complexes.
- Investigated gas insertion with lanthanide complexes to synthesize non-classical carbocation.

**Physical Chemistry: Undergraduate Student Researcher** Gettysburg, PA  
Advisor: Michael R. Wedlock.  

- Utilized Raman spectroscopy to study the photodissociation of small molecules.
- Directed monochromatic light from a Nd:YAG laser to excite organic sample.
- Analyzed the emission spectrum to describe the photodissociation process in the excited state.

Publications

"Reactivity of the Ln$^{2+}$ Complexes [K(2.2.2-cryptand)][(C$_5$H$_4$SiMe$_3$)$_3$Ln]: Reduction of Naphthalene and Biphenyl." Christopher M. Kotyk, Matthew R. MacDonald, Joseph W. Ziller, and William J. Evans. *Organometalics*, 2015, 34, 2287

"Isolation of +2 Rare Earth Ions with Three Anionic Carbocyclic Rings: Bimetallic Bis(cyclopentadienyl) Reduced Arene Complexes of La$^{2+}$ and Ce$^{2+}$ are Four Electron Reductants." Christopher M. Kotyk, Megan E. Fieser, Joseph W. Ziller, Filipp Furche, and William J. Evans. *Manuscript Submitted.*

Awards

**Most Promising Future Teacher** Irvine, CA  
Department of Chemistry, University of California, Irvine,  
(6/2015)

Presentations

**Research in Organometallic Chemistry at 2015 ACS Conference** Denver, CO  
*Reactivity of the Ln$^{2+}$ Complexes [K(2.2.2 cryptand)][(C$_5$H$_4$SiMe$_3$)$_3$Ln]: Reduction of Aromatic Hydrocarbons.*  
(3/2015)

**Research in Physical Chemistry at 2008 ACS Conference** New Orleans, LA  
*Polarized Emission Spectroscopy of Dimethyl Disulfide.*  
(4/2008)
Industry Experience

**QinetiQ North America / Foster-Miller: Associate Chemist**
Waltham, MA

- Carried out chemical synthesis for multi-year programs funded by DARPA, DHS and NavAir.
- Synthesized hyper-adsorptive polymers, UV curable resins, and metal organic frameworks.
- Developed self-decontaminating fabrics for biochemical materials.
- Selected as Lab Manager of Polymer Processing lab and Applied Chemistry lab.

**Covidien / Tyco Healthcare: Research Technician**
North Haven, CT

- Participated on a small team assigned to synthesize bioadhesive.
- Responsible for testing new experimental procedures.
- Prepared in-vitro and in-vivo samples for bio-surgery research staff.
- Analyzed characteristics of surgical adhesives and sprayable sealants.
- Assisted with investigations of novel materials (e.g. hydrogels) for endoscopic use.

Service Experience

**Chemistry Outreach Program: UC Irvine**
Irvine, CA

- Travelled to local elementary schools to demonstrate exciting chemistry experiments for classrooms and school assemblies and to discuss the importance of chemistry and its impact on day-to-day life.

- Regularly participated in the LEAPS program (Laboratory Experiments in the Physical Sciences), demonstrating chemistry experiments for middle school and high school students in our graduate research laboratory, introducing young scientists to the lanthanide elements and the intricacies of air-free chemistry.

**Residence Assistant / Coordinator: Gettysburg College**
Gettysburg, PA

- Responsible for fostering a safe environment in residence halls.
- Oversaw training and management of residential assistants.
- Provided a safe community for over 150 undergraduate students and assisted first-year orientation.

**Community Service Corps.: Apache Reservation**
San Carlos, AZ

- Constructed housing for families in local reservation community.
- Worked with Rec and Wildlife on animal population control.
- Lived with Apache family to learn about heritage and customs.
Abstract of the Dissertation

Expanding Synthetic Aspects of Redox and Mechanical Organometallic Chemistry of Rare Earth Complexes

by

Christopher M. Kotyk

Doctor of Philosophy in Chemistry

University of California, Irvine, 2015

Professor William J. Evans, Chair

This dissertation describes the synthesis, characterization, and reactivity of organometallic complexes of yttrium and the lanthanides in an effort to more completely understand the nature of a recently-discovered class of +2 ions of these rare earth metals. The reactivity of complexes of a new set of Ln$^{2+}$ ions (Ln = rare earth metal) with unprecedented 4f$^n$5d$^1$ electron configurations has been explored to expand the unique chemistry possible with the rare earth elements. The isolation of unexpected reaction products is described as well as the discovery of a new divalent lanthanide system and the utilization of solvent-free mechanochemical synthesis for established rare earth organometallic species.

In Chapter 1, the reactivity of the highly-reducing, air-, moisture-, and temperature-sensitive divalent lanthanide complexes [K(2.2.2-cryptand)][Cp′₃Ln] (Ln = Y, La, Ce, Dy) is characterized by examining reactions with aromatic organic substrates of known reduction potential. Complexes of the 4f$^n$5d$^1$ Ln$^{2+}$ ions reduce naphthalene and biphenyl within minutes to form a new class of reduced aromatic complexes, [K(2.2.2-cryptand)][Cp′₂Ln($\eta^4$-C$_{10}$H$_8$)] (Ln = Y, La, Ce, Dy) and [K(2.2.2-cryptand)][Cp′₂Y($\eta^6$-C$_6$H$_5$Ph)], respectively. The naphthalene
reactions also produced the previously unobserved ligand redistribution products [K(2.2.2-cryptand)][Cp′4Ln] (Ln = Y, La), which show the effect of the lanthanide contraction on structure as the lanthanum complex has four $\eta^3$-Cp′ rings while yttrium has three $\eta^3$-Cp′ rings and one $\eta^1$-Cp′ ring.

Chapter 2 describes the synthesis and characterization of a new class of 4f$^{n}$5d$^1$ Ln$^{2+}$ complexes in which a reduced benzene dianion bridges two metal centers: [K(2.2.2-cryptand)]$_2$[(Cp′$_2$)La(µ-η$^6$:η$^6$-C$_6$H$_6$)] (Ln = La, Ce). In these complexes, the (C$_6$H$_6$)$^{2−}$ dianion formally takes the place of a (Cp$^{n−1}$ anion in the [K(2.2.2-cryptand)][Cp′3Ln] complexes above and suggests a pattern that three anionic carbocyclic rings can stabilize the new Ln$^{2+}$ ions. In accordance with the presence of two metal centers of 4f$^{n}$5d$^1$ electron configurations and (C$_6$H$_6$)$^{2−}$ dianions, these complexes react as four electron reductants to reduce two equiv of naphthalene to two equiv of [K(2.2.2-cryptand)][Cp′$_2$Ln(η$^4$-C$_{10}$H$_8$)] (Ln = La, Ce). This constitutes a better synthesis of these complexes than the one above since no (Cp′$_3$Ln)$^{1−}$ byproducts are formed.

Chapter 3 describes the solvent-free synthesis of the previously established complexes (C$_5$Me$_5$)$_3$Y, Cp′$_3$Y, [Cp′$_2$Y(µ-Cl)]$_2$, Y[N(SiMe$_3$)$_2$]$_3$, and U[N(SiMe$_3$)$_2$]$_3$ by mechanochemical ball milling. Not only do these reactions show the feasibility of ball milling as an alternative method to synthesizing organometallic rare earth complexes, but these preliminary results also show promising routes that shorten reaction times and limit the generation of organic solvent waste. This new method of solid-state synthesis is especially important for the isolation of (C$_5$Me$_5$)$_3$Y as the established synthetic route must avoid aromatic hydrocarbons.

Chapter 4 describes a study of the reactivity of organometallic rare earth non-classical carbocation complexes (C$_5$Me$_5$)$_2$Ln[(OC)$_2$C$_3$Me$_5$-κ$^2$-O,O′] (Ln = La, Sm) obtained from sterically crowded (C$_5$Me$_5$)$_3$Ln and carbon monoxide. Investigation of the reactivity is
consistent with DFT analysis that suggests the LUMO of the La complex is the 5d\textsubscript{2}\textsuperscript{z} orbital of the metal center rather than an orbital centered on the carbocation.

Also described in this dissertation are the synthesis and structural and spectroscopic characterization of two previously unreported rare earth amide complexes, Y(NCy\textsubscript{2})\textsubscript{3}(THF) and Y(NPh\textsubscript{2})\textsubscript{3}(THF)\textsubscript{2} (Chapter 5), the insertion of CO\textsubscript{2} into a Y–C bond for the first time with the Cp′ ligand to form [Cp′\textsubscript{2}Y\{µ-O\textsubscript{2}C[3-(Me\textsubscript{3}Si)C\textsubscript{5}H\textsubscript{4}]\textsuperscript{−}\textsuperscript{κ-2}O,O′\}'\textsubscript{2}] (Appendix A), the synthesis and structural characterization Cp′\textsubscript{2}Ln metalloocene complexes of unsubstituted phenyl ligands, Cp′\textsubscript{2}LnPh(THF) (Ln = Y, Dy) (Appendix B), and the attempted synthesis of a bimetallic bridging monoanionic benzene rare earth complexes with the aim of developing a new class of single molecule magnets (Appendix C).
**Introduction**

Common misconceptions about the rare earth metals (Sc, Y, lanthanides) are that they are scarce and by extension expensive, they are chemically well-understood, and generally uninteresting given their apparently limited range of oxidation states in comparison to transition metals.\(^1\) However, rare earth metals are not all that rare, as the lanthanides Ce, La, and Nd are more earth-abundant than Co and Pb, and the natural abundances of all of the rare earths are greater than Hg and the precious metals, Au, Ag, Pt, and Rh.\(^2\) Further, the U. S. Department of Energy has classified rare earth elements, Dy, Nd, Tb, Eu, and Y as critically important to clean energy technologies projected for 2015-2025.\(^3\) It is therefore great interest to study and understand the fundamental chemistry of these highly valuable rare earth metals.

One of the most important fundamental types of chemical reactivity is redox chemistry. The transfer of electrons affects the formal oxidation state of a species and allows many types of chemical reactions to be possible including important natural and industrial catalytic processes. It is therefore of fundamental importance to understand the limits of oxidation states and this has inspired extensive study across the periodic table, including the f block.

The predominant oxidation state for rare earth elements, Ln (Ln = Sc, Y, lanthanides), is +3, but it was discovered in 1906 that complexes of three of these elements, Eu, Yb, and Sm, could be isolated containing +2 ions.\(^4\) Progress toward synthesizing complexes of other Ln\(^{2+}\) ions as molecular species was intermittent. The next three, Tm\(^{2+}\), Dy\(^{2+}\), and Nd\(^{2+}\), were not observed as molecular species until 1997-2000.\(^5\)-\(^9\) An increase in the number of rare earth metals available in the +2 oxidation state beyond the traditional six divalent lanthanides, Eu\(^{2+}\), Yb\(^{2+}\), Sm\(^{2+}\), Tm\(^{2+}\), Dy\(^{2+}\), and Nd\(^{2+}\), began with the discovery by Lappert that silyl-cyclopentadienyl ligands were particularly suited to stabilize low-valent lanthanide ions. Preliminary evidence for
additional complexes of Ln$^{2+}$ was discovered when Lappert and co-workers isolated reduced arene species, Figure 0.1.a, that were theorized to be Ln$^{2+}$ complexes with bridging (C$_6$H$_6$)$^{1-}$ and (C$_6$H$_5$CH$_3$)$^{1-}$ ligands in 1998 and 2000, respectively, as $[(\text{LnCp}^\text{RR})_2(\mu-\eta^6:\eta^6$-C$_6$H$_5$R')]$^{1-}$ (Ln = La, R = 'Bu, R' = H; Ln = La, Ce, R = SiMe$_3$, R' = Me).$^{10,11}$ However, ambiguity regarding the oxidation state of the metal made it unclear if they were indeed Ln$^{2+}$ complexes.$^{10,11}$ Unequivocal evidence for La$^{2+}$ and Ce$^{2+}$ in molecular complexes was discovered in 2008$^{12}$ with the and (Cp''$_3$Ln)$^{1-}$ (Cp'' = C$_5$H$_5$(SiMe$_3$)$_2$-1,3; Ln = La, Ce),$^{12}$ Figure 0.1.a and Figure 0.1.b, respectively. The use of (Cp''$^{1-}$ ligand made clear the importance of the trimethylsilyl substituent on Cp, which led to the discovery other Ln$^{2+}$ complexes with (Cp')$^{1-}$, [K(18-crown-6)][Cp'$_3$Ln] (Cp' = C$_5$H$_4$SiMe$_3$; Ln = Y, Ho, Er.$^{13,14}$ Ultimately these complexes inspired the isolation of yttrium and all of the lanthanides (except radioactive promethium) in the +2 oxidation state for the first time in one system, [K(2.2.2-cryptand)][Cp'$_3$Ln] (Ln = Y, lanthanides), Figure 0.1.c.$^{13-15}$

![Diagram of complexes](image)

**Figure 0.1:** Anions of low-valent cyclopentadienyl lanthanide complexes a) $[(\text{LnCp}^\text{RR})_2(\mu-\eta^6:\eta^6$-C$_6$H$_5$R')]$^{1-}$, b) (Cp''$_3$Ln)$^{1-}$, and c) (Cp'$_3$Ln)$^{1-}$.

With the emergence of the +2 oxidation state for Y and all of the lanthanides (except radioactive promethium), the natural progression of characterizing the (Cp'$_3$Ln)$^{1-}$ species was to
examine the Ln$^{2+}$/Ln$^{3+}$ redox couple. However, as a result of their highly reactive nature, reproducible electrochemistry results were elusive. Traditionally, the reductive capacity of isolable rare earth reducing agents too reactive for electrochemical experiments has been tested against aromatic hydrocarbons of known reduction potential.\textsuperscript{16-20} For example, decamethylsamarocene, Sm(C$_5$Me$_5$)$_2$, was shown to reduce polycyclic aromatic hydrocarbons anthracene, pyrene, 2,3-benzantracene, 9-methylantracene, acenaphthylene, cyclooctatetraene, and stilbene.\textsuperscript{16,20,21} The chemistry of the LnA$_2$ (A = anion) system has also revealed unexpected byproducts, as was the case when the reduction of cyclooctatetraene by Sm(C$_5$Me$_5$)$_2$ produced the first tris(pentamethylcyclopentadienyl) metal complex, Sm(C$_5$Me$_5$)$_3$, eq 0.1.\textsuperscript{20} It was therefore of interest to study the reactivity of [K(2.2.2-crytand)][Cp$^*$Ln] and to determine if these complexes behaved analogously to the Ln$^{2+}$ ions of the LnA$_2$ system.

Other reducing agents based on the rare earth metals take advantage of the LnA$_3$/M system, where a Ln$^{3+}$ complex, LnA$_3$, is combined with an alkali metal, M, in situ. By this method, substrates of low reduction potential including dinitrogen,\textsuperscript{22-26} benzene,\textsuperscript{10,27,28} and toluene,\textsuperscript{11} have been reduced to form anions coordinated to rare earth metals. The products of these reactions have also afforded revealed interesting properties. Reduced dinitrogen species containing a dianionic (N$_2$)$_2^{-}$ ligand bridging two lanthanide centers has itself been shown to act as a reductant, reducing aromatic organic substrates phenazine, anthracene, eq. 0.2, and azobenzene, as well as the small molecule carbon monoxide.\textsuperscript{29} Further, bridging radical ligands
such as \((N_2)^{3-}\) or \((\text{arene})^{1-}\) between paramagnetic lanthanides have been shown to behave as single molecule magnets (SMMs).\(^{30}\) Although the \((\text{Cp}^\prime)^{1-}\) ligand was shown to support Ln\(^{2+}\) ions as isolable species, it remained to be seen if this apparent stabilizing effect could be harnessed by the LnA\(_3\)/M route to develop bridged arene reducing agents or radical SMMs.

The research presented in this dissertation has examined the reactivity of Ln\(^{2+}\) systems. Complexes of \((\text{Cp}^\prime_3\text{Ln})^{1-}\) were treated with polycyclic hydrocarbons of known reduction potential\(^{16-19}\) and were found to reduce naphthalene and biphenyl to form \([K(2.2.2\text{-cryptand})][\text{Cp}_2\text{Ln}(\eta^4\text{-C}_{10}\text{H}_8)]\) \((\text{Ln} = \text{Y}, \text{La}, \text{Ce}, \text{Dy})\) and \([K(2.2.2\text{-cryptand})][\text{Cp}_2\text{Y}(\eta^4\text{-C}_{10}\text{H}_8)]\), respectively.\(^{31}\) Although the isolation of a benzene anion was not observed directly from \((\text{Cp}^\prime_3\text{Ln})^{1-}\) complexes, the combination of \text{Cp}^\prime_3\text{Ln} with two equiv potassium in situ did reduced benzene by two electrons. This produced dianionic benzenide species bridging two Ln(II) metal centers, \([K(2.2.2\text{-cryptand})]_2[(\text{Cp}_2\text{Ln})_2(\mu-\eta^6:\eta^6\text{-C}_6\text{H}_6)]\) \((\text{Ln} = \text{La}, \text{Ce})\), which marks the discovery yet another Ln\(^{2+}\) system. Efforts to use the LnA\(_3\)/M system to make precursors to SMMs and bridging monoanionic benzenide species and are also described here as well as a solvent-free mechanochemical approach to synthesizing rare earth complexes.
References

Chapter 1

Reactivity of the Ln$^{2+}$ Complexes [K(2.2.2-cryptand)][(C$_5$H$_4$SiMe$_3$)$_3$Ln]:

Reduction of Naphthalene and Biphenyl

Introduction

From 2008-2013, the number of +2 ions available in the lanthanide series in soluble molecular complexes has been expanded from the traditional list of six, namely Eu$^{2+}$, Yb$^{2+}$, Sm$^{2+}$, Tm$^{2+}$, Dy$^{2+}$, and Nd$^{2+}$, to the rest of the lanthanides except radioactive promethium via the potassium-graphite reactions shown in equations 1.1 and 1.2. The availability of these complexes allowed the reaction chemistry of these new oxidation states to be investigated for the first time. The traditional way of investigating new oxidation states, by their electrochemistry, proved to be difficult with these highly reactive complexes.

† Portions of this chapter have been published: Kotyk, C. M., MacDonald, M. R., Ziller, J. W., Evans, W. J. Organometallics 2015, 34, 2287.
A traditional way to characterize reducing agents too reactive for reproducible electrochemistry is to treat them with polycyclic aromatic hydrocarbons of known reduction potential. This method was initially used to characterize the reactivity of \((C_5Me_5)_2Sm\) and subsequently used for \(NdI_2\) and \(DyI_2\). \((C_5Me_5)_2Sm\) can reduce anthracene \((-1.98 \text{ V vs SCE})\) to form \([((C_5Me_5)_2Sm)]_2(\mu-C_{14}H_{10})\), but it does not reduce naphthalene \((-2.60 \text{ V vs SCE})\). The stronger reductants, \(NdI_2\) and \(DyI_2\), reduce naphthalene in 1,2-dimethoxyethane (DME) and THF to produce \([NdI_2(THF)_3]_2(\mu-C_{10}H_8)\) and \((C_{10}H_8)DyI(DME)_2\), respectively. Although other reduced naphthalene complexes of the rare earth ions are known, their preparations either involve (a) initial reduction of naphthalene by an alkali metal followed by complexation to the rare earth metal ion or (b) addition of an alkali metal to a mixture of a \(Ln^{3+}\) complex and naphthalene, which could also involve reduction of naphthalene by the alkali metal.

In this Chapter, a description of the reductive power of the new \(Ln^{2+}\) complexes is presented by examining the reactivity of \([\text{K}(2.2.2\text{-cryptand})][\text{Cp}'_3\text{Ln}]\), \(1-Ln\), with naphthalene and biphenyl \((-2.60 \text{ V and } -2.80 \text{ V vs SCE})\) respectively. Yttrium was the initial metal of choice due to its favorable NMR characteristics associated with a 100% naturally abundant \(I = \frac{1}{2}\) \(^{89}\text{Y}\) nucleus. To contrast the chemistry of this smaller rare earth ion with that of larger metal ions, the analogous reactions with the largest lanthanides, lanthanum and cerium, were examined. The dysprosium analog was also studied as a typical open-shell lanthanide and a
member of the set of traditional six Ln\(^{2+}\) ions described above. Not only was reduction of aromatic substrates observed, but these reactions also led to the isolation of the tetrakis(trimethylsilylcyclopentadienyl) complexes, (Cp\(^{1}\))Ln\(^{1-}\).

Results

Naphthalene Reduction By Y\(^{2+}\). Dark maroon [K(2.2.2-cryptand)][Cp\(^{3}\)Y], 1-Y, reacts with naphthalene to form a deep blue solution from which black crystals of [K(2.2.2-cryptand)][Cp\(^{2}\)Y(\(\eta^{4}\)-C\(_{10}\)H\(_{8}\))], 2-Y, Figure 1.1, colorless crystals of [K(2.2.2-cryptand)][Cp\(^{4}\)Y], 3-Y, Figure 1.2, and colorless crystals of [K(2.2.2-cryptand)][Cp\(^{1}\)], 4, Figure 1.3, could be isolated. Each of these products was crystallized from the same reaction mixture and definitively identified by X-ray diffraction. Since these complexes have solubility similar enough to preclude quantitative separation, each was also independently synthesized in pure form for full analytical and spectroscopic characterization as described below. The formal stoichiometric transformation of the anion in 1-Y to the anions in 2-Y and 3-Y is shown in equation 1.3.

The structural parameters on 2-Y, discussed below, are consistent with the presence of a (C\(_{10}\)H\(_{8}\))\(^{2-}\) dianion, which indicates that the Y\(^{2+}\) ion in 1-Y can reduce naphthalene by two electrons. Since the reduction requires two equiv of 1-Y and forms a bis(cyclopentadienyl) naphthenidene complex from tris(cyclopentadienyl) precursors, one yttrium center must lose a (Cp\(^{1}\))\(^{1-}\) anion in the reduction process. If that (Cp\(^{1}\))\(^{1-}\) anion is trapped by Cp\(^{5}\)Y, an intermediate
that could be present after an equivalent of 1-Y has transferred an electron, this would form 3-Y, the stoichiometric byproduct shown in equation 1.3. If the (Cp')\(^{-1}\) anion does not form 3-Y, the anion can form [K(2.2.2-cryptand)][Cp'], 4, which is also isolated as a byproduct. \(^1\)H NMR analysis of the crude reaction mixture with cyclooctane as an internal standard shows that the yield of 2-Y is about 67% yield of that expected based on the stoichiometry of equation 1.3. 2-Y and 3-Y are present in a 1:1 ratio, but after crystallization, NMR analysis of a solution of the recovered crystals reveals a 5:1 molar ratio of 2-Y to 3-Y while the dried mother liquor showed extensive decomposition.

![Molecular structure of the anion of 2-Y, [Cp\(_{2}\)Y(\(\eta^4\)-C\(_{10}\)H\(_8\))]\(^{-1}\). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.](image)

**Figure 1.1.** Molecular structure of the anion of 2-Y, [Cp\(_{2}\)Y(\(\eta^4\)-C\(_{10}\)H\(_8\))]\(^{-1}\). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.
Figure 1.2. Molecular structure of $[\text{K}(2.2.2\text{-cryptand})][\text{Cp}_4\text{Y}]$, 3-Y, with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity.

Figure 1.3. Molecular structure of $[\text{K}(2.2.2\text{-cryptand})][\text{Cp}_4]$, 4, with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity.
Independent Synthesis of Reaction Products. [K(2.2.2-cryptand)][Cp’5Y(η4-C10H8)], 2-Y, was synthesized in pure form using a route commonly successful with bis(pentamethylcyclopentadienyl) metallocene complexes, namely the displacement of a (BPh₄)⁻ anion from (C₅Me₅)₂Ln(μ-Ph₂BPh₂).²⁰⁻²⁷ The necessary precursor bis(trimethylsilylcyclopentadienyl)yttrium tetraphenylborate salt, [Cp’₂Y(THF)]₂[BPh₄], 5-Y,² did not require desolvation to make a direct analog of (C₅Me₅)₂Ln(μ-Ph₂BPh₂)²⁰⁻²⁷ for this reaction. A mixture of [Cp’₂Y(THF)]₂[BPh₄], naphthalene, and 2.2.2-cryptand reacts with potassium graphite in THF within 30 min to generate a deep blue solution from which black crystals of 2-Y were grown, eq 3.4. The ¹H NMR spectrum of 2-Y shows sets of resonances characteristic of Cp’ and 2.2.2-cryptand as well as resonances at 5.76, 5.64, 5.07, and 3.47 ppm of equal intensity consistent with the naphthalenide dianion identified by X-ray crystallography, Figure 1.1. The ¹³C {¹H} NMR spectrum of 2-Y had a doublet resonance at 63.0 ppm consistent with coupling to yttrium with ¹JYC = 25.4 Hz. This is in the range of coupling expected for Y–C bonds.²⁸⁻³³

$$\begin{align*}
\text{[Cp’₂Y(THF)]₂[BPh₄]} &\quad + 2 \text{KC₈} \\
&\quad + 2 \text{(2.2.2-cryptand)} \\
&\quad + \text{THF, Ar, rt} \\
&\quad - \text{graphite} \\
&\quad - \text{[K(2.2.2-cryptand)]}[BPh₄] \\
&\quad \rightarrow \text{2-Y}
\end{align*}$$

[K(2.2.2-cryptand)][Cp’₄Y], 3-Y, was synthesized by reacting Cp’₃Y with KCp’ and 2.2.2-cryptand, eq 3.5. Complex 3-Y could be obtained in 86% yield as a colorless crystalline solid. The ¹H NMR spectrum of 3-Y shows a single set of Cp’ resonances that indicate that all Cp’ rings are equivalent in solution at room temperature. Since the solid-state structure,
discussed below, has both $\eta^1$ and $\eta^5$ rings, the ligands must be fluxional in solution. The $^1$H NMR spectrum at 175 K shows a 3:1 ratio of Me$_3$Si resonances consistent with the solid-state structure.

The third product of the reaction of 1-Y with naphthalene, namely [K(2.2.2-cryptand)][Cp'], 4, was independently synthesized by reaction of KCp’ with 2.2.2-cryptand in 96% yield, eq 3.6.

$$
\text{KCp'} + \text{2.2.2-cryptand} \xrightarrow{\text{THF, rt}} [\text{K(2.2.2-cryptand)][Cp']} \quad (1.6)
$$

**Lanthanum, Cerium, and Dysprosium.** 1-La, 1-Ce, and 1-Dy$^{19}$ react similarly with naphthalene to make the reduced naphthalenide complexes 2-La, 2-Ce, and 2-Dy in analogy to equation 1.3, Figure 1.4, Figure 1.5, Figure 1.6., respectively. The reduction of naphthalene in each case was confirmed by crystallographic identification. Complex 2-Dy is isomorphous with 2-Y. Complexes 2-La and 2-Ce are structurally similar to 2-Y, but the lanthanum complex crystallizes with THF in the lattice and the cerium complex has Et$_2$O in the lattice.
Figure 1.4. Molecular structure of the anion of 2-La, $[\text{Cp}'_2\text{La}(\eta^4\text{-C}_{10}\text{H}_8)]^{1-}$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and disordered atoms in Cp' and naphthalenide ligands omitted for clarity.

Figure 1.5. Molecular structure of the anion of 2-Ce, $[\text{Cp}'_2\text{Ce}(\eta^4\text{-C}_{10}\text{H}_8)]^{1-}$. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms omitted for clarity.
Figure 1.6. Molecular structure of the anion of 2-Dy, [Cp’₂Dy(η⁴-C₁₀H₈)]⁻. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms omitted for clarity.

In the La, Ce, and Dy reactions analogous to equation 1.3, colorless byproduct crystals are also observed. Only in the lanthanum case were these crystals suitable for X-ray analysis. These crystals were identified as [K(2.2.2-cryptand)][Cp’₅La], 3-La, by X-ray diffraction, Figure 1.7. ¹H NMR analysis of the crude lanthanum reaction mixture shows that 2-La and 3-La are present in a 1:1 ratio. After crystallization, ¹H NMR analysis of a solution of the recovered crystals reveals a 47:1 molar ratio of 2-La to 3-La, while the dried mother liquor had a 1:33 molar ratio.

Complex 3-La was also synthesized independently in analogy to equation 1.5. Like 3-Y, 3-La displays a single set of cyclopentadienyl resonances in the ¹H NMR spectrum showing the rings are not locked into one configuration in solution. However, in the solid state, the larger lanthanum has all the (Cp)⁻⁻ rings in a pentahapto binding mode as discussed in the next section.
Figure 1.7. Molecular structure of [K(2.2.2-cryptand)][Cp′₄La], 3-La, with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity.

Crystallographic Data on the Naphthalene Reaction Products. Structural data for the [K(2.2.2-cryptand)][Cp′₂Ln(η⁴-C₁₀H₈)] complexes, 2-Ln (Ln = La, Ce, Dy, Y), are compared in Table 1.1. Disorder in the lanthanum complex, 2-La, prevented detailed comparison of the coordinated naphthalenide ligand.

In each 2-Ln complex, a (Cp′₂Ln)⁺ metallocene unit is oriented toward four carbon atoms of one ring of the C₁₀ unit. The shortest Ln–C distances in each complex are Ln–C₁₇ and Ln–C₂₀ with Ln–C₁₈ and Ln–C₁₉ being the next shortest lengths. All four of these Ln–C distances are much shorter than the average Ln–C(Cp′) distances. For example, the values for 2-Y are 2.517(2) Å (Y–C₂₀), 2.528(2) Å (Y–C₁₇), 2.619(2) Å (Y–C₁₉), and 2.633(2) Å (Y–
C18) compared to 2.725(7) Å for the average Y–C(Cp') distance. In contrast, the 3.042(2) Å Y–C21 and 3.060(2) Å Y–C26 distances involving the carbon atoms closest to yttrium in the planar C6 ring are significantly longer than the Y–C(Cp')avg length, 2.725(7) Å, i.e. the C21-C26 ring does not have a significant interaction with the metal.

Table 1.1. Selected Bond Distances (Å) and Angles (°) for [K(2.2.2-cryptand)][Cp'2Ln(η4-C10H8)], 2-Ln (Ln = La, Ce, Dy, Y).

<table>
<thead>
<tr>
<th></th>
<th>2-La</th>
<th>2-Ce</th>
<th>2-Dy</th>
<th>2-Y</th>
</tr>
</thead>
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<tr>
<td>Ln1–Cnt1</td>
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<tr>
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<td>2.437</td>
<td>2.433</td>
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<td>2.114</td>
<td>2.098</td>
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<td>2.837(2)</td>
<td>2.731(7)</td>
<td>2.725(7)</td>
</tr>
<tr>
<td>Ln1–C17</td>
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<td>2.622(2)</td>
<td>2.543(4)</td>
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</tr>
<tr>
<td>Ln1–C18</td>
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</tr>
<tr>
<td>Ln1–C19</td>
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</tr>
<tr>
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<td>2.519(3)</td>
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</tr>
<tr>
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<td>3.024(2)</td>
<td>3.071(3)</td>
<td>3.042(2)</td>
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<tr>
<td>Ln1–C26</td>
<td>3.052(3)</td>
<td>2.992(2)</td>
<td>3.076(3)</td>
<td>3.060(2)</td>
</tr>
<tr>
<td>C18–C19</td>
<td>1.371(3)</td>
<td>1.363(5)</td>
<td>1.358(4)</td>
<td>1.358(4)</td>
</tr>
<tr>
<td>C17–C18</td>
<td>1.453(3)</td>
<td>1.456(5)</td>
<td>1.459(4)</td>
<td>1.459(4)</td>
</tr>
<tr>
<td>C19–C20</td>
<td>1.440(3)</td>
<td>1.449(5)</td>
<td>1.449(4)</td>
<td>1.449(4)</td>
</tr>
<tr>
<td>C20–C21</td>
<td>1.474(3)</td>
<td>1.474(5)</td>
<td>1.465(4)</td>
<td>1.465(4)</td>
</tr>
<tr>
<td>C17–C26</td>
<td>1.473(3)</td>
<td>1.453(6)</td>
<td>1.467(3)</td>
<td>1.467(3)</td>
</tr>
<tr>
<td>C21–C22</td>
<td>1.403(3)</td>
<td>1.386(5)</td>
<td>1.406(4)</td>
<td>1.406(4)</td>
</tr>
<tr>
<td>C21–C26</td>
<td>1.435(3)</td>
<td>1.442(5)</td>
<td>1.407(4)</td>
<td>1.407(4)</td>
</tr>
<tr>
<td>C22–C23</td>
<td>1.389(3)</td>
<td>1.400(5)</td>
<td>1.378(4)</td>
<td>1.378(4)</td>
</tr>
<tr>
<td>C23–C24</td>
<td>1.388(3)</td>
<td>1.377(6)</td>
<td>1.379(4)</td>
<td>1.379(4)</td>
</tr>
<tr>
<td>C24–C25</td>
<td>1.391(3)</td>
<td>1.387(6)</td>
<td>1.380(4)</td>
<td>1.380(4)</td>
</tr>
<tr>
<td>C25–C26</td>
<td>1.399(3)</td>
<td>1.404(5)</td>
<td>1.402(3)</td>
<td>1.402(3)</td>
</tr>
<tr>
<td>Cnt1–Ln1–Cnt2</td>
<td>117.3</td>
<td>117.5</td>
<td>118.7</td>
<td>118.7</td>
</tr>
<tr>
<td>Pln1–Pln2</td>
<td>155.5</td>
<td>154.8</td>
<td>147.4</td>
<td>145.5</td>
</tr>
</tbody>
</table>

*Cnt1 and Cnt2 are the centroids of the cyclopentadienyl groups labeled (C1-C5) and (C9-C13), respectively.
*Mid1 is the midpoint of the vector between C17 and C20.
*Not available due to disorder
*Pln1 and Pln2 are the planes of (C17-C20) and (C17, C20-C26), respectively.
Bond distances in the analogous lanthanide complexes, **2-La**, **2-Ce**, and **2-Dy** follow similar trends and change as expected on the basis of their ionic radii: La, 1.22 Å; Ce, 1.20 Å; Dy, 1.08 Å; Y, 1.08 Å (9-coordinate radii). For example, the distance of the metal to the midpoint of the C17–C20 vector (Mid1) decreases with the ionic radius: 2.230 Å (La); 2.225 Å (Ce); 2.114 Å (Dy); 2.098 Å (Y).

Examination of the C–C distances in the naphthalenide ligands of **2-Ce**, **2-Dy**, and **2-Y** reveals that the C18–C19 distances are the shortest with a range of 1.358(4)-1.371(3) Å. This suggests some localization in the non-planar C6 ring (C17-C21, C26) with negative charge on both C17 and C20 and more double bond character in C18–C19. This has been observed in other monometallic rare earth naphthalenide complexes such as (C$_3$H$_5$)Lu(C$_{10}$H$_8$)(DME)$_3$ and (C$_{10}$H$_8$)DyI(DME)$_2$ and in the terminal naphthalenide ligands of the triple-decker naphthalene complex \{[Tm(DME)]$_2$(η$^2$-C$_{10}$H$_8$)$_2$(μ-η$^4$:η$^4$-C$_{10}$H$_8$)\}. The four carbon atoms, C17-C20, of the C6 ring closest to the rare earth metal are not coplanar with the remaining six carbon atoms, C21-C26. The angle between the plane of C17-C20 (Pln1) and the plane of C17 and C20-C26 (Pln2) decreases with radial size resulting in a more bent structure for the smaller metals: 155.5° (La); 154.8° (Ce); 147.4° (Dy); 145.5° (Y). This increased bending may reflect a greater polarization of the (C$_{10}$H$_8$)$_2^-$ dianion by the more Lewis acidic smaller metals.

The two tetrakis(trimethylsilylcyclopentadienyl) complexes, \[K(2.2.2-cryptand)][Cp'4Ln], **3-Y** and **3-La**, differ in the solid state in that **3-Y** has three (η$^5$-Cp')$^{1-}$ligands and one (η$^1$-Cp')$^{1-}$ ligand, whereas all four (Cp')$^{1-}$ ligands are bound η$^5$ in the complex of the larger metal, lanthanum. The coordination environment of the ion in **3-Y** resembles that in the polymeric complex \[(C_3H_5)_3Ln\]$_n$ (Ln = Lu, Sc) and the tetrameric methylcyclopentadienyl
complexes [(C₅H₄Me)₃Ce]₄³⁷ and [(C₅H₄Me)₃La]₄³⁸ where three η⁵- and one η¹-cyclopentadienyl ligands are also present. The structure of 3-La is similar to the monomeric actinide complexes, Cp₄U³⁹ and Cp₄Th⁴⁰ (Cp = C₅H₅), where each metal center is bound to four (η⁵-Cp)¹⁻ ligands.

Complex 3-Y has a 2.479(10) Å Y–(η⁵-Cp′ Cntavg) bond length similar to that of 2-Y, 2.447(5) Å, but the 2.724(4) Å distance in 3-La is significantly longer than that in 2-La, 2.601(3) Å. The La–(η⁵-Cp′ Cntavg) distance in 3-La is even longer than the 2.642 Å distance in stERICALLY crowded (C₅Me₅)₃La.⁴¹ The 0.245 Å difference in Ln–(η⁵-Cp′ Cntavg) distances of 3-Y and 3-La is significantly greater than the difference in their 9-coordinate radii, 0.141 Å, a result of the different [(η⁵-Cp′)₃(η¹-Cp′)Y]¹⁻ vs. [(η⁵-Cp′)₄La]¹⁻ structures.

The structure of [K(2.2.2-cryptand)][Cp′], 4, Figure 1.3, contains a cyclopentadienyl ring that is not near the counteration since the potassium is encapsulated in the cryptand ligand. Several structures of isolated cyclopentadienyl ligands are in the literature⁴²-⁴⁸ and the effect of Me₃Si groups in providing "naked" cyclopentadienyls has been discussed.⁴⁷ The C–C and C–Si bond distances in 4 are similar to those in (LiCp′)-TMEDA⁴⁸ and polymeric (LiCp′)ₙ⁴⁹ and (KCP′)ₙ⁵⁰, Table 1.2. Evidently, encapsulation of the cation in 4 by the cryptand to isolate it from the cyclopentadienyl anion does not affect bond distances compared to the alkali metal bridged complexes.

**Table 1.2.** Selected Bond Distances (Å) for (LiCp′)-TMEDA,⁴⁸ (LiCp′)ₙ⁴⁹ (KCP′)ₙ⁵₀ and [K(2.2.2-cryptand)][Cp′], 4.

<table>
<thead>
<tr>
<th></th>
<th>(LiCp′)-TMEDA</th>
<th>(LiCp′)ₙ</th>
<th>(KCP′)ₙ</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–Cnt, M= Li, K</td>
<td>1.92</td>
<td>1.96</td>
<td>2.78</td>
<td>7.063</td>
</tr>
<tr>
<td>C–C range</td>
<td>1.38(1)-1.421(8)</td>
<td>1.400(5)-1.436(5)</td>
<td>1.368-1.442</td>
<td>1.398(2)-1.424(2)</td>
</tr>
<tr>
<td>C–C_avg</td>
<td>1.38(1)</td>
<td>1.41(1)</td>
<td>1.408</td>
<td>1.410(3)</td>
</tr>
<tr>
<td>Si–C(Cp′)</td>
<td>1.825(6)</td>
<td>1.858(3)</td>
<td>1.820</td>
<td>1.8285(16)</td>
</tr>
</tbody>
</table>
Biphenyl Reduction. No color change is observed when biphenyl is added to a dark maroon solution of \([\text{K}(2.2.2\text{-cryptand})][\text{Cp}^3\text{Y}],\) 1-Y, in THF, but reaction indeed occurs as evidenced by the isolation of black crystals of \([\text{K}(2.2.2\text{-cryptand})][\text{Cp}^2\text{Y}(\eta^6\text{-C}_6\text{H}_5\text{Ph})],\) 6-Y, Figure 1.8, eq 1.7. The reaction is similar to the naphthalene reaction in equation 1.3, except that now a biphenyl dianion, \((\eta^6\text{-C}_6\text{H}_5\text{Ph})^2^-\), is formed as shown by the crystallographic data described below. In contrast to the naphthalene reduction described above, neither the tetrakis(cyclopentadienyl) byproduct, 3-Y, nor the potassium cyclopentadienide, 4, were isolated in these reactions, although other byproducts were present that proved difficult to identify definitively. The yield of 6-Y is 67% as determined by an NMR-scale reaction with a cyclooctane internal standard.

![Molecular structure of the anion of 6-Y, \([\text{Cp}^2\text{Y}(\eta^6\text{-C}_6\text{H}_5\text{Ph})]^{1-}\). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms and co-crystallized Et_2O are omitted for clarity.](image-url)
Attempts to synthesize 6-Y independently from a mixture of [Cp’₂Y(THF)₂][BPh₄], 5-Y, biphenyl, 2.2.2-cryptand, and KC₈ in THF in analogy to equation 1.4 were unsuccessful. A red color change was observed, but only colorless crystals of [K(2.2.2-cryptand)][BPh₄], 7, were isolated, Figure 1.9.

**Figure 1.9.** Molecular structure of [K(2.2.2-cryptand)][BPh₄], 7, with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity.
Crystallographic Data on [K(2.2.2-cryptand)][Cp’₂Y(η⁶-C₆H₅Ph)], 6-Y. Structures of reduced biphenyl anions are rare in the literature. To our knowledge, they are all bimetallic complexes: in some cases with one metal coordinated to each ring, e.g. \([\{P₂N₂]Ln\}_2\{\eta^6:\eta^6’-(C₆H₅)₂\} \quad (Ln = Y, \text{Ho, Lu}; \quad P₂N₂ = \text{PhP(CH₂SiMe₂NSiMe₂CH₂)}_2\text{PPh})\), and in other cases with both metals coordinated to a single ring, e.g. \([\{P₂N₂]Y\}_2\{\eta^6:\eta^6’-\text{C₆H₄Me-4'}\} \quad \text{[}((\text{NN}^{\text{fc}})\text{Ln}]_2\text{K(toluene)}\}_2(\mu\text{-biphenyl}) \quad (Ln = \text{Sc, Y, La, Lu}; \quad \text{NN}^{\text{fc}} = \{\text{C₃H₄}[\text{N(SiBuMe}_2)]\}_2\text{Fe})\), and \([\text{K(18-crown-6)(THF)}_2\text{[}((\text{NN}^{\text{fc}})\text{Y}]_2(\mu\text{-biphenyl})]\). \text{6-Y appears to be the first rare earth example of a monometallic biphenylide complex, Figure 1.6.}

Structural data on \text{6-Y} are presented in Table 1.3. The phenyl ring oriented toward the \((\text{Cp’}_2\text{Y})^{1+}\) cation involving C17-C22 is non-planar with a boat-like structure and an angle of 153.3° between the plane defined by C17, C18, C19, and C22 and the plane of C19, C20, C21, and C22. The common atoms of these two planes make the shortest connections to yttrium, i.e., the 2.480(2) Å Y–C19 and 2.561(2) Å Y–C22 distances. The other four carbon atoms have Y–C distances in the range 2.697(2)-2.730(2) Å, which are comparable to the 2.733(8) Å Y–C(Cp’) average distance in this complex. The 1.355(3) Å C17–C18 distance and the 1.353(3) Å C20–C21 distance are the shortest C–C bonds in this ring and are in the double bond range. The other four C–C bonds are in the range 1.444(4)-1.466(3) Å. Hence, this ring has a localized structure consistent with a dianion with negative charge at both C19 and C22.

The structure is like that in the naphthalene complexes \text{2-Ln} except that all six carbons of the ring are oriented toward yttrium. The dianionic ring of the biphenylide ligand is also similar in geometry and bond distances to a \((C₆H₆)_2^{2-}\) "benzene 1,4-dianion" described by Lappert and co-workers in the complex \([\text{K(18-crown-6)}]\text{[}([\text{C₅H₃(SiMe}_3]_2}\text{La(C₆H₆)}), \text{Table 1.4.}

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Table 1.3. Selected Bond Distances (Å) and Angles (°) for [K(2.2.2-cryptand)][Cp'2Y(η6-C6H5Ph)], 6-Y.

| 6-Y |  |
|-----|-----|-----|
| Y1–Cnt1<sup>a</sup> | 2.467 | C17–C18 | 1.355(3) |
| Y1–Cnt2<sup>a</sup> | 2.442 | C17–C22 | 1.464(3) |
| Y1–Mid1<sup>b</sup> | 2.057 | C18–C19 | 1.450(3) |
| Y1–C17 | 2.716(2) | C19–C20 | 1.444(4) |
| Y1–C18 | 2.697(2) | C20–C21 | 1.353(3) |
| Y1–C19 | 2.480(2) | C21–C22 | 1.466(3) |
| Y1–C20 | 2.716(2) | C22–C23 | 1.460(3) |
| Y1–C21 | 2.730(2) | C23–C24 | 1.415(3) |
| Y1–C22 | 2.561(2) | C23–C28 | 1.422(3) |
| Cnt1–Ln1–Cnt2 | 117.2 | C24–C25 | 1.372(4) |
| Pln1–(C19, C22)–Pln2<sup>c</sup> | 153.3 | C25–C26 | 1.391(4) |
|  |  | C26–C27 | 1.385(4) |
|  |  | C27–C28 | 1.371(4) |

<sup>a</sup>Cnt1 and Cnt2 are the centroids of the cyclopentadienyl rings (C1-C5) and the centroids of the cyclopentadienyl rings (C1-C5) and (C9-C13).

<sup>b</sup>Mid1 is the midpoint of vector between C19 and C22.

<sup>c</sup>Pln1 and Pln2 are the planes of (C17-C19, C22) and (C19–C22).

Table 1.4. Comparison of C–C bond distances (Å) in the coordinated biphenylide ring of 6-Y and the (C6H6)<sup>2−</sup> dianion in {[C5H3(SiMe3)2]2La(C6H6)<sup>1−</sup>}<sup>54</sup>

<table>
<thead>
<tr>
<th>6-Y</th>
<th>{[C5H3(SiMe3)2]2La(C6H6)&lt;sup&gt;1−&lt;/sup&gt;}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C17–C18</td>
<td>1.355(3)</td>
</tr>
<tr>
<td>C18–C19</td>
<td>1.450(3)</td>
</tr>
<tr>
<td>C19–C20</td>
<td>1.444(4)</td>
</tr>
<tr>
<td>C20–C21</td>
<td>1.353(3)</td>
</tr>
<tr>
<td>C21–C22</td>
<td>1.466(3)</td>
</tr>
<tr>
<td>C22–C17</td>
<td>1.464(3)</td>
</tr>
</tbody>
</table>
The other C6 ring in 6-Y has 1.371(4)-1.422(3) Å C–C bond distances with a 1.393(7) Å average that is consistent with a normal phenyl substituent on the benzene dianion composed of C17-C22. The 1.460(3) Å C22–C23 bond connecting the two rings is typical for a Csp2–Csp2 bond.

**Discussion**

The reduction of naphthalene by the complexes [K(2.2.2-crypt)][Cp’,Ln], 1-Ln, (Ln = La, Ce, Dy, Y), demonstrates that the new Ln2+ rare earth ions in these complexes are powerful reducing agents. They are more reactive than (C5Me5)2Sm, which can reduce stilbene (~2.22 V vs. SCE) but not naphthalene, and are at least as reducing as NdI2 and DyI2. Structural data on the reduced naphthalene products, 2-Ln, are consistent with two-electron reduction. Since the two electrons come from two equiv of 1-Ln and the aromatic reduction product contains only one (Cp’2Ln)1+ unit, the formal byproducts from the two equiv of 1-Ln are (Cp’)1− and Cp’,Ln. In the case of the Y and La reactions, these byproducts can be observed together in the form of the tetrakis(cyclopentadienyl) complexes, (Cp’4Ln)1−, 3-Ln, identified by NMR and X-ray crystallography. Since [K(2.2.2-crypt)][Cp’] is also found as a byproduct, the capture of the (Cp’)1− by Cp’2Ln to make 3-Ln is not the only fate of the byproducts.

Although the reaction of 1-Ln with naphthalene leads to new reduced aromatic complexes and demonstrates the reduction power of 1-Ln, the formation of 3-Ln as a stoichiometric byproduct with 2-Ln limits the synthetic utility of these reactions. Therefore it is fortunate that the naphthalenide complex, 3-Ln, can be made independently from the solvated cation, [Cp’2Y(THF)2][BPh4], 5-Y. Interestingly, this Cp’ metallocene cation can display the chemistry of the unsolvated (C5Me5)1− metallocene cations, (C5Me5)2Ln(µ-Ph2)BPh2,20-27
without the need for THF desolvation. The \((\text{Cp}'_4\text{Ln})^{1^-}\), \textbf{3-Ln}, byproduct complexes also can be made independently for yttrium and lanthanum. Although \text{Cp}_4\text{U}^{39} \text{ and } \text{Cp}_4\text{Th}^{40} \text{ are known and examples exist of polymeric rare earth and actinide complexes that show the metal center interacting with four cyclopentadienyl ligands,}^{36-38,56} \text{ complexes } \textbf{3-Y} \text{ and } \textbf{3-La} \text{ are the first examples of monomeric rare earth } [(\text{C}_5\text{R}_5)_4\text{Ln}]^{1^-} \text{ species. The lanthanum and yttrium examples of } (\text{Cp}'_4\text{Ln})^{1^-}, \textbf{3-Y} \text{ and } \textbf{3-La}, \text{ clearly show the effects of the lanthanide contraction on structure since the lanthanum complex has an } [(\eta^5\text{-Cp}')_3\text{La}]^{1^-} \text{ structure while yttrium has one } \eta^1\text{-ring, } [(\eta^5\text{-Cp}')_3(\eta^1\text{-Cp}')\text{Y}]^{1^-}.

The reduction of biphenyl by \textbf{1-Y} \text{ not only demonstrates that } \text{Y}^{2+} \text{ can reduce substrates with more negative reduction potentials than naphthalene, but it also leads to a previously unobserved type of biphenyldie complex, } \textbf{6-Y}. \text{ The fact that this complex has just one metal coordinated to just one ring differentiates it from other } [(\text{C}_6\text{H}_5)_2]^{2^-} \text{ complexes in the literature. This dianion is typically isolated in bimetallic complexes with metals on both sides of the } \text{C}_6 \text{ rings.}^{51-53} \text{ Whether the unique structure arises due to the } (\text{Cp}')_{1^-} \text{ ancillary ligands or from the reductive pathway provided by } \text{Y}^{2+} \text{ remains to be determined as more examples are defined.}

\textbf{Conclusion}

The [K(2.2.2-cryptand)][\text{Cp}'_3\text{Ln}] \text{ complexes of the new Ln}^{2+} \text{ ions are powerful reductants capable of reducing naphthalene and biphenyl. Their reductive chemistry to form complexes of the naphthalenide dianion, } (\eta^4\text{-C}_{10}\text{H}_8)^{2^-}, \text{ that are characterizable by X-ray crystallography shows that the } (\text{C}_5\text{H}_4\text{SiMe}_3)^{1^-} \text{ ancillary ligand used to make the Ln}^{2+} \text{ complexes is suitable to fully define reductive reaction products as has been previously demonstrated with the } (\text{C}_3\text{Me}_3)^{1^-} \text{ auxiliary ligand. The isolation of a complex containing the } (\eta^6\text{-C}_6\text{H}_5\text{Ph})^{2^-} \text{ dianion for the first}
time by this route demonstrates that these Ln$^{2+}$ species can lead to new options in reduction chemistry.

**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 argon (Praxair) 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 prior to use. Anhydrous LnCl$_3$ (Ln = Y, La, Ce, Dy),$^{57}$ KCp’ (Cp’ = C$_5$H$_4$SiMe$_3$),$^{58}$ KC$_8$,$^{59}$ Cp’$_3$Ln (Ln = Y,$^2$ La,$^{58}$ Ce,$^{37}$ Dy$^{19}$), [K(2.2.2-cryptand)][Cp’$_3$Y]·THF, 1-Y, (Ln = Y, La, Ce, Dy),$^{4,19}$ and [Cp’$_2$Y(THF)$_2$][BPh$_4$],$^{2}$ were prepared according to the literature. 2.2.2-Cryptand, (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane), (Aldrich) was placed under vacuum (10$^{-3}$ Torr) for 12 h before use. $^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) 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 Perkin-Elmer 2400 Series II CHNS elemental analyzer.

**Reaction of 1-Y with Naphthalene.** In a glovebox, a solution of naphthalene (5 mg, 0.04 mmol) in THF (3 mL) was added to a stirred dark maroon solution of [K(2.2.2-cryptand)][Cp’$_3$Y]·THF, 1-Y, (67 mg, 0.068 mmol) in THF (3 mL). The solution was stirred for 5 min, during which time it turned deep blue. The solvent was removed under vacuum and the resulting deep blue oil was redissolved in Et$_2$O (3 mL) and stored at −35 °C. Black crystals, identified as [K(2.2.2-cryptand)][Cp’$_2$Y($\eta^4$-C$_{10}$H$_8$)], 2-Y, by X-ray crystallography, deposited
overnight. Colorless crystals were also isolated and found to be [K(2.2.2-cryptand)][Cp’4Y], 3-Y, and [K(2.2.2-cryptand)][Cp’], 4, by X-ray crystallography and 1H NMR spectroscopy (see below). The similar solubilities of these complexes did not allow analytically pure samples to be obtained by this route.

[K(2.2.2-cryptand)][Cp’2Y(η^4-C_{10}H_{8})], 2-Y. In a glovebox, naphthalene (25 mg, 0.20 mmol), 2.2.2-cryptand (148 mg, 0.393), and [Cp’2Y(THF)][BPh_{4}]_2 (162 mg, 0.196 mmol), were dissolved in THF (8 mL). Addition of KC_8 (53 mg, 0.39 mmol) to this stirred solution caused an immediate color change to deep blue. After 30 min, the mixture was filtered to remove black solids and the solvent was slowly removed under vacuum until the volume was 0.5 mL. Et_2O (5 mL) was added and the solution was allowed to sit at room temperature for 1 h during which time [K(2.2.2-cryptand)][BPh_{4}], 5, formed as a colorless precipitate that was identified by X-ray crystallography. The deep blue solution was filtered again and stored at −35 °C for 2 days producing analytically pure 2-Y as black crystals (53 mg, 30%). 1H NMR (THF-d_8): δ 5.99 (m, C_5H_4SiMe_3, 2H), 5.76 (s, C_{10}H_8, 2H), 5.64 (s, C_{10}H_8, 2H), 5.57 (m, C_5H_4SiMe_3, 4H), 5.07 (s, C_{10}H_8, 2H), 3.85 (m, C_5H_4SiMe_3, 2H), 3.56 (s, OCH_2CH_2O, 12H), 3.52 (t, ^3J_{HH} = 4.5 Hz, NCH_2CH_2O, 12H), 3.47 (s, C_{10}H_8, 2H), 2.54 (t, ^3J_{HH} = 4.5 Hz, NCH_2CH_2O, 12H), 0.16 (s, C_5H_4SiMe_3, 18H). 13C NMR (THF-d_8): δ 145.2 (C_5H_4SiMe_3), 120.8 (C_5H_4SiMe_3), 117.8 (C_5H_4SiMe_3), 117.4 (C_5H_4SiMe_3, C_{10}H_8), 113.4 (C_5H_4SiMe_3), 109.5 (C_{10}H_8), 106.9 (C_{10}H_8), 71.4 (OCH_2CH_2O), 68.5 (NCH_2CH_2O), 63.0 (d, ^1J_{CY} = 25.4 Hz, C_{10}H_8), 54.8 (NCH_2CH_2O), 1.9 (C_5H_4SiMe_3), 1.7 (C_5H_4SiMe_3). IR: 3080w, 3036w, 2947m, 2885m, 2816m, 2361w, 1557w, 1478w, 1447m, 1359m, 1299w, 1262s, 1241s, 1183m, 1135m, 1105s, 1037s, 1007w, 950s, 933m, 905m, 832s, 762s, 736s, 683m, 628m, 590m, 525s cm\(^{-1}\). Anal. Calcd for C_{44}H_{70}N_2O_6KSi_2Y, 2-Y: C, 58.25; H, 7.78; N, 3.09. Found: C, 57.98; H, 7.65; N, 3.09.
[K(2.2.2-cryptand)][Cp′₄Y], 3-Y. In a glovebox, a solution of KCp′ (67 mg, 0.38 mmol) in THF (2 mL) was added to a stirred solution of Cp′₄Y (190 mg, 0.380 mmol) and 2.2.2-cryptand (142 mg, 0.380 mmol) in THF (3 mL). After 5 min, the colorless solution was concentrated to 1 mL under vacuum, layered with Et₂O (10 mL), and stored at −35 °C overnight to yield 3-Y as colorless crystals (343 mg, 86%). ¹H NMR (THF-d₈): δ 6.11 (m, C₅H₄SiMe₃, 8H), 5.74 (m, C₅H₄SiMe₃, 8H), 3.48 (s, OCH₂CH₂O, 12H), 3.45 (t, ³J_HH = 4.5 Hz, NCH₂CH₂O, 12H), 2.48 (t, ³J_HH = 4.5 Hz, NCH₂CH₂O, 12H), 0.23 (s, C₅H₄SiMe₃, 36H). ¹³C NMR (THF-d₈): δ 121.3 (C₅H₄SiMe₃), 114.3 (C₅H₄SiMe₃), 110.5 (C₅H₄SiMe₃), 71.4 (OCH₂CH₂O), 68.5 (NCH₂CH₂O), 54.8 (NCH₂CH₂O), 1.7 (C₅H₄SiMe₃). IR: 3089w, 3069m, 3034w, 2950s, 2890s, 2820m, 2762m, 2732w, 1927w, 1480m, 1445m, 1411w, 1359m, 1300m, 1260m, 1247s, 1197w, 1182m, 1134m, 1105s, 1082m, 1039m, 949m, 933m, 904m, 831s, 791m, 751s, 730m, 641m, 630m, 605s, 569m, 524s cm⁻¹. Anal. Calcd for C₅₉H₈₈N₂O₆KSi₄Y, 3-Y: C, 57.00; H, 8.42; N, 2.66. Found: C, 56.66; H, 8.64; N, 2.62.

[K(2.2.2-cryptand)][Cp′], 4. In a glovebox, a solution of 2.2.2-cryptand (68 mg, 0.18 mmol) in Et₂O (3 mL) was added to a solution of KCp′ (32 mg, 0.18 mmol) in Et₂O (3 mL) and stirred for 5 min. The colorless solution was filtered and the solvent was removed under vacuum to yield [K(2.2.2-cryptand)][Cp′] as a white microcrystalline solid (96 mg, 96%). Colorless crystals of [K(2.2.2-cryptand)][Cp′] were grown from a concentrated THF solution at −35 °C. ¹H NMR (THF-d₈): δ 5.75 (m, C₅H₄SiMe₃, 2H), 5.62 (m, C₅H₄SiMe₃, 2H), 3.43 (s, OCH₂CH₂O, 12H), 3.41 (t, ³J_HH = 4.5 Hz, NCH₂CH₂O, 12H), 2.44 (t, ³J_HH = 4.5 Hz, NCH₂CH₂O, 12H), 0.03 (s, C₅H₄SiMe₃, 9H). ¹³C NMR (THF-d₈): δ 111.6 (C₅H₄SiMe₃), 106.8 (C₅H₄SiMe₃), 103.3 (C₅H₄SiMe₃), 71.3 (OCH₂CH₂O), 68.5 (NCH₂CH₂O), 54.9 (NCH₂CH₂O), 2.8 (C₅H₄SiMe₃).
Reaction of 1-La with Naphthalene. In a glovebox, a solution of naphthalene (7 mg, 0.06 mmol) in THF (1 mL) was added to a stirred dark purple solution of [K(2.2.2-cryptand)][Cp’3La]-THF, 1-La, (109 mg, 0.105 mmol) in THF (2 mL). The solution was stirred for 5 min, during which time the solution turned deep green. The solvent was removed under vacuum and the resulting deep green oil was redissolved in Et2O (2 mL) and stored at −35 °C. Black crystals and colorless crystals deposited overnight (79 mg). These were determined to be [K(2.2.2-cryptand)][Cp’2La(η4-C10H8)], 2-La, and [K(2.2.2-cryptand)][Cp’4La], 3-La, respectively, by X-ray crystallography and 1H NMR spectroscopy. An analytically pure sample of 2-La was obtained *a la Pasteur* (33 mg, 48%). 1H NMR (THF-d8): δ 5.88 (s, C5H4SiMe3, 4H), 5.63 (s, C10H8, 2H), 5.59 (s, C5H4SiMe3, 4H), 5.02 (s, C10H8, 2H), 3.61 (s, OCH2CH2O, 12H), 3.57 (s, NCH2CH2O, 12H), 3.35 (s, C10H8, 2H), 3.23 (s, C10H8, 2H), 2.59 (s, NCH2CH2O, 12H), 0.14 (s, C5H4SiMe3, 18H). IR: 3072m, 2950s, 2887s, 2814s, 2497w, 2091w, 1866w, 1694w, 1601w, 1553w, 1476m, 1445s, 1399m, 1360s, 1298m, 1242s, 1186s, 1039s, 951s, 830s, 747s, 681m, 625m cm⁻¹. Anal. Calcd for C44H70N2O6KSi2La, 2-La: C, 55.21; H, 7.37; N, 2.93. Found: C, 54.82; H, 7.57; N, 2.86.

[K(2.2.2-cryptand)][Cp’4La], 3-La. In a glovebox, a solution of KCp’ (56 mg, 0.32 mmol) in THF (2 mL) was added to a stirred solution of Cp’3La(THF), (192 mg, 0.308 mmol) and 2.2.2-cryptand (116 mg, 0.308 mmol) in THF (2 mL). After 5 min, the colorless solution was concentrated to 1 mL under vacuum, layered with Et2O (10 mL), and stored at −35 °C overnight to yield 3-La as colorless crystals (299 mg, 88%). 1H NMR (THF-d8): δ 6.21 (s, C5H4SiMe3, 8H), 5.83 (m, C5H4SiMe3, 8H), 3.54 (s, OCH2CH2O, 12H), 3.50 (t, 3JHH = 4.5 Hz,
NCH₂CH₂O, 12H), 2.52 (t, \(^3J_{HH} = 4.5\) Hz, NCH₂CH₂O, 12H), 0.27 (s, C₅H₄SiMe₃, 36H). \(^{13}\)C NMR (THF-\(d_8\)): \(\delta\) 121.3 (C₅H₄SiMe₃), 114.3 (C₅H₄SiMe₃), 110.5 (C₅H₄SiMe₃), 71.4 (OCH₂CH₂O), 68.5 (NCH₂CH₂O), 54.8 (NCH₂CH₂O), 1.7 (C₅H₄SiMe₃).

IR: 3089w, 2951w, 2890w, 2814w, 2384w, 2349w, 1476m, 1444m, 1354m, 1296m, 1261m, 1243m, 1186m, 1134m, 1105m, 1079m, 1040m, 981m, 952m, 934m, 905m, 832m, 742m, 682w, 624m cm\(^{-1}\). Anal. Calcd for C\(_{50}\)H\(_{88}\)N\(_2\)O\(_6\)KSi\(_4\)La, 3-La: C, 54.42; H, 8.04; N, 2.52. Found: C, 54.28; H, 7.95; N, 2.62.

**Reaction of 1-Ce with Naphthalene.** In a glovebox, a solution of naphthalene (6 mg, 0.05 mmol) in THF (1 mL) was added to a stirred dark purple solution of [K(2.2.2-cryptand)][Cp’\(_3\)Ce]·THF, 1-Ce, (90 mg, 0.087 mmol) in THF (2 mL). The solution was stirred for 5 min, during which time the solution turned deep green. The solvent was removed under vacuum and the resulting deep green oil was redissolved in Et₂O (2 mL) and stored at \(-35\) °C. Black crystals and colorless crystals deposited overnight. The black crystals were determined to be [K(2.2.2-cryptand)][Cp’\(_2\)Ce(\(\eta^4\)-C\(_{10}\)H\(_8\))], 2-Ce, by X-ray crystallography, but the colorless crystals were too small to examine by X-ray crystallography.

**Reaction of 1-Dy with Naphthalene.** In a glovebox, a solution of naphthalene (4 mg, 0.03 mmol) in THF (1 mL) was added to a stirred dark maroon solution of [K(2.2.2-cryptand)][Cp’\(_3\)Dy]·THF, 1-Dy, (60 mg, 0.057 mmol) in THF (3 mL). The solution was stirred for 5 min, during which time the solution turned deep blue. The solvent was removed under vacuum and the resulting deep blue oil was redissolved in Et₂O (2 mL) and stored at \(-35\) °C. Black crystals and colorless crystals deposited overnight. The black crystals were determined to be [K(2.2.2-cryptand)][Cp’\(_2\)Dy(\(\eta^4\)-C\(_{10}\)H\(_8\))], 1-Dy, by X-ray crystallography but the colorless crystals were too small to examine by X-ray crystallography.
**Reaction of 1-Y with Biphenyl.** In a glovebox, a solution of biphenyl (4 mg, 0.03 mmol) in THF (1 mL) was added to a stirred dark maroon solution of [K(2.2.2-cryptand)][Cp’2Y]·THF, 1-Y, (48 mg, 0.049 mmol) in THF (1 mL). The solution was stirred for 2 h. The solvent was removed under vacuum and the resulting deep maroon oil was redissolved in Et₂O (2 mL) and stored at −35 °C for several hours. The dark maroon solution was then layered with Et₂O (15 mL) and stored at −35 °C. Black crystals and colorless crystals deposited overnight (50 mg). The black crystals were determined to be [K(2.2.2-cryptand)][Cp’2Y(η⁶-C₆H₅Ph)], 6-Y, by X-ray crystallography, but the structure of the colorless crystals could not be solved. An analytically pure sample of [K(2.2.2-cryptand)][Cp’2Y(η⁶-C₆H₅Ph)] could not be obtained from this reaction due to the similar solubilities of the two types of crystals. One set of resonances among the many in the ¹H NMR spectrum was consistent with the structure determined crystallographically. HMQC and HMBC experiments did not give definitive assignments. Only plausible assignments are given here. ¹H NMR (THF-d₈): δ 7.96 (d, ³J₃HH = 7.2 Hz, C₆H₅Ph, 2H), 7.62, 7.29, 7.14 (d, ³J₃HH = 7.4 Hz, C₆H₅Ph, 2H), 7.11 (t, ³J₄HH = 7.4 Hz, C₆H₅Ph, 1H), 6.27, 5.97 (s, C₅H₄SiMe₃, 4H), 5.87 (s, C₅H₄SiMe₃, 4H), 5.76, 5.14, 3.52 (s, OCH₂CH₂O, 12H), 3.48 (t, ³J₄HH = 4.6 Hz, NCH₂CH₂O, 12H), 2.50 (t, ³J₄HH = 4.5 Hz, NCH₂CH₂O, 12H), 1.29 (s, C₆H₅Ph, 5H), 0.88, 0.24, 0.11 (s, C₅H₄SiMe₃, 18H). A separate reaction was done in d₈-THF of 1-Y (47 mg, 0.048 mmol) with biphenyl (4 mg, 0.03 mmol) and a known amount of cyclooctane (6 mg, 0.05 mmol) was added at the end of the reaction. The resonance at 5.98 ppm in the ¹H NMR spectrum attributed to four aromatic Cp’ protons 6-Y integrated to a 40% molar ratio compared to cyclooctane, i.e., 0.02 mmol of 6-Y was obtained from 0.03 mmol of biphenyl, a crude yield of 67%.
X-ray Data Collection, Structure Determination, and Refinement. Crystallographic details for compounds [K(2.2.2-cryptand)][Cp’2Ln(η4-C10H8)], 2-Ln (Ln = La, Ce, Dy, Y), [K(2.2.2-cryptand)][Cp’4Ln], 3-Ln (Ln = La, Y), [K(2.2.2-cryptand)][Cp’], 4, [K(2.2.2-cryptand)][Cp’2Y(η6-C6H5Ph)], 6-Y, and [K(2.2.2-cryptand)][BPh4], 7, are summarized in Tables 1.5, 1.6, and 1.7.

X-ray Data Collection, Structure Solution and Refinement for 2-Y. A green crystal of approximate dimensions 0.517 x 0.299 x 0.136 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX260 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 SAINT61 and SADABS62 to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL63 program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group P ̅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 factors64 for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR² = 0.0968 and Goof = 1.038 for 511 variables refined against 11145 data (0.78 Å), R1 = 0.0409 for those 8457 data with I > 2.0σ(I). There were several high residuals present in the final difference-Fourier map that was probably due to diethylether solvent. The solvent did not refine well. The SQUEEZE routine in the PLATON65 program package was used to account for the electrons in the solvent accessible voids.

X-ray Data Collection, Structure Solution and Refinement for 2-La. A green crystal of approximate dimensions 0.217 x 0.512 x 0.526 mm was mounted on a glass fiber and
transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{66} 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{61} and SADABS\textsuperscript{67} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{68} 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 $F^2$ by full-matrix least-squares techniques\textsuperscript{62}. The analytical scattering factors\textsuperscript{64} for neutral atoms were used throughout the analysis. Hydrogen atoms were either located from a difference-Fourier map and refined $(x,y,z)$ or included using a riding model. Several carbon atoms were disordered and were included using multiple components with partial site-occupancy-factors. There was a molecule of tetrahydrofuran solvent present. At convergence, $wR2 = 0.0891$ and Goof = 1.045 for 589 variables refined against 12661 data (0.0.75Å), $R1 = 0.0338$ for those 11497 data with $I > 2.0\sigma(I)$. 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 an additional molecule of tetrahydrofuran solvent was present. The SQUEEZE routine in the PLATON\textsuperscript{69} program package was used to account for the electrons in the solvent accessible voids.

**X-ray Data Collection, Structure Solution and Refinement for 2-Ce.** A green crystal of approximate dimensions $0.212 \times 0.207 \times 0.167$ mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{70} 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{71} and SADABS\textsuperscript{67} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{72}
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$^{64}$ for neutral atoms were used throughout the analysis. There was one molecule of diethyl ether solvent per formula unit. Hydrogen atoms were included using a riding model. At convergence, $wR^2 = 0.0664$ and $Goof = 1.017$ for 558 variables refined against 13663 data (0.73 Å), $R1 = 0.0305$ for those 10803 data with $I > 2.0\sigma(I)$.

**X-ray Data Collection, Structure Solution and Refinement for 2-Dy.** A purple crystal of approximate dimensions $0.132 \times 0.152 \times 0.263$ mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2$^{73}$ 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$^{61}$ and SADABS$^{67}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL$^{68}$ 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 using the coordinates from the yttrium analogue and refined on $F^2$ by full-matrix least-squares techniques.$^{63}$ The analytical scattering factors$^{64}$ for neutral atoms were used throughout the analysis. Hydrogen atoms H(17) and H(20) were located from a difference-Fourier map and refined (x,y,z). The remaining hydrogen atoms were included using a riding model. At convergence, $wR^2 = 0.0856$ and $Goof = 1.047$ for 517 variables refined against 9720 data (0.80Å), $R1 = 0.0357$ for those 8080 data with $I > 2.0\sigma(I)$.

**X-ray Data Collection, Structure Solution and Refinement for 3-Y.** A blue crystal of approximate dimensions $0.240 \times 0.219 \times 0.034$ mm was mounted on a glass fiber and transferred
to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{74} program package was used to determine the unit-cell parameters and for data collection (40 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT\textsuperscript{61} and SADABS\textsuperscript{62} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{68} 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.\textsuperscript{63} The analytical scattering factors\textsuperscript{64} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, $wR_2 = 0.0972$ and $Goof = 1.015$ for 577 variables refined against 13538 data (0.75 Å), $R_1 = 0.0439$ for those 9993 data with $I > 2.0\sigma(I)$.

**X-ray Data Collection, Structure Solution and Refinement for 3-La.** A colorless crystal of approximate dimensions 0.167 x 0.259 x 0.305 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{73} 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{75} and SADABS\textsuperscript{67} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{64} 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.\textsuperscript{76} The analytical scattering factors\textsuperscript{64} for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined ($x,y,z$ and $U_{iso}$). At convergence,
wR2 = 0.0507 and Goof = 1.030 for 929 variables refined against 13387 data (0.77Å), R1 = 0.0248 for those 11016 data with I > 2.0σ(I).

**X-ray Data Collection, Structure Solution and Refinement for 4.** A colorless crystal of approximate dimensions 0.381 x 0.176 x 0.091 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 mmn and the systematic absences were consistent with the orthorhombic space group Pbca 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. At convergence, wR2 = 0.0880 and Goof = 1.006 for 328 variables refined against 7008 data (0.75 Å), R1 = 0.0356 for those 5346 data with I > 2.0σ(I).

**X-ray Data Collection, Structure Solution and Refinement for 6-Y.** A red crystal of approximate dimensions 0.146 x 0.247 x 0.383 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. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group P1̅ 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.\(^{63}\) The analytical scattering factors\(^ {64}\) for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model or were fixed during refinement. There was one-half molecule of diethylether present per formula-unit. The solvent was disordered about an inversion center and was included using partial site-occupancy-factors. At convergence, \( wR^2 = 0.0962 \) and \( \text{Goof} = 1.037 \) for 576 variables refined against 11300 data (0.78\(\AA\)), \( R_1 = 0.0398 \) for those 8755 data with \( I > 2.0\sigma(I) \).

**X-ray Data Collection, Structure Solution and Refinement for 7.** A purple crystal of approximate dimensions 0.226 x 0.291 x 0.492 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX\(^ 2 \)\(^{73} \) 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\(^ 75 \) and SADABS\(^ 67 \) to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\(^ 63 \) 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 \( F^2 \) by full-matrix least-squares techniques. The analytical scattering factors\(^ {64}\) for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were two molecules of the formula-unit present (\( Z = 4 \)). There was one molecule of tetrahydrofuran and one-half molecule of diethylether present per formula-unit. Least-squares analysis yielded \( wR^2 = 0.2074 \) and \( \text{Goof} = 1.050 \) for 1074 variables refined against 17929 data (0.82\(\AA\)), \( R_1 = 0.0711 \) for those 13571 data with \( I > 2.0\sigma(I) \).
Table 1.5. X-ray Data and Collection Parameters for \([\text{K(2.2.2-cryptand)}][\text{Cp’}_2\text{Ln}(\eta^4\text{C}_{10}\text{H}_8)]\),

\(2\text{-Ln} (\text{Ln} = \text{La}, \text{Ce}, \text{Dy}, \text{Y}).\)

<table>
<thead>
<tr>
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<th>2-La</th>
<th>2-Ce</th>
<th>2-Dy</th>
<th>2-Y</th>
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<tbody>
<tr>
<td>Empirical Formula</td>
<td>(\text{C}<em>{44}\text{H}</em>{70}\text{N}_2\text{O}_8\text{KSi}_2\text{La})</td>
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\(^a\)Definitions: R1 = Σ||\(F_o\)| - |\(F_c||/Σ|F_o|, wR2 = [Σw(\(F_o^2 - F_c^2\))^2/Σw(\(F_o^2\))^2]^{1/2}
Table 1.6. X-ray Data and Collection Parameters for \([K(2.2.2\text{-cryptand})][\text{Cp}_4\text{Ln}], \text{3-La (Ln = La, Y)}, [K(2.2.2\text{-cryptand})][\text{Cp}_2\text{Y(}^{9}\text{-C}_6\text{H}_3\text{Ph})], \text{6-Y}\).

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<td>Triclinic</td>
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\(^a\)Definitions: R1 = \(\Sigma||F_o| - |F_c||/\Sigma|F_o|\), wR2 = \(\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\)^\(1/2\)
Table 1.7. X-ray Data and Collection Parameters for [K(2.2.2-cryptand)][Cp'], 4, [K(2.2.2-cryptand)][BPh₄], 7.

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<td>0.1886</td>
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*Definitions: R1 = Σ||F_o| - |F_c||/Σ|F_o|, wR2 = [Σw(F_o² - F_c²)²/Σw(F_o²)²]*
References

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(73) APEX2 Version 2013.6-2, Bruker AXS, Inc.; Madison, WI 2013.
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Chapter 2

Isolation of +2 Rare Earth Ions with Three Anionic Carbocyclic Rings:

Bimetallic Bis(cyclopentadienyl) Reduced Arene Complexes of La$^{2+}$ and Ce$^{2+}$

are Four Electron Reductants

Introduction

One of the most fundamental aspects of any element is the number of oxidation states accessible to it. Since this defines the range of chemistry possible with the element, the limits of oxidation states for each element have been heavily probed for decades and are well-established. From 2008-2013 nine oxidation states were discovered in the rare earth series of elements.$^{1-4}$

The discovery of the nine Ln$^{2+}$ ions required,$^{1-4}$ in each case, a coordination environment composed of three cyclopentadienyl rings, specifically $(\text{Cp''}_3)^{3-}$ or $(\text{Cp'}_3)^{3-}$ ($\text{Cp''} = \text{C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}$; $\text{Cp'} = \text{C}_5\text{H}_4\text{SiMe}_3$), eq. 2.1. In this tris(cyclopentadienyl) ligand field, it was found that reduction of a $4f^n$ Ln$^{3+}$ ion added an electron, not to the 4f valence orbitals to make a $4f^{n+1}$ Ln$^{2+}$ ion, but to an orbital with a higher principal quantum number, a 5d$e_2$ orbital, to give Ln$^{2+}$ ions best described by $4f^n5d^1$ electron configurations. This was rationalized by the fact that the d$e_2$ orbital is the lowest energy d orbital in a tris(cyclopentadienyl) coordination environment complex.$^{1-11}$
It was of interest to determine if these Ln$^{2+}$ ions could be isolated in other coordination environments to examine the general accessibility of these new oxidation states. Crystallographic evidence that Ln$^{2+}$ complexes could be made with an anionic reduced benzene ligand was previously reported by Lappert et al.,$^{12,13}$ eq. 2.2. Reduction of Cp$^\text{III}$La (Cp$^\text{III}$ = C$_5$H$_5$(CMe$_3$)$_2$)-1,3 with 1.5 equiv of potassium in the presence of benzene gave a compound that was postulated to be a La$^{2+}$ complex of a (C$_6$H$_5$)$_1^-$ bridging ligand rather than a Ln$^{3+}$ complex of (C$_6$H$_5$)$_3^-$. With the silyl analogs, [C$_5$H$_3$(SiMe$_3$)$_2$]$_3$Ln (Ln = La, Ce), in toluene, similar reactions to form (C$_6$H$_5$CH$_3$)$_1^-$ complexes were reported.$^{13}$ The known difficulty in assigning oxidation states in bridging arene systems$^{14-23}$ complicated the assignments until unambiguous examples of La$^{2+}$ and Ce$^{2+}$ were found via equation 2.1.$^1$

In a small variation of equation 2.2, reaction involving excess K instead of 1.5 equiv per Ln led to the formation of Ln$^{3+}$ products, rather than Ln$^{2+}$ complexes, and reduction of benzene
to \((C_6H_6)^{2-}\) rather than \((C_6H_6)^{1-}\) in the compounds, \([K(18\text{-crown-6})][(C_6H_6)LnCp’’]\) (Ln = La, Ce, Pr, Nd), eq. 2.3. In a further variation with \((C_5H_4SiMe_2CMe_3)_3Ln\) precursors in toluene, Ln\(^{3+}\) hydride products were found. All of these reactions were postulated to involve Ln\(^{2+}\) intermediates.

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{Ln} & \quad + 2 \text{K} + 18\text{-crown-6} \\
\text{C}_6\text{H}_6 & \quad - \text{[K(18\text{-crown-6})][Cp’’]} \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{Ln} & \quad \text{SiMe}_3 \\
\end{align*}
\]

Further variability in this arene rare earth reduction chemistry was subsequently observed with Cp’ ligands in reactions of crystallographically characterized Ln\(^{2+}\) complexes, \([K(2.2.2\text{-cryptand})][Cp’Ln], 1-Ln\) (Ln = Y, La, Ce, Dy). These compounds reduce naphthalene (−2.50 V vs SCE\(^{17}\)) and biphenyl (−2.69 V vs SCE\(^{17}\) ), but were not observed to reduce benzene (−3.43 V vs SCE\(^{17}\)). These reactions differed from equations 2.2 and 2.3 not only in the Cp’ ligand, but also in that they started with bona fide Ln\(^{2+}\) precursors and not a combination of a Ln\(^{3+}\) precursor and potassium that could form a Ln\(^{2+}\) intermediate.

In light of these results, it was of interest to see how the Cp’ complexes would behave in reactions analogous to equations 2.2 and 2.3. This ligand has given yet another variation on benzene reduction and has led to a new series of rare earth complexes in the formal +2 oxidation state. These results show the generality of using three anionic carbocyclic ligands to stabilize Ln\(^{2+}\) and provide a new type of four-electron reductant.
Results and Discussion

Reactions of solutions of Cp′₃Ln, 8-Ln (Ln = La, Ce), in benzene with 2 equiv of potassium-graphite (KC₈) in the presence of 2.2.2-cryptand produce thick black precipitates. After stirring at room temperature for 4 h, extraction with THF followed by centrifugation to remove graphite produces deep purple solutions from which deep purple crystals of [K(2.2.2-cryptand)]₂[(Cp′₂Ln)(µ-η⁶:η⁶-C₆H₆)], 9-Ln, were isolated. Single crystals were grown from THF and identified by X-ray diffraction, although 9-La gave good metrical data, Figure 2.1, while 9-Ce was gave only connectivity-only, Figure 2.2. The byproduct [K(2.2.2-cryptand)][Cp′] was identified by ¹H NMR spectroscopy.

Figure 2.1. Molecular structure of the anion of [K(2.2.2-cryptand)]₂[(Cp′₂La)(µ-η⁶:η⁶-C₆H₆)], 9-La. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and co-crystallized benzene and THF were omitted for clarity.
Figure 2.2. Connectivity-only molecular structure of the anion of \([\text{K}(2.2.2\text{-cryptand})]_2[(\text{Cp}'_2\text{Ce})_2(\mu-\eta^6:\eta^6-\text{C}_6\text{H}_6)]\), 9-Ce. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and co-crystallized benzene were omitted for clarity.

The reaction formally involves the addition of four equiv of KC₈ to two equiv of Cp'₃Ln with loss of one (Cp')⁻⁻ anion per metal complex as \([\text{K}(2.2.2\text{-cryptand})][\text{Cp}']\) and formation of a reduced benzene ligand bridging two bis(cyclopentadienyl) metal units, eq. 4. The \([(\text{Cp}'_2\text{Ln})_2(\mu-\eta^6:\eta^6-\text{C}_6\text{H}_6)]^{2-}\) product could be described by two extreme forms as either two Ln²⁺ ions and a \((\text{C}_6\text{H}_6)^{2-}\) dianion or two Ln³⁺ ions and a \((\text{C}_6\text{H}_6)^{4-}\) tetraanion.
$^{1}$H NMR analysis of 9-La shows multiple resonances at chemical shifts typical of aromatic Cp' protons (5.5 to 6.0 ppm), known 2.2.2-cryptand resonances, and peaks in the 0.0 to 0.5 ppm range typical of trimethylsilyl protons. A peak at 2.03 ppm in the $^{1}$H NMR spectrum was assigned to the reduced arene since it was missing in the analogous reaction using C$_6$D$_6$. The product of the reaction described in equation 2.4 with C$_6$D$_6$ gives a product with a resonance at 2.03 ppm in the $^{2}$H NMR spectrum.

The structural parameters for [K(2.2.2-cryptand)]$_2$[(Cp'$_2$La)$_2$(µ-η$^6$:η$^6$-C$_6$H$_6$)], 9-La, are summarized in Table 2.1. The 1.446(6)-1.459(6) Å C–C bonds of the C$_6$ unit in the solid-state structure of 9-La are longer than the bond lengths in free benzene, which has an average C–C bond length of 1.397(9) Å.$^{26}$ This is consistent with reduction of C$_6$H$_6$. The C$_6$H$_6$ moiety is not planar and has a dihedral angle of 11° between the planes defined by C34-C37 and C33, C34, C37, C38. This is more consistent with (C$_6$H$_6$)$_2^-$ than (C$_6$H$_6$)$_4^-$, since (C$_6$H$_6$)$_4^-$ is reported to be planar.$^{17}$ Interestingly, the 2.690 Å La–(Cp' ring centroid) distances are significantly longer than those of either the La$^{3+}$ complex, Cp'$_3$La, 2.559 Å,$^{27}$ or the La$^{2+}$ complex, [K(2.2.2-cryptand)][Cp'$_3$La], 9-La, 2.586 Å.$^{4}$ Traditionally, bond distances in 4f$^{n+1}$ Ln$^{2+}$ complexes are 0.1-0.2 Å larger than those of 4f$^n$ Ln$^{3+}$ complexes, but bond distances for 4f$^n$5d$^1$ complexes of the recently discovered Ln$^{2+}$ ion complexes are only 0.02-0.03 Å longer.$^{4}$
Table 2.1. Selected Bond Distances (Å) and Angles (°) for [K(2.2.2-cryptand)]$_2$[(Cp$_2$La)$_2$(μ-η$^6$:η$^6$-C$_6$H$_6$)], 9-La.

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$^a$Cnt1, Cnt2, Cnt3, and Cnt4 are the centroids of the Cp$'$ groups.
$^b$Cnt5 is the centroid of the C$_6$ unit labeled C33-C38.
$^c$Pln1 and Pln2 are the planes of (C33-C36) and (C33, C36, C37, C38), respectively.

The UV-vis spectra for 9-Ln are shown in Figure 2.3 and compared to the Ln$^{2+}$ complexes, [K(2.2.2-cryptand)][Cp$'_3$Ln], 1-Ln. The spectra of 9-Ln are similar to those of 1-Ln, but the extinction coefficients are much higher: ~ 8000 M$^{-1}$cm$^{-1}$ in the high-energy visible region. This is particularly unusual since the 1000-2000 M$^{-1}$cm$^{-1}$ extinction coefficients for 1-Ln are already much higher than those of analogous complexes of traditional 4f$^2$ Ln$^{2+}$ complexes of 1-Ln which are all lower than 900 M$^{-1}$cm$^{-1}$.
Figure 2.3. Experimental UV-vis spectra of [K(2.2.2-cryptand)]$_2$[(Cp'$_2$Ln)$_2$(µ-$\eta^6$-$\eta^6$-C$_6$H$_6$)], 9-Ln (dark), and [K(2.2.2-cryptand)][Cp'$_3$Ln], 1-Ln (light), in THF (1 mM) at 298 K (Ln = La, solid; Ln = Ce, dotted).

DFT calculations were used to examine the energies of the possible electron configurations of 9-La. All calculations were performed using the Turbomole quantum chemistry software$^{28}$ and the TPSSh functional.$^{29}$ Calculations on [(Cp'$_2$Ln)$_2$(µ-$\eta^6$-$\eta^6$-C$_6$H$_6$)]$^{2-}$ 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. The calculations also showed long La–(Cp’ ring centroid) distances, similar to those found experimentally. Although this singlet ground state 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 cm$^{-1}$) and
62 kcal/mol (21,800 cm\(^{-1}\)) higher than the singlet ground state, respectively. When a geometry optimization of the quintet state was performed, the optimized structure had only three carbon atoms of the bridging C\(_6\)H\(_6\) ligand coordinated to one metal and the other three carbon atoms coordinated to the other metal. This large difference from the experimental structure indicated that this quintet state is not a viable description of 9-La.

The two highest occupied molecular orbitals (HOMO and HOMO–1) of the singlet state show significant mixing between the metal orbitals and the \(\pi^*\) orbitals of the C\(_6\)H\(_6\) ring, Figure 2.4. Mulliken population analyses (MPA)\(^30\) 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, and is primarily a \(d_{z^2}\) orbital.

**Figure 2.4.** Molecular orbital plots of (a) the 183a orbital (HOMO) and (b) the 182a orbital (HOMO–1) of the dianion in 9-La, using a contour value of 0.05.
Natural population analysis (NPA)\textsuperscript{31} of the dianion in 9-La suggests that each La center has approximately 1.4 5d electrons, Table 2, which is more than the 1.2 electrons and 0.9 electrons found in calculations on (Cp’3La)\textsuperscript{1−} and Cp’3La, 8-La, respectively.\textsuperscript{4} Since there is more electron density on each La center in 9-La than even that for the La\textsuperscript{2+} complex, [K(2.2.2-cryptand)][Cp’3La], 1-La,\textsuperscript{4} 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. The mixed arene/d orbital character of the HOMO and HOMO−1 orbitals suggests that access to a low lying d\textsubscript{z} orbital is not a rigid requirement for isolation of Ln\textsuperscript{2+} complexes of metals such as lanthanum and cerium.

\textbf{Table 2.2.} MPA and NPA analysis of the dianion in 9-La. The % metal character indicates the total metal contribution to the molecular orbital 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>(HOMO−1) MPA</th>
<th>(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>

Time dependent DFT (TDDFT)\textsuperscript{32} calculations were performed to simulate the UV–vis spectrum of 9-La. The simulated spectrum of the singlet state gave the best match to the experimental spectrum as shown in Figure 2.5. The predicted UV–vis spectrum contains three broad absorptions, one of which matches the low energy absorption in the experimental spectrum, while the combination of the other two fit under the experimentally-determined high-energy absorption. The excitations between 300 and 1000 nm are comprised of excitations from the HOMO and HOMO−1 orbitals shown in Figure 2.4. 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.

**Figure 2.5.** Experimental (solid) and calculated (dotted) UV–vis spectra of 9-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.

The reductive reactivity of 9-Ln was probed by examining the reaction with naphthalene. Two equiv of naphthalene are reduced by four electrons to produce 2 equiv of [K(2.2.2-cryptand)][Cp'2Ln(η4-C10H8)], 2-Ln (Ln = La, Ce), eq. 2.5.33 The four electron reduction is consistent with the presence of two Ln²⁺ ions and a (C₆H₆)²⁻ dianion, but does not provide definitive evidence on this because a (C₆H₆)⁴⁻ anion would also be a 4-electron reductant. This reaction does provide a clean route to 2-Ln, which are originally made from 1-Ln in a reaction that has an inseparable byproduct, [K(2.2.2-cryptand)][Cp'₄Ln] (Ln = Y, La).33
In summary, a new type of rare earth compound has been identified that is best described as a bimetallic complex of two Ln$^{2+}$ ions bridged by (C$_6$H$_6$)$_2^{-}$. This result constitutes an intriguing variation of the arene reduction reactions in equations 2.2 and 2.3 in which complexes are found with either (C$_6$H$_6$)$_1^{-}$ and two Ln$^{2+}$ ions or with (C$_6$H$_6$)$_2^{-}$ and one Ln$^{3+}$ ion. Clearly, small variations in these reactions and in the substituents on the cyclopentadienyl rings can have a significant effect on the product isolated in the tris(cyclopentadienyl)rare earth/alkali metal reductions of arenes.

**Conclusion**

The isolation of 9-Ln demonstrates the generality of isolating Ln$^{2+}$ ions with three anionic carbocyclic rings beyond the (Cp"$^3$)^{3−} and (Cp′$^3$)^{3−} coordination environments. In 9-Ln, a (C$_6$H$_6$)$_2^{-}$ dianion shared between two metals takes the place of a cyclopentadienyl anion in the monometallic Ln$^{2+}$ systems.$^{1-3}$ This is not a common substitution in organometallic chemistry since arene anions are only formed under highly reducing conditions. DFT studies on 9-La show that this heteroleptic three ring ligand system differs from the tris(cyclopentadienyl) complexes in that the HOMOs have much more ligand character than in the (Cp"$^3$)^{3−} and (Cp′$^3$)^{3−}-ligated
complexes, in which the HOMOs are primarily $d_{z^2}$. These results suggest that other variations of three carbocyclic rings with orbital character beyond that found in tris(cyclopentadienyl) ligand environments could also stabilize unusual Ln$^{2+}$ ions.

It is important to note that 9-La displays some unexpected properties, i.e. the long La–(Cp’ ring centroid) distances in the crystal structure, the long La–C(C$_6$H$_6$) distances in the DFT calculations, and the extremely high (for a rare earth) extinction coefficients. Determining the origin of these properties will require the isolation of more examples of other ligand systems for these Ln$^{2+}$ ions. Although the electronic nature of these Ln$^{2+}$ complexes may not be completely understood, it is clear they can function as multi-electron reductants that can provide four electrons from a single molecule. Hence, these complexes demonstrate a new approach using f element chemistry to multi-electron reducing systems, which are not very common.

**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 argon (Praxair) 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 prior to use. Anhydrous Cp’$_3$La(THF),$^{27}$ Cp’$_3$Ln (Ln = Ce,$^{34}$ Pr,$^3$ Nd$^{35}$), and KC$_8$,$^{36}$ were prepared according to the literature. 2.2.2-Cryptand, (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane), (Aldrich) was placed under vacuum ($10^{-3}$ Torr) for 12 h before use. $^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) 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 Jasco FT/IR-4700 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS elemental analyzer.

\[ \text{[K(2.2.2-cryptand)]}_2[(\text{Cp'}_2\text{La})_2(\mu-\eta^6:\eta^6-C_6H_6)]} \], 9-La. In an argon-filled glovebox, benzene (10 mL) was added to a vial containing Cp'La(THF), (156 mg, 0.251 mmol), 2.2.2-cryptand (189 mg, 0.502 mmol), and KC\(_8\) (68 mg, 0.503 mmol). The mixture was allowed to stir vigorously for 5 hours. When stirring ceased, the suspension was allowed to settle and colorless benzene was pipetted out of the vial and discarded leaving behind a black oil. 2 mL of THF was added to the oil and stirred for 5 minutes before centrifugation for 10 min to remove graphite. The dark purple supernatant was filtered into a vial and chilled at \(-35^\circ\text{C}\) for an hour. The solution was layered with room temperature Et\(_2\)O (10 mL) and stored at \(-35^\circ\text{C}\), producing dark purple crystals overnight (72 mg, 33 %). X-ray quality crystals were grown from a concentrated THF solution at \(-35^\circ\text{C}\) over 5 days. \(^1\)H NMR (THF-\(d_8\)): \(\delta 5.70\) (s, \(\text{CH}_4\text{SiMe}_3\), 8H), 5.62 (s, \(\text{CH}_4\text{SiMe}_3\), 8H), 3.55 (s, \(\text{OCH}_2\text{CH}_2\text{O}\), 24H), 3.50 (s, \(\text{NCH}_2\text{CH}_2\text{O}\), 24H), 2.53 (s, \(\text{NCH}_2\text{CH}_2\text{O}\), 24H), 2.04 (s, \(\text{C}_6\text{H}_6\), 6H), 0.21 (s, \(\text{C}_5\text{H}_4\text{SiMe}_3\), 27H). \(^{13}\)C NMR (THF-\(d_8\)): \(\delta 113.7\) (\(\text{CH}_4\text{SiMe}_3\)), 109.1 (\(\text{CH}_4\text{SiMe}_3\)), 71.7 (\(\text{OCH}_2\text{CH}_2\text{O}\)), 69.6 (\(\text{C}_6\text{H}_6\)), 68.7 (\(\text{NCH}_2\text{CH}_2\text{O}\)), 55.4 (\(\text{NCH}_2\text{CH}_2\text{O}\)), 2.9 (\(\text{C}_5\text{H}_4\text{SiMe}_3\)). IR: 3068w, 2946s, 2883s, 2811s, 1478m, 1444m, 1385m, 1360s, 1354s, 1299m, 1259m, 1237m, 1179m, 1134s, 1104s, 1079s, 1037m, 950s, 933m, 904m, 831s, 749s, 732m, 689w, 678w, 668w, 634m. Anal. Calcd for \(\text{C}_{74}\text{H}_{130}\text{K}_2\text{La}_2\text{N}_4\text{O}_{12}\text{Si}_4\cdot2\text{THF}\), 2-La: C, 52.38; H, 7.83; N, 2.98. Found: C, 52.52; H, 7.78; N, 3.00.

\[ \text{[K(2.2.2-cryptand)]}_2[(\text{Cp'}_2\text{Ce})_2(\mu-\eta^6:\eta^6-C_6H_6)]} \], 9-Ce. In an argon-filled glovebox, benzene (10 mL) was added to a vial containing Cp'Ce (175 mg, 0.387 mmol), 2.2.2-cryptand (296 mg, 0.791 mmol), and KC\(_8\) (108 mg, 0.799 mmol). The mixture was allowed to stir vigorously for 4 hours. When stirring ceased, the suspension was allowed to settle and colorless
benzene was pipetted out of the vial and discarded leaving behind a black oil. 2 mL of THF was added to the oil and stirred for 5 minutes before centrifugation for 10 min to remove graphite. The dark black supernatant was filtered into a vial and chilled at −35 °C for an hour. The solution was layered with room temperature Et2O (10 mL) and stored at −35 °C, producing black crystals overnight (174 mg, 26 %). IR: 3068w, 2946s, 2882s, 2813s, 1478m, 1445m, 1388m, 1360s, 1354s, 1300m, 1258m, 1236m, 1179m, 1134s, 1104s, 1080s, 1036m, 950s, 932m, 904m, 828s, 749s, 730m, 716m, 678m, 634m, 628m. Anal. Calcd for C74H130K2Ce2N4O12Si4•C6H6, 2-Ce: C, 52.89; H, 7.55; N, 3.08. Found: C, 53.09; H, 7.87; N, 3.20.

**Reaction of 9-La with Naphthalene.** In an argon-filled glovebox, a solution of naphthalene (3 mg, 0.02 mmol) in THF (1 mL) was added to a stirred dark purple solution of 9-La (20 mg, 0.012 mmol) in THF (1 mL). The solution was stirred for 10 min, during which time the solution turned deep green. The solvent was removed under vacuum, and the resulting solids were washed with hexane and dried to give [K(2.2.2-cryptand)][Cp’2La(η4-C10H8)], 2-La, as a deep green powder (19 mg, 86 %).

**Reaction of 9-Ce with Naphthalene.** In an argon-filled glovebox, a solution of naphthalene (11 mg, 0.08 mmol) in THF (1 mL) was added to a stirred dark purple solution of 9-Ce (72 mg, 0.04 mmol) in THF (2 mL). The solution was stirred for 10 min, during which time the solution turned deep green. The solvent was removed under vacuum, and the resulting solids were washed with hexane and dried to give [K(2.2.2-cryptand)][Cp’2Ce(η4-C10H8)], 2-Ce, as a deep green powder (72 mg, 91 %).
X-ray Data Collection, Structure Solution and Refinement for 9-La.

A purple crystal of approximate dimensions 0.077 x 0.175 x 0.299 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2\textsuperscript{37} 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 SAIN\textsuperscript{38}T\textsuperscript{39} and SADABS\textsuperscript{39} to yield the reflection data file. Subsequent calculations were carried out using the SHELX\textsuperscript{40}TL\textsuperscript{40} program. The diffraction symmetry was mmm and the systematic absences were consistent with the orthorhombic space group Pccn 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{41} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There was one molecule of tetrahydrofuran and one-half molecule of benzene present per formula-unit. The benzene was located about an inversion center. Potassium atoms K(2) and K(3) were located on two-fold rotation axes.

At convergence, wR2 = 0.1305 and Goof = 1.211 for 933 variables refined against 18865 data (0.80Å), R1 = 0.0553 for those 16255 data with I > 2.0σ(I).

**Table 2.3.** Crystal data and structure refinement for 9-La.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C\textsubscript{74} H\textsubscript{130} La\textsubscript{2} K\textsubscript{2} N\textsubscript{4} O\textsubscript{12} Si\textsubscript{4} • 1.5(C\textsubscript{6}H\textsubscript{6}) • C\textsubscript{4}H\textsubscript{8}O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1847.35</td>
</tr>
<tr>
<td>Temperature</td>
<td>88(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pccn</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 20.3261(11) Å</td>
</tr>
<tr>
<td></td>
<td>b = 54.668(3) Å</td>
</tr>
<tr>
<td></td>
<td>c = 16.5827(9) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>18426.5(17) Å³</td>
</tr>
</tbody>
</table>
Z

Density (calculated) 1.332 Mg/m³
Absorption coefficient 1.114 mm⁻¹
F(000) 7736
Crystal color purple
Crystal size 0.299 x 0.175 x 0.077 mm³
Theta range for data collection 1.069 to 26.372°
Index ranges -25 ≤ h ≤ 25, -68 ≤ k ≤ 68, -20 ≤ l ≤ 20
Reflections collected 194473
Independent reflections 18865 [R(int) = 0.0505]
Completeness to theta = 25.500° 100.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7457 and 0.6462
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 18865 / 0 / 933
Goodness-of-fit on F² 1.211
Final R indices [I>2sigma(I) = 16255 data] R1 = 0.0553, wR2 = 0.1258
R indices (all data, 0.80Å) R1 = 0.0650, wR2 = 0.1305
Largest diff. peak and hole 2.510 and -1.474 e.Å⁻³

Table 2.4. Crystal data and structure refinement for 9-Ce.

Empirical formula C₇₄ H₁₃₀ Ce₂ K₂ N₄ O₁₂ Si₄ • 1.5(C₆H₆)
Formula weight 1855.77
Temperature 138(2) K
Wavelength 0.71073 Å
Crystal system Monoclinic
Space group P2₁/c
Unit cell dimensions a = 27.776(6) Å α = 90°.
b = 20.229(4) Å β = 100.194(3)°.
c = 16.486(4) Å γ = 90°.
Volume 9116(3) Å³
Z 4
Density (calculated) 1.352 Mg/m³
Absorption coefficient 1.187 mm⁻¹
F(000) 3884
Crystal color black
Crystal size 0.233 x 0.153 x 0.139 mm³
References


(38) SAINT Version 8.34a, Bruker AXS, Inc.; Madison, WI 2013.
Chapter 3
Mechanochemical Synthesis of Rare Earth and Actinide
Organometallic Species in the Solid State

Introduction

Mechanochemistry is a subset of solid-state chemistry that involves the fracturing and welding of solids in the absence of solvent through ball milling.\(^1\) In this process, energy is generated from collisions between stainless steel balls and the sample container that can be harnessed for chemical reactivity\(^2\) to achieve solid-state chemical reactions including ionic metathesis reactions and ligand rearrangements.\(^3\) In ball milling, impact points of ball/ball and ball/container collisions create very high, but short-lived local temperatures. This thermal energy allows for molecular reactions to take place, but it is dissipated before decomposition can occur.\(^4\)

The use of ball milling to perform ionic metathesis reactions is an attractive alternative to solution-state chemistry as it diminishes solvent use and the generation of organic waste. In addition, ball milling can be a means to avoid participatory solvents such as THF that can rigidly bind rare earth metals, which can interfere with reactivity\(^5,6\) and require heat and high vacuum to desolvate.\(^7,8\) Mechanochemistry can also afford reactivity that is otherwise not possible in solution. Aylmore and co-workers used ball milling to effect a formal oxidation of \(\text{Yb}^0\) and \(\text{Eu}^0\) by \(\text{nTlCp}\) (\(\text{Yb}, n = 2; \text{Eu}, n = 3; \text{Cp} = \text{cyclopentadienyl}\)) to produce the Cp-substituted rare earth (Ln) complexes, \(\text{LnCp}_n\), eq 3.1.\(^2\) The same technique was used with \(\text{Fe}^0\) to make ferrocene through a synthetic route not possible in solution, eq 3.1.\(^2\) More recently, Hanusa and co-workers have used ball milling to synthesize the first example of an unsolvated tris(allyl)
organoaluminum species and have extended the chemistry to rare earth metals by synthesizing the analogous Sc complex, eq 3.2.9

\[
\begin{align*}
\text{Ln}^0 + n\text{TiCp} & \xrightarrow{\text{ball mill}} \text{LnCp}_n \xrightarrow{\text{solvent } S} \text{LnCp}_n S^+ \\
\text{Ln} &= \text{Yb; } n = 2; S = \text{DME} \\
\text{Ln} &= \text{Eu; } n = 3; S = \text{pyr} \\
\text{Ln} &= \text{Fe; } n = 2; S = \text{Et}_2\text{O}
\end{align*}
\]

Mechanochemistry is appealing in the f element area due to the problems associated with the synthesis of many types of organolanthanide complexes. The synthesis of Cp’5Y (Cp’ = C5H4SiMe3) is typical of chemical reactions involving rare earth metals in that it requires rigorously dried solvents, generates organic waste, and requires extended reaction times, eq 3.3.10

\[
\begin{align*}
\text{MX}_3 + 3\left[ \text{K} \left[ \text{Me}_3\text{Si} - \text{SiMe}_3 \right] \right] & \xrightarrow{\text{ball mill}} \text{ball mill} \\
\text{M} &= \text{Al; } X = \text{Cl, Br, I} \\
\text{M} &= \text{Sc; } X = \text{Cl}
\end{align*}
\]

In some cases, rare earth complexes react with solvents. For example, traditionally, tris(pentamethycyclopentadienyl) rare earth complexes such as (C5Me5)3Gd are made by reacting KC5Me5 with (C5Me5)2Gd(µ-Ph)2BPh2 in benzene, eq 3.4.11 However, for smaller rare earth metals like yttrium, the steric bulk of the (C5Me5)33– ligand set causes (C5Me5)3Y to react with benzene and toluene to form (C5Me5)2Y(C6H5) and (C5Me5)2Y(CH2C6H5), respectively.11
An alternative route was developed for the synthesis and isolation of \( (\text{C}_5\text{Me}_5)_3\text{Y} \) that avoids aromatic hydrocarbon solvents susceptible to metalation by reacting \( [(\text{C}_5\text{Me}_5)_2\text{Y(\mu-H)}]_2 \) with 2 equiv of 1,2,3,4-tetramethylfulvene (TMF), eq 3.5. However, TMF is not commercially available and is synthesized in a reaction that involves a pyrophoric material, \( \text{n-BuLi} \), and requires the acutely toxic pseudohalide cyanogen bromide (BrCN), eq 3.6.

The synthesis \( \text{U}[\text{N(SiMe}_3)_2]_3 \) is another example of a problematic reaction in that this complex is prone to reactivity in solution that produces the cyclometalated U(IV) species \( \text{U}[(\text{SiMe}_3)_2\text{N}]_2[\text{k}^2-\text{CH}_2\text{Me}_2\text{SiN(SiMe}_3)_2] \) and \( \text{H(NSiMe}_3)_2 \) as byproducts. This requires that \( \text{U}[\text{N(SiMe}_3)_2]_3 \) be purified by sublimation.

In this study, preliminary mechanochemical reactions are pursued to test the feasibility of ball milling as a solid-state alternative to solution-mediated reactions with rare earth and actinide complexes. Particular attention was paid to reactions that produce solvent-sensitive substrates or are prone to decomposition in solution.
Results

Colorless solids of YCl\textsubscript{3} and KCp’ were combined in a 100 mL round bottom flask containing stainless steel ball bearings (8 mm) and turned on a rotary evaporator for 8 h. Extraction with hexane yielded a pale yellow product. Analysis by \textsuperscript{1}H NMR spectroscopy revealed that Cp’\textsubscript{3}Y, 8-Y, was synthesized in a 5:3 ratio with [Cp’\textsubscript{2}Y(\mu-Cl)]\textsubscript{2}, eq 3.7.

\[
\text{YCl}_3 + 3\text{KCp'} \xrightarrow{\text{ball mill}} \text{Cp’}_3\text{Y} + \text{Cp’}_2\text{Y} (\mu-\text{Cl}) \text{Cl}^{-} \text{YCp’}_2
\]  

(3.7)

In a typical procedure, colorless solids of [(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Y][BPh\textsubscript{4}] and an excess of KC\textsubscript{5}Me\textsubscript{5} were combined in a 35 x 10 mm stainless steel capsule, Figure 3.1, with a single ball bearing (5 mm) and milled in a wig-l-bug grinding mill for 20 min. Extraction with hexane freshly collected from the drying column produced an orange product. Analysis by \textsuperscript{1}H NMR spectroscopy revealed the formation of (C\textsubscript{5}Me\textsubscript{5})\textsubscript{3}Y, 10-Y, 1.97 ppm, and [(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Y](\mu-O), 2.02 ppm, in C\textsubscript{6}D\textsubscript{12}, in a 10:1 ratio, eq. 3.8.

Figure 3.1: Stainless steel capsule with threaded cap and stainless steel ball for wig-l-bug ball milling.
To test the feasibility of extending mechanochemistry with the [N(SiMe$_3$)$_2$]$^{1-}$ ligand to actinides, a test reaction to synthesize Y[N(SiMe$_3$)$_2$]$^{15}$ in the solid state was first attempted. Colorless solids of YCl$_3$ and KN(SiMe$_3$)$_2$ were combined in the 1.5-inch stainless steel capsule with a single ball bearing (5 mm) and milled in a wig-l-bug grinding mill for 20 min. Extraction with hexane produced a colorless product. Analysis by $^1$H NMR revealed the formation of Y[N(SiMe$_3$)$_2$]$_3$, 11-Y, as well as the presence of HN(SiMe$_3$)$_2$ and KN(SiMe$_3$)$_2$ in a 3:1:1 ratio, respectively, eq. 3.9.

\[
\text{YCl}_3 + 3\text{KN(SiMe}_3\text{)}_2 \xrightarrow{\text{ball mill}} \text{Y[N(SiMe}_3\text{)}_2]_3 + \text{KN(SiMe}_3\text{)}_2 + \text{HN(SiMe}_3\text{)}_2
\]

In a similar reaction, black solids of UI$_3$ and colorless solids of KN(SiMe$_3$)$_2$ were milled in a wig-l-bug grinding mill for 20 min to produce a black solid. Extraction with hexane produced a red product. Analysis by $^1$H NMR spectroscopy revealed the formation of U[N(SiMe$_3$)$_2$]$_3$, 11-U, as well as the cyclometalated species U[(SiMe$_3$)$_2$N]$_2$[$\kappa^2$-CH$_2$Me$_2$SiN(SiMe$_3$)] and H(NSiMe$_3$)$_2$ in a ratio of 11:3:6, respectively, eq 3.10. The similar solubilities of KN(SiMe$_3$)$_2$ and HN(SiMe$_3$)$_2$ did not allow analytically pure samples of Y[N(SiMe$_3$)$_2$]$_3$ and U[N(SiMe$_3$)$_2$]$_3$ to be obtained by this route.
Discussion

Initial test reactions have shown that Cp\textquotesingle_3Y can be synthesized without solvent from YCl_3 and KCp\textquotesingle simply by slowly grinding the solids together with 8 mm stainless steel balls over 8 h. However, by this method full conversion to Cp\textquotesingle_3Y was not accomplished, as evidenced by the formation of [Cp\textquotesingle_2Y(μ-Cl)]_2. Although grinding in a round bottom flask was inexpensive and sufficient for testing initial reactivity, the stainless steel capsule for ball milling proved to be more efficient, diminishing reaction times to the order of minutes. By this method (C_5Me_5)_3Y was produced directly from [(C_5Me_5)_2Y][BPh_4] in the solid state, thereby avoiding unfavorable metalation reactions with benzene and toluene. In order to unequivocally confirm the production of (C_5Me_5)_3Y, it would be of interest to grow single crystals of the orange product. Further evidence would be to test reactivity with benzene and toluene and observe by \textsuperscript{1}H NMR spectroscopy the formation of the respective metalation products.

Through ball milling reactions with the stainless steel capsule, Y[N(SiMe_3)_2]_3 and U[N(SiMe_3)_2]_3 were synthesized for the first time in the solid state directly from their trihalide precursors. Although the formation of the cyclometalated species U[(SiMe_3)_2N]_2[k^2-CH_2Me_2SiN(SiMe_3)] through ball milling was unexpected, it implies that the formation of this U(IV) byproduct is not dependent on a solution-mediated reaction.
Conclusion

Several initial test reactions have shown that it is possible to effect metathesis reactions in the solid-state for rare earth metals and uranium through mechanochemical routes with (Cp')\(^{-}\), (C\(_5\)Me\(_5\))\(^{-}\), and [N(SiMe\(_3\))\(_2\)]\(^{-}\) ligands. During ball milling, incomplete mixing may result from the spherical stainless steel balls not conforming to the angled shape of the capsule. With complete mixing, a clean mechanochemical synthesis for Cp\(_3\)Y and (C\(_5\)Me\(_5\))\(_3\)Y would reduce solvent use and organic waste generation. Further, the mechanochemical synthesis of (C\(_5\)Me\(_5\))\(_3\)Y avoids metalation reactions with benzene and toluene, as well as toxic precursors necessary to make TMF. In the mechanochemical synthesis of U[N(SiMe\(_3\))\(_2\)]\(_3\), the formation of the cyclometalated species U[(SiMe\(_3\))\(_2\)N][κ\(_2\)2-CH\(_2\)Me\(_2\)SiN(SiMe\(_3\))] was observed, which to our knowledge is the first example of this byproduct formed from a solid-state reaction.

Experimental Details

The syntheses and manipulations described below were conducted under argon and nitrogen with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were sparged with UHP argon (Praxair) 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 prior to use. Anhydrous YCl\(_3\),\(^{16}\) UI\(_3\),\(^{17}\) KCp' (Cp' = C\(_5\)H\(_4\)SiMe\(_3\)),\(^{18}\) [(C\(_5\)Me\(_5\))\(_2\)Y][BPh\(_4\)],\(^{11}\) were prepared according to the literature. KC\(_5\)Me\(_5\) was synthesized from a 1:1 molar reaction of HC\(_5\)Me\(_5\) (Strem) and potassium bis(trimethylsilylamide) (Aldrich) in toluene. Sodium hexafluoroacetylacetonate was synthesized from refluxing hexafluoroacetylacetone (Aldrich) with excess sodium in toluene. \(^1\)H NMR (500 MHz) were
obtained on a Bruker GN500 or CRYO500 MHz spectrometer at 298 K. Rotary grinding was performed with a Büchi Rotovapor R-200. Ball milling was performed with Biospec Mini-Beadbeater wig-l-bug in a 1.5-inch stainless steel capsule, Figure 3.1. Disperser milling was performed with an Ultra-Turrax Tube Drive and BMT-20-S tubes, both purchased from IKA Works, Inc., Wilmington, NC, USA.

**Synthesis of Cp’3Y, 8-Y, by Rotary Grinding.** A 100 mL round bottom flask was charged with YCl3 (232 mg, 1.19 mmol), KCp’ (640 mg, 3.63 mmol), and stainless steel ball bearings (8 mm diameter, 20 count) in a glovebox containing an atmosphere of argon. The round bottom flask was wrapped in electrical tape and sealed with a Teflon-sealable adaptor. The air-free apparatus was removed from the glovebox, attached to a rotary evaporator, and allowed to revolve on low speed for 8 h. The apparatus was transferred to a glovebox containing an atmosphere of argon. The solids were extracted with hexane under an atmosphere of argon and dried under reduced pressure to reveal a 5:3 ratio of Cp’3Y and [Cp’2Y(µ-Cl)]2 as a pale yellow solid (76 mg). 1H NMR (C6D6): δ 6.78 (m, [(C5H4(SiMe3))2Y(µ-Cl)]2) 6.53 (m, [C5H4(SiMe3)]3Y), 6.47 (m, [(C5H4(SiMe3))2Y(µ-Cl)]2), 6.22 (m, [C5H4(SiMe3)]3Y), 0.29 (s, [(C5H4(SiMe3))2Y(µ-Cl)]2) 0.21 (s, [C5H4(SiMe3)]3Y).

**Synthesis of (C5Me5)3Y, 10-Y, by Ball milling.** A stainless steel capsule was charged with [(C5Me5)2Y][BPh4] (75 mg, 0.11 mmol), KC5Me5 (37 mg, 0.21 mmol), and stainless steel ball bearings (5 mm diameter, 2 count) in a glovebox containing an atmosphere of argon and tightly sealed. The air-free capsule was removed from the glovebox and locked into the ball milling apparatus and milled for 20 min on the medium setting. The capsule was transferred to a glovebox containing an atmosphere of argon. The solids were extracted with freshly dried
hexane under an argon atmosphere and dried under reduced pressure to reveal an orange solid.  

$^1$H NMR (C$_6$D$_{12}$): $\delta$ 2.02 (s, [(C$_5$Me$_3$)$_2$Y]$_2$(µ-O)), 1.97 (s, (C$_5$Me$_3$)$_3$Y), 1.94 (s).

**Synthesis of Y[N(SiMe$_3$)$_2$]$_3$, 11-Y, by Ball Milling.** A stainless steel capsule was charged with YCl$_3$ (41 mg, 0.21 mmol), KN(SiMe$_3$)$_2$ (126 mg, 0.63 mmol), and a stainless steel ball bearing (5 mm diameter) in a glovebox containing an atmosphere of argon and tightly sealed. The capsule was locked into the ball milling apparatus and milled for 20 min on the medium setting. The capsule was transferred to a glovebox containing an atmosphere of argon. The solids were extracted with hexane under an argon atmosphere and dried under reduced pressure to reveal a colorless solid. $^1$H NMR (C$_6$D$_6$): $\delta$ 0.30 (s, Y[N(SiMe$_3$)$_2$]$_3$), 0.13 (s, KN(SiMe$_3$)$_2$), 0.10 (s, HN(SiMe$_3$)$_2$).

**Synthesis of U[N(SiMe$_3$)$_2$]$_3$, 11-U, by Ball Milling.** A stainless steel capsule was charged with UI$_3$ (88 mg, 0.14 mmol), KN(SiMe$_3$)$_2$ (85 mg, 0.43 mmol), and a stainless steel ball bearing (5 mm diameter) in a glovebox containing an atmosphere of argon and tightly sealed. The capsule was locked into the ball milling apparatus and milled for 20 min on the medium setting. The capsule was transferred to a glovebox containing an atmosphere of argon. The solids were extracted with pentane under an argon atmosphere and dried under reduced pressure to reveal 11-U as a red solid. $^1$H NMR (C$_6$D$_6$): $\delta$ 11.40 (s, U[(SiMe$_3$)$_2$N]$_2$[κ$^2$-CH$_2$Me$_2$SiN(SiMe$_3$)]), 9.74 (s, U[(SiMe$_3$)$_2$N]$_2$[κ$^2$-CH$_2$Me$_2$SiN(SiMe$_3$)]), 0.11 (s, HN(SiMe$_3$)$_2$), $-11.04$ (s, U[N(SiMe$_3$)$_2$]$_3$), $-13.20$ (s, U[(SiMe$_3$)$_2$N]$_2$[κ$^2$-CH$_2$Me$_2$SiN(SiMe$_3$)]).
References

Chapter 4

Investigation of a Rare-Earth Non-Classical Carbocation

Introduction

Since the first reported synthesis of tris(pentamethylcyclopentadienyl) samarium, (C$_5$Me$_5$)$_3$Sm, in 1991,$^1$ (C$_5$Me$_5$)$_3$Ln, $^{10}$-Ln (Ln = La,$^2$ Ce,$^3$ Pr,$^3$ Nd,$^4$ Sm$^5$), complexes have proven to be interesting for reactivity based on the relief of unprecedented steric crowding. Through sterically induced reduction (SIR), (C$_5$Me$_5$)$_3$Sm has shown similar reductive chemistry to divalent (C$_5$Me$_5$)$_2$Sm, i.e., both complexes can act as reducing agents, eq. 4.1 and 4.2.$^5$

\[
(C_5M_5)_2Sm \rightarrow e^- + [(C_5M_5)_2Sm]^+ \quad (4.1)
\]

\[
(C_5M_5)_3Sm \rightarrow e^- + [(C_5M_5)_2Sm]^+ + \frac{1}{2} (C_5M_5)_2 \quad (4.2)
\]

The typical $\eta^5$ binding mode in (C$_5$Me$_5$)$_3$Ln is proposed to access a highly reactive $\eta^1$ mode$^3$ so that when it reacts with carbon monoxide$^6$ the remarkable complexes (C$_5$Me$_5$)$_2$Ln[(OC)$_2$C$_5$Me$_5$-$\kappa^2$-O,O'], (C$_5$Me$_5$)$_2$Ln(O$_2$C$_7$Me$_5$), $^{12}$-Ln (Ln = La, Ce, Pr, Nd, Sm), can form, eq 4.3. These are rare examples of crystallographically-characterizable non-classical carbocation moieties.$^{3,7,8}$

![Diagram](image-url)
A non-classical carbocation is a carbonium ion that is stabilized through the delocalization of 2 electrons between 3 $\sigma$-bonds.\(^9\) Previously reported crystal structures of $(C_{5}Me_{5})_2Ln(O_2C_7Me_5)$ ($Ln = Sm$, Nd) show that the cationic carbon is trigonal planar and formally interacts with the internal olefin indicating a 2-electron-3-center bond and a non-classical carbocation.\(^7,8\) It is of interest to explore the reactivity of the CO insertion product, $(C_{5}Me_{5})_2Ln(O_2C_7Me_5)$, under conditions that promote cationic polymerization.

**Results and Discussion**

Since the initial synthesis of $(C_{5}Me_{5})_3Sm$ from $(C_{5}Me_{5})_2Sm$ and 1,3,5,7-cyclooctatetraene,\(^1\) the general preparation of $(C_{5}Me_{5})_3Ln$, **10-Ln**, has been improved to a more efficient synthetic route described by Evans and co-workers in 1998.\(^4\) By this method, **10-Sm** and **10-La** were synthesized in good yields (**10-Sm**, 73%; **10-La**, 78%) through identical reaction pathways, Figure 4.1.

---

**Figure 4.1.** Synthesis of $(C_{5}Me_{5})_3Ln$, **10-Ln** ($Ln = Sm$, La).
Synthesis of the non-classical carbocation complex \((C_5\text{Me}_5)_2\text{Sm}(O_2\text{C}_7\text{Me}_5)\), \textbf{12-Sm}, was accomplished through the addition of CO (1 atm) to degassed \((C_5\text{Me}_5)_3\text{Sm}\), \textbf{10-Sm}, at room temperature over 20 min on a high vacuum line, eq 4.4. \textbf{12-Sm} was synthesized in 42% yield, and confirmed by \(^1\text{H}\) NMR spectroscopy in \(C_6\text{D}_6\).\(^7\) The synthesis of \((C_5\text{Me}_5)_2\text{La}(O_2\text{C}_7\text{Me}_5)\), \textbf{12-La}, was performed and isolated in 32% yield. Spectroscopic evidence by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy, IR spectroscopy, and elemental analysis is consistent with the formation of \textbf{12-La}.

While the synthesis of \((C_5\text{Me}_5)_3\text{Ln}\) was nearly identical for the La and Sm metals, Figure 4.1, the CO insertion reaction performed to generate \textbf{12-Sm} and \textbf{12-La} varied drastically as shown in equation 4.4. While \((C_5\text{Me}_5)_2\text{Sm}(O_2\text{C}_7\text{Me}_5)\), \textbf{12-Sm}, forms in a matter of minutes at room temperature, \((C_5\text{Me}_5)_2\text{La}(O_2\text{C}_7\text{Me}_5)\), \textbf{12-La}, requires 5 days heated at 55 °C and is isolated in 32% yield. Both \((C_5\text{Me}_5)_3\text{Ln}\) compounds, \textbf{10-Sm} and \textbf{10-La}, have the potential for an \(\eta^1\) binding mode for one of the \((C_5\text{Me}_5)^{1-}\) ligands. However, due to a smaller ionic radius, the samarium species is more sterically crowded, which may facilitate the more reactive \(\eta^1\) mode and allow CO insertion more readily.

\((C_5\text{Me}_5)_2\text{La}(O_2\text{C}_7\text{Me}_5)\), \textbf{12-La}, was isolated by forcing precipitation of the product from toluene with the addition of hexane. The structure and purity were confirmed by NMR spectroscopy in THF-\(d_8\) and elemental analysis, respectively. It is interesting that \textbf{12-La} is hexane-insoluble while the Ce, Pr, Nd, and Sm homologues are not. It is therefore of interest to crystallize \textbf{12-La} to determine if the solid-state structure is isomorphous with \textbf{12-Sm}.
To investigate the reactivity of this non-classical carbocation, \((\text{C}_5\text{Me}_5)_2\text{Sm(O}_2\text{C}_7\text{Me}_5)\), 12-Sm, was subjected to a number of reactions to probe for cationic-initiated polymerization. Isoprene was added by vacuum-transfer to 12-Sm in C\(_6\)D\(_6\). No reaction was observed after 24 h at room temperature or 24 h at 40 °C. In a second attempt at cationic-initiated polymerization, 9-vinylcarbazole was added to 12-Sm in C\(_6\)D\(_6\). No reaction was observed after 24 h at 40 °C or 2 days at 60 °C. Further, styrene was added by vacuum-transfer to \((\text{C}_5\text{Me}_5)_2\text{La(O}_2\text{C}_7\text{Me}_5)\), 12-La, in C\(_6\)D\(_6\). No reaction was observed after 24 h at room temperature or 24 h at 50 °C.

To investigate the lack of reactivity, the electronic structure of 12-La was studied via density functional theory (DFT) by Megan Fieser. Using the previously reported crystal structure of 12-Sm\(^7\), the studies indicate the LUMO is not the empty 2p orbital located on the carbocation. Instead, the DFT analysis predicts the LUMO to be the 5d\(_{z^2}\) orbital of metal center and the LUMO +1 as the \(\pi^*\) anti-bonding orbital on the external olefin, Figure 4.2.

![LUMO and LUMO+1 of (C\(_5\)Me\(_5\))\(_2\)La(O\(_2\)C\(_7\)Me\(_5\)), 12-La.](image-url)
Conclusion

Attempts at using the rare earth non-classical carbocations, \((\text{C}_5\text{Me}_5)_2\text{Ln}(\text{O}_2\text{C}_7\text{Me}_5)\), \textbf{12-Ln} (Ln = La, Sm) for cationic-initiated polymerization have proven unsuccessful. When taking into consideration the results of DFT calculations, it may be possible to perform polymerizations or nucleophilic additions in a small, linear solvent such as acetonitrile, which could activate the complex by coordinating to the metal center and donating into the 5d\(_\text{z}^2\) orbital. Although spectroscopically similar to the analogous compounds with Ce, Pr, Nd, and Sm, the non-classical carbocation \((\text{C}_5\text{Me}_5)_2\text{La}(\text{O}_2\text{C}_7\text{Me}_5)\), \textbf{12-La}, was shown to be insoluble in aliphatic hydrocarbon solvents. It would be of interest to crystallize the product to determine whether the molecular structure is isomorphous with \((\text{C}_5\text{Me}_5)_2\text{Sm}(\text{O}_2\text{C}_7\text{Me}_5)\), \textbf{12-Sm}.

Experimental Details

All manipulations described below were performed with meticulous exclusion of oxygen and moisture using glovebox, Schlenk, and high vacuum line techniques. Tris(pentamethylyclopentadienyl) lanthanide complexes, \((\text{C}_5\text{Me}_5)_3\text{Ln}\), are especially reactive and were handled under an argon atmosphere free of coordinating solvents (THF, Et\(_2\)O, etc.) using silylated glassware to suppress oxide formation. All appropriate glassware was silylated using 1\% Siliclad (Gelest) in deionized water. All solvents were dried on columns containing Q-5 and 4 Å molecular sieves. NMR solvents benzene-\(d_6\) (\(\text{C}_6\text{D}_6\)) and tetrahydrofuran-\(d_8\) (THF-\(d_8\)) were dried over sodium-potassium alloy and benzophenone ketyl, degassed by 3 freeze-pump-thaw cycles, and vacuum-transferred on a high vacuum line prior to use. \(\text{LnCl}_3\) (Ln = La, Sm) was purified by sublimation under high vacuum at 350 °C.\(^{11,12}\) \(\text{KC}_5\text{Me}_5\) was synthesized from a 1:1 molar reaction of \(\text{HC}_5\text{Me}_5\) (Strem) and potassium
bis(trimethylsilylamide) (Aldrich) in toluene. HNEt₃BPh₄ was synthesized from a 1:1 molar reaction of NaBPh₄ and Et₃N·HCl in deionized water and dried thoroughly under high vacuum for several days before use. Ultra high-purity carbon monoxide was purchased from Airgas and used as received. 9-vinylcarbazole (Aldrich) was placed under vacuum (10⁻³ Torr) for 12 h prior to use. ¹H and ¹³C NMR spectra were collected with a Bruker CRYO 500 MHz spectrometer at 25 °C. IR spectra were collected from KBr pellets with Varian 1000 FT-IR spectrometer. Elemental analyses were conducted using a PerkinElmer Series II 2400 C/H/N elemental analyzer.

**General Procedure for Synthesizing (C₅Me₅)₂LnCl₂K(THF)₂.**¹³ K(C₅Me₅) was slowly tapped into a round bottom flask containing a stirred white slurry of LnCl₃ in THF, resulting in an immediate color change. The flask was sealed and allowed to stir for 2 days. The reaction mixture was centrifuged, and the supernatant was evaporated to dryness. The solids were washed with toluene and hexane, and collected by filtration. **Sm:** 0.7 g SmCl₃ (2.9 mmol); 1.0 g K(C₅Me₅) (5.8 mmol); 30 mL THF; 1.1 g orange-red solid (57%). **La:** 1.7 g LaCl₃ (7.1 mmol); 2.3 g K(C₅Me₅) (13 mmol); 50 mL THF, 2.8 g yellow solid (58%).

**General Procedure for Synthesizing (C₅Me₅)₂Ln(C₃H₅).**¹⁴ A graduated syringe was used to add (C₃H₅)MgCl (2.0 M solution in THF) dropwise to a stirred suspension of (C₅Me₅)₂LnCl₂K(THF)₂ in toluene. The flask was wrapped with aluminum foil to prevent exposure to light and allowed to stir overnight. The solvent was then removed under reduced pressure and the remaining tacky solids were left to stir in hexane with 1% 1,4-dioxane overnight wrapped in aluminum foil. The resulting slurry was filtered and the transparent filtrate was collected. The solvent was removed under reduced pressure and the solid product was transferred to a sublimation tube and placed under high vacuum (10⁻⁶ torr) with the temperature
carefully adjusted to just below the sublimation point (50-65 °C, 3 d) to remove coordinated THF. The desolvated product was transferred to an argon-filled glovebox free of coordinating solvents and extracted with hexane.  **Sm:** 15 g (C₅Me₅)₂SmCl₂K(THF)₂ (22 mmol); 13 mL of 2 M (C₅H₅)MgCl solution (27 mmol); 0.3 L toluene; yield 8.0 g red solids (80%). ¹H NMR (500 MHz, C₆D₆): δ 15.5 (br s, 1H, CH₂C₅H₅CH₂), 7.25 (d, 3JHH = 12.5 Hz, 2H, anti-CH₂CHCH₂), 3.82 (d, 3JHH = 8 Hz, 2H, syn-CH₂CHCH₂), 1.20 (s, 15H, C₅Me₅), 0.96 (s, 15H, C₅Me₅).

**La:** 2.8 g (C₅Me₅)₂LaCl₂K(THF)₂ (4.2 mmol); 2.5 mL of 2.0 M (C₅H₅)MgCl solution (5.0 mmol); 80 mL toluene; yield 1.4 g yellow solid (62%). ¹H NMR (500 MHz, C₆D₆): δ 6.56 (tt, 3JHH = 15.5, 9.0 Hz, 1H, CH₂C₅H₅CH₂), 3.18 (d, 3JHH = 15.5 Hz, 2H, anti-CH₂CHCH₂), 2.56 (d, 3JHH = 9.0 Hz, 2H, syn-CH₂CHCH₂), 1.91 (br s, 30H, C₅Me₅).

**General Procedure for Synthesizing of [(C₅Me₅)₂Ln][(µ-Ph)₂BPh₄].**¹⁴ In a nitrogen-filled glovebox, HNEt₃BPh₄ was slowly added to a round bottom flask containing a stirred solution (C₅Me₅)₂Ln(C₅H₅) in toluene. The resulting suspension was allowed to stir in an open flask for 3 h to allow gaseous propene to escape. The flask was then sealed with a greased stopper. After 18 h, the solid product was collected by filtration and washed with hexane.  **Sm:** 0.5 g (C₅Me₅)₂SmC₃H₅ (1.1 mmol); 0.4 g HNEt₃BPh₄ (1.0 mmol); 40 mL toluene; 0.6 g red solid (76%). ¹H NMR (500 MHz, C₆D₆): δ 8.43 (br s, 8H, BPh₄), −0.34 (s, 30H, C₅Me₅).  **La:** 1.8 g of (C₅Me₅)₂LaC₃H₅ (4.0 mmol); 1.7 g HNEt₃BPh₄ (4.0 mmol); 0.1 L toluene; yield 2.5 g pale yellow solid (86%). ¹H NMR (500 MHz, C₆D₆): δ 7.69 (br d, J = 6.0 Hz, 8H, o-BPh₄), 7.22 (t, 3JHH = 7.0 Hz, 8H, m-BPh₄), 7.08 (t, 3JHH = 7.0 Hz, 4H, p-BPh₄), 1.60 (s, 30H, C₅Me₅).

**General Procedure for Synthesizing (C₅Me₅)₃Ln, 10-Ln.**¹⁴ In an argon-filled glovebox, with vigorous stirring K(C₅Me₅) was slowly added to a suspension of [(C₅Me₅)₂Ln][(µ-Ph)₂BPh₄] in benzene. The reaction vessel was sealed and allowed to stir. After 48 h, ¹H NMR
spectroscopy confirmed product formation. The reaction mixture was centrifuged and the supernatant was filtered. Removal of the solvent under reduced pressure afforded \((\text{C}_5\text{Me}_5)_3\text{Ln}\).

**10-Sm:** 1.6 g of \[((\text{C}_5\text{Me}_5)_2\text{Sm})[\text{(µ-Ph)}_2\text{BPh}_4]\) (2.2 mmol); 0.8 g \text{K(C}_5\text{Me}_5\) (4.4 mmol); 30 mL benzene; yield 0.9 g red solid (73%). \(^1\text{H NMR (500 MHz, C}_6\text{D}_6\):} \(\delta -1.23 \) (s, 45H, \text{C}_5\text{Me}_5).

**10-La:** 0.4 g of \[((\text{C}_5\text{Me}_5)_2\text{La})[\text{(µ-Ph)}_2\text{BPh}_4]\) (0.5 mmol); 0.2 g \text{K(C}_5\text{Me}_5\) (1.4 mmol); 10 mL benzene; yield 0.2 g yellow solid (78%). \(^1\text{H NMR (500 MHz, C}_6\text{D}_6\):} \(\delta 2.01 \) (s, 45H, \text{C}_5\text{Me}_5).

\((\text{C}_5\text{Me}_5)_2\text{Sm(C}_6\text{Me}_4-2,2'-\text{CMe},\text{µ-1,1',κ}^2\text{-O,O')}, \text{ 12-Sm.}^{15}\) A deep red solution of \((\text{C}_5\text{Me}_5)_3\text{Sm}\) (0.2 g, 0.3 mmol) in toluene (10 mL) in a side arm Schlenk flask (50 mL) was degassed by 3 freeze-pump-thaw cycles on a high vacuum line. CO (1 atm) was introduced to the flask, which was then sealed, and the solution was allowed to stir at room temperature. After 20 min, the solution had changed color from deep red to bright yellow. The solvent and CO were removed under reduced pressure before being transferred to a non-coordinating glovebox containing argon. The resulting yellow solids were extracted with hexane, and removal of the solvent under reduced pressure afforded \textbf{12-Sm} as a yellow solid (74 mg, 42%). \(^1\text{H NMR (500 MHz, C}_6\text{D}_6\):} \(\delta 3.64 \) (s, 3H, \text{CMe},\text{µ-1,1'}), 2.31 (s, 6H, 2,2'-\text{C}_6\text{Me}_4), 1.29 (s, 6H, 3,3'-\text{C}_6\text{Me}_4), 1.07, 0.99 (s, 15H, \text{C}_5\text{Me}_5).

\((\text{C}_5\text{Me}_5)_2\text{La(C}_6\text{Me}_4-2,2'-\text{CMe},\text{µ-1,1',κ}^2\text{-O,O')}, \text{ 12-La.}^{15}\) An amber solution of \((\text{C}_5\text{Me}_5)_3\text{La}\) (0.7 g, 1.4 mmol) in toluene (50 mL) in a side arm Schlenk flask (100 mL) was degassed with 3 freeze-pump-thaw cycles on a high vacuum line. CO (1 atm) was introduced to the flask, which was then sealed, and the solution was allowed to stir at 55 °C for 5 days with no color change. CO was removed with 3 freeze-pump-thaw cycles on high vacuum line. The flask was transferred to a non-coordinating glovebox containing argon and the solution was concentrated to 2 mL under reduced pressure. Hexane (50 mL) was added to precipitate \textbf{12-La}
as white solid, which was collected by filtration (0.3 g, 32%). $^1$H NMR (500 MHz, THF-$d_8$): $\delta$ 1.87, 1.78 (s, 15H, C$_5$Me$_5$), 1.64 (s, 6H, 2,2'-C$_6$Me$_4$), 1.28 (s, 3H, CMe,μ-1,1'), 1.20 (s, 6H, 3,3'-C$_6$Me$_4$). $^{13}$C NMR (125 MHz, THF-$d_8$): $\delta$ 133.85 (2,2'-C$_6$Me$_4$), 128.68 (1,1'-C$_2$), 127.92 (CMe,μ-1,1'), 125.05, 116.71, 116.63 (C$_5$Me$_5$), 10.58 (2,2'-C$_6$Me$_4$), 10.30, 10.20 (C$_5$Me$_5$), 6.86 (3,3'-C$_6$Me$_4$), 2.79 (CMe,μ-1,1'). IR: 2969m, 2910m, 2855m, 2721w, 1539s, 1438m, 1409s, 1367s, 1301w, 1088m, 957w, 892w, 800w, 731m, 695m, 574w, 493m cm$^{-1}$. Anal. Calcd for C$_{32}$H$_{45}$O$_2$La: C, 63.99; H, 7.55. Found: C, 64.14; H 7.70.

**DFT Analysis on 12-La.**$^{16}$ Starting from the available crystal data of 12-Sm and replacing the Sm metal center with La, calculations were performed using the TPSSh$^{17}$ hybrid meta-GGA functional. Split valence basis sets with polarization functions on non-hydrogen atoms (SV(P)) were used for light atoms and triple-zeta valence basis sets with two sets of polarization functions (def2-TZVP) for La.$^{18,19}$ TPSSh was chosen due to its established performance for transition metal compounds, and reductive Ln chemistry.$^{20-22}$ Relativistic small-core pseudopotentials$^{23}$ were employed for La. All computations were performed using the TURBOMOLE program package.$^{24}$ All molecular orbitals were computed with SV(P) basis sets using contour values of 0.05.$^{25}$
References

(16) DFT data was collected and compiled by Megan Fieser and Jeb Bates.
Chapter 5
Development of a Rare Earth Reducing Agent
With Simple Amide Ligands

Introduction

Since the 1970s, rare earth elements have been explored for use as single electron reductants through a highly reducing divalent oxidation state. In 1980, Kagan and co-workers discovered that the lanthanide compound samarium diiodide (SmI₂) could be used to selectively reduce aldehydes, perform coupling reactions, deoxygenate epoxides, and react with ketones in the presence of alkyl halides to form tertiary alcohols. In 1987, it was discovered that the effectiveness of SmI₂ toward the reduction of organic halides could be significantly enhanced in the presence of hexamethylphosphoramide (HMPA). The combination of SmI₂ and HMPA has been an extremely valuable tool for many classes of organic reactions that require a single-electron reducing agent. However, HMPA has been recognized as a potent carcinogen and SmI₂/HMPA reactions are largely limited to use in THF.

Described in this Chapter are attempts to develop a well-defined reducing agent with a rare earth metal center that is compatible with a range of organic reactions in multiple solvents as an alternative to the SmI₂/HMPA system that currently dominates reduction reactions in organic chemistry. To this end, an isolable reagent was pursued in the form of a reduced nitrogen species, \((A_2Ln)_2(\mu-\eta^2:\eta^3-N_2)\) (Ln = Sc, Y, lanthanides; A = anion).

Reduced dinitrogen complexes with rare earth metals (Ln) can be made via the LnA₃/M system (M = alkali metal) in which an Ln³⁺ salt is combined with an alkali metal to give reactivity equivalent to LnA₂. Utilizing the ancillary ligand bis(trimethylsilyl)amide,
[N(SiMe₃)₂]⁻, first reported by Bradley in 1973,¹⁹ the Ln[N(SiMe₃)₂]₃ complexes (Ln = Tm, Dy, Y) have proven to be valuable precursors to the (N₂)²⁻ products, {[(Me₂Si)N(THF)]Ln₂(µ-η²:η²-N₂)}.²⁰,²¹ However, the reaction produces a number of byproducts including an (N₂)³⁻ species, {[(Me₂Si)₂N(THF)]Ln₂(µ-N₂H₂)}, and an undesirable metallacyclic species, {[(Me₂Si)₂N]Ln[CH₂Si(Me₂)NSiMe₃]}[K(THF)₂], resulting from C–H bond activation of SiMe₃.²²

The neutral bimetallic rare earth complex [(C₅Me₅)₂(THF)La](µ-η²:η²-N₂)¹² that contains a bridging (N₂)²⁻ has been shown to act as reducing agent. [(C₅Me₅)₂(THF)La](µ-η²:η²-N₂) can reduce aromatic organic substrates phenazine, anthracene, and azobenzene by two electrons and has also shown interesting reactivity with CO.¹⁷ However, despite the reducing power of this dinitrogen system, complexes with Cp ligands have not found significant use as reducing agents in organic syntheses. The work in this Chapter is therefore devoted to synthesizing (A₂Ln)₂(µ-η²:η²-N₂) complexes where A is not [N(SiMe₃)₂]⁻ or cyclopentadienyl. The new compounds were to be made by the LnA₃/M and to accomplish this, new LnA₃ complexes had to be made.

In this study, a number of LnA₃ complexes with Ln = Y were synthesized toward the development of a new (A₂Ln)₂(µ-η²:η²-N₂) species. In the framework of an LnA₃/M system, the anionic ancillary ligand was varied where A = dicyclohexyl amide, (Cy₂N)⁻, diphenyl amide, (Ph₂N)⁻, diisopropyl amide, (Pr₂N)⁻, and 2,3-dimethylindolide (DMI)⁻, to avoid formation of the metallacyclic product that is observed when A = the [N(SiMe₃)₂]⁻ during nitrogen reduction. Yttrium was chosen as the rare earth metal to be used for the LnA₃/M reduction reaction due to its I = ½ nuclear spin, which is useful analytically for NMR and EPR spectroscopy, as well as its low reduction potential²³ and small ionic radius, making it a model system for the smaller
In the Ln[N(SiMe$_3$)$_2$]$_3$/M reduction process with larger lanthanides (Ln = La, Ce, Pr), the $(\text{N}_2)^{2-}$ product was observed by NMR spectroscopy but could not be isolated as crystals.$^{15}$

**Results and Discussion**

**Synthesis of YA$_3$ Complexes.** A colorless suspension of YCl$_3$ and three equiv of LiNCy$_2$ in THF reacts by metathesis to form a colorless solution of $(\text{Cy}_2\text{N})_3\text{Y}(\text{THF})$, 13, in 60% yield, eq 5.1. Compound 13 was crystallized from toluene and definitively identified by X-ray diffraction, Figure 5.1. Despite a smaller ionic radius,$^{24}$ the Y$^{3+}$ ion is able to accommodate the same ligand set as an analogous Ce$^{3+}$ complex reported by Lappert, $(\text{Cy}_2\text{N})_3\text{Ce}(\text{THF})$, which is isomorphous with 13.$^{25}$

Following a similar procedure for 13, a colorless suspension of YCl$_3$ and three equiv of KNPh$_2$ in THF reacts by metathesis to form a colorless solution of $(\text{Ph}_2\text{N})_3\text{Y}(\text{THF})$, 14, in 90% yield, eq 5.2. Compound 14 was crystallized from Et$_2$O and definitively identified by X-ray diffraction, Figure 5.1.
Figure 5.1. ORTEP\textsuperscript{26} representation of 13 with thermal ellipsoids drawn at the 50\% probability level. Hydrogen atoms have been omitted for clarity.

Figure 5.2. ORTEP\textsuperscript{26} representation of 14 with thermal ellipsoids drawn at the 50\% probability level. Hydrogen atoms have been omitted for clarity.
A similar reaction was attempted between YCl3 and LiNPr2 to produce (iPr2N)3Y(THF), a synthetic route first reported by Ghotra and Hart for (iPr2N)3Ln(THF) (Ln = Y, Nd, Yb). The product was sacrificed for single crystal X-ray diffraction and found to match the unit cell of a tetrakis-amido complex, (THF)2Li[µ-(NPr2)]2Y(iPr2)2, 15, eq 2.3, reported by Aspinall. As a result of a sterically smaller diisopropylamido ligand, the only product isolated was 15, a compound commonly produced under these reaction conditions.

An alternative route to (iPr2N)3Y(THF) is described by Anwander and co-workers that proceeds through a protolysis of (Me3SiH2C)3Y(THF)2 by HNPr2 rather than by the conventional metathesis used successfully for 13 and 14. A colorless solution of LiCH2SiMe3 in hexane was added to YCl3 to precipitate (Me3SiH2C)3Y(THF)2, 16, as a pale yellow solid, eq 5.4. The synthesis of 16 was confirmed by 1H NMR spectroscopy, which demonstrates a 2-bond coupling of 2.5 Hz between yttrium and the methylene protons of the (Me3SiH2C)− ancillary ligand, as both Y and H nuclei have a nuclear spin of ½.

A colorless solution of 16 in hexane reacts with HNPr2 to form (iPr2N)3Y(THF)2, 17, as a colorless solid, eq 5.5. Compound 17 was crystallized from hexane and definitively identified by X-ray crystallography. A colorless solution of 16 in hexane reacts with HDMI to form (DMI)3Y(THF)2, 18, as a yellow solid. Compound 18 was identified by NMR spectroscopy.
Crystallographic Data on (R₂N)₃Y(THF)ₙ Complexes. Crystallographic data for compounds (Cy₂N)₃Y(THF), 13, and (Ph₂N)₃Y(THF)₂, 14, are summarized in Table 5.1. Compound 13 is 4-coordinate and tetrahedral (τ₄ = 0.77 where 0 = ideal square planar and 1 = ideal tetrahedral)³¹ while compound 14 is 5-coordinate and is neither trigonal bipyramidal nor square pyramidal (τ₅ = 0.50 where 0 = ideal trigonal bipyramidal and 1 = ideal square pyramidal).³² If 14 were considered from a trigonal planar point of view, the THF ligands would be axial. However, the O1–Y1–O2 bond angle is only 160.31(4)° and not 180°. The [(NPh₂)₃]³⁻ ligands of 14 are nearly trigonal planar about the yttrium metal center, with Y1 sitting just 0.100 Å above the plane of N1, N2, and N2, Pln1. The diphenylamido ligand, (NPh₂)⁻, is less sterically demanding than (NCy₂)⁻, which allows for the coordination of a second THF ligand. The 2.201(1)-2.232(2) Å Y–N bonds in 4-coordinate 13 are numerically shorter than the 2.240(2)-2.287(1) Å analogs in 5-coordinate 14, although the longest bond of 13, the 2.232(2) Å Y1–N3, is comparable with the shortest bond of 14, Y1–N1, 2.240(2) Å, respectively. Average Y–N bond lengths for 13 and 14, 2.215(16) and 2.263(19) Å, are comparable with that of Y[N(SiMe₃)₂]₃, 2.224(6) Å.³³
Table 5.1: Selected Bond Distances (Å) and Angles (deg) for (Cy₂N)₃Y(THF), 13, and (Ph₂N)₃Y(THF)₂, 14.

<table>
<thead>
<tr>
<th></th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y1–N1</td>
<td>2.2008(14)</td>
<td>2.2612(14)</td>
</tr>
<tr>
<td>Y1–N2</td>
<td>2.2123(14)</td>
<td>2.2399(14)</td>
</tr>
<tr>
<td>Y1–N3</td>
<td>2.2316(15)</td>
<td>2.2869(14)</td>
</tr>
<tr>
<td>Y1–O1</td>
<td>2.4260(12)</td>
<td>2.3526(11)</td>
</tr>
<tr>
<td>Y1–O2</td>
<td>-</td>
<td>2.3838(12)</td>
</tr>
<tr>
<td>Pln₁⁻⁻⁻–Y1</td>
<td>-</td>
<td>0.100</td>
</tr>
<tr>
<td>N1–Y1–N2</td>
<td>108.29(5)</td>
<td>106.77(5)</td>
</tr>
<tr>
<td>N1–Y1–N3</td>
<td>122.44(5)</td>
<td>130.61(5)</td>
</tr>
<tr>
<td>N2–Y1–N3</td>
<td>109.27(5)</td>
<td>122.03(5)</td>
</tr>
<tr>
<td>O1–Y1–O2</td>
<td>-</td>
<td>160.31(4)</td>
</tr>
</tbody>
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Pln₁ is the plane of N1, N2, and N3

Reactivity of (Cy₂N)₃Y(THF), 13. To test the ability of compound 13 to reduce N₂ in the presence of an alkali metal, a reaction was performed between 13 and potassium-graphite, KC₈, eq 5.7. After the addition of KC₈ to a THF solution of (Cy₂N)₃Y(THF), the reaction was stirred for 5 h to make a yellow intermediate that goes on to form a red product after 24 h, which deepens to a dark red product after 9 d. The reaction in eq 5.7 was repeated overnight with ¹⁵N₂ on a high vacuum line to form a red product. The product of the ¹⁵N₂ reaction was investigated by ¹⁵N NMR. No peaks were observed.

(Cy₂N)₃Y(THF) + KC₈ → Red Oil

(THF, N₂, rt) (5.7)

The reaction in equation 5.7 was repeated under argon as a control reaction. After 5 days, a deep red product was observed that was found to also be identical to the ¹H NMR spectrum collected for the product in equation 5.7. Two control reactions, under ¹⁵N₂ and argon, as well as an absence of bound THF by ¹H NMR indicate that a bridging N₂ species has not been
synthesized. Without structural information, the identity of the red product of equation 5.7 cannot be assigned.

**Conclusion**

(Cy$_2$N)$_3$Y(THF), 13, and (Ph$_2$N)$_3$Y(THF)$_2$, 14, were synthesized and characterized for the first time. Although initially there was a color change in the reaction of (Cy$_2$N)$_3$Y(THF) with KC$_8$ under an atmosphere of N$_2$, the absence of peaks by $^{15}$N NMR spectroscopy and a control reaction performed under argon indicate that N$_2$ reduction has not taken place. It is possible that the product forming is a bridging oxide, such as [(Cy$_2$N)$_2$Y](µ-O), which would be of interest because deliberate attempts at synthesizing [(SiMe$_3$)$_2$N]$_2$Y(µ-O), a by-product of the reaction between (N$_2$)$_3$$^{3-}$ and NO, remain unsuccessful.

The ability of (Ph$_2$N)$_3$Y(THF)$_2$, 14, (′Pr$_2$N)$_3$Y(THF)$_2$, 17, and (DMI)$_3$Y(THF)$_2$, 18, to reduce N$_2$ in the presence of KC$_8$ is also of interest, although it is unlikely that the similar (′Pr$_2$N)$_3$$^{3-}$ system of 17 would react differently. The (Ph$_2$N)$_3$$^{3-}$ and (DMI)$_3$$^{3-}$ ligand sets for 14 and 18, respectively, may be less electron-donating and in that regard react similarly to [N(SiMe$_3$)$_2$]$_3$$^{3-}$. If a reduced N$_2$ product is formed, it may be possible to assist crystallization of an (N$_2$)$^{3-}$ product with a crown ether, to oxidize any (N$_2$)$^{3-}$ with Hg to increase yield of (N$_2$)$^{2-}$.

If it is confirmed that a given (R$_2$N)$_3$Y/M system can reduce N$_2$, that same system can be used to attempt the reductions of the aromatic compounds phenazine and anthracene to assess the reducing power of these new reductants relative to the known [N(SiMe$_3$)$_2$]$^{1-}$ system. Further, the development of a tetraphenylborate salt analogous to {[(Me$_3$Si)$_2$N]$_2$(THF)$_2$Y}{BPh$_4$}$^{34}$ may allow access to the reduction of dinitrogen through an alternative pathway through analogous [Y(NR$_2$)$_2$]$^{+}$ cations.
Experimental Details

All manipulations described below were performed with meticulous exclusion of oxygen and moisture using glovebox, Schlenk, and high vacuum line techniques. All solvents were dried on columns containing Q-5 and 4 Å molecular sieves. NMR solvents benzene-$d_6$ (C$_6$D$_6$) and tetrahydrofuran-$d_8$ (THF-$d_8$) were dried over sodium-potassium alloy and benzophenone ketyl, degassed by 3 freeze-pump-thaw cycles, and vacuum-transferred on a high vacuum line prior to use. YCl$_3$ (was purified by sublimation under high vacuum at 350 °C$^{36,37}$ HNCy$_2$ (Acros) and HNPr$_2$ (Aldrich) were dried over activated molecular sieves overnight prior to use. HNPh$_2$ and HDMI (Aldrich) were placed under vacuum ($10^{-3}$ Torr) for 12 h prior to use. KH was washed with hexane prior to use. LiCH$_2$SiMe$_3$ (1.0 M solution in pentane) was purchased from Aldrich and dried prior to use. n-Butyllithium (2.5 M solution in hexane) was purchased from Aldrich and used as received. $^1$H and $^{13}$C NMR spectra were collected with a Bruker CRYO 500 MHz spectrometer at 25 °C. IR spectra were collected from KBr pellets with Varian 1000 FT-IR spectrometer. Elemental analyses were conducted using a PerkinElmer Series II 2400 C/H/N elemental analyzer. Raman experiments were performed in a quartz cell sealed with a Teflon stopcock with a Renishaw inVia confocal Raman Microscope using 532 nm laser excitation (10% laser power, laser focus 50% at 100 s exposure).

Synthesis of LiNCy$_2$. In a glovebox containing nitrogen, a solution of HNCy$_2$ (5.0 g, 28 mmol) in THF (30 mL) was prepared in a pear-shaped Schlenk flask. The flask was transferred to a Schlenk line and cooled to 0 °C. Under a positive pressure of N$_2$, a 2.5 M solution of n-butyllithium (10 mL, 25 mmol) was added to the reaction vessel dropwise, creating an amber solution that was allowed to stir overnight at room temperature. The solvent was removed under reduces pressure yielding a tacky yellow product. The solids were stirred in
hexane overnight, dried under reduced pressure, and placed under high vacuum (10^{-6} torr) overnight. Hexane was used to precipitate LiNCy\textsubscript{2} from residual THF as a white powder, collected by filtration (1.7 g, 36%). \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta\) 2.81 (app t, \(^3J_{HH} = 10.7\) Hz, 1H, \(CH(\text{CH}_2)_5\)), 2.61 (app t, \(^3J_{HH} = 10.7\) Hz, 1H, \(CH(\text{CH}_2)_5\)), 2.12 (d, \(^3J_{HH} = 10\) Hz, 2H, (\text{o,eq})-CH(\text{CH}_2)_5), 1.94 (d, \(^3J_{HH} = 11\) Hz, 2H, (\text{o,eq})-CH(\text{CH}_2)_5), 1.85 (t, \(^3J_{HH} = 13.2\) Hz, 4H, (\text{m,eq})-CH(\text{CH}_2)_5), 1.71 (t, \(^3J_{HH} = 14.5\) Hz, 2H, (\text{p,eq})-CH(\text{CH}_2)_5), 1.41 (quin, \(^3J_{HH} = 13.1\) Hz, 4H, (\text{m,ax})-CH(\text{CH}_2)_5), 1.21 (m, 2H, (\text{p,ax})-CH(\text{CH}_2)_5), 1.08 (quin, \(^3J_{HH} = 10.5\) Hz, 4H, (\text{o,ax})-CH(\text{CH}_2)_5).

**Synthesis of \((\text{Cy}_2\text{N})_3\text{Y(THF)}\), 13.** \textsuperscript{39} YCl\textsubscript{3} (0.2 g, 1.2 mmol) was stirred for 3 days in THF (20 mL) in a pear-shaped Schlenk flask to ensure complete solvation. Under a positive pressure of N\textsubscript{2} on a Schlenk line, a solution of LiNCy\textsubscript{2} (0.6 g, 3.4 mmol) in THF (15 mL) was added dropwise to YCl\textsubscript{3} at 0 °C over 15 min. The reaction vessel was allowed to warm to room temperature and after 1 h the solvent was removed under reduced pressure to yield a tacky white solid. In a glovebox containing nitrogen, the white solids were extracted with toluene, filtered, and concentrated to 2 mL. Layering with hexane and storing at \(-28\) °C for 4 days yielded colorless crystals of 13 (0.5 g, 60%). \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta\) 3.86 (m, 4H, \(THF\)), 3.01 (m, 6H, \(CH(\text{CH}_2)_5\)), 2.03 (d, \(^3J_{HH} = 11.5\) Hz, 12H, (\text{o,eq})-CH(\text{CH}_2)_5), 1.94 (d, \(^3J_{HH} = 13.0\) Hz, 12H, (\text{m,eq})-CH(\text{CH}_2)_5), 1.74 (d, \(^3J_{HH} = 12.5\) Hz, 6H, (\text{p,eq})-CH(\text{CH}_2)_5), 1.63 (app q, \(^3J_{HH} = 13.0\) Hz, 12H, (\text{m,ax})-CH(\text{CH}_2)_5), 1.51 (app q, \(^3J_{HH} = 13.0\) Hz, 12H, (\text{o,ax})-CH(\text{CH}_2)_5), 1.32 (tt, \(^3J_{HH} = 12.5\), 3.5 Hz, 6H, (\text{p,ax})-CH(\text{CH}_2)_5), 1.25 (m, 4H, \(THF\)). \textsuperscript{13}C NMR (125 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta\) 72.30 (\(THF\)), 57.98, 38.77, 27.75, 27.35 (\text{C}_6\text{H}_{11}), 25.35 (\(THF\)). IR: 2905m, 2758m, 2663m, 2583m, 1462m, 1447m, 1396m, 1358m, 1338m, 1290w, 1243m 1177m, 1143m, 1117m, 1087m, 1067m, 1038m, 1017m, 983m, 947m, 887m, 865m, 842m, 798m, 776w, 658m, 621m, 580m, 492m,
Anal. Calcd for C$_{40}$H$_{74}$N$_3$OY: C, 68.44; H, 10.63; N, 5.99. Found: C, 68.25; H, 10.40; N, 5.51.

**X-ray Data Collection, Structure Solution and Refinement for (Cy$_2$N)$_3$Y(THF), 13.**

A colorless crystal of approximate dimensions 0.38 x 0.24 x 0.19 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2$^{41}$ 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$^{42}$ and SADABS$^{43}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL$^{44}$ 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 by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors$^{45}$ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There was one molecule of toluene solvent present. At convergence, wR2 = 0.0831 and Goof = 1.021 for 470 variables refined against 10772 data (0.75 Å), $R_1 = 0.0356$ for those 8407 data with $I > 2.0\sigma(I)$.

**Synthesis of KNPh$_2$.**$^{38}$ Under positive pressure of N$_2$ on a Schlenk line, a solution of HNPh$_2$ (9.3 g, 55 mmol) in THF (45 mL) was added dropwise to a suspension of KH (2.0 g, 50 mmol) in THF (70 mL) at 0 °C over 15 min. The resulting yellow solution was allowed to stir overnight at room temperature. The solvent was removed under reduced pressure and washing with hexane yielded KNPh$_2$ as a white solid (10 g, 99%). $^1$H NMR (500 MHz, THF-$d_8$): $\delta$ 6.84 (app q, $^3J_{HH} = 8.16$ Hz, 8H, $(o,m)$-C$_6$H$_5$), 6.12 (app t, $^3J_{HH} = 3.0$ Hz, 2H, $p$-C$_6$H$_5$).

**Synthesis of (Ph$_2$N)$_3$Y(THF)$_2$, 14.**$^{39}$ YCl$_3$ (0.63 g, 3.2 mmol) was stirred for 2 days in THF (30 mL) in a pear-shaped Schlenk flask to ensure complete solvation. Under positive
pressure of N$_2$ on a Schlenk line, a solution of KNPh$_2$ (1.9 g, 9.1 mmol) in THF (30 mL) was added dropwise to the YCl$_3$ suspension in THF at 0 °C over 15 min. The reaction vessel was allowed to warm to room temperature, and after 1 h, the solvent was removed under reduced pressure to yield a white solid. In a glovebox containing a N$_2$ atmosphere, the product was extracted with toluene and evaporated to dryness. The resulting solids were washed with hexane to yield 14 as a white solid (2.2 g, 90%). The white solid was dissolved in Et$_2$O and stored at −28 °C for 3 days to yield colorless crystals of 14. $^1$H NMR (500 MHz, C$_6$D$_6$): δ 7.17 (dd, $^3$J$_{HH}$ = 7.5, 7.0 Hz, 12H, o-C$_6$H$_5$), 7.06 (d, $^3$J$_{HH}$ = 8.0 Hz, 12H, m-C$_6$H$_5$), 6.80 (dd, $^3$J$_{HH}$ = 7.5, 7.0 Hz, 6H, p-C$_6$H$_5$), 3.49 (br s, 8H, THF), 0.87 (br s, 8H, THF). $^{13}$C NMR (125 MHz, C$_6$D$_6$): δ 130.46 (o-C$_6$H$_5$), 122.34 (m-C$_6$H$_5$), 119.92 (p-C$_6$H$_5$), 72.14, 26.31 (THF). IR: 3051w, 3008w, 2976w, 2902w, 2581w, 2477w, 1928w, 1581s, 1482s, 1332s, 1283s, 1199s, 1177s, 1073m, 1012s, 989s, 961m, 911s, 864s, 843s, 748s, 696s, 649m, 518m, 497s cm$^{-1}$. Anal. Calcd for C$_{44}$H$_{46}$N$_3$O$_2$Y: C, 71.63; H, 6.28; N, 5.70. Found: C, 71.67; H, 6.25; N, 5.51.

**X-ray Data Collection, Structure Solution and Refinement for (Ph$_2$N)$_3$Y(THF)$_2$, 14.** A colorless crystal of approximate dimensions 0.37 x 0.38 x 0.57 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 $P2_1/c$ 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. At convergence, wR2 = 0.0812 and Goof = 1.035 for 451 variables refined against 8829 data (0.75Å), R1 = 0.0313 for those 7562 data with I > 2.0σ(I).

**Synthesis of LiN\text{\textit{i}}\text{\textit{Pr}}\text{\textsubscript{2}}.**\textsuperscript{38}\textsuperscript{38} Under positive pressure of N\textsubscript{2} on a Schlenk line, a 2.5 M solution of \textsuperscript{\textit{n}}-butyllithium in hexane (14 mL, 36 mmol) was added to a solution of HN\text{\textit{i}}\text{\textit{Pr}}\text{\textsubscript{2}} (4.0 g, 40 mmol) in hexane (40 mL) dropwise over 20 min at 0 °C. The resulting colorless solution was allowed to stir overnight at room temperature. The solvent was removed under reduced pressure and the remaining white solids were washed with hexane to give LiN\text{\textit{i}}\text{\textit{Pr}}\text{\textsubscript{2}} as a white solid (1.9 g, 50%). \textsuperscript{1}H NMR (500 MHz, THF-\textit{d}\textsubscript{8}): δ 3.02 (m, 2H, C\text{\textit{H}}(CH\text{\textsubscript{3}})\text{\textsubscript{2}}), 0.98 (d, 12H, CH(C\text{\textsubscript{H}}\text{\textsubscript{3}})\text{\textsubscript{2}}).

**Synthesis of (THF)\textsubscript{2}Li[\textmu-(N\text{\textit{i}}\text{\textit{Pr}}\text{\textsubscript{2}})]\textsubscript{2}Y(N\text{\textit{i}}\text{\textit{Pr}}\text{\textsubscript{2}})\textsubscript{2}, 15.**\textsuperscript{39,46} YCl\textsubscript{3} (0.8 g, 4.1 mmol) was stirred overnight in THF (30 mL) to ensure complete solvation. Under positive pressure of N\textsubscript{2} on a Schlenk line, a solution of LiN\text{\textit{i}}\text{\textit{Pr}}\text{\textsubscript{2}} (1.2 g, 12 mmol) in THF (30 mL) was added dropwise to the suspension of YCl\textsubscript{3} in THF at 0 °C over 20 min. The resulting clear solution was allowed to stir overnight. The solvent was removed under vacuum to yield a tacky yellow-tinted solid. The product was stirred in hexane overnight and centrifuged. The supernatant was filtered and reduced to 5 mL then stored overnight at −28 °C to yield colorless crystals of 15. \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}): δ 3.57 (br s, 8H, C\text{\textit{H}}(CH\text{\textsubscript{3}})\text{\textsubscript{2}}), 3.35 (br s, 4H, THF), 1.39 (s, 48H, CH(C\text{\textsubscript{H}}\text{\textsubscript{3}})\text{\textsubscript{2}}), 1.16 (m, 4H, THF).

**Synthesis of (Me\textsubscript{3}SiH\textsubscript{2}C)\textsubscript{3}Y(THF)\textsubscript{2}, 16.**\textsuperscript{47} In a glovebox containing nitrogen, YCl\textsubscript{3} (0.7 g, 3.7 mmol) was stirred for 5 days to ensure complete solvation. The solvent was removed under reduced pressure. A solution of LiCH\textsubscript{2}SiMe\textsubscript{3} (1.0 g, 11 mmol) in hexane (30 mL) was added dropwise to the suspension of YCl\textsubscript{3} and allowed to stir overnight at room temperature. A white precipitate formed and the resulting mother liquor was decanted and placed under vacuum
to yield 16 as a pale yellow solid (0.58 g, 33%). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 3.95, 1.30 (m, 8H, THF), 0.30 (s, 27H, CH$_2$Si(CH$_3$)$_3$), −0.68 (d, $^2$J$_{YH}$ = 2.5 Hz, 6H, CH$_2$Si(CH$_3$)$_3$).

**Synthesis of (iPr$_2$N)$_3$Y(THF)$_2$, 17.$^{47}$** In a glovebox containing nitrogen, a solution of HNiPr$_2$ (102 mg, 1.0 mmol) in hexane (3 mL) was added dropwise to a stirred solution of 16 (164 mg, 0.3 mmol) in hexane (5 mL) and allowed to stir overnight at room temperature and centrifuged. The supernatant was filtered and stored at −28 °C for 7 days to yield colorless crystals of 17. Crystals were sacrificed to collect a unit-cell.

**Synthesis of (DMI)$_3$Y(THF)$_2$, 18.$^{48}$** In a glovebox containing nitrogen, a solution of HDMI (292 mg, 2.0 mmol) in toluene (6 mL) was added dropwise to a stirred solution of 16 (325 mg, 0.7 mmol) in toluene (15 mL) and allowed to stir for 2 h. The solvent was removed under vacuum to yield 18 as a yellow solid (427 mg, 33%). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 7.76 (d, $^3$J$_{HH}$ = 7.7 Hz, 1H, Ar-DMI), 7.68 (d, $^3$J$_{HH}$ = 8.0 Hz, 3H, Ar-DMI), 7.3 (app t, $^3$J$_{HH}$ = 7.1 Hz, 3H, Ar-DMI), 7.19 (app d, $^3$J$_{HH}$ = 7.1 Hz, 3H, Ar-DMI), 3.33 (br s, 8H, THF), 2.47 (s, 9H, Me-DMI), 2.44 (s, 9H, Me-DMI), 0.73 (br s, 8H, THF).

**Reaction of (Cy$_2$N)$_3$Y(THF)/KC$_8$ with N$_2$.$^{49}$** In a glovebox containing nitrogen, THF was added to a vial containing solids 13 (0.2 g, 0.2 mmol) and KC$_8$ (68 mg, 0.5 mmol). After 3 hours of vigorous stirring, the suspension had changed color from bronze to black. The suspension was allowed to stir overnight at room temperature. After centrifugation, the supernatant was filtered and the solvent was removed under reduced pressure to yield a red oil. $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 2.65 (s, 8H, CH(CH$_2$)$_3$), 1.83 (d, $^3$J$_{HH}$ = 10.5 Hz, 16H, (o,eq)-CH(CH$_2$)$_3$), 1.67 (d, $^3$J$_{HH}$ = 10 Hz, 16H, (m,eq)-CH(CH$_2$)$_3$), 1.54 (d, $^3$J$_{HH}$ = 9.5 Hz, 8H, (p,eq)-CH(CH$_2$)$_3$), 1.15 (m, 27H, (m,p,ax)-CH(CH$_2$)$_3$), 1.04 (m, 12H, (o,ax)-CH(CH$_2$)$_3$).
Control Reaction of (Cy₂N)₃Y(THF)/KC₈ under Argon. In a glovebox containing Argon, THF was added to a vial containing solids 13 (325 mg, 0.5 mmol) and KC₈ (190 mg, 1.4 mmol). The suspension was allowed to stir for 5 days at room temperature. After centrifugation, the supernatant was filtered and the solvent was removed under reduced pressure to yield a red oil. 

H NMR (500 MHz, C₆D₆): δ 2.53 (m, 6H, CH(CH₂)₅), 1.82 (app d, \(^3J_{HH} = 4.66\) Hz, 12H, (o,eq)-CH(CH₂)₅), 1.67 (m, 12H, (m,eq)-CH(CH₂)₅), 1.54 (m, 7H, (p,eq)-CH(CH₂)₅), 1.22 (m, 20H, (m,p,ax)-CH(CH₂)₅), 1.04 (m, 6H, (o,ax)-CH(CH₂)₅).

Reaction of (Cy₂N)₃Y(THF)/KC₈ with \(^{15}\)N₂. In a glovebox containing nitrogen, KC₈ (220 mg, 1.6 mmol) and 13 (380 mg, 0.6 mmol) were added to a side arm Schlenk flask (100 mL) with a stir bar, transferred to a high-vacuum Schlenk line, and placed under vacuum. THF, degassed with 3 freeze-pump-thaw cycles, was added to 13 and KC₈ by vacuum-transfer. \(^{15}\)N₂ (1 atm) was introduced to the flask, which was then sealed. The suspension was allowed to stir at room temperature overnight. The suspension was degassed with 3 freeze-pump-thaw cycles before the flask was transferred to a non-coordinating glovebox containing argon. After centrifugation the supernatant was filtered and the solvent was removed under reduced pressure to yield a red oil.
References


(40) X-ray crystal data was collected and compiled by Jordan Corbey and Joseph Ziller.

(41) APEX2 Version 2011.4-1, Bruker AXS, Inc.; Madison, WI 2011.

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


Appendix A

**CO₂ Insertion Chemistry with Cp’₃Y to Make**

\[ [\text{Cp’}_2\text{Y}\{\mu-O_2C[3-(\text{Me}_3\text{Si})\text{C}_5\text{H}_4]-\kappa^2\text{O},\text{O’}]\}]_2 \]

**Introduction**

Although the insertion of CO₂ has been studied extensively as a method for creating more stable carboxylate complexes from reactive metal–carbon bonds,¹⁻⁴ the reported examples of rare earth metals (Ln) activating this substrate are less common. It has been shown that CO₂ can be reduced by a porphyrin-supported organosamarium species to form a bridging bimetallic carbonate complex,⁵ as well as by a Cp-supported species (Cp = cyclopentadienyl), \((\text{C}_5\text{Me}_5)_2\text{Sm(THF)}_2\), to form a bridging bimetallic oxalate complex, eq A.1.⁶⁻⁸

\[
2(\text{C}_5\text{Me}_5)_2\text{Sm(THF)}_2 + \text{CO}_2 \xrightarrow{\text{THF}} (\text{C}_5\text{Me}_5)_2\text{Sm} \quad \text{O} \quad \text{Sm(}\text{C}_5\text{Me}_5)_2 \quad \text{O} \quad \text{O} \quad \text{O} (\text{A.1})
\]

In other cases, CO₂ can be inserted directly into Cp-supported Ln–C bonds of alkyl amines⁹ and \(\eta^3\)-allyl ligands,¹⁰ creating more stable carboxylate linkages as Cp remains an inert ancillary ligand. Interesting, although the insertion of CO₂ into metal–carbon single bonds is well known, the reported examples of CO₂ insertion with cyclopentadienyl groups are limited to only the sterically congested \((\text{C}_5\text{Me}_5)_3\text{Ln}\) and \((\text{C}_5\text{Me}_4\text{H})_3\text{Ln}\) systems, eq A.2.¹¹
It is suggested that the insertion of \( \text{CO}_2 \) and into the Ln–Cp linkage is made possible by steric bulk of the ligands causing the \( \eta^5 \)-Cp to be in equilibrium with an \( \eta^1 \)-alkyl structural isomer, eq A.3.\(^{12,13}\)

In this study, \( \text{CO}_2 \) insertion with the Cp’ ligand (Cp’ = C\(_5\)H\(_4\)SiMe\(_3\)) was examined. Initially, \( \text{CO}_2 \) reaction with Cp’\(_3\)Y, \( 8\)-Y,\(^{14}\) produced \( [\text{Cp’}_2\text{Y}\{\mu-\text{O}_2\text{C}[3-(\text{Me}_3\text{Si})\text{C}_5\text{H}_4]-\kappa^2\text{O},\text{O’}\}]_2 \), \( 19 \), in high yield. To contrast the chemistry of a smaller rare earth ion with that of a larger ion, analogous reactivity was studied with Cp’\(_3\)La(THF), \( 8\)-La·THF.\(^{15,16}\)

**Results and Discussion**

Pale yellow Cp’\(_3\)Y, \( 8\)-Y, reacts with an equivalent of \( \text{CO}_2 \) to form a cloudy, colorless suspension from which \( [\text{Cp’}_2\text{Y}\{\mu-\text{O}_2\text{C}[3-(\text{Me}_3\text{Si})\text{C}_5\text{H}_4]-\kappa^2\text{O},\text{O’}\}]_2 \), \( 19 \), was isolated as a colorless solid, eq A.4. \( 19 \) was crystallized from toluene and definitively identified by X-ray diffraction, Figure A.1, Figure A.2.
**Figure A.1:** Molecular structure of 19, [Cp₂Y{μ-O₂C[3-(Me₃Si)C₅H₄]-κ²O₂}₂]. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.
Figure A.2: Molecular structure of 19, [Cp’2Y{µ-O2C[3-(Me3Si)C5H4]-κ2O,O’}]2. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and cyclopentadienyl groups were omitted for clarity.

Preliminary structural data for 19 are summarized in Table A.1. The two independent Y1–Cnt distances, 2.374 Å and 2.372 Å, are equivalent, while the Y1–O1 and Y1–O2 distances, 2.526 Å and 2.323 Å, respectively, differ by 0.203 Å. This is not unexpected as O1 bridges between yttrium metal centers in the dimeric unit. The C17–O1 and C17–O2 bond distances are comparable with typical C–O bonds in carboxylic acids.\(^\text{17}\) The C17–C18 bond distance, 1.465 Å, is typical for a conjugated Csp\(^2\)–Csp\(^2\) bond.\(^\text{17}\) The C18–C19 and C21–C22 bond distances, 1.320 Å and 1.324 Å, respectively, are typical for cis Csp\(^2\)=Csp\(^2\) bonds, while the C18–C22 bond, 1.439 Å, is typical of an Csp\(^2\)=Csp\(^2\) bond.\(^\text{17}\) The C19–C20 and C20–C21 bond distances,
1.445 Å and 1.452 Å, respectively, are slightly shorter than typical C\textit{sp}^3–C\textit{sp}^2 bonds.\textsuperscript{17} The H20a–C20–Si3 angle is 109.6°, typical for a tetrahedral \textit{sp}^3 hybridized carbon,\textsuperscript{18} with Si3 bent out of the plane of the C\textsubscript{5} unit by 126°.

**Table A.1:** Preliminary Bond Distances (Å) and Angles (deg) for [Cp\textprimed\textsubscript{2}Y{\textmu-}O\textsubscript{2}C[3-(Me\textsubscript{3}Si)C\textsubscript{5}H\textsubscript{4}]-\textkappa{2}O,O\textsuperscript{'}]\textsubscript{2}, \textbf{19}.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y1–Cnt1\textsuperscript{a}</td>
<td>2.374</td>
</tr>
<tr>
<td>Y1–Cnt2\textsuperscript{a}</td>
<td>2.372</td>
</tr>
<tr>
<td>Y1–O1</td>
<td>2.526</td>
</tr>
<tr>
<td>Y1–O2</td>
<td>2.323</td>
</tr>
<tr>
<td>Y1–O1\textsuperscript{b}</td>
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</tr>
<tr>
<td>C17–O1</td>
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</tr>
<tr>
<td>C17–O2</td>
<td>1.259</td>
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<tr>
<td>C17–C18</td>
<td>1.465</td>
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<tr>
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<td>1.320</td>
</tr>
<tr>
<td>C18–C22</td>
<td>1.439</td>
</tr>
<tr>
<td>C19–C20</td>
<td>1.445</td>
</tr>
<tr>
<td>C20–C21</td>
<td>1.452</td>
</tr>
<tr>
<td>C21–C22</td>
<td>1.324</td>
</tr>
<tr>
<td>Cnt1–Y1–Cnt2\textsuperscript{a}</td>
<td>126.4</td>
</tr>
<tr>
<td>Cnt3\textsuperscript{a}–C20–Si3</td>
<td>126.0</td>
</tr>
<tr>
<td>H20a–C20–Si3</td>
<td>109.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Cnt1, Cnt2, and Cnt3 are the centroids of the cyclopentadienyl groups C1–C5, C9–C13, and C18–C22, respectively.

\textsuperscript{b}bridging bond between monomeric units

Complex \textbf{19} differs from the previous examples of reactions of CO\textsubscript{2} with rare earth complexes with cyclopentadienyl ligands in that the cyclopentadienyl carbon that is attached to the carbon of CO\textsubscript{2} has no other substituent. Hence C20, not C18, is an \textit{sp}^3 hybridized carbon and has both H and SiMe\textsubscript{3} substituents. This could occur by H or SiMe\textsubscript{3} migration depending on which C is involved in the insertion reaction.
To test the analogous reaction with a larger rare earth metal, a colorless solution of Cp’3La(THF) was treated with an equivalent of CO₂ and monitored by ¹H NMR spectroscopy. No color change was observed and the addition of CO₂ had no effect on the ¹H NMR spectrum, even after stirring overnight at room temperature, eq A.5. It is possible that reactivity was frustrated by the THF ligand bound to metal center and that unsolvated Cp’3La may allow for CO₂ insertion.

Conclusion

Cp’3Y reacts to insert CO₂ into a Y–C bond for the first time with the Cp’ ligand to form \([\text{Cp’}2\text{Y}\{\mu-O_2C[3-(\text{Me}_3\text{Si})\text{C}_5\text{H}_4]\kappa^2\text{O}_2\text{O’}\}]_2\), 19. The insertion product is compositionally similar to the product of CO₂ insertion with the \((\text{C}_5\text{Me}_5)_3\text{Ln}\) system except that the C17 carbon originating with the CO₂ reagent is bound to an \(sp^2\) hybridized rather than \(sp^3\) hybridized carbon, C18, and the C20 carbon in the ring has both H and SiMe₃ substituents. This may imply a reaction mechanism that differs from CO₂ insertion with \((\text{C}_5\text{Me}_5)_3\text{Ln}\). The analogous CO₂ insertion reaction with Cp’3La(THF) does not occur. The lack of reactivity with Cp’3La(THF) may be the result of a solvated metal center.
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 argon (Praxair) 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 prior to use. Anhydrous Cp’sY and Cp’sLa(THF) were prepared according to the literature. CO2 (99.98%) was purchased from AirGas and used as received. 1H NMR (500 MHz) were obtained on a Bruker GN500 or CRYO500 MHz spectrometer at 298 K.

Synthesis of [Cp’sY{µ-O2C[3-(Me3Si)C5H4]-κ2O,O’}]2, 19. A 50 mL side arm Schlenk flask fitted with a greaseless stopper containing a pale yellow solution of Cp’sY (189 mg, 0.377 mmol) in hexane (10 mL) was connected to a glass T-joint on a high-vacuum line. The other end of the glass T-joint was attached to a 47 mL side arm Schlenk flask fitted with a greaseless stopper that was used to measure the amount of CO2 assuming ideal gas behavior. The hexane solution of Cp’sY was degassed by three freeze-pump-thaw cycles and frozen in liquid N2. CO2 gas was then slowly introduced to the 47 mL Schlenk flask to a pressure of 15 torr. The stopper of the 47 mL Schlenk flask was then closed and the system evacuated under high vacuum. The CO2 gas was then condensed into the flask with liquid nitrogen over 1 h. The flask was sealed and the solution was allowed to stir at room temperature overnight. The yellow solution changed color to a colorless cloudy suspension that was dried under reduced pressure and washed with minimal hexane. The product was dried under reduced pressure to yield 19 as a colorless solid (199 mg, 97%). X-ray quality crystals were grown overnight at −35 °C from a toluene solution.

1H NMR (C6D6): δ 6.72 (s, C5H4SiMe3, 4H), 6.57 (s, C5H4SiMe3, 4H), 1.36 (s, 3-(Me3Si)C5H4, 2H), 1.24 (s, 3-(Me3Si)C5H4, 2H), 0.40 (s, C5H4SiMe3, 18H), −0.01 (s, 3-(Me3Si)C5H4, 9H).
References

Appendix B

Synthesis of an Unsubstituted Phenyl Rare Earth Metalloocene

Introduction

As the +2 oxidation state has become more available for rare earth ions beyond the six traditional divalent lanthanides, the number of ligand sets capable of stabilizing non-traditional Ln²⁺ ions (Ln = rare earth metal) has expanded from Cp'' (Cp'' = C₅H₃-1,3-(SiMe₃)₂)² to Cp' (Cp' = C₅H₄SiMe₃).³⁻⁵ It is possible that the trimethysilyl groups, as less electron-donating substituents,⁶,⁷ may allow the Cp ligands to stabilize the low-valent Ln²⁺ ion. With η¹ hapticity, phenyl ligands contribute less electron density to the metal center than η⁵ Cp ligands and could afford new Ln²⁺ ions supported by less electron-donating groups.

There are few structurally characterized phenyl complexes on Cp-supported rare earth metals,⁸⁻¹⁴ with (C₅Me₅)₂Sm(C₆H₅)(THF), 20-Sm, as the only example with an unsubstituted phenyl ligand.¹⁵ Although (C₅Me₅)₂Sm(C₆H₅)(THF) was synthesized by reducing (C₆H₅)₂Hg with (C₅Me₅)₂Sm(THF)₂, eq B.1,¹⁵ Atwood and co-workers showed that it was possible to synthesize rare earth phenyl complexes through a metathesis reaction with a lithium salt, eq. B.2.⁸

\[
\begin{array}{c}
\text{Sm}^{2+} \text{THF}^n + (\text{C}_6\text{H}_5)_2\text{Hg} \to \text{toluene} - \text{Hg}^0 \to \text{Sm}^{2+} \text{THF}^n \text{C}_6\text{H}_5
\end{array}
\]

(B.1)
In this study, phenyllithium was reacted with \([\text{Cp}^{\prime}_2\text{Y}(\text{THF})_2][\text{BPh}_4]\), \(5-\text{Y}\), to form a mixed ligand complex with an unsubstituted phenyl ligand \(\text{Cp}^{\prime}_2\text{YPH}(\text{THF})\), \(21-\text{Y}\). To extend this chemistry to a lanthanide of similar size,\(^{16}\) phenyllithium was reacted with \([\text{Cp}^{\prime}_2\text{Dy}(\text{THF})_2][\text{BPh}_4]\), \(5-\text{Dy}\), to form \(\text{Cp}^{\prime}_2\text{DyPH}(\text{THF})\), \(21-\text{Dy}\).

**Results and Discussion**

Colorless \([\text{Cp}^{\prime}_2\text{Ln}(\text{THF})_2][\text{BPh}_4]\), \(5-\text{Ln}\), reacts with an equivalent of phenyllithium to form \(21-\text{Ln}\) as a colorless solid in high yield (\(\text{Ln} = \text{Y, 96%}; \text{Dy, 97%}\)), eq B.3. The \(21-\text{Ln}\) complexes were crystallized from hexane and definitively identified by X-ray diffraction as isomorphous complexes, Figure B.1, Figure B.2.
Figure B.1: Preliminary molecular structure of 21-Y, Cp₂YPh(THF). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

Figure B.2: Preliminary molecular structure of 21-Dy, Cp₂DyPh(THF). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.
Preliminary structural data for \textbf{21-Ln} are summarized in Table \textbf{B.1}. The Ln1–Cnt, Ln1–C17, and Ln1–O1 distances for \textbf{21-Y} and \textbf{21-Dy} are comparable considering a 0.008 Å difference in ionic radius for a 8-coordinate system.\textsuperscript{16} The planar C17-C22 C\textsubscript{6} ring is bound \(\eta^1\) with C–C bond distances that are typical for aromatic \(\text{Csp}^2-\text{Csp}^2\) bonds.\textsuperscript{17} Ln1–C17 bond distances are shorter for \textbf{21-Ln} than the analogous bond in \textbf{20-Sm}, Table \textbf{B.2}. This may be the result of the more sterically bulky \([(\text{C}_5\text{Me}_5)_2]^2^-\) ligand set, as evidenced by a larger Cnt1–Ln1–Cnt2 bond angle.

\textbf{Table B.1:} Preliminary Bond Distances (Å) and Angles (deg) for \(\text{Cp}_2\text{LnPh(THF)}, \textbf{21-Ln}\).

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<tr>
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<td>Cnt1–Ln1–Cnt2</td>
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</table>

\textsuperscript{a}Cnt1 is the centroid for the cyclopentadienyl group C1-C5
\textsuperscript{b}Cnt2 is the centroid for the cyclopentadienyl group C9-C13
Table B.2: Comparison of Selected Bond Distances (Å) and Angles (deg)

For 20-Sm, 21-Y, and 21-Dy.

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<td>2.422</td>
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</tr>
<tr>
<td>ionic radius&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.079</td>
<td>1.019</td>
<td>1.027</td>
</tr>
<tr>
<td>Ln–C(C₆H₅)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.432</td>
<td>1.403</td>
<td>1.392</td>
</tr>
<tr>
<td>Cnt1–Ln1–Cnt2</td>
<td>135.9</td>
<td>132.1</td>
<td>132.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> value determined for an 8-coordinate system

<sup>b</sup> distance to C(C₆H₅) adjusted for ionic radius

Metal centers in mixed ligand complexes like 21-Ln may be able to accept additional electron density from an alkali metal reductant as a means to isolate new examples of Ln<sup>2+</sup> ions.<sup>3-5</sup> It may also be interesting to react 21-Ln with an equivalent of CO₂ for small molecule insertion into the Ln–C(C₆H₅) bond, which may resemble reactivity of 20-Sm to make a bimetallic carboxylate complex, [(C₅Me₅)₂Sm(THF)₂][µ-η²:η²-1,4-(O₂C)C₆H₅].<sup>18</sup>

Conclusion

Mixed ligand rare earth metal complexes Cp'₂LnPh(THF), 21-Ln (Ln = Y, Dy), were synthesized in high yield from a simple metathesis reaction with phenyllithium and [Cp'₂Ln(THF)₂][BPh₄], 5-Ln. These complexes mark the second and third examples of structurally characterized complexes of rare earth metals bound η¹ to an unsubstituted phenyl ligand, and the first examples with the (Cp')²⁻ ligand set.
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 argon (Praxair) and passed through columns containing Q-5 and molecular sieves before use. Phenyllithium was purchased as a solution (Aldrich) and dried under reduced pressure prior to use. Anhydrous [Cp’2Y(THF)2][BPh4], 5-Y, was prepared according to the literature, [Cp’2Dy(THF)2][BPh4], 5-Dy, was prepared similarly. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS elemental analyzer.

Synthesis of Cp’2YPh(THF), 21-Y. A colorless solution of [Cp’2Y(THF)][BPh4] (94 mg, 0.11 mmol) and LiPh (10 mg, 0.12 mmol) in THF (5 mL) was stirred for 30 min. THF was removed under reduced pressure revealing a tacky colorless solid. Hexane (5 mL) was added to the solid and stirred as a suspension for 30 min before centrifugation for 10 min to remove insoluble material. The colorless supernatant was filtered into a vial and dried under reduced pressure to reveal 21-Y as a white solid (56 mg, 96%). X-ray quality crystals were grown overnight at −35 °C from a saturated hexane solution. Anal. Calcd for C26H39OSi2Y, 21-Y: C, 60.91; H, 7.67. Found: C, 60.77; H, 7.78.

Synthesis of Cp’2DyPh(THF), 21-Dy. A colorless solution of [Cp’2Dy(THF)][BPh4] (92 mg, 0.10 mmol) and LiPh (6 mg, 0.10 mmol) in THF (5 mL) was stirred for 30 min. THF was removed under reduced pressure revealing a tacky colorless solid. Hexane (5 mL) was added to the solid and stirred as a suspension for 30 min before centrifugation for 10 min to remove insoluble material. The colorless supernatant was filtered into a vial and dried under reduced pressure to reveal 21-Dy as a white solid (58 mg, 97%). X-ray quality crystals were grown overnight at −35 °C from a saturated hexane solution.
References

Appendix C

Development of Arene Radical Bridged Bimetallic Rare Earth

Metallocene Complexes For Evaluation as Single Molecule Magnets

Introduction

Single molecule magnets (SMMs) are molecules that exhibit magnetization in the presence of an external magnetic field and are able to retain their magnetism after the field is removed.\(^1\) Through the combination of a rare earth complex with an alkali metal, LnA\(_3\)/M (Ln = Sc, Y, lanthanides; A = anion; M = alkali metal) under an atmosphere of N\(_2\), powerful bimetallic SMMs have been developed with rare earth metals that take advantage of a radical dinitrogen bridge.\(^2\)\(^-\)\(^4\) Bimetallic complexes containing radical bridging systems derived from reduced aromatic complexes between rare earth metal centers have also been shown to display SMM properties.\(^1\),\(^5\)\^-\(^14\)

Recently, several new Ln\(^{2+}\) ions have been identified as described in Chapter 1. Magnetic susceptibility studies on these new ions in a collaboration between the Evans group and that of Professor Jeff Long at UC Berkeley have revealed that some of these new ions can display higher magnetic moments than ever observed for a monometallic species. Specifically, the Ho(II) complex, [Cp’\(^{3}\)Ho][(2.2.2-cryptand)] (Cp’ = C\(_5\)H\(_4\)SiMe\(_3\)), displays the highest magnetic moment for a single ion to date.\(^15\),\(^16\)

It is therefore of interest to synthesize a bimetallic rare earth complex with highly paramagnetic Ln(II) metal centers (Ln = Tb, Dy, Ho) that takes advantage of a bridging radical
species in the development of a new class of SMMs. Lappert and co-workers have reported the synthesis of the crystallographically characterized bimetallic rare earth complex \[ \text{[K(18-crown-6)(\eta^2-C_6H_6)(LaCp''_2)\_2-(\mu-\eta^6:\eta^6-C_6H_6)]} \] \( \text{(Cp''} = \text{C}_5\text{H}_3\text{('Bu)}_2) \), with a monoanionic arene radical bridging two La(II) metal centers, eq C.1.\(^{17} \)

![Diagram](C.1)

In this Appendix, attempts to synthesize a bimetallic complex with a bridging arene radical between two paramagnetic Ln\(^{2+}\) ions are described using \( \text{Cp'Y, [Cp'Y(THF)\_2][BPh}_4] \) and \( \text{(Cy}_2\text{N)}_3\text{Y(THF)} \) as precursors. Yttrium was used as a model for the smaller paramagnetic lanthanides Tb, Dy, and Ho, which have demonstrated SMM properties,\(^{2,3,18,19} \) because it is of similar size\(^{20} \) and it has favorable spectroscopic characteristics associated with a 100% naturally abundant \( I = \frac{1}{2} \text{^{89}Y} \) nucleus. The synthesis of such a bimetallic bridging arene radical species depends on the ability of the metal centers to maintain a +2 charge, which has proven to be possible with \( \text{(Cp')}^{1-} \) as a stabilizing ligand.\(^{21-24} \) The \( \text{[(Cy}_2\text{N)}_3]^{3-} \) system was also tested as the dicyclohexyl amide ligands may avoid a cyclometallation product often formed in the presence of an external reductant as described in Chapter 5.\(^{25} \)

**Results and Discussion**

**Reactions with Benzene.** A pale yellow solution of \( \text{Cp'Y} \) in benzene was added to a vial containing a thin smear of potassium metal, which precipitated a maroon solid after stirring
vigorously for 4 h, eq C.2. The solids were collected and analysis by EPR spectroscopy at 295 K showed an axial signal with a g-value of 1.985, Figure C.1.

\[
\begin{align*}
\text{SiMe}_3 & \quad \text{Me}_3\text{Si} \\
\text{Y} & \quad + \quad \text{C}_6\text{H}_6 \\
\text{SiMe}_3 & \quad \text{Maroon Solids} \quad \text{(C.2)}
\end{align*}
\]

Figure C.1. EPR spectrum of the reaction product of Cp’3Y with potassium in benzene at 295 K.

In an analogous reaction with a chelating agent present, the reaction changed color from pale yellow to red within minutes, eq C.2. With 18-crown-6 as the chelating agent, the reaction produced a red solution, which showed isotropic signals at 77 K and 295 K and g-values of 2.001 by EPR spectroscopy, Figure C.2 The color of the solution changed to brown upon addition of THF, but the EPR signals were unaffected. With 2.2.2-cryptand as the chelating agent, the reaction produced an insoluble red oil, which showed an axial signal at 77 K with hyperfine coupling \((A = 35.5 \text{ G})\) centered at \(g = 1.987\) and an isotropic signal 295 K with hyperfine coupling \((A = 36.1)\) centered at \(g = 1.989\) by EPR spectroscopy, Figure C.3. The red oil changed
color to a soluble brown solution upon addition of THF, but the EPR signals were unaffected. Using potassium spheres\textsuperscript{26} rather than a thin smear of potassium showed no change in reactivity or the EPR spectra in the reaction with 2.2.2-cryptand.

\[
\text{SiMe}_3
\text{Me}_3\text{Si}
\text{Me}_3\text{Si}
\text{Y} - \begin{array}{c}
\text{C}_6\text{H}_6 \\
\text{(chelate)}
\end{array}
\rightarrow
\text{Red Product}
\]

Figure C.2. EPR spectra at a) 77 K and b) 295 K of the reaction product of \(\text{Cp}'_3\text{Y}\) and 18-crown-6 with potassium in benzene.
A colorless suspension of \([\text{Cp}'_2\text{Y(THF)}_2][\text{BPh}_4]\) and 18-crown-6 in benzene was treated with potassium-graphite to produce a deep orange solution, eq C.4. The product was analyzed by EPR spectroscopy at 77 K and 295 K and showed axial signals with g values of 1.994 and 1.984, respectively, with unresolved hyperfine coupling, Figure C.4.

\[
\begin{align*}
\text{[Cp}'_2\text{Y(THF)}_2][\text{BPh}_4] 
& \quad + \quad 2.0 \text{KC}_8 + 1.5 \text{(18-crown-6)} 
\quad \xrightarrow{\text{C}_6\text{H}_6} 
\text{Orange Product} \quad \text{(C.4)}
\end{align*}
\]
Figure C.4. EPR spectra at a) 77 K and b) 295 K of the reaction product of [Cp'2Y][BPh₄] and 18-crown-6 with potassium in benzene.

A colorless suspension of [Cp'2Y(THF)₂][BPh₄] and 2.2.2-cryptand in benzene was treated with potassium-graphite to produce a black precipitate after stirring for 40 min, eq C.5. Analysis of the purple benzene solution by EPR spectroscopy at 77 K and 295 K and showed axial signals with g values of 1.994 and 2.003, respectively, with unresolved hyperfine coupling, Figure C.5. Extraction of the black precipitate with THF gave a soluble brown solution that showed similar EPR spectra.

\[
\begin{array}{c}
\text{[Cp'2Y(THF)₂][BPh₄]} \\
\text{+ 2.0 KC₈ + 2.0 (2.2.2-cryptand)} \rightarrow \text{Purple Product} \quad \text{(C.5)}
\end{array}
\]
Figure C.5. EPR spectra at a) 77 K and b) 295 K of the reaction product of [Cp’2Y][BPh₄] and 2.2.2-cryptand with potassium in benzene.

A colorless solution of (Cy₂N)₃Y(THF) and 18-crown-6 in benzene was added to a vial containing potassium metal and stirred vigorously for 2 h, eq C.6. A black oil formed initially, but dispersed to become a red solution after stirring. Analysis of the red solution by EPR spectroscopy at 77 K and 295 K and showed isotropic signals with hyperfine coupling (A = 2.7) centered at $g = 2.003$, Figure C.6.

$$\begin{align*}
\text{Cy}_2\text{N}^\text{THF} & \quad \text{Y} \quad \text{NCy}_2 \\
+ \quad 1.5 \text{ K} & \quad + \quad 1.5 \ (18\text{-crown-6}) \\
\text{C}_6\text{H}_6 & \quad \rightarrow \quad \text{Red Product} \quad \text{(C.6)}
\end{align*}$$
Figure C.6. EPR spectra at a) 77 K and b) 295 K of the reaction product of \((\text{Cy}_2\text{N})_3\text{Y(THF)}\) and 18-crown-6 with potassium in benzene.

A colorless solution of \((\text{Cy}_2\text{N})_3\text{Y(THF)}\) and 2.2.2-cryptand in benzene was added to a vial containing a thin smear of potassium metal and stirred vigorously for 1 h, eq C.7. A black oil formed initially, but dispersed to become a red solution after stirring. Analysis of the red solution by EPR spectroscopy at 77 K and 295 K showed isotropic signals with hyperfine coupling \((A = 3.6)\), centered at \(g = 1.919\) and \(g = 2.003\), respectively, Figure C.7.

\[
\begin{align*}
\text{Cy}_2\text{N} & \quad \text{THF} \\
\text{Y} & \quad \text{NCy}_2 \\
+ \quad 1.5 \text{ K} & \quad + \quad 1.5 \ (2.2.2\text{-cryptand}) \\
& \quad \text{C}_6\text{H}_6 \\
\rightarrow & \quad \text{Red Product} \\
\end{align*}
\]
**Figure C.7.** EPR spectra at **a)** 77 K and **b)** 295 K of the reaction product of $(\text{Cy}_2\text{N})_3\text{Y(THF)}$ and 2.2.2-cryptand with potassium in benzene.

**Reactions with Toluene.** A pale yellow solution of $\text{Cp}^{\prime}\text{Y}$ in toluene was added to a vial containing a thin smear of potassium metal, which precipitated a maroon solid after stirring vigorously overnight, eq C.8. The solids were collected and analysis by EPR spectroscopy at 77 K and 295 K showed a rhombic signal with g-values of 1.986 and 1.985, respectively, Figure C.8. Extraction with THF caused the product to change color to brown and isotropic signals were observed at 77 K and 295 K with g-values of 2.002.
Figure C.8. EPR spectra at **a)** 77 K and **b)** 295 K of the reaction product of Cp’3Y with potassium in toluene.

When Cp’3Y in toluene was added to a vial containing a thin smear of potassium metal with a chelating agent was present, the reaction changed color from pale yellow to red within minutes, eq C.9. With 18-crown-6 as the chelating agent, the reaction produced a red solution, which showed an isotropic signal with hyperfine coupling at 77 K with a g-value of 2.001 by EPR spectroscopy, Figure C.9. With 2.2.2-cryptand as the chelating agent, the reaction produced an insoluble red oil, which showed an axial signal at 77 K with hyperfine coupling (A = 33.8 G) centered at g = 1.989 and an isotropic signal 295 K with hyperfine coupling (A = 35.5) centered at g = 1.988 by EPR spectroscopy, Figure C.10. The red oil changed color to a soluble brown solution upon addition of THF, but the EPR signals were unaffected.

\[
\begin{array}{c}
\text{SiMe}_3 \\
\text{Y} \\
\text{Me}_3\text{Si} \\
\text{SiMe}_3
\end{array} + \text{1.5 K} + \text{1.5 (chelate)} \rightarrow \text{Toluene} \rightarrow \text{Red Product} \quad (C.9)
\]
Figure C.9. EPR spectra at 77 K of the reaction product of Cp₃Y and 18-crown-6 with potassium in toluene.

Figure C.10. EPR spectra at a) 77 K and b) 295 K of the reaction product of Cp₃Y and 2.2.2-cryptand with potassium in toluene.

Reactions with 1,4-Bis(trimethylsilyl)benzene. A pale yellow solution of Cp₃Y and 18-crown-6 with 1,4-bis(trimethylsilyl)benzene in Et₂O was treated with potassium graphite to produce a deep red solution, eq C.10. The product was analyzed by EPR spectroscopy and showed an axial signal at 77 K with hyperfine coupling (A = 36.0 G) centered at g = 1.987 and
an isotropic signal 295 K with hyperfine coupling \((A = 35.5)\) centered at \(g = 1.990\) by EPR spectroscopy, Figure C.11. The red oil changed color to a soluble brown solution upon addition of THF, but the EPR signals were unaffected.

\[
\begin{align*}
\text{Red Product} &\rightarrow \text{Me}_3\text{Si} \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} &+ 1.5 \text{KC}_8 + 1.5 (18\text{-crown-6}) \rightarrow \text{SiMe}_3 \quad \text{Me}_3\text{Si} \\
\end{align*}
\]

\(\text{eq C.11}\)

**Figure C.11.** EPR spectra at a) 77 K and b) 295 K of the reaction product of \(\text{Cp}'_3\text{Y}\) and 2.2.2-cryptand with potassium in toluene.

A pale yellow solution of \(\text{Cp}'_3\text{Y}\) and 2.2.2-cryptand with 1,4-bis(trimethylsilyl)benzene in hexane was treated with potassium graphite and allowed to stir vigorously for 2.5 h, eq C.11. While stirring, a black precipitate was observed forming on the walls of the vial. When stirring was ceased, the remaining colorless hexane solution was removed and the black precipitate was extracted with THF. X-ray quality maroon crystals were grown from a concentrated solution of THF layered with \(\text{Et}_2\text{O}\) overnight at \(-35\) °C. The color and unit cell of these crystals matched
data collected for the $\text{Y}^{2+}$ complex $[\text{Cp}_3\text{Y}][\text{K}(2.2.2\text{-cryptand})]\cdot\text{THF}$, 1-Y. This was a surprising result as the synthesis of 1-Y by precipitating the product as it forms from the reaction solvent was previously unknown.

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{Y} & \quad + 1.5 \text{K}_8 + 1.5 (2.2.2\text{-cryptand}) & \text{Red Product} \\
\text{Hexane} & \quad \text{Me}_3\text{Si} & \quad \text{(C.11)}
\end{align*}
\]

**Conclusion**

As the product of the reaction of Cp$_3$Y and 1,4-bis(trimethylsilyl)benzene in the presence of KC$_8$ and 2.2.2-cryptand produced crystals of $[\text{K}(2.2.2\text{-cryptand})][\text{Cp}_3\text{Y}]$, 1-Y, it is possible that 1-Y also forms in the reactions of Cp$_3$Y and potassium in benzene and toluene, as described in eq C.3 and eq C.9, respectively, with 2.2.2-cryptand as the chelating agent. These products also show axial signals at 77 K and isotropic signals at 295 K with g values and coupling constants that are similar to 1-Y. However, it was previously unknown that 1-Y could be synthesized by precipitating the product directly out of a hydrocarbon reaction solvent as it forms. Interestingly, the most simple reactions of Cp$_3$Y and potassium in benzene and toluene without a chelating agent, described in eq C.2 and eq C.8, respectively, yielded unique spectra by EPR spectroscopy that do not match 1-Y. If the products of these reactions are bridging arene radical complexes, it may be possible to add a chelating agent after isolating the solid product, or repeating the reaction with Tb, Dy, or Ho and simply testing the magnetic behavior of the solid product. Without crystallographically characterized products from the reactions of arenes with $[\text{Cp}_2\text{Y}(\text{THF})_2][\text{BPh}_4]$, and (Cy$_2$N)$_3\text{Y}(\text{THF})$ with potassium in the presence of a chelating agent
a detailed discussion of these reactions is limited. However, analysis of these products by EPR spectroscopy indicates hyperfine coupling that differs from the product of Cp′₃Y reactions and is an order of magnitude smaller.

**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 argon (Praxair) and passed through columns containing Q-5 and molecular sieves before use. Anhydrous Cp′₃Y,¹¹ [Cp′₂Y(THF)₂][BPh₄]₂¹¹ K₈,²⁷ and K spheres²⁶ were prepared according to the literature. (NCy₂)₃Y(THF) was prepared according to the synthesis described in Chapter 5. 18-Crown-6 (Aldrich) was sublimed before use. 2,2,2-Cryptand, (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane), (Aldrich) was placed under vacuum (10⁻³ Torr) for 12 h before use. Electron paramagnetic resonance spectra were collected using a Bruker EMX spectrometer equipped with an ER041XG microwave bridge. The magnetic field was calibrated with DPPH (g = 2.0036).

**Reaction of Cp′₃Y with K in benzene.** A pale yellow solution of Cp′₃Y (61 mg, 0.12 mmol) in benzene (3 mL) was added to a vial containing a thin smear of potassium (7 mg, 0.18 mmol) and stirred vigorously at room temperature. Over 4 h the solution changed from pale yellow to dark red suspension. Stirring was ceased, precipitating a maroon solid. EPR data were collected on the suspension in benzene.

**Reaction of Cp′₃Y with K in benzene with 18-crown-6.** A pale yellow solution of Cp′₃Y (30 mg, 0.06 mmol) and 18-crown-6 (24 mg, 0.09 mmol) in benzene (2 mL) was added to a vial containing a thin smear of potassium (4 mg, 0.1 mmol) and stirred vigorously at room
temperature. The solution changed color from pale yellow to a red solution in 20 min. EPR data were collected on red solution in benzene and in THF.

**Reaction of Cp’3Y with K in benzene with 2.2.2-cryptand.** A pale yellow solution of Cp’3Y (30 mg, 0.06 mmol) and 2.2.2-cryptand (34 mg, 0.09 mmol) in benzene (2 mL) was added to a vial containing a thin smear of potassium (4 mg, 0.1 mmol) and stirred vigorously at room temperature. The solution changed color from pale yellow to a red suspension in 5 min. Hexane was added to precipitate a red oil, which was dried under reduced pressure. Addition of THF created a brown solution. EPR data were collected on the suspension in benzene and in solution by extraction with THF. Layering with hexane or Et2O at −35 °C did not produce crystals.

**Reaction of Cp’3Y with K spheres in benzene with 2.2.2-cryptand.** K spheres (13 mg, 0.33 mmol) were added to a stirred pale yellow solution of Cp’3Y (110 mg, 0.220 mmol) and 2.2.2-cryptand (83 mg, 0.220 mmol). After stirring for 15 min at room temperature, the solution color changed from pale yellow to a red suspension. After stirring was ceased, a yellow tinted benzene solution was decanted leaving behind a red oil, which was dried under reduced pressure. Addition of THF created a brown solution. Layering with hexane or Et2O at −35 °C did not produce crystals.

**Reaction of [Cp’2Y(THF)2][BPh4] with K in benzene with 18-crown-6.** KC8 (30 mg, 0.22 mmol) was added to a stirred colorless suspension of [Cp’2Y(THF)2][BPh4] (91 mg, 0.11 mmol) and 18-crown-6 (44 mg, 0.17 mmol) in benzene (5 mL). After stirring at room temperature for 20 min, the mixture was filtered revealing a deep orange solution. EPR data were collected on the solution in benzene. Layering with hexane at −35 °C did not produce crystals from a THF solution.
Reaction of [Cp’₂Y(THF)₂][BPH₄] with K in benzene with 2.2.2-cryptand. KC₈ (36 mg, 0.27 mmol) was added to a stirred colorless suspension of [Cp’₂Y(THF)₂][BPH₄] (111 mg, 0.134 mmol) and 2.2.2-cryptand (101 mg, 0.268 mmol) in benzene (5 mL). The mixture was allowed to stir vigorously for 40 min. When stirring ceased, the suspension was allowed to settle and a purple solution was pipetted out of the vial leaving behind a black oil. THF (5 mL) was added to the oil and stirred for 5 min before centrifugation for 10 min to remove graphite, revealing a brown solution. EPR data were collected on the solution in benzene and THF. Layering with Et₂O at −35 °C did not produce crystals from a THF solution.

Reaction of (Cy₂N)₃Y(THF) with K in benzene with 2.2.2-cryptand. A colorless solution of (Cy₂N)₃Y(THF) (50 mg, 0.07 mmol) and 2.2.2-cryptand (40 mg, 0.11 mmol) in benzene (3 mL) was added to a vial containing a thin smear of potassium (4 mg, 0.1 mmol) and stirred vigorously at room temperature. Upon stirring, a black oil began forming off the potassium smear. After 1 h, the black oil suspension changed color to a red solution. EPR data were collected on red solution in benzene.

Reaction of (Cy₂N)₃Y(THF) with K in benzene with 18-crown-6. A colorless solution of (Cy₂N)₃Y(THF) (128 mg, 0.182 mmol) and 18-crown-6 (73 mg, 0.28 mmol) in benzene (5 mL) was added to a vial containing potassium (11 mg, 0.28 mmol) and stirred vigorously at room temperature. Upon stirring, a black oil began to form. After 2 h, the black oil suspension changed color to a red solution. EPR data were collected on red solution in benzene.

Reaction of Cp’₃Y with K in toluene. A pale yellow solution of Cp’₃Y (97 mg, 0.19 mmol) in toluene (3 mL) was added to a vial containing a thin smear of potassium (11 mg, 0.28 mmol) and stirred vigorously at room temperature. No color change was observed after 4 h. Stirring overnight changed the color to a red suspension. When stirring was ceased, a red solid
precipitated. EPR data were collected on the suspension in toluene and in solution by extraction with THF.

**Reaction of Cp’₃Y with K in toluene with 18-crown-6.** A pale yellow solution of Cp’₃Y (30 mg, 0.06 mmol) and 18-crown-6 (24 mg, 0.09 mmol) in toluene (2 mL) was added to a vial containing a thin smear of potassium (7 mg, 0.2 mmol) and stirred vigorously at room temperature. The solution changed color from pale yellow to a red solution in 40 min. EPR data were collected on red solution in toluene.

**Reaction of Cp’₃Y with K in toluene with 2.2.2-cryptand.** A pale yellow solution of Cp’₃Y (35 mg, 0.07 mmol) and 2.2.2-cryptand (39 mg, 0.10 mmol) in toluene (3 mL) was added to a vial containing a thin smear of potassium (5 mg, 0.1 mmol) and stirred vigorously at room temperature. The solution changed color from pale yellow to a red suspension in 40 min. EPR data were collected on red suspension in toluene and in THF.

**Reaction of Cp’₃Y and 1,4-bis(trimethylsilyl)benzene with K and 18-crown-6.** KC₈ (17 mg, 0.13 mmol) was added to a stirred pale yellow solution of Cp’₃Y (33 mg, 0.07 mmol), 1,4-bis(trimethylsilyl)benzene (80 mg, 0.36 mmol), and 18-crown-6 (30 mg, 0.11 mmol) in Et₂O (5 mL). After stirring at room temperature for 40 min the mixture was filtered revealing a red solution. EPR data were collected on the suspension in benzene and in solution by extraction with THF. Layering with hexane or Et₂O at −35 °C did not produce crystals.

**Reaction of Cp’₃Y and 1,4-bis(trimethylsilyl)benzene with K and 2.2.2-cryptand.** KC₈ (35 mg, 0.26 mmol) was added to a stirred pale yellow solution of Cp’₃Y (85 mg, 0.17 mmol), 1,4-bis(trimethylsilyl)benzene (19 mg, 0.06 mmol), and 2.2.2-cryptand (96 mg, 0.26 mmol) in hexane (8 mL). The mixture was allowed to stir vigorously for 2.5 h. When stirring ceased, the suspension was allowed to settle and a colorless solution was pipetted out of the vial.
and discarded leaving behind a black oil. THF (5 mL) was added to the oil and stirred for 5 min before centrifugation for 10 min to remove graphite. The deep red supernatant was filtered into a vial and chilled at −35 °C for an hour. The solution was layered with room temperature Et₂O (10 mL) and stored at −35 °C, producing X-ray quality maroon crystals overnight. The unit cell of the crystalline produce matched [Cp',Y][K(2.2.2-cryptand)]·THF.²³
References