Title
Rare earth arene-bridged complexes obtained by reduction of organometallic precursors

Permalink
https://escholarship.org/uc/item/8mr462nv

Journal
Handbook on the Physics and Chemistry of Rare Earths, 45

ISSN
0168-1273

Authors
Huang, W
Diaconescu, PL

Publication Date
2014

DOI
10.1016/B978-0-444-63256-2.00266-7

Peer reviewed
Rare Earth Arene-bridged Complexes Obtained by Reduction of Organometallic Precursors

Wenliang Huang and Paula L. Diaconescu*

Department of Chemistry & Biochemistry, University of California, Los Angeles, California 90095

ABSTRACT

Rare earth chemistry has witnessed remarkable advances in recent years. In particular, ancillary ligands other than cyclopentadienyl derivatives have been introduced to the organometallic chemistry and their complexes exhibit distinct reactivity and properties compared to the metallocene or half-sandwiched analogues. The present chapter reviews arene-bridged rare earth complexes with an emphasis on those compounds obtained by reduction reactions. A particular emphasis is placed on rare earth complexes supported by 1,1′-ferrocenediyl diamides since they show the most diverse chemistry with arenes: fused arenes, such as naphthalene and anthracene, formed inverse-sandwiched complexes, in which the arene is dianionic; weakly conjugated arenes, such as biphenyl, p-terphenyl, and 1,3,5-triphenylbenzene, were unexpectedly reduced by four electrons and led to 6-carbon, 10-π electron aromatic systems; on the contrary, (E)-stilbene, which has a carbon-carbon double bond between the two phenyl rings, could only be reduced by two electrons, which were located on the carbon-carbon double bond instead of the phenyl rings. The reactivity of some rare earth arene-bridged complexes is also discussed with noticeable examples being the activation of white phosphorus (P_4) by rare earth naphthalene complexes. Stoichiometric P_4 activation led to polyphosphide (P_8^4- or P_7^3-), which could then be transferred to phosphorus-containing organic molecules.
1. INTRODUCTION

1.1 General Remarks about the Organometallic Chemistry of Rare Earths

This review summarizes recent advances in arene rare earth chemistry with an emphasis on complexes obtained by reduction and supported by non-cyclopentadienyl ancillary ligands. In order to discuss this area in context, a brief historical view of rare earth organometallic chemistry, in general, is included in the first section, and of bridging arene complexes, in particular, is included in the second section. The other sections describe chemistry from our group and include previously reported examples that are relevant to a particular section.

Bochkarev wrote a comprehensive review on rare earth arene complexes in 2002 (Bochkarev, 2002) and Nief provided a complete summary of molecular low-valent rare earth
complexes in 2010 (Nief, 2010). However, in the past several years, significant advances in these two intrinsically related fields, arene complexes and molecular low-valent complexes, have been accomplished by some laboratories including ours. In addition, with the ever growing power of computational tools and characterization methods, chemists are now able to understand the electronic structures of fascinating molecular structures better than it was possible even a decade ago.

In the periodic table, the rare earths are placed between alkaline earths and group 4 metals. As a consequence, four of them, scandium, yttrium, lanthanum, and lutetium, are also classified as group 3 metals. Unlike transition metals, which usually have multiple common oxidation states, most rare earths only have one common oxidation state, +3. Another significant difference between rare earths and transition metals is that the valence electrons of the former are f electrons, which are barely affected by the ligand field, while the ligand field has a major influence on the d electrons of the latter. Rare earths also differ from main group metals, such as group 13 elements, in part because of their empty d orbitals available for ligand coordination. Therefore, rare earth metal chemistry provides unique opportunities for synthetic chemists.

Organometallic rare earth chemistry witnessed major advances in the decades after the discovery of ferrocene (Kealy and Pauson, 1951; Miller et al., 1952), once π ligands were found to bind rare earth ions strongly (Bombieri and Paolucci, 1998). The most popular π ligands are cyclopentadienyl ((η^5-C\(_5\)H\(_5\))^−, commonly referred to as Cp) and its derivatives. Rare earths are highly electropositive elements and prefer ionic binding similar to alkali and alkali earth metals. As a consequence, rare earth metal-carbon bonds are highly polarized with a significant amount of negative charge built up on carbon. Because Cp is a 5-carbon, 6π-electron aromatic system, it can readily diffuse the negative charge through resonance. Therefore, cyclopentadienyls bind
tightly to rare earth metals and usually serve as good ancillary ligands, facilitating many reactivity studies of organometallic rare earth chemistry (Chart 1) (Arndt and Okuda, 2002; Ephritikhine, 1997; Evans and Davis, 2002). Binary rare earth cyclopentadienyl complexes, Cp₃M (M = Sc, Y, La, Ce, Pr, Nd, Sm, and Gd), were first synthesized by Wilkinson (Wilkinson and Birmingham, 1954), followed by the metallallocenes Cp₂MCl (M = Sm, Gd, Dy, Ho, Er, Yb, Lu) and (Me-Cp)₂MCl (M = Gd, Er, Yb) (Maginn et al., 1963) and half-sandwich CpMCl₂ (M = Sm, Eu, Gd, Dy, Ho, Er, Yb, Lu) (Manastyrskyj et al., 1963) complexes. Substituted cyclopentadienyls were developed next in order to adjust their electronic and steric properties. The most important substituted-Cp ligand is pentamethylcyclopentadienyl ((η⁵-C₅Me₅)⁻, commonly referred to as Cp*), which is more electron donating and more sterically demanding than the non-substituted cyclopentadienyl. Brintzinger and Bercaw pioneered the Cp* chemistry for group 3 and 4 metals (Bercaw et al., 1972; Manriquez and Bercaw, 1974; Manriquez et al., 1976; Piers et al., 1990; Roddick et al., 1985; Wolczanski et al., 1979; Wolczanski and Bercaw, 1980). Among the first heteroleptic pentamethylcyclopentadienyl complexes synthesized with various lanthanides were Cp*₂NdCl (Wayda and Evans, 1980), Li[Cp*MX₃] and [Cp*₂MX₂], M = Yb, Lu, X = Cl, I (Watson et al., 1981), as well as [M’(solvent)][Cp*₂MCl₂], M’ = Li, Na, M = Nd, Sm, Yb; Cp*₂NdCl(THF), Cp*₂Nd(N[SiMe₃]₂), Cp*₂YbCl(THF); [Na(OEt₂)₂][Cp*NdCl₃], and Cp*Nd(N[SiMe₃]₂)₂ (Tilley and Andersen, 1981).

The coordination chemistry of other π ligands has also been explored (Chart 1) (Bombieri and Paolucci, 1998; Edelmann et al., 2002). The cyclooctatetraene dianion, (η⁸-C₈H₈)²⁻, commonly referred to as COT, also famous for the isolation of uranocene (Avdeef et al., 1972; Streitwieser and Mueller-Westerhoff, 1968), is known to stabilize lanthanides in all three oxidation states (+2, +3, +4). In fact, the first COT lanthanide complexes to be prepared were solvated Ln(COT) species
with Ln = Eu, Yb (Hayes and Thomas, 1969). Most rare earth COT complexes, which feature both mono- and bis-COT, are, however, of the trivalent lanthanides (Bombieri and Paolucci, 1998). Cerocene, Ce(COT)₂, merits a special mention since its electronic structure is still being actively investigated (Ferraro et al., 2012; Kerridge, 2013; Kumari et al., 2013; Walter et al., 2009).

Aromatic heterocycles that mimic cyclopentadienyl by functioning as multidentate ligands, such as boratabenzene (η⁶-C₅H₅BR)⁻, (first reported rare earth examples: (C₅H₅B-Ph)ScPh₂(THF) and (C₅H₅B-Ph)₂ScPh(THF)) (Putzer et al., 1999), tetramethylphosphophylyl (η⁵-C₄Me₄P)⁻ (first reported rare earth examples: [Yb(μ-Cl)(η⁵-C₄Me₄P)(THF)₂]₂ and [Yb(μ-SPh)(η⁵-C₄Me₄P)(THF)₂]₂) (Nief and Ricard, 1994), and other heterocyclopentadienyl ligands (Nief, 2001) form rare earth complexes that are far less numerous than those of cyclopentadienyl derivatives because of their relative inaccessibility and difficult modification.
CHART 1 Important organometallic complexes, selected π ligands for organometallic rare earth complexes, and selected examples of rare earth complexes supported by certain π ligands (abbreviations are the same as in text).

In the last two decades, well defined ancillary ligands other than the aforementioned π ligands have been developed by various groups (Chart 2). They are usually electron rich and sterically demanding, in order to compensate the high Lewis acidity and high coordination number of rare earth ions. Some examples will be mentioned here with relevant compounds described later.
in the review, but the list is not meant to be exhaustive since several reviews cover the area of non-cyclopentadienyl rare earth chemistry (Arnold and Casely, 2009; Diaconescu, 2008; Edelmann et al., 2002; Edelmann, 2009; Konkol and Okuda, 2008; Li et al., 2010; Piers and Emslie, 2002; Reznichenko and Hultsch, 2010; Trifonov, 2010; Zeimentz et al., 2006). Fryzuk and co-workers pioneered the use of multidentate amidophosphine ligands, which combine soft phosphine and hard amide donors, and incorporated such motifs into the coordination sphere of group 3 metals, including the tridentate [N(SiMe2CH2PPr2)2] (P2N) in (P2N)ScR2 (R = Me, Et, CH2SiMe3) (Fryzuk et al., 1996), tetradentate (PhP[CH2(SiMe2)N(SiMe2)CH2]2PPh)2- (P2N2) in (P2N2)Y[CH(SiMe3)2] (Fryzuk et al., 1997), and, recently, the tetradentate fc(NPPr2)2 in [(fc(NPPr2)2)Sc(THF)(μ-H)]2 (Halcovitch and Fryzuk, 2013). J. Arnold popularized porphyrins as supporting ligands for scandium organometallic complexes (Arnold and Hoffman, 1990; Arnold et al., 1993), and, recently, synthesized lanthanum and terbium corrole complexes (Buckley et al., 2013). Several groups reported on the use of mono- and bis-amidinate rare earth complexes as analogues of Cp*2M (Duchateau et al., 1993; Hagadorn and Arnold, 1996; Wedler et al., 1990). Piers used bulky β-diketiminato ligands (nacnac) to obtain scandium dialkyl (Hayes et al., 2001) and cationic monoalkyl species (Hayes et al., 2002), and developed a salicylaldiminato ligand to afford group 3 metal hydrides upon hydrogenation by H2 (Emslie et al., 2002). Takats worked extensively with sterically demanding pyrazolylborate ligands (scorpionate) (Marques et al., 2002; Stainer and Takats, 1982), with early reports on alkyl and hydride divalent lanthanide complexes (Ferrence et al., 1999; Hasinoff et al., 1994). Scott achieved the synthesis of triamidoamine complexes of rare earths using N(CH2CH2NSiMe3)3 (Roussel et al., 1998). Bercaw introduced the neutral 1,4,7-trimethyl-1,4,7-triazacyclononane (TACN) on group 3 metals (Hajela et al., 1997) that was later modified by Mountford with a monoanionic pendant arm as an anchor (Bylikin et
al., 2001). Gade and Mountford also developed a series of diamidopyridine and diamidoamine ligands with flexible backbones for the synthesis of scandium alkyl or aryl complexes (Ward et al., 2002).
New, non-cyclopentadienyl ligands made possible the synthesis of bonding motifs that seemed elusive a decade ago (Chart 3). Mindiola (Scott and Mindiola, 2009) incorporated a pincer-type, rigid tridentate PNP ligand, N(2-PPr2-4-methylphenyl)2, on scandium and isolated rare scandium methylidene and oxo complexes (Scott et al., 2008), and, later, a scandium phosphinidene (Wicker et al., 2010). Y. Chen developed a series of tridentate monoanionic (Xu et al., 2010) or dianionic (Lu et al., 2011) β-diketiminato ligands and was able to characterize an unsupported scandium terminal imide (Lu et al., 2010) and studied its reactivity (Chu et al., 2011; Chu et al., 2012a; Lu et al., 2012). Other examples of transient (Scott and Mindiola, 2009; Wicker et al., 2011) or isolated (Chu et al., 2012b; Rong et al., 2013) scandium terminal imide complexes have also been reported. A recent development in this field is the synthesis of a terminal cerium(IV) oxide supported by the sterically encumbering Kläui tripod ligand [CoCp(P(O)(OEt)2)3] and stabilized by hydrogen bonding with a molecule of acetamide (So et al., 2014). These developments, as well as the report of transient (Thomson et al., 2010) and isolated (King et al., 2012) uranium nitride complexes, bide well for the discovery of other interesting bonding motifs with f elements. Recently, a P3-containing rare earth complex, [K(toluene)](μ-I)4[Y4(THF)4(μ-PAr)4YI](μ-P) (Ar = 2,6-di-iso-Pr-C6H3), was isolated from YI2(THF)3(P[SiMe3][Ar]) (Chart 3) (Lv et al., 2011).
CHART 3  Examples of rare earth-element multiple bonds and phosphide reported by various groups (abbreviations are the same as in text).

The list of rare earth-element multiple bonds is still missing terminal metal carbenes. However, Cavell (Aparna et al., 2000), Le Floch (Cantat et al., 2005), and Liddle (Mills et al., 2010) (Chart 4) synthesized formal rare earth carbene complexes by incorporating the carbene in the framework of a chelating bis(iminophosphorano)methylene ($N_2C_2^-$) or bis(diphenylthiophosphinoyl)methylene ($S_2C_2^-$) ligand. Also, P. Arnold reported numerous examples of interesting reactivity of f-block complexes supported by N-heterocyclic carbenes (NHCs) (Chart 4) (Arnold and Casely, 2009; Liddle and Arnold, 2005).
Another chapter of interesting bonding motifs is that of heterometallic complexes between the rare earths and transition metals with unsupported metal-metal bonds. Although the first structurally characterized lanthanide-transition metal bonds were reported in the early 1990s, \([(\text{MeCN})_3\text{YbFe(CO)}_4\cdot\text{MeCN}]^{\infty}\) (Deng and Shore, 1991) and \(\text{Cp}_2\text{Lu(THF)-RuCp(CO)}_2\) (Beletskaya et al., 1993), the field started developing at a fast pace only in the last decade (Arnold et al., 2009; Butovskii et al., 2010; Liddle and Mills, 2009; Minasian et al., 2009; Oelkers et al., 2012), spurred by Kempe’s report of \([\text{O(SiMe}_2\text{N-2-C}_5\text{H}_3\text{N-4-Me)}_2]\text{NdRh(\eta}^2\text{-C}_2\text{H}_4)]\) and \([\text{O(SiMe}_2\text{N-2-C}_5\text{H}_3\text{N-4-Me)}_2]\text{Nd(THF)PdMe}\) in 1998 (Chart 5) (Spannenberg et al., 1998). Probably the most thought-provoking molecule reported in this area is \(\text{Sm(ReCp)}_3\), also by Kempe,
which does not feature any traditional supporting ligands for samarium and, instead, is bound solely by transition metals (Chart 5) (Butovskii et al., 2010).

**CHART 5** Top and middle: Initial examples of rare earth-transition metal unsupported bonds. Bottom: Synthesis of Sm(ReCp)_3 reported by Kempe’s group (Butovskii et al., 2010).

Although most rare earth organometallic complexes are discrete mono or binuclear species, the chemistry of small nuclearity clusters shows that new reactivity can be discovered in the area of inert molecule activation when several rare earths act in concert (Chart 6) (Hou et al., 2007). In
2003, Hou et al. reported the synthesis and structural characterization of polyhydrido lanthanide cluster complexes, \([\text{C}(\text{Me})\text{Me}_2\text{SiMe}_3]\text{Ln}(\mu\text{-H})_4(\text{THF})_n\) (\text{Ln} = \text{Lu}, \text{Y}, n = 0-2) (Tardif et al., 2003), which represented the first examples of structurally well-defined, salt-free lanthanide polyhydrido clusters (Hou et al., 2001). These clusters and their derivatives could break strong bonds such as the C-O bond in CO (Shima and Hou, 2006) and CO\(_2\) (Tardif et al., 2004) and showed interesting polymerization activity (Li et al., 2006). A related trinuclear titanium polyhydride was found to be able to induce dinitrogen cleavage followed by partial hydrogenation in the presence of dihydrogen (Shima et al., 2013).

**CHART 6** Selected examples of small nuclearity rare earth polyhydride clusters reported by Hou’s group.

Somewhat related to the small nuclearity clusters described above are organoaluminum rare earth heterometallic complexes (Chart 7) studied as models of Ziegler-type catalysts used in diene polymerization. Efforts in this area were initiated by Pearce and Lappert, who reported \(\text{Cp}_2\text{M}(\mu\text{-Me})_2\text{AlR}_2\) (\text{R} = \text{Me} and \text{M} = \text{Sc}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Tm}, \text{or Yb}; \text{R} = \text{Et} and \text{M} = \text{Sc} or \text{Y}) (Ballard and Pearce, 1975; Holton et al., 1976), and were continued by Anwander (Fischbach and
Anwander, 2006), who developed homoleptic tetraalkylaluminate rare earth complexes (Dietrich et al., 2011; Occhipinti et al., 2011) and bridging methyldienes (Dietrich et al., 2006b) and methyldynes (Dietrich et al., 2006a) as part of rare earth aluminum small clusters. Interestingly, the crystal structures of isostructural bridging hexacoordinate carbides, \([([\text{TMTAC}]M)[M_2(\mu-\text{CH}_3)](\mu_6-\text{C})(\mu(\text{CH}_3)_2)(\text{CH}_3)_3)((\mu(\mu(\mu(\text{CH}_3)_2))\text{Al}(\text{CH}_3)_2)_2] (\text{TMTAC} = 1,3,5\text{-trimethyl-1,3,5-triazacyclohexane, } M = Y, \text{Sm}), were also reported (Venugopal et al., 2009).
Our group previously synthesized group 3 metal monoalkyl complexes supported by ferrocene diamide ligands (Chart 8) (Diaconescu, 2010a; Diaconescu, 2010b) and studied their reactivity toward various organic substrates, including aromatic N-heterocycles (Carver and
Diaconescu, 2008; Miller et al., 2009) and other unsaturated substrates (Carver and Diaconescu, 2009). The 1,1′-ferrocenediyl (fc) diamide ligands have the general formula fc(NR)₂; the system studied the most by us has R = SiBuMe₂ (Carver et al., 2008), while other versions, such as R = SiMe₃ (Monreal et al., 2007), SiPhMe₂ (Duhović and Diaconescu, 2013), adamantyl (Wong et al., 2010), 2,4,6-trimethylphenyl, and 3,5-dimethylphenyl (Lee et al., 2011) have been explored only briefly. Group 3 metal alkyl complexes supported by a pincer-type pyridine diamide ligand, 2,6-bis(2,6-di-iso-propylanilidomethyl)pyridine (N₂N²py) (Guerin et al., 1995), were also synthesized for a reactivity comparison study (Chart 8) (Jie and Diaconescu, 2010).

CHART 8 Examples of rare earth complexes supported by chelating diamide ligands reported by Diaconescu’s group.

The continuous development of ancillary ligands has focused recently on nitrogen donors in the field of organometallic rare earth chemistry, as shown in the special issue “Recent Advances in f-Element Organometallic Chemistry” appeared in *Organometallics* in 2013 (Marks, 2013). Although the non-cyclopentadienyl organometallic chemistry of rare earths has been relatively underdeveloped, more than two thirds of the research articles in that issue used ancillary ligands other than cyclopentadienyl and its derivatives.
1.2 Reduction Chemistry of Organometallic Rare Earth Complexes

As mentioned previously, rare earth chemistry differs mainly from transition metal chemistry in that most rare earth ions are redox inactive under ordinary conditions. However, a few lanthanides can support the +2 or +4 oxidation state. Lanthanide chemistry in the +4 oxidation state is mostly limited to cerium(IV) compounds (Nair et al., 2003). On the other hand, low-valent chemistry is more nuanced than its high-valent counterpart (Nief, 2010). Table 1 lists the ionic radii for $M^{3+}$ (Shannon, 1976) and the spectroscopically estimated values for $E^0(M^{3+}/M^{2+})$ (Nugent et al., 1973).

**TABLE 1** Ionic radii for $M^{3+}$ (effective ionic radii are listed) and spectroscopically estimated values for $M^{3+/2+}$ (all values referenced to the normal hydrogen electrode, values in brackets are experimentally determined, NA = not applicable). Values were adapted from Shannon (1976) and Nugent et al. (1973).

<table>
<thead>
<tr>
<th>Element</th>
<th>$r$ (Å)</th>
<th>$E^0(M^{3+}/M^{2+})$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>0.74</td>
<td>NA</td>
</tr>
<tr>
<td>Y</td>
<td>0.90</td>
<td>NA</td>
</tr>
<tr>
<td>La</td>
<td>1.03</td>
<td>-3.1</td>
</tr>
<tr>
<td>Ce</td>
<td>1.02</td>
<td>-3.2</td>
</tr>
<tr>
<td>Pr</td>
<td>0.99</td>
<td>-2.7</td>
</tr>
<tr>
<td>Nd</td>
<td>0.98</td>
<td>-2.6</td>
</tr>
<tr>
<td>Pm</td>
<td>0.97</td>
<td>-2.6</td>
</tr>
<tr>
<td>Sm</td>
<td>0.96</td>
<td>-1.6 (-1.55)</td>
</tr>
<tr>
<td>Eu</td>
<td>0.95</td>
<td>-0.3 (-0.35)</td>
</tr>
<tr>
<td>Gd</td>
<td>0.94</td>
<td>-3.9</td>
</tr>
<tr>
<td>Tb</td>
<td>0.92</td>
<td>-3.7</td>
</tr>
<tr>
<td>Dy</td>
<td>0.91</td>
<td>-2.6</td>
</tr>
<tr>
<td>Ho</td>
<td>0.90</td>
<td>-2.9</td>
</tr>
<tr>
<td>Element</td>
<td>Value</td>
<td>( E_{1/2} )</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
<td>----------------</td>
</tr>
<tr>
<td>Er</td>
<td>0.89</td>
<td>-3.1</td>
</tr>
<tr>
<td>Tm</td>
<td>0.88</td>
<td>-2.3 (-2.2)</td>
</tr>
<tr>
<td>Yb</td>
<td>0.87</td>
<td>-1.1 (-1.1)</td>
</tr>
<tr>
<td>Lu</td>
<td>0.86</td>
<td>NA</td>
</tr>
</tbody>
</table>

An interesting study, relevant to organometallic rare earth chemistry, found that most LnI\(_2\) could be synthesized using solid state techniques with two different types of structures: those with a \([Xe]d^0fn\) configuration and those with a \([Xe]d^1fn-1\) configuration (Meyer et al., 2004). The former (including NdI\(_2\), SmI\(_2\), EuI\(_2\), DyI\(_2\), TmI\(_2\), and YbI\(_2\)) are genuine \([M^{2+}][I^-]_2\) salts, while the latter (the rest of LnI\(_2\)) should be viewed as \([M^{3+}][I^-]_2[e^-]\) due to their metallic character (the valence d electron is not localized on the metal but is found in the conduction band). This phenomenon is well correlated to the spectroscopically estimated values of \(M^{3+/2+}\): the salt-like LnI\(_2\) are those of rare earths having smaller values for the \(M^{3+/2+}\) reduction potential, while the metallic LnI\(_2\) are those with a \(M^{3+/2+}\) reduction potential close to or lower than \(-3.0\) V (the alkali metals have \(M^{1+/0}\) reduction potentials around \(-3.0\) V). These characteristics are also reflected in the organometallic chemistry of these elements: Eu(II) is so stable that it is just as common as Eu(III) in organometallic rare earth chemistry (Bombieri and Paolucci, 1998; Zimmermann and Anwander, 2010). Indeed, no homoleptic Eu(III) alkyl complexes have been reported yet (Zimmermann and Anwander, 2010), likely because the alkyl group is readily oxidized by Eu(III). Yb(II) is also common (Bombieri and Paolucci, 1998; Zimmermann and Anwander, 2010). A major breakthrough in this field was the isolation of organosamarium(II) complexes. Divalent samarium complexes, such as Cp\(^*\)\(_2\)Sm, are strong reductants. For example, Cp\(^*\)\(_2\)Sm could reduce N\(_2\) to form the first dinitrogen complex of an f element, \((\text{Cp}^*\text{Sm})_2(\mu-\eta^2:\eta^2-\text{N}_2)\) (Chart 9) (Evans et al., 1988). The synthesis of molecular thulium, dysprosium, and even neodymium(II) complexes could be achieved from the corresponding metal diiodides with the appropriate ligands (Nief, 2010).
Cyclopentadienyls with bulky substituents like trimethylsilyl or tert-butyl, such as 1,3-(Me₃Si)₂C₅H₃, Me₃SiC₅H₄, and their tert-butyl counterparts, proved to be successful in isolating relatively stable divalent rare earth metal complexes. Some of them were crystallographically characterized, including [1,3-(Me₃Si)₂C₅H₃]₂Tm(THF) (Evans et al., 2002) and [(1,2,4-(Bu₃C₅H₂)₂Dy(μ-Z)K(18-crown-6)] (Z = BH₄, Br) (Jaroschik et al., 2007a), while others were proposed as reaction intermediates (Jaroschik et al., 2009).
$2 \text{LnZ}_3 + 2 \text{KC}_8 \xrightarrow{\text{N}_2, \text{THF}} \text{ZLnN}_2\text{LnZ}_3 \text{THF}_x$

or

$2 \text{LnZ}_2\text{Z'} -2 \text{KZ} \text{or} -2 \text{KZ'}$

$\text{Ln} = \text{Sc, La, Ce, Pr, Nd, Gd, Tb, Dy, Y, Ho, Er, Tm, Lu}$

$\text{Z} = \text{N(SiMe}_3)_2, 2,6-\text{OC}_6\text{H}_3\text{Bu}_2, \text{C}_5\text{Me}_5, \text{C}_5\text{H}_4\text{SiMe}_3, \text{C}_5\text{Me}_4\text{H, C}_5\text{H}_2\text{Bu}_3$

$\text{Z'} = \text{BPH}_4, \text{I}$

**LnZ₃/KC₈ system**

**CHART 9** Selected examples of reduced dinitrogen organometallic rare earth complexes reported by Evans’s group.
Besides isolated divalent rare earth metal complexes, systems that behave as M(II) are usually included with low-valent organometallic rare earth compounds (Nief, 2010). Perhaps the most famous system is LnZ₃/KC₈ developed by Evans, where Z may be various monoanionic ligands, including amides, aryloxides, and cyclopentadienyls, and Ln may be any rare earth (Chart 9). This combination can reduce dinitrogen to form (N₂)²⁻ (Evans et al., 2005; Evans, 2007). Recently, lanthanide complexes of the radical trianion (N₂)³⁻ have been isolated and characterized crystallographically (Evans et al., 2009; Fang et al., 2011; Farnaby et al., 2012; Fieser et al., 2013). It is important to note that some lanthanide (N₂)³⁻ complexes behave as single molecule magnets due to the spin exchange between the lanthanide ions and (N₂)³⁻ (Rinehart et al., 2011a), and one of them, [K(18-crown-6)(THF)₂][([(Me₃Si)₂N]₂(THF)Tb)(μ-η²:η²-N₂)] (Chart 9), has one of the highest blocking temperatures (14 K) for a single molecule magnet (Rinehart et al., 2011b).

In 2008, Lappert isolated the first compound in a series of metal complexes with an ambiguous electronic structure: [K(18-crown-6)(Et₂O)][[1,3-(Me₃Si)₂C₅H₃]₃La] (Hitchcock et al., 2008). The authors proposed that it contains a lanthanum(II) ion. Recently, Evans extended this chemistry to almost all the lanthanides (Chart 10) (MacDonald et al., 2011; MacDonald et al., 2012; MacDonald et al., 2013a). The charge balance requires the lanthanide ion to be in +2 oxidation state. However, intriguingly, the density functional theory (DFT) calculations reported by the authors suggest that all lanthanides have a [Xe]4f⁰5d¹6s⁰ configuration, which is the same as that of solid state LnI₂ salts. As mentioned earlier, the latter are considered to be (Ln³⁺)(I⁻)₂(e⁻) (Meyer et al., 2004; Meyer, 2014). Despite the ambiguity in their electronic structure, the isolation of these complexes is nonetheless a remarkable achievement in the reduction chemistry of rare earth metals. Moreover, the advantage of using the [η⁵-C₅H₅SiMe₃]₃M platform has proved to be useful beyond...
supporting lanthanides: it was employed in the first structurally characterized molecular uranium(II) complex, also reported by Evans’s group (MacDonald et al., 2013b).

![Chart 10](image)

**CHART 10** Examples of reduced tris-cyclopentadienyl rare earth complexes reported by Lappert’s and Evans’s groups.

Overall, the reduction chemistry of organometallic rare earth compounds is a fast developing field with a lot of recent exciting discoveries (Evans, 2007). Although cyclopentadienyls feature prominently, non-cyclopentadienyl ligands have not been explored in detail (Nief, 2010) and may hold the key to unlock new bonding motifs and reactivity.

2. PREVIOUS STUDIES OF ARENE-BRIDGED RARE EARTH COMPLEXES

Arenes have outstanding stability due to their aromaticity; however, the accessibility of both their $\pi$ and $\pi^*$ orbitals allows them to serve as multi-electron neutral or anionic ligands. Rare earths ions, because of their large ionic radii and high positive charge, can have high coordination
numbers without sacrificing the strength of interactions with a ligand. Therefore, neutral and anionic arenes serve as excellent ligands for rare earth ions (Bochkarev, 2002).

Rare earth metal arene complexes were reviewed extensively by Bochkarev in 2002 (Bochkarev, 2002). The first authentic arene-lanthanide complex was reported in 1986 and contained a neutral C₆Me₆ ligand (Cotton and Schwotzer, 1986). Rare earth complexes of reduced arenes have been targeted for a long time due to their fundamental importance as well as their potential use as multi-electron sources for reduction reactions (Bochkarev, 2002). Among them, inverted sandwiches of naphthalene are the most studied and have been synthesized and characterized for almost all rare earths (Bochkarev, 2002). In compounds with anionic arene ligands, the metal is usually found in the +3 oxidation state, while the additional electrons rest in the $\pi^*$ orbitals of the arene ligand. Because of the relatively high energy of these orbitals, such complexes can serve as strong reductants.

The prototypical example in the class of arene-bridged complexes is the reduced benzene ligand. Lappert and coworkers isolated two types of bridged, reduced benzene complexes (Chart 11): [K([18]-crown-6)][Ln(C₅H₅(SiMe₃)₂-1,3)₂(C₆H₆)] (Ln = La, Ce, Pr, Nd) and [K([18]-crown-6)(C₆H₆)₂][Ln(C₅H₅(t-Bu)₂-1,3)₂(C₆H₆)] (Cassani et al., 2002; Cassani et al., 1996; Cassani et al., 1998; Cassani et al., 1999). The two classes differ by the substituent of the cyclopentadienyl ligand (SiMe₃ versus tert-butyl, the latter is more sterically demanding due to the shorter C-C than Si-C distance) and the nature of the benzene anion. Based on X-ray crystallography studies, it was proposed that the first class contains a 1,4-hexadiene-2,5-diy ligand, while the latter contains a benzenide anion (monoanionic benzene). These differences are reflected in the color of these compounds: while the former are dark red, the latter are dark green. The dark green toluene radical anion was later isolated as a potassium salt from potassium metal, 18-crown-6, and toluene in a
THF solution. The corresponding benzene radical anion could not be obtained probably due to its high reactivity, but, instead, the radical coupled dimer [K(18-crown-6)]2(μ-η⁵-C⁶H⁶-C⁶H⁶) was isolated. It was suggested that the dimer readily dissociated to C⁶H₆⁻ in solution (Hitchcock et al., 2001). Although the CCC angles of the benzene anion are similar for the potassium and lanthanum species, the C-C distances differ, with an average of 1.40 and 1.44 Å, respectively. It is interesting to note that the average C-C distance in the 1,4-hexadiene-2,5-diy1 lanthanum complex is intermediate between those two values, 1.42 Å.

CHART 11 Inverse sandwiches of anionic benzene rare earth complexes as a 1,4-hexadiene-2,5-diy1 (left) and as a benzene radical anion (right) ligand reported by Lappert’s group.

Biphenyl-bridged rare earth complexes are the least numerous in the class of polyaromatic complexes. As shown later in our chemistry, they can differ greatly from their corresponding fused arene (naphthalene or anthracene) counterparts. The examples from Fryzuk’s group (Figure 1) also show divergent chemistry: biphenyl-bridged complexes of yttrium and lutetium supported by the macrocyclic P₂N₂ ligand were obtained through C-C bond formation of proposed phenyl intermediates (Chart 12) (Fryzuk et al., 1997). Depending on the biphenyl ligand, two types of compounds were isolated: from phenyl, the resulting compound featured yttrium ions coordinated
to different rings, while from *meta*- and *para*-tolyl, complexes with both yttrium ions coordinated to the same ring were identified. Variable temperature NMR spectroscopy indicated that the dimethylbiphenyl complexes show fluxional behavior in solution. It was proposed that both types of biphenyl complexes would show such behavior (Fryzuk et al., 1997).

**CHART 12** Inverse sandwiches of dianionic biphenyl yttrium complexes reported by Fryzuk’s group.
FIGURE 1 Molecular structures of inverse sandwiches of dianionic biphenyl yttrium complexes reported by Fryzuk’s group. Figures were redrawn after Fryzuk et al. (1997).

Rare earth complexes in which the naphthalene is reduced and bridges two metal ions are rather numerous and all examples previous to our work were reviewed by Bochkarev (Bochkarev, 2002). In order to be consistent, those compounds will also be described here since it will allow us to have a perspective view of the field.
CHART 13 Inverse sandwiches of dianionic naphthalene lanthanide complexes reported by Bochkarev’s group.

Figure 2 Molecular structure of $[\text{Tm(DME)}]_2(\eta^2-\text{C}_{10}\text{H}_8)_2(\mu-\eta^4:\eta^4-\text{C}_{10}\text{H}_8)$ reported by Bochkarev’s group. Figure was adapted from Bochkarev et al. (1997).

Bochkarev’s group pioneered the synthesis of bridging, reduced naphthalene complexes (Chart 13) by isolating and structurally characterizing $[\text{LaI}_2(\text{THF})_3]_2(\mu-\eta^4:\eta^4-\text{C}_{10}\text{H}_8)$ and
[EuI(DME)₂]₂(μ-η⁴:η⁴-C₁₀H₈) (Fedushkin et al., 1995). Shortly after, the series of lanthanide diiodides and an additional ytterbium(II) complex were reported (Bochkarev et al., 1996). A triple decker binary thulium(III) naphthalene complex [Tm(DME)]₂(η²-C₁₀H₈)₂(μ-η⁴:η⁴-C₁₀H₈) (Figure 2) was also isolated from the reaction of TmI₂ and lithium naphthalenide in 1,2-dimethoxyethane (DME) solution (Bochkarev et al., 1997). In all these complexes, the bridging naphthalene ligand is dianionic and coordinates in a μ-η⁴:η⁴ mode. Samarium and ytterbium dinuclear complexes supported by cyclopentadienyl were also synthesized and reported to adopt the same coordination mode for the bridging naphthalene based on infra-red (IR) spectroscopic data, but an X-ray structural analysis was not included (Protchenko et al., 1996).

A similar bridging mode was observed by Fryzuk’s group, who synthesized naphthalene-bridged complexes of yttrium and lutetium supported by the macrocyclic P₂N₂ ligand ([(P₂N₂)Ln]₂(μ-η⁴:η⁴-C₁₀H₈), Ln = Y, Lu, Figure 3) from the reduction with KC₈ of the corresponding chloride-bridged bimetallic starting materials (Chart 14) (Fryzuk et al., 2000). Similarly to what was found for the dianionic, bridging biphenyl rare earth complexes supported by the same ligand, fluxional behavior was observed for the naphthalene complexes.
CHART 14 Inverse sandwiches of anionic naphthalene yttrium and lutetium complexes reported by Fryzuk’s group.

FIGURE 3 Molecular structure of \([([P_2N_2]Y)_2(\mu-\eta^4:\eta^4-C_{10}H_8)]\) reported by Fryzuk’s group. Figure adapted from Fryzuk et al. (2000).

Probably the most interesting anionic naphthalene complex from the point of view of the naphthalene coordination mode is \([(\text{Cp}^*\text{Lu})_3(C_{10}H_8)(C_{10}H_7)(H)][\text{Na(THF)}_3]]_2[C_{10}H_8]\), which was isolated from the reaction of \([\text{Cp}^*\text{LuCl}_2]\text{NaCl}\) with \(C_{10}H_8\text{Na}\) (Chart 15) (Protchenko et al., 1997). X-ray analysis indicated that there is an interstitial dianionic naphthalene, which does not coordinate any cation but balances the charge for the two trinuclear lutetium clusters. In addition, one of the bridging naphthalenes is a dianion (indicated in Chart 15 by an \(\eta^6\) coordination to Lu2), while the other is a trianion that coordinates \(\eta^4\) to Lu3 and \(\eta^1\) to Lu2. Since the cluster is diamagnetic, charge balance requires the presence of a hydride ligand. This proposal has not been verified directly, but was supported by the isolation of neodymium and dysprosium naphthalene complexes from hydride-containing starting materials (Burin et al., 2011).
Crystallographically characterized bridging, reduced anthracene complexes are less numerous than their naphthalene counterparts. For anthracene, there is the possibility that the two metal ions bind symmetrically involving both terminal rings or to a terminal and the middle ring (Chart 16). In the first case, a $\mu$-$\eta^3$ coordination mode was observed for $(\text{Cp}^*2\text{Ln})_2(\text{C}_{14}\text{H}_{10})$ ($\text{Ln} = \text{Sm, La}$) (Evans et al., 1994; Thiele et al., 1996), in which the two lanthanides bind symmetrically to a terminal and the middle ring, while a $\mu$-$\eta^4$ coordination mode was observed for $[(\text{P}_2\text{N}_2)\text{Ln}]_2(\mu$-$\eta^3$-$\eta^4$-$\text{C}_{14}\text{H}_{10})$ ($\text{Ln} = \text{Y, Lu}$) (Fryzuk et al., 2000), akin to that of naphthalene in the analogous complexes. The solid-state molecular structures of $[(\text{P}_2\text{N}_2)\text{Ln}]_2(\mu$-$\eta^3$-$\eta^4$-$\text{C}_{14}\text{H}_{10})$ (Figure 4) indicate an unsymmetrical binding of the two lanthanides, however, variable temperature NMR spectroscopy pointed to a fluxional behavior and a symmetrical solution structure.

**Chart 15** Proposed structure of a bridging naphthalene hydride trilutetium complex reported by Bochkarev’s group (Protchenko et al., 1997).
CHART 16  Bridging dianionic anthracene rare earth complexes.

FIGURE 4  Molecular structure of $\left(\left[P_2N_2\right]Y\right)_2(\mu-\eta^4:\eta^4-C_{14}H_{10})$ reported by Fryzuk’s group.

Figure was adapted from Fryzuk et al. (2000).
Complexes of bridging, reduced polycyclic arenes with more than three fused phenyl rings were also reported and various coordination modes identified (Chart 17). These range from \((\text{Cp*}_2\text{Sm})_2(\mu-\eta^3:\eta^3:\text{C}_{16}\text{H}_{10})\) (Evans et al., 1994) to \([(\text{Cp*La})_3(\mu-\text{Cl})_3(\text{THF})(\mu-\eta^2:\eta^6:\eta^6:\text{C}_{16}\text{H}_{10})]\) (Thiele et al., 1998) in pyrene compounds and \((\text{Cp*}_2\text{Sm})_2(\mu-\eta^3:\eta^3:\text{C}_{18}\text{H}_{12})\) (Evans et al., 1994) in a 2,3-benzanthracene complex.

Overall, the molecules mentioned in this section show that a bridging anionic aromatic ligand can adopt a variety of coordination modes in the corresponding rare earth complexes. A feature worth noticing is that, when studied, all these compounds showed fluxional behavior and it is likely that most of them would do so in solution. This is explained, in part, by the ionic nature of the interaction between the lanthanide ions and the bridging anionic arenes.

**Chart 17** Bridging, dianionic pyrene and 2,3-benzanthracene rare earth complexes.
3. PREVIOUS STUDIES OF METAL COMPLEXES SUPPORTED BY FERROCENE-BASED DIAMIDE LIGANDS AND DEVELOPMENT OF NEW RARE EARTH STARTING MATERIALS

3.1 Advantages of 1,1′-ferrocenediyl Diamide Ligands

In 2000, J. Arnold reported a reliable synthesis of 1,1′-diaminoferrocene (Shafir et al., 2000) and introduced the trimethylsilyl version fc(NHSiMe3)2 (H2(NN\text{TM}S)) to group 4 metals, titanium and zirconium, to afford metal dimethyl and dibenzyl complexes (NN\text{TM}S)TiMe2 and (NN\text{TM}S)ZrBn2 (Bn = CH2Ph) (Chart 3-1) (Shafir et al., 2001). [(NN\text{TM}S)ZrBn][(\mu-Bn)B(C6F5)3] could be obtained by treating (NN\text{TM}S)ZrBn2 with 1 equivalent of B(C6F5)3 and its reactivity toward olefin polymerization was studied (Shafir and Arnold, 2003). Our group introduced the 1,1′-ferrocenediyl diamide ligands to uranium and reported the synthesis and characterization of (NN\text{TB}S)2U (NN\text{TB}S = 1,1′-fc(NSi\text{t}BuMe2)2) and its one electron oxidation product [(NN\text{TB}S)2U][BPh4] in 2007 (Chart 18). The redox process was studied in detail and it was found that the electronic communication between the two iron centers was mediated by uranium in the mixed-valent (Fe(II) and Fe(III)) complex, [(NN\text{TB}S)2U][BPh4] (Monreal et al., 2007). At the time, it was also observed that the tert-butyldimethylsilyl version, 1,1′-fc(NHSi\text{t}BuMe2)2 (H2(NN\text{TB}S)), was easier to handle because of its improved solubility, which allowed many compounds to crystallize easily. As a consequence, later efforts focused on this particular ligand platform. Group 3 metal monoalkyl complexes with the general formula (NN\text{TB}S)M(CH2Ar)(THF) (M = Sc (Carver et al., 2008) and Lu (Carver et al., 2009), Ar = 3,5-C6H3Me2; M = Y (Carver and Diaconescu, 2008) and La (Miller et al., 2009), Ar = C6Hs) and the uranium dialkyl complex (NN\text{TB}S)UBn2 (Monreal and Diaconescu, 2008) were successfully synthesized (Chart 18 and Figure 5). The electron donating 1,1′-ferrocenediyl group (Sauro and Workentin, 2002) makes the amide donor bind
strongly to the highly electropositive group 3 metals and uranium(IV) ion. By using NNTBS as the ancillary ligand for d⁰₉ metal alkyl complexes, the C-H bond activation of aromatic heterocycles (Williams et al., 2011), successive C-C bond coupling (Carver et al., 2009; Carver et al., 2010; Monreal and Diaconescu, 2010; Williams et al., 2010), dearomatization of aromatic heterocycles (Miller et al., 2009), and the unprecedented ring-opening of 1-methylimidazole (Carver and Diaconescu, 2008; Monreal et al., 2009), 1-methylbenzimidazole (Miller et al., 2010), or other aromatic heterocycles (Duhović et al., 2010) were observed and studied (Diaconescu, 2010a; Diaconescu, 2010b).
CHART 18  Group 4, uranium, and group 3 metal complexes supported by 1,1’-ferrocenediyl diamide ligands.
FIGURE 5 Molecular structure of \((\text{NN}^{\text{TBS}})\text{Sc(CH}_2\text{Ar})(\text{THF})\) (Ar = 3,5-C\text{6}H\text{3}Me\text{2}). Figure was adapted from Carver et al. (2008).

It is likely that the ferrocene backbone has a specific role in facilitating the unique reactivity observed by our group. Our hypothesis is that when the electron rich iron center of ferrocene and the electropositive metal ion are brought into close proximity, a donor-acceptor interaction takes place between iron and the metal (Bauer et al., 2012). This type of Lewis acid-Lewis base interaction was observed previously with both electrophilic early and late transition metals (Chart 19): Seyferth suggested a weak, dative Fe-to-Pd bond in \([\text{Fe}(\eta^5-C\text{5}H\text{4}S)_2]\text{Pd}(\text{PPh}_3)\) (Seyferth et al., 1983); Akabori later provided a comprehensive study based on \([M(\eta^5-C\text{3}H\text{4}O)_2]M'(\text{PPh}_3)\) (M = Fe or Ru, M' = Pd or Ni) that supported a dative M-M' interaction (Akabori et al., 1987); Nataro recently reported on the electronic structure of palladium(II) and platinum(II) compounds of 1,1'-bis(phosphino)metalocenes (Gramigna et al., 2013). In the area of early transition metals, J. Arnold suggested a dative Fe to Ti bond based on the short Fe-Ti distance in \(([(\text{NN}^{\text{TMS}})\text{Ti}(\mu-Cl)]_2)[\text{B(C}_6\text{F}_5)_4]_2\) (Shafir and Arnold, 2001), and Stephan showed the importance of a ferrocenyl-
titanium or zirconium interaction in stabilizing reactive cations (Ramos et al., 2009). More interestingly, J. Arnold observed that the Fe-Ti distance in a series of compounds with the NN\textsuperscript{TMS} ligand varied according to the electrophilicity of the titanium center: Fe-Ti distance is 3.32 Å in the neutral dialkyl complex (NN\textsuperscript{TMS})TiMe\textsubscript{2}, but it shortens to 3.07 Å in the Lewis adduct [(NN\textsuperscript{TMS})TiMe][(μ-Me)B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}] and reaches the shortest value, 2.49 Å, in the chloride-bridged dicationic complex ([(NN\textsuperscript{TMS})Ti(μ-Cl)]\textsubscript{2})[B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\textsubscript{2}. Our group observed a similar trend for group 3 metal complexes supported by the NN\textsuperscript{TBS} ligand: the Fe-Sc distance is 3.16 and 2.80 Å in (NN\textsuperscript{TBS})Sc(CH\textsubscript{2}C\textsubscript{6}H\textsubscript{5}Me\textsubscript{2}-3,5)(THF) (Figure 5) and [(NN\textsuperscript{TBS})Sc(μ-Cl)]\textsubscript{2} (Figure 6), respectively (Carver et al., 2008). Recently, our group also reported a dative Fe-Ru interaction in [Fe(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{4}NH\textsubscript{2})Ru(PPh\textsubscript{3})\textsubscript{2}] and characterized it by spectroscopic methods and DFT calculations (Green et al., 2013).
CHART 19  Metalloocene complexes containing dative iron-metal bonds (indicated as red dashed lines).
Besides the weak Fe-M interaction, ferrocene-based ligands inherit the redox-active nature of ferrocene. The ferrocenium-ferrocene redox couple is usually reversible (Connelly and Geiger, 1996). Therefore, the ferrocene unit can serve as a redox-switch providing an indirect control of active sites for polymerization or other chemical transformations (Gregson et al., 2006; Yoon et al., 2010). Recently, our group reported a redox-switchable catalyst used for ring-opening polymerization and the synthesis of biodegradable materials (Broderick et al., 2011). This result highlighted the potential of the redox-active ferrocene backbone in tuning the reactivity of the metal center found in the vicinity of ferrocene. On the other hand, the possibility to reduce ferrocene was evidenced by the reversible redox event observed for ferrocene in 1,2-dimethoxyethane at -3.45 V (referenced to ferrocene+/0) (Ito et al., 1983).

Based on experimental observations and computational studies on the organometallic compounds supported by the 1,1′-ferrocenediyl diamide ligands, the following advantages/features were attributed to this type of ligands (Figure 7): (1) the weak, dative iron-metal interaction stabilizes complexes of the Lewis acidic metal center, and, probably more important, this interaction is flexible since the barrier for the ferrocene unit to move toward or away from the metal center is low (nearly free rotation of C_{ipso}-N bonds); (2) the 1,1′-ferrocenediyl diamide blocks one side of the metal leaving the other side widely open for substrate coordination. This is particularly important when comparing it to substituted cyclopentadienyls. From our point of view, substituted cyclopentadienyls are usually sterically demanding, which facilitates the isolation of unstable compounds but hinders their reactivity (Evans and Davis, 2002).
FIGURE 7 Advantages/features of 1,1′-ferrocenediyl diamide ligands to support electrophilic d⁰fⁿ metals.

3.2 (NN^{TBS})MI(THF)₂ (M = Sc, Y, La, and Lu) as Precursors for Reduction Chemistry

In rare earth reduction chemistry, the metal precursor complex is crucial. For example, Evans and co-workers synthesized the first scandium dinitrogen complex by using a specific Sc(III) cationic species, [(C₅Me₄H)₂Sc][(μ-Ph)BPh₃], as the precursor (Demir et al., 2010). Similarly, in our chemistry, initial attempts using [(NN^{TBS})Sc(μ-Cl)]₂ (Carver et al., 2008) and potassium graphite (KC₈) in common organic solvents such as hexanes, toluene, diethyl ether (Et₂O), tetrahydrofuran (THF) did not result in any products that could be identified. However, the iodide analogue proved to be a good starting material.

(NN^{TBS})ScI(THF)₂ could be readily prepared from (NN^{TBS})Sc(CH₂C₆H₃Me₂-3,5)(THF) on a gram scale. Clean conversion to (NN^{TBS})MI(THF)₂ (M = Sc, Y, La, and Lu) was achieved by stirring 2 equivalents of Me₃SiI and (NN^{TBS})M(CH₂Ar)(THF) in toluene at 25 °C for 1 hour (Scheme 1). Compounds (NN^{TBS})MI(THF)₂ are barely soluble in saturated hydrocarbons, but
readily soluble in aromatic solvents and ethers. Except for \(\text{NN}^{\text{TBS}}\text{ScI(THF)}_2\), which crystallized in the space group \(C2/c\), all other \(\text{NN}^{\text{TBS}}\text{MI(THF)}_2\) crystallized in the same space group, \(P-1\), and differed only slightly in their structural parameters (Figure 8). In all \(\text{NN}^{\text{TBS}}\text{MI(THF)}_2\) structures, the rare earth ion is coordinated by two nitrogen, two oxygen, and one iodide ligand, while the ferrocene backbone sits oppositely to iodide. If iron coordination is taken into account, the metal center has a pseudo-octahedral geometry. However, the Fe-M interaction is in the “off” mode (indicated by long Fe-M distances) in the presence of two coordinating THF molecules, which supply enough electron density to the metal center.

\[\text{SCHEME 1} \quad \text{Synthesis of } \text{NN}^{\text{TBS}}\text{MI(THF)}_2 \quad (M = \text{Sc, Y, La and Lu, } \text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2 \text{ or C}_6\text{H}_5)\]

\[\text{FIGURE 8} \quad \text{Molecular structure of } \text{NN}^{\text{TBS}}\text{ScI(THF)}_2 \text{ (left) and } \text{NN}^{\text{TBS}}\text{YI(THF)}_2 \text{ (right). Figures were adapted from Huang et al. (2011) and Huang and Diaconescu (2012).}\]
A molecular orbital analysis by using DFT calculations was performed for \((\text{NN}^{\text{TBS}})\text{MI}(\text{THF})_2\) (Figure 9). From the point of view of reduction chemistry, the LUMO of \((\text{NN}^{\text{TBS}})\text{MI}(\text{THF})_2\) is of particular interest because it may indicate whether the ferrocene backbone is involved in the reduction process. Somewhat surprisingly, the LUMO of various metal iodides was not the same, although HOMO and HOMO-1 were always the 3d orbitals of iron. For \((\text{NN}^{\text{TBS}})\text{ScI}(\text{THF})_2\), the LUMO was localized on the 3d orbital of scandium, while the LUMO+1 was the \(\pi^*\) orbital of the ferrocene backbone; however, for \((\text{NN}^{\text{TBS}})\text{YI}(\text{THF})_2\), both the LUMO and LUMO+1 were the \(\pi^*\) orbitals of the ferrocene backbone. Since the reduction usually involves population of the LUMO from an external electron source, this difference suggests that the ferrocene backbone might serve as an electron shuttle in addition to a direct reduction pathway of the rare earth halide that is operative in other rare earth halides.
3.3 Reaction Conditions for Reduction Chemistry

It is well documented that reaction conditions are crucial to the outcome of reduction chemistry. As a typical heterogeneous reductant, KC₈ forms a suspension in common organic solvents such as n-pentane, Et₂O, and THF (Bergbreiter and Killough, 1978). However, the reaction of KC₈ with acidic protons (water, methanol, and other alcohols) in different solvents resulted in a different amount of evolved hydrogen gas. It was suggested that this difference in
reactivity was caused by the fact that the suspensions formed by KC₈ in n-pentane and Et₂O are not as well dispersed as those formed in THF (Bergbreiter and Killough, 1978).

![Space-filling model of KC₈: left, side view; right, top view. Use granted by Ben Mills from the Wikimedia Commons.](image)

**FIGURE 10** Space-filling model of KC₈: left, side view; right, top view. Use granted by Ben Mills from the Wikimedia Commons.

Potassium graphite (commonly referred to as KC₈) is the most potassium rich form of a series of graphite intercalation compounds with potassium (Rüdorff and Schulze, 1954). A space-filling model of KC₈ is shown in Figure 10. KC₈ is probably the most widely used reductant in organometallic rare earth chemistry (Nief, 2010). The system composed of trivalent lanthanide precursors LnZ₃ (Z represents a monoanionic ligand) and KC₈ developed by Evans proved successful in reducing dinitrogen to form stable lanthanide dinitrogen complexes with the general formula (Z₂Ln)₂(μ-η²:η²-N₂) (Evans et al., 2005). In addition, KC₈ was used in obtaining a series of divalent lanthanide complexes [K(2.2.2-cryptand)][(C₅H₄SiMe₃)₃Ln] (Chart 10) (MacDonald et al., 2013a). The strategy of using KC₈ as a reductant was also employed in main group chemistry to obtain structurally fascinating and fundamentally important molecules such as
LB(H)=B(H)L (Wang et al., 2007) and LSi=SiL (Wang et al., 2008) (L = :C[N(2,6-Pr2C6H3)CH]2),
containing a B=B bond and a Si=Si bond, respectively, although similar molecules,
L:B(Br)=B(Br):L and L:B≡B:L, could also be prepared using sodium naphthalenide as a reductant
by another group (Braunschweig et al., 2012). The use of KC₈ as a reductant in organic synthesis
has also been explored (Bergbreiter and Killough, 1978). It was concluded that, as a reducing agent,
it behaved similarly or poorly compared to its homogeneous analogue sodium naphthalenide, but
it had the advantage that it did not form any soluble byproducts. This advantage is particularly
important in organometallic chemistry (Jensen et al., 1965; Schwindt et al., 1990; Ungurenasu and
Palie, 1975).

4. SYNTHESIS OF RARE EARTH FUSED-ARENE COMPLEXES AND THEIR
REACTIVITY TOWARD P₄ ACTIVATION

4.1 Scandium Fused-arene Complexes: Synthesis, Characterization, and Reactivity

Previous to our work, rare earth reduced naphthalene complexes were missing examples
of scandium compounds. Similarly, no scandium complex with another fused arene, such as
anthracene, was known, although reduced anthracene complexes with other rare earths are
common (Bochkarev, 2002). The synthesis of scandium arene complexes had been limited to the
co-condensation of scandium metal vapors and benzene derivatives with bulky substituents (1,3,5-
t-Bu₃C₆H₃) (Cloke et al., 1991) or heteroaromatic hydrocarbons (2,4,6-t-Bu₃C₅H₂N and 2,4,6-t-
Bu₃C₃P₃) to give sandwich, formally zero-valent and sub-valent scandium arene complexes (Chart
20) (Arnold et al., 1996; Arnold et al., 1998; Cloke, 1993). The gas-phase reaction of scandium
ion with benzene and its derivatives led to products that could only be characterized by mass
spectrometry (Huang et al., 1987). Neutral arene scandium(III) complexes supported by β-
diketiminato ligands were isolated and structurally characterized by Piers’s group (Chart 21) (Hayes et al., 2003; Hayes et al., 2007). The reports from Piers’s group highlighted the strong Lewis acidity of scandium(III).

**CHART 20** Formally zero-valent and sub-valent scandium arene complexes.
CHART 21 Coordination of neutral arene to cationic scandium(III) species reported by Piers’s group.

The observed lack of scandium reduced arene complexes may be related to the unique characteristics of scandium. Scandium(III) is the smallest among rare earths: its ionic radius of 0.74 Å is 0.12 Å smaller than that of lutetium(III) (Shannon, 1976). The large difference in ionic radius between scandium and other rare earths leads to special properties and reactivity of scandium complexes (Moeller et al., 1965; Zimmermann and Anwander, 2010). This is best illustrated by the product from the co-condensation of scandium metal and 1,3,5-tert-Bu3C6H3 (Cloke et al., 1991). While other rare earths gave the formally zero-valent sandwich complexes (1,3,5-tert-Bu3C6H3)Ln (Ln = Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Lu) (Anderson et al., 1989), in the case of scandium, a second product arising from the insertion of scandium into the C–H bond of the tert-butyl groups was also observed (Cloke et al., 1991).

The NN\textsuperscript{TBS} ligand proved to be the right choice for supporting inverse sandwiches of reduced arene scandium complexes: the reaction between (NN\textsuperscript{TBS})ScI(THF)\textsubscript{2} (NN\textsuperscript{TBS} = 1,1′-fc(NHSi′BuMe\textsubscript{2})\textsubscript{2}) and 0.5 equiv naphthalene (Scheme 2a) led to the first scandium naphthalene complex, [(NN\textsuperscript{TBS})Sc]_{2}(\mu-\eta^{4}:\eta^{4}-C_{10}H_{8}) (Sc\textsubscript{2}-naph) (Figure 11) (Huang et al., 2011). The
analogous anthracene complex, [(NN\text{TBS})Sc]_2(\mu-\eta^6:\eta^6-C_{14}H_{10}) \text{(Sc}_2\text{-anth)}, could be obtained by following a similar protocol (Scheme 2b) and was also crystallographically characterized (Figure 11).

**SCHEME 2** a) Synthesis of Sc\textsubscript{2}-naph; b) synthesis of Sc\textsubscript{2}-anth; c) conversion of Sc\textsubscript{2}-naph to Sc\textsubscript{2}-anth. Adapted with permission from Huang et al. (2011). Copyright © 2011, American Chemical Society.
The molecular structure of \textit{Sc}_2-naph (Figure 11) was reminiscent of previously reported yttrium naphthalene complexes (Fryzuk et al., 2000). The naphthalene is distorted from planarity with C2/C3 and C2A/C3A bending in opposite directions from the plane composed of the other six carbon atoms (ca. 20° torsion angle). The C-C bonds within the naphthalene are best described as two isolated double bonds (C2=C3 and C2A=C3A), with short distances averaging 1.37 Å, and a 6C, 8π-electron system for the six co-planar center carbon atoms. Each scandium ion binds \( \eta^4 \) to C1 through C4 (or C1A through C4A) with similar distances averaging 2.51 Å. These features are also reminiscent of those of the lithium naphthalene dianion \([\text{Li(TMEDA)}]_2(\mu-\eta^4:\eta^4-\text{C}_{10}\text{H}_8)\) (TMEDA = tetramethylethlenediamine) (Melero et al., 2009).

Besides common structural parameters with previously reported rare earth or alkali metal naphthalene dianion complexes, \textit{Sc}_2-naph featured a short Fe-Sc distance of 2.83 Å, which was significantly shorter than that of (NN\textsuperscript{TBS})ScI(THF)_2 (3.12 Å) and among the shortest Fe-Sc distances observed by our group with the NN\textsuperscript{TBS} ligand (Diaconescu, 2010b; Huang et al., 2010), indicative of a relatively strong interaction between scandium and iron; this interaction is likely
essential to the stability of \textbf{Sc$_2$-naph}. Geometrically, with the short Fe-Sc distance, the scandium ion is sterically protected because it is shielded by the ferrocene backbone. An even shorter Fe-Sc distance of 2.74 Å was observed in \textbf{Sc$_2$-anth}. When using a non-ferrocene-based amide complex, [(Me$_3$Si)$_2$N]$_2$ScI(THF), instead of (NN$^{TBS}$)ScI(THF)$_2$, no formation of a scandium naphthalene complex was observed. This result highlighted the advantages of the NN$^{TBS}$ ligand in stabilizing highly electrophilic scandium(III) complexes.

The solid-state molecular structure of \textbf{Sc$_2$-anth} (Figure 11) was similar to that of ((P$_2$N$_2$)$_2$Y)$_2$(μ-C$_{14}$H$_{10}$) (Figure 4) (Fryzuk et al., 2000), featuring an unsymmetrical coordination mode of the two metals. The two scandium ions are bound to opposite sides of the middle and an outer ring. $^1$H NMR spectroscopy, however, indicated that the solution structure of \textbf{Sc$_2$-anth} was symmetrical at 25 °C in C$_6$D$_6$. A variable temperature NMR experiment conducted with a toluene-$d_8$ solution of \textbf{Sc$_2$-anth} indicated that coalescence took place at -15 °C and further cooling led to the appearance of new, sharp peaks, which were correlated with the unsymmetrical molecular structure obtained by X-ray crystallography. As previously mentioned, a similar fluxional behavior was reported for ((P$_2$N$_2$)$_2$Y)$_2$(μ-C$_{14}$H$_{10}$) (Fryzuk et al., 2000).
FIGURE 12 Variable temperature $^1$H NMR spectra of Sc$_2$-anth in aromatic solvents (209 K to 298 K in C$_7$D$_8$; 326 K to 359 K in C$_6$D$_6$). NN$^{Fc}$ = NN$^{TBS}$. Peaks corresponding to low T and high T structures are labeled and highlighted with L and H. The coalescence peaks were labeled and highlighted with C. Adapted with permission from Huang et al. (2011). Copyright © 2011, American Chemical Society.

DFT calculations carried out on the full molecule of Sc$_2$-naph indicated that the naphthalene dianion has an electronic structure similar to that found in other rare earth naphthalene complexes. It was found that the HOMO was comprised mostly of naphthalene orbitals, consistent with its dianionic nature (Figure 13), and that the negative charge was mainly localized on C1 and C4 (average -0.30), while C5 had the least (-0.07), and C2 and C3 were in the middle (average -
0.14), confirming the $\eta^4$ coordination mode observed in the solid state. The nearly degenerate HOMO-1 and HOMO-2 (HOMO-5 for $\text{Sc}_2\text{-anth}$, Figure 13) showed some orbital mixing between the 3d orbitals of iron and scandium together with the 2p orbitals of nitrogen and carbon of the NN$^{TBS}$ ligand supporting the presence of the iron-scandium interaction. That interaction was also supported by the Mayer bond order of 0.41, and Mulliken charges, calculated to be +1.02 for scandium and -0.04 for iron, which indicated that the interaction between scandium and iron was mainly electrostatic, with iron serving as a donor and scandium being the acceptor. Similar results were obtained from DFT calculations carried out on $\text{Sc}_2\text{-anth}$.

**FIGURE 13** Top: Selected molecular orbitals of $\text{Sc}_2\text{-naph}$: HOMO (left); HOMO-1 (right). Bottom: HOMO-5 of $\text{Sc}_2\text{-anth}$. Reproduced with permission from Huang et al. (2011). Copyright © 2011, American Chemical Society.

Although few examples of converting a bridging, reduced arene rare earth complex into another have been reported (Bochkarev, 2002), these studies are important in understanding and supporting bonding considerations. Conversion of $\text{Sc}_2\text{-naph}$ to $\text{Sc}_2\text{-anth}$ could be achieved by heating a 1:1 mixture of $\text{Sc}_2\text{-naph}$ and anthracene at 50 °C in C$_6$D$_6$ for five days (Scheme 2c),
indicating that the naphthalene ligand in Sc$_2$-naphe is more reducing than the anthracene ligand in Sc$_2$-anth.

Rare earth arene complexes are good precursors for difficult-to-synthesize rare earth compounds (Bochkarev, 2002) and the same was true for the scandium arene complexes supported by NN$^{TBS}$. Hessen previously showed that a scandium complex of the 2,2$'$-bipyridyl radical anion could be readily accessed from a reduced 1,3-diene scandium complex (Beetstra et al., 2003). Similarly, the addition of 2,2$'$-bipyridine to a C$_6$D$_6$ solution of Sc$_2$-naphe (Scheme 3a) led to the formation of the previously reported radical anionic bipyridyl complex (NN$^{TBS}$)Sc(2,2$'$-bipyridine) (Williams et al., 2010).
SCHEME 3  a) Reaction of Sc$_2$-naph with 2,2′-bipyridine to form (NN$^{TBS}$)Sc(2,2′-bipyridine) with the elimination of free naphthalene; b) reaction of Sc$_2$-naph with pyridine to form [(NN$^{TBS}$)Sc(NC$_5$H$_5$)$_2$[µ-(NC$_5$H$_5$-C$_3$H$_5$N)]] with the elimination of free naphthalene; c) reaction of Sc$_2$-naph with phenylacetylene to form [(NN$^{TBS}$)Sc(µ-C$_{1}$CPh)$_2$] with the elimination of dihydronaphthalene. Reproduced with permission from Huang et al. (2011). Copyright © 2011, American Chemical Society.

The reaction of Sc$_2$-naph with excess pyridine (Scheme 3b) led to the isolation of a rare, reductively 4,4′-C-C coupled diamide linker that bridges the two scandium ions in the complex [(NN$^{TBS}$)Sc(NC$_5$H$_5$)$_2$[µ-(NC$_5$H$_5$-C$_3$H$_5$N)]]. A similar reduction was reported in the reactions of divalent thulium complexes (Fedushkin et al., 2003; Jaroschik et al., 2007b) and, recently, samarium(II) (Labouille et al., 2012) with pyridine, however, the reaction of a rare earth arene complex with pyridine had not been reported previously.

A common substrate used with rare earth arene complexes is phenylacetylene (Bochkarev, 2002). The reaction of Sc$_2$-naph with 2 equivalents of phenylacetylene led to the immediate formation of [(NN$^{TBS}$)Sc(µ-C$_{1}$CPh)$_2$] (Scheme 3c) presumably from protonation of the naphthalene dianion since a mixture of dihydronaphthalene isomers was also observed as byproducts. X-ray crystallography confirmed the isolation of the phenylacetylde bridging dimer with a short Fe-Sc (2.89 Å) distance.

4.2 P$_4$ Activation by Rare Earth Arene Complexes

4.2.1 P$_4$ Activation by Scandium Arene Complexes
White phosphorous (P₄) activation has been long targeted by synthetic chemists (Caporali et al., 2010; Cossairt et al., 2010b; Scheer et al., 2010). Unlike main group elements and late transition metals (Caporali et al., 2010; Scheer et al., 2010), the number of Pₙ-containing early transition metal complexes formed from direct P₄ activation is much smaller (Chirik et al., 2002; Cossairt et al., 2010b; Hey et al., 1987; Scherer et al., 1988; Seidel et al., 2009). Among early transition metals, rare earths are more Lewis acidic, leading to a more pronounced mismatch in binding between their ions and phosphorous anions (Cui et al., 2008; Lv et al., 2011; Masuda et al., 2008). All known examples of lanthanide (Chart 22) (Konchenko et al., 2009; Li et al., 2011) and actinide (Scherer et al., 1991; Stephens, 2004) mediated P₄ activation had involved low-valent metal complexes prior to our reports. For example, (Cp*₂Sm)₄P₈ was obtained by vapor transfer of P₄ to a toluene solution of Cp*₂Sm over the course of a week in a low yield (ca. 10%). The heterometallic Sm-Fe P₅ complex was obtained by reacting Cp*Fe(η⁵-P₅) with samarium reagents. It is worth noting that late transition metal arene complexes have also been used for P₄ activation recently (Schnöckelborg et al., 2011).

**CHART 22** Examples of rare earth Pₙ-containing complexes reported by P. Roesky’s group.
Because the scandium naphthalene complex **Sc₂-naph** was found to be an excellent two-electron reductant toward a variety of substrates, its reactivity toward P₄ was investigated. The reaction took place smoothly at ambient conditions and was accompanied by the generation of free naphthalene (Scheme 4). The formation of [(NNTBS)Sc]₄(μ₄-η²:η²:η²:η²-P₈) (Sc₄P₈) was supported by X-ray crystallography (Huang and Diaconescu, 2012). Sc₄P₈ was also characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy. Although the solid-state molecular structure had only C₂ symmetry, the ¹H spectrum of Sc₄P₈ indicated that all four [(NNTBS)Sc] fragments were equivalent in solution on the NMR timescale. The ³¹P NMR spectrum featured an AA'AM'MM'M'M'' spin system.

**SCHEME 4** Reactions of **Sc₂-naph** and **Sc₂-anth** with P₄ to form [(NNTBS)Sc]₄(μ₄-η²:η²:η²:η²-P₈) (Sc₄P₈) and [(NNTBS)Sc]₃(μ₃-η²:η²:η²-P₇) (Sc₃P₇) with the elimination of free naphthalene or anthracene. Adapted with permission from The Royal Society of Chemistry from Huang and Diaconescu (2012).
The molecular structure of $\text{Sc}_4\text{P}_8$ (Figure 14) has a realgar-type $\text{P}_8$ unit in the center and four $[(\text{NN}^{TBS})\text{Sc}]$ fragments at the corners, each binding to two anionic phosphorus atoms. A short Fe-Sc distance of 2.80 Å was observed again and it was proposed to play a role in stabilizing the structural motif of $\text{Sc}_4\text{P}_8$. The $\text{P}_8$ unit showed local $C_{2v}$ symmetry, with two distinct types of P-atoms: $\text{P}_{\text{inner}}$ (three neighboring P atoms) and $\text{P}_{\text{corner}}$ (two neighboring P atoms). The average $\text{P}_{\text{inner}}-\text{P}_{\text{inner}}$ distance is 2.31 Å, 0.11 Å longer than that of $\text{P}_{\text{inner}}-\text{P}_{\text{corner}}$. The average $\text{P}_{\text{inner}}-\text{P}_{\text{corner}}$ distance of 2.20 Å is close to the P-P interatomic distance in $\text{P}_4$ (2.21 Å) (Corbridge and Lowe, 1952) or a recent updated gas phase value 2.1994(3) Å (Cossaïrt et al., 2010a). The structure of the $\text{P}_8$ unit resembled that of $(\text{Cp}^*\text{Sm})_4\text{P}_8$ (Konchenko et al., 2009). The $\text{P}_8$ unit had been previously observed in some late transition metal complexes, which were obtained from the photolysis reaction of $\text{P}_4$ with cyclopentadienyl iron or iridium carbonyl species (Barr et al., 1991; Scheer et al., 1996), and in the tricyclic [3.3.0.0$^{3,7}$]octaphosphane (Butts et al., 2008).
FIGURE 14  Molecular structures of \([\text{NN}^{\text{TBS}}\text{Sc}]_4(\mu_4-\eta^2:\eta^2:\eta^2:\eta^2-\text{P8})\) (left) and \([\text{NN}^{\text{TBS}}\text{Sc}]_3(\mu_3-\eta^2:\eta^2:\eta^2-\text{P7})\) (right). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Redrawn after Huang and Diaconescu (2012).

A second product was also obtained from the reaction of \(\text{Sc}_2\text{naph}\) and \(\text{P4}\) and was isolated based on its solubility properties, different from those of \(\text{Sc}_4\text{P8}\). X-ray crystallography indicated it to be the first early transition metal \(\text{P7}\) compound, \([\text{NN}^{\text{TBS}}\text{Sc}]_3(\mu_3-\eta^2:\eta^2:\eta^2-\text{P7})\) (\(\text{Sc}_3\text{P7}\)) (Figure 14). It was also found that the product distribution could be tuned by either changing the stoichiometry of \(\text{P4}\) or using a different scandium arene starting material: employing 1.0 equivalent or a sub-stoichiometric amount of \(\text{P4}\) favored the formation of \(\text{Sc}_4\text{P8}\), while using excess \(\text{P4}\) or the less reactive but more labile \(\text{Sc}_2\text{anth}\) (as indicated by its fluxional behavior in solution) favored the formation of \(\text{Sc}_3\text{P7}\).

\(\text{Sc}_3\text{P7}\) was the first example of a Zintl-type \(\text{P}_7^{3-}\) compound formed directly from \(\text{P4}\) activation without using an alkali metal or its equivalent as reducing agents (Baudler and Faber, 1980; Charles et al., 1996; Fritz et al., 1990; Scheer et al., 2010; Schnöckelborg et al., 2011). Three types of phosphorous atoms were found to be present in \(\text{Sc}_3\text{P7}\): \(\text{P}_{\text{apex}}\), \(\text{P}_{\text{edge}}\), and \(\text{P}_{\text{bottom}}\). The difference in \(\text{P-P}\) distances was smaller than that observed in \(\text{Sc}_4\text{P8}\), with almost identical \(\text{P}_{\text{apex}}\)-\(\text{P}_{\text{edge}}\) and \(\text{P}_{\text{edge}}\)-\(\text{P}_{\text{bottom}}\) distances of 2.20 Å and a slightly longer \(\text{P}_{\text{bottom}}\)-\(\text{P}_{\text{bottom}}\) distance of 2.23 Å. The \(\text{P}_7^{3-}\) unit in \(\text{Sc}_3\text{P7}\) resembles that of the solid-state structure of \(\text{Li}_3\text{P7}\), although in the latter case, the difference in \(\text{P-P}\) distances is larger. Similarly to \(\text{Sc}_4\text{P8}, \text{Sc}_3\text{P7}\) also bears a short \(\text{Fe-Sc}\) distance of 2.80 Å. The \(^{31}\text{P}\) NMR spectrum showed three sets of peaks, at \(\delta = +23.1 -118.9, \text{and} -131.4\) ppm, in a 3:1:3 ratio, featuring an AA'A"MM'M"X spin system similar to the previously reported \(\text{Li}_3\text{P7}, \text{Fe}_3\text{P7}\) and \(\text{P}_7\text{R3}\) (\(\text{R} = \text{silyl or alkyl}\)) cases (Ahlrichs et al., 1996; Fritz and Härer, 1983).
DFT calculations on model molecules of $\text{Sc}_4\text{P}_8$ and $\text{Sc}_3\text{P}_7$ indicated that the two polyphosphide complexes exhibit mostly ionic interactions between the metal and the polyphosphide anion as described for $(\text{Cp}^*_2\text{Sm})_4\text{P}_8$ (Konchenko et al., 2009). The examination of bonding orbitals with the same symmetry, HOMO-15 for $\text{Sc}_4\text{P}_8$ and HOMO-18 for $\text{Sc}_3\text{P}_7$ (Figure 15), revealed some overlapping between the 3d orbitals of scandium and the 3p orbitals of phosphorous. In addition, the calculated Mayer bond order for Sc-P was found to be 0.53 and 0.51 for $\text{Sc}_4\text{P}_8$ and $\text{Sc}_3\text{P}_7$, respectively. DFT calculations also supported the existence of an iron-scandium interaction: Mayer bond orders of Fe-Sc interaction were found to be 0.44 and 0.42 for $\text{Sc}_4\text{P}_8$ and $\text{Sc}_3\text{P}_7$, respectively.
FIGURE 15 Selected molecular orbitals of $\text{Sc}_4\text{P}_8$ and $\text{Sc}_3\text{P}_7$. Top: HOMO-12 (left) and HOMO-15 (right) for $\text{Sc}_4\text{P}_8$. Bottom: HOMO-17 (left) and HOMO-18 (right) for $\text{Sc}_3\text{P}_7$. Reproduced with permission from The Royal Society of Chemistry from Huang and Diaconescu (2012).

4.3 Yttrium, Lanthanum, and Lutetium Naphthalene Complexes: Synthesis, Characterization, and Reactivity toward $\text{P}_4$ Activation

The success of direct $\text{P}_4$ activation by scandium arene complexes was mirrored when other rare earths, such as yttrium, lanthanum, and lutetium, were employed. The yttrium, lanthanum, and lutetium naphthalene complexes were prepared by a similar protocol to that of $\text{Sc}_2\text{-naph}$ (Scheme 5). Different from $\text{Sc}_2\text{-naph}$, which did not coordinate THF, the other rare earth naphthalene complexes were synthesized with the general formula of $[(\text{NN}^{\text{TBS}})\text{M(THF)}]_2(\mu-\eta^4:\eta^4-$C$_{10}$H$_8)$ ($\text{M}_2\text{-naph}$, M = Y, La, and Lu) (Huang and Diaconescu, 2012, 2013), containing one THF per metal center. With the complete series of diamagnetic rare earth naphthalene complexes supported by the $\text{NN}^{\text{TBS}}$ ligand, it was possible to compare their physical properties. $\text{Sc}_2\text{-naph}$ is a black solid barely soluble in hexanes but soluble in aromatic solvents. However, $\text{Y}_2\text{-naph}$ is a dark-red solid barely soluble in hexanes, aromatic solvents, and diethyl ether, but only soluble in
THF. While **Lu$_2$-naph** has similar physical properties to **Y$_2$-naph**, **La$_2$-naph**, with the largest ionic radius of all rare earths and same molecular formula as **Y$_2$-naph** and **Lu$_2$-naph**, has physical properties similar to **Sc$_2$-naph**: it is a black solid soluble in aromatic solvents and even slightly soluble in hexanes. These counterintuitive observations show that, in the present case, the properties of rare earth complexes do not follow the trend of their metal ion size.

**SCHEME 5** (a) Synthesis of **M$_2$-naph** (M = Y, La, and Lu); (b) exclusive formation of [**(NN$^{TBS}$)M(THF)]$_3$(μ$_3$-η$^2$-η$^2$-P$_7$) (**M$_3$P$_7$**) from P$_4$ activation by employing **M$_2$-naph**. Adapted with permission from Huang and Diaconescu (2013). Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

All **M$_2$-naph** were characterized by $^1$H and $^{13}$C NMR spectroscopy, X-ray crystallography, and elemental analysis. While the proton chemical shifts of the scandium, yttrium, and lutetium
naphthalene complexes were close to each other, the proton chemical shifts of the naphthalene fragment in La$_2$-naph were shifted significantly upfield compared to the other three complexes (Table 2). However, it was found that the $^{13}$C chemical shifts for La$_2$-naph were similar to those of other rare earth naphthalene complexes (Huang and Diaconescu, 2013).

**TABLE 2** Summary of $^1$H and $^{13}$C NMR chemical shifts (unit in ppm) of (C$_{10}$H$_8$)$_2^-$ unit and structural parameters (distance in Å) for M$_2$-naph (M = Sc, Y, La, and Lu).

<table>
<thead>
<tr>
<th></th>
<th>Sc$_2$-naph</th>
<th>Y$_2$-naph</th>
<th>La$_2$-naph</th>
<th>Lu$_2$-naph</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-CH and $\beta$-CH</td>
<td>5.06, 4.02</td>
<td>5.09, 3.94</td>
<td>4.28, 2.73</td>
<td>5.17, 4.23</td>
</tr>
<tr>
<td>ipso-$C$, $\alpha$-$C$, $\beta$-$C$</td>
<td>158, 120, 95</td>
<td>158, 118, 94</td>
<td>157, 122, 100</td>
<td>155, 118, 95</td>
</tr>
<tr>
<td>$C_{\alpha}$-$C_{\beta}$</td>
<td>1.428(7)</td>
<td>1.441(6)</td>
<td>1.433(4)</td>
<td>1.444(6)</td>
</tr>
<tr>
<td>$C_{\beta}$-$C_{\beta}$</td>
<td>1.368(7)</td>
<td>1.376(7)</td>
<td>1.374(4)</td>
<td>1.374(6)</td>
</tr>
<tr>
<td>$C_{\text{ipso}}$-$C_{\alpha}$</td>
<td>1.421(6)</td>
<td>1.423(6)</td>
<td>1.418(3)</td>
<td>1.424(6)</td>
</tr>
<tr>
<td>$C_{\text{ipso}}$-$C_{\text{ipso}}$</td>
<td>1.445(9)</td>
<td>1.450(6)</td>
<td>1.451(5)</td>
<td>1.452(6)</td>
</tr>
</tbody>
</table>

Although M$_2$-naph (M = Y, La, and Lu) crystallized in different space groups, they were shown to have similar structural parameters (Huang and Diaconescu, 2013). The molecular structure of Y$_2$-naph is shown in Figure 16 as a representative for M$_2$-naph. Despite differences in the strength of the iron-metal interaction, as determined by the ratio of the sum of the covalent radii of the two metals and the observed distance, compounds M$_2$-naph were found to contain the usual $\mu$-$\eta^4,\eta^4$ coordination motif of the bridging naphthalene ligand.
The reactivity of $M_2$-naph (M = Y, La, and Lu) toward P$_4$ was also tested. Regardless of the stoichiometry of P$_4$ versus $M_2$-naph, a single product was formed with the general formula of \([(\text{NN}^{\text{TBS}})M(\text{THF})]_3(\mu_3-\eta^2:\eta^2:\eta^2-P_7)\) ($M_3P_7$) (Huang and Diaconescu, 2012, 2013). The exclusive formation of $M_3P_7$ from $M_2$-naph raises an interesting question about the mechanism of P$_4$ activation by rare earth arene complexes. It seems plausible that there are two competing reaction pathways: the first leads to the formation of $M_4P_8$ and the second leads to the formation of $M_3P_7$. For scandium, the two pathways have similar activation barriers since both products Sc$_4P_8$ and Sc$_3P_7$ are observed; for other rare earths, the pathway to form $M_3P_7$ is more favorable, so $M_3P_7$ forms exclusively in the reaction.

Compounds $M_3P_7$ (M = Y, La, and Lu) were isolated in good yield after crystallization from various organic solvents. It was found that La$_3P_7$ was more soluble than Y$_3P_7$ and Lu$_3P_7$ in common organic solvents: La$_3P_7$ was soluble in hexanes and aromatic solvents, while Y$_3P_7$ and
Lu$_3$P$_7$ were barely soluble in hexanes and slightly soluble in aromatic solvents. While the solubility of Lu$_3$P$_7$ was similar to that of the previously reported Y$_3$P$_7$, the solubility of La$_3$P$_7$ was different but similar to that of the THF free compound Sc$_3$P$_7$. The unexpected solubility properties of M$_3$P$_7$ (M = Sc, Y, La, Lu) echoed the different solubilities of M$_2$-naph described above.

The molecular structure of Y$_3$P$_7$ is shown in Figure 16 as a representative for M$_3$P$_7$. While Lu$_3$P$_7$ is isostructural to Y$_3$P$_7$, La$_3$P$_7$ crystallized in a different space group, and two out of the three lanthanum ions were coordinated by diethyl ether instead of THF. It was mentioned that different batches of La$_3$P$_7$ showed different ratios between THF and diethyl ether as a coordinating solvent. Similarly to La$_3$P$_7$, some batches of La$_2$-naph also had diethyl ether replacing THF. This lack of selectivity for the coordinating solvent was attributed to the weaker Lewis acidity of lanthanum(III) compared to that of yttrium(III) and lutetium(III) (Tsuruta et al., 1999).

**TABLE 3** P-P distances of M$_3$P$_7$ (unit: Å, error in brackets, all are average values).

<table>
<thead>
<tr>
<th>M$_3$P$_7$</th>
<th>P$<em>{\text{apex}}$-P$</em>{\text{edge}}$</th>
<th>P$<em>{\text{edge}}$-P$</em>{\text{bottom}}$</th>
<th>P$<em>{\text{bottom}}$-P$</em>{\text{bottom}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$_3$P$_7$</td>
<td>2.201(2)</td>
<td>2.197(2)</td>
<td>2.229(2)</td>
</tr>
<tr>
<td>Lu$_3$P$_7$</td>
<td>2.183(2)</td>
<td>2.181(2)</td>
<td>2.233(2)</td>
</tr>
<tr>
<td>Y$_3$P$_7$</td>
<td>2.188(2)</td>
<td>2.176(3)</td>
<td>2.238(2)</td>
</tr>
<tr>
<td>La$_3$P$_7$</td>
<td>2.191(2)</td>
<td>2.161(2)</td>
<td>2.258(2)</td>
</tr>
</tbody>
</table>

[a] Unlike other M$_3$P$_7$, Sc$_3$P$_7$ has no solvent molecule coordinated to scandium.

All M$_3$P$_7$ structures feature a central Zintl-type polyphosphide P$_{7^-}$ anion surrounded by three [(NN$^{TBS}$)M(solvent)] fragments (Huang and Diaconescu, 2013). Except for Sc$_3$P$_7$, which does not coordinate any THF, all the other M$_3$P$_7$ adopt a similar coordination environment. Despite this difference in the coordination environment, P-P distances (listed in Table 3) followed a trend
consistent with the size of the metal ion: the larger the rare earth, the shorter the $P_{\text{edge}}-P_{\text{bottom}}$ distance. In alkali-earth metal stabilized $P_7^{3-}$ compounds, the three distinguishable $P$-$P$ bonds also have different distances, with the shortest being the $P_{\text{edge}}-P_{\text{bottom}}$ and the longest being the $P_{\text{bottom}}-P_{\text{bottom}}$ distance (Baudler and Glinka, 1993). For instance, in $\text{Sr}_3P_{14}$, $P_{\text{apex}}-P_{\text{edge}}$, $P_{\text{edge}}-P_{\text{bottom}}$, and $P_{\text{bottom}}-P_{\text{bottom}}$ are 2.21, 2.17, and 2.25 Å, respectively. (Dahlmann and Schnering, 1972) For $\text{La}_3P_7$, the difference among the $P$-$P$ distances is comparable to those of alkali earth $P_7^{3-}$ binary complexes; for $\text{Sc}_3P_7$, the difference among the $P$-$P$ distances is at the minimum and is close to that observed for silyl substituted $P_7R_3$ compounds. For instance, in $P_7(SiMe_3)_3$, $P_{\text{apex}}-P_{\text{edge}}$, $P_{\text{edge}}-P_{\text{bottom}}$, and $P_{\text{bottom}}-P_{\text{bottom}}$ distances are 2.180(4), 2.192(4), and 2.214(4) Å (Hönle and Schnering, 1978). As a consequence, the $P$-$P$ distances were taken as an indication of the bonding character of the $M$-$P$ interaction: for covalent Si-$P$ bonds, the difference among the three types of $P$-$P$ bonds is the smallest; for highly ionic Sr-$P$ interactions, the difference among the three types of $P$-$P$ bonds is the largest. Those considerations indicated that the larger the rare earth ion, the more ionic is the bond character.

4.4 Tautomerization of $M_3P_7$ Studied by Variable-temperature NMR Spectroscopy

$P_7^{3-}$ is the major product of $P_4$ activation by strong reductants or nucleophiles as well as the “dead-end” of the decompositions of other polyphosphide species (Baudler and Glinka, 1993; Scheer et al., 2010). Intense experimental and theoretical studies have been performed on its alkali and alkali earth metal complexes. For example, $\text{Li}_3P_7$ was studied by variable temperature and 2D $^{31}P$ NMR spectroscopy (Baudler et al., 1979; Baudler et al., 1980; Baudler and Hahn, 1990), and it was found that the $^{31}P$ NMR spectrum of $\text{Li}_3P_7$ in THF-$d_8$ is temperature dependent: at low temperature (-60 °C), three distinguishable signals were observed for the three different types of
phosphorus atoms in P$_7^{3-}$; however, upon warming, coalescence took place and, eventually, at high temperature (50 °C) only one peak was observed. That phenomenon was attributed to a fluxional behavior of P$_7^{3-}$ (Baudler and Glinka, 1993). The free P$_7^{3-}$ anion can tautomerize to essentially the same tautomer (there are 1680 of them) (Baudler et al., 1979) by simultaneously breaking one P$_{\text{bottom}}$-P$_{\text{bottom}}$ bond and forming a new P-P bond between two P$_{\text{edge}}$ atoms right next to the two P$_{\text{bottom}}$ atoms of the P-P bond that breaks. This tautomerization mechanism, which is analogous to bullvalene tautomerization (Schröder et al., 1965), was calculated to have a low energy barrier (Böhm and Gleiter, 1981) and was further supported by a topology study (Randic et al., 1986). Apparently, the tautomerization only takes place in highly ionic compounds such as Li$_3$P$_7$ and Cs$_3$P$_7$ (Kraus et al., 2003); no tautomerization was observed for silyl substituted P$_7$R$_3$ compounds (Baudler and Glinka, 1993).

The $^{31}$P NMR spectra of Sc$_3$P$_7$, Y$_3$P$_7$, and Lu$_3$P$_7$, at 25 °C in benzene-$d_6$ or toluene-$d_8$, were similar and showed three well resolved peaks that integrated to a 3:1:3 ratio, indicating that the tautomerization of the P$_7^{3-}$ anion was frozen (Huang and Diaconescu, 2013). However, the $^{31}$P NMR spectrum (25 °C, benzene-$d_6$) of La$_3$P$_7$ showed only one, broad signal centered at -75 ppm, similarly to Li$_3$P$_7$ in THF-$d_8$. $^{31}$P NMR spectra (Figure 17 left) collected from -75 °C to 107 °C showed the fluxional behavior of P$_7^{3-}$ in La$_3$P$_7$ and a coalescence temperature comparable to that of Li$_3$P$_7$. 
FIGURE 17  Left: Overlay of $^{31}$P NMR spectra (toluene-$d_8$) of $\text{La}_3\text{P}_7$ at different temperatures. Right: Proposed mechanism for valence tautomerization of $\text{P}_7^{3-}$ in $\text{La}_3\text{P}_7$. NN$^{\text{TBS}}$ ligands and solvent molecules were omitted for clarity. The pink solid line represents the La-P bond to break. The pink dashed line represents the La-P bond to form. The green solid line represents the P-P bond to break. The green dashed line represents the P-P bond to form. The grey solid lines represent La-P and P-P bonds not affected by this particular tautomerization process. Adapted with permission from Huang and Diaconescu (2013). Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The fluxional behavior took place in non-polar solvents (benzene-$d_6$ or toluene-$d_8$) for $\text{La}_3\text{P}_7$, while for $\text{Li}_3\text{P}_7$ it was only observed in polar and strongly coordinating solvents such as THF, DME (1,2-dimethoxyethane), and TMEDA (tetramethylethylenediamine); without a strongly coordinating solvent, $\text{Li}_3\text{P}_7$ decomposed. This difference was explained by the migration
of the (NN\textsuperscript{TBS})La(THF) fragment from one phosphorous atom to another, allowing the valence
tautomerization to occur (Huang and Diaconescu, 2013). This mechanism for P\textsuperscript{7+} tautomerization
in La\textsubscript{3}P\textsubscript{7} requires the simultaneous breaking and formation of four La-P bonds (Figure 17 right).
The tautomerization involves one of the five-member rings of P\textsuperscript{7+}: a P\textsubscript{bottom}-P\textsubscript{bottom} bond breaks
while a P\textsubscript{edge}-P\textsubscript{edge} bond forms; at the same time, the lanthanum fragment coordinated to that face
migrates from two P\textsubscript{edge} atoms to two P\textsubscript{bottom} atoms. The other two lanthanum ions only break and
form one La-P bond each. Such a process, together with the necessary breaking and formation of
P-P bonds, is made possible by the coordination of lanthanum to two neighbouring P\textsubscript{edge} atoms and
two neighbouring P\textsubscript{bottom} atoms. To support this hypothesis, the average La-P\textsubscript{edge} distance is 3.10 Å, while the average La-P\textsubscript{bottom} distance is 3.54 Å. The 0.44 Å difference is smaller than the
corresponding distance difference in the other M\textsubscript{3}P\textsubscript{7} (M = Sc: 0.67 Å, Lu: 0.57 Å, Y: 0.53 Å). If it
is assumed that the metal-P distances vary linearly with the strength of the metal-P interaction,
then it will be easier to form new metal-P bonds for La\textsubscript{3}P\textsubscript{7} than for Y\textsubscript{3}P\textsubscript{7} > Lu\textsubscript{3}P\textsubscript{7} > Sc\textsubscript{3}P\textsubscript{7}.
Consequently, it was found that the tautomerization also took place in Y\textsubscript{3}P\textsubscript{7} but at a high
temperature (coalescence temperature higher than 75 °C). Unfortunately, the low solubility of
Y\textsubscript{3}P\textsubscript{7} in aromatic solvents and the high coalescence temperature prevented a detailed variable
temperature \textsuperscript{31}P NMR spectroscopy study for this complex (Huang and Diaconescu, 2013).

4.5 Synthesis of Organic P-containing Compounds from P\textsubscript{4}

Transferring the activated polyphosphide is essential to generate organophosphorus
compounds (Cossairt et al., 2010b). The reaction of Sc\textsubscript{3}P\textsubscript{7} or Y\textsubscript{3}P\textsubscript{7} (Scheme 6) with 3 equiv Me\textsubscript{3}SiI
led to the formation of the corresponding rare earth iodide and P\textsubscript{7}(SiMe\textsubscript{3})\textsubscript{3} (Huang and Diaconescu,
2012), as confirmed by \textsuperscript{31}P NMR spectroscopy (Fritz and Härer, 1983).
SCHEME 6 Reaction of $\text{M}_3\text{P}_7$ with $\text{Me}_3\text{SiI}$. Adapted with permission from The Royal Society of Chemistry from Huang and Diaconescu (2012).

5. SYNTHESIS AND CHARACTERIZATION OF RARE EARTH BIPHENYL COMPLEXES: 6C, 10\(\pi\)-ELECTRON AROMATIC SYSTEMS

5.1 Synthesis and Structural Characterization of Rare Earth Biphenyl Complexes

A DFT study predicted in 2005 that the barium complex of the benzene tetraanion would be stable as an inverse sandwich, $\text{Ba}_2(\text{C}_6\text{H}_6)$, with $D_{6h}$ symmetry (Diefenbach and Schwarz, 2005). The C-C distance was calculated to be 1.466 Å. Charge calculations and molecular orbitals suggested that the benzene moiety is reduced by four electrons as a 10\(\pi\)-electron system. The calculated nuclear-independent chemical shift (NICS) confirmed the (C\(_6\)H\(_6\))\(_4^\text{−}\) formulation. The report suggested some suitable metal centers, such as thorium, to stabilize the highly electron-rich (C\(_6\)H\(_6\))\(^{+}\). This suggestion, based on the Lewis acid character of thorium is in line with what is described in section 2, where several benzene/arene polyanions stabilized by coordination to lanthanides are presented. For actinides, several groups reported that benzene or its derivatives can serve as a bridging ligand between two uranium ions (Arnold et al., 2012; Diaconescu et al., 2000; Diaconescu and Cummins, 2012; Evans et al., 2004; Monreal et al., 2011; Patel et al., 2011). Magnetic susceptibility measurements, X-ray absorption near edge structure (XANES) spectroscopy, and DFT studies showed that most of these complexes can be described as having a
benzene (or a substituted benzene) dianion bridging two U(III) centers (Diaconescu and Cummins, 2012; Evans et al., 2004). Liddle and coworkers suggested a [toluene]⁺ ligand in [U(TsXy)]₂(μ-η⁶:η⁶-C₆H₅Me)] (TsXy = HC(SiMe₂NAr)₃; Ar=3,5-Me₂C₆H₃) (Patel et al., 2011; Patel et al., 2013); however, XANES spectroscopy studies have not been reported for this or the other uranium examples, [U(OSi(O'Bu)₃)₃]₂(μ-η⁶:η⁶-C₇H₈), K[U(OSi(O'Bu)₃)₃]₂(μ-η⁶:η⁶-C₇H₈), K₂[U(OSi(O'Bu)₃)₃]₂(μ-η⁶:η⁶-C₇H₈) (Camp et al., 2013), with proposed [toluene]⁺ ligands.

Compound [(NN TBS)Y]₂[K(toluene)]₂(μ-biphenyl) (Y₂K₂-biph) was obtained by addition of potassium graphite to a pre-mixed tetrahydrofuran (THF) solution of (NN TBS)YI(THF)₂ and biphenyl (Scheme 7) and was crystallographically characterized (Figure 18) (Huang et al., 2013). The two yttrium ions coordinate to opposite sides of the same phenyl ring in an η⁶ fashion, while the two potassium ions coordinate to the other biphenyl ring in an η⁶ fashion as well. Based on charge balance, by assuming that yttrium is Y(III) and potassium is K(I), a 4- charge was assigned to the biphenyl ligand. XANES spectroscopy studies agreed with this formulation for Y₂K₂-biph.
SCHEME 7 Synthesis of quadruply reduced substituted benzene complexes \( M_2K_2\text{-biph} \) (\( M = \text{Sc, Y, La, and Lu} \)), \( Y_2K_2\text{-terph} \), and \( \text{Lu}_2K_2\text{-TPB} \). Adapted from Huang et al. (2013). Copyright © 2013, Rights Managed by Nature Publishing Group.

FIGURE 18 Thermal-ellipsoid (50% probability) representation of \( Y_2K_2\text{-biph} \) (left) and the anion of \( [\text{K(18-crown-6)(THF)}_{1.5}]_2[[\text{NN}^{\text{TBS}}\text{Y}_2(\mu\text{-biphenyl})]]_2(\mu\text{-biphenyl})\) (right). Details of structural parameters are presented in Figure 20 and Table 6. Redrawn after Huang et al. (2013).

It was shown that the unusual binding mode of biphenyl in \( Y_2K_2\text{-biph} \) with yttrium and potassium coordinating to different rings was maintained in solution. The \(^1\text{H}\) NMR spectra of \( Y_2K_2\text{-biph} \) at 25 °C, -45 °C, or -89 °C in THF-\( d_8 \) all showed two distinct sets of signals for the phenyl rings. The \(^1\text{H}\) NMR pattern for the ring coordinated to the yttrium centers is shifted upfield, while that for the other ring appeared in the expected aromatic region (complete assignment of \(^1\text{H}\), \(^{13}\text{C}\) chemical shifts is summarized in Table 4). In addition, \(^{13}\text{C}[^1\text{H}]\) NMR spectroscopy showed that the signals for the \textit{ortho-} and \textit{meta-}carbon atoms of the ring coordinating to yttrium were...
triplets due to coupling to $^{89}\text{Y}$; the \textit{para}- and \textit{ipso}-carbon atoms, being the farthest from the yttrium ions, were not coupled to them and appeared as singlets.

As mentioned previously (Fryzuk et al., 1997), reported lanthanide complexes of reduced biphenyl exhibited fluxional behavior in solution even when their solid-state structures indicated that the two metal centers coordinated in a non-symmetrical fashion. In the case of $\text{Y}_2\text{K}_2\text{-biph}$, no fluxional behavior was observed in solution. In addition, the isolation of the 18-crown-6 version of $\text{Y}_2\text{K}_2\text{-biph}$, $[\text{K}(18\text{-crown-6})(\text{THF})_{1.5}]_2[[(\text{NN}^{\text{TBS}})\text{Y}]_2(\mu\text{-biphenyl})]$ ($\text{Y}_2\text{biph}-\text{K}_2\text{-crown}_2$, Figure 18), indicated that the coordination of potassium ions to the biphenyl ligand was not required to maintain the rigid structure.

The stability imparted by the aromatic character of the bridged tetraanionic biphenyl ligand was also manifested when attempts to isolate the corresponding dianionic species failed (Scheme 8). For example, $\text{Y}_2\text{K}_2\text{-biph}$ was formed exclusively even when sub-stoichiometric amounts of KC$_8$ were used and the comproportionation reaction between (NN$^{\text{TBS}}$)Y(THF)$_2$ and $\text{Y}_2\text{K}_2\text{-biph}$ did not occur. Selective oxidation of the quadruply reduced arene to the doubly reduced species also failed (Scheme 8).
SCHEME 8  Oxidation attempts involving $\text{Y}_2\text{K}_2\text{-biph}$ and $\text{Y}_2\text{-biphe-K}_2\text{-crown}_2$. Adapted from Huang et al. (2013). Copyright © 2013, Rights Managed by Nature Publishing Group.

The structural motif of $\text{Y}_2\text{K}_2\text{-biph}$ was not restricted to yttrium and/or biphenyl: other group 3 metals, namely, scandium, lanthanum, and lutetium formed $\text{Sc}_2\text{K}_2\text{-biph}$, $\text{La}_2\text{K}_2\text{-biph}$, and $\text{Lu}_2\text{K}_2\text{-biph}$, respectively, following a synthetic protocol analogous to that for $\text{Y}_2\text{K}_2\text{-biph}$ (Figure 18). These compounds show $^1\text{H}$ and $^{13}\text{C}$ NMR spectra and solid-state molecular structures similar to $\text{Y}_2\text{K}_2\text{-biph}$. Other non-fused arenes (Scheme 7) such as $p$-terphenyl or 1,3,5-triphenylbenzene...
(TPB) led to \([(N{\text{N}^{\text{TB5}}})_2Y_2[K(\text{THF})_2]_{\mu-\text{p-terphenyl}}]\) (\text{Y}_2\text{K}_2-\text{terph}) and \[(N{\text{N}^{\text{TB5}}})_2\text{Lu}[\text{K}(\text{THF})_2]_{\mu-1,3,5-\text{C}_6\text{H}_3\text{Ph}_3}\] (\text{Lu}_2\text{K}_2-\text{TPB}, \text{Ph} = \text{C}_6\text{H}_5), respectively (Figure 19) (Huang et al., 2013). Table 4 summarizes the \(^1\text{H}\) and \(^{13}\text{C}\) NMR chemical shifts of related substituted bridging benzene complexes. Table 5 compares the \(^1\text{H}\) and \(^{13}\text{C}\) NMR chemical shifts with literature values for anionic biphenyl species. Table 6 summarizes the representative structural parameters for \(\text{M}_2\text{K}_2-\text{arene}\) complexes; while Table 7 compares those values with literature examples of anionic biphenyl or benzene species.

**TABLE 4** Summary of \(^1\text{H}\) and \(^{13}\text{C}\) NMR chemical shifts (in ppm) for \(\text{M}_2\text{K}_2-\text{biph}\) (\(\text{M} = \text{Sc}, \text{Y}, \text{La}, \text{and Lu}\)), and \(\text{Y}_2\text{K}_2-\text{terph}, \text{Lu}_2\text{K}_2-\text{TPB}, \text{and Y}_2\text{-biph-K}_2\text{-crown}_2\) (all measured at -40 to -50 °C) (Huang et al., 2013).\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>\text{Y}_2\text{K}_2-\text{biph}</th>
<th>\text{Sc}_2\text{K}_2-\text{biph}</th>
<th>\text{La}_2\text{K}_2-\text{biph}</th>
<th>\text{Lu}_2\text{K}_2-\text{biph}</th>
<th>\text{Y}_2\text{-biph-K}_2\text{-crown}_2</th>
<th>\text{Y}_2\text{K}_2-\text{terph}</th>
<th>\text{Lu}_2\text{K}_2-\text{TPB}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{H1}</td>
<td>4.02</td>
<td>4.23</td>
<td>4.20</td>
<td>3.76</td>
<td>3.83</td>
<td>4.13</td>
<td>3.77</td>
</tr>
<tr>
<td>\text{H2}</td>
<td>3.85</td>
<td>4.17</td>
<td>3.89</td>
<td>3.59</td>
<td>3.76</td>
<td>3.82</td>
<td>3.77</td>
</tr>
<tr>
<td>\text{H3}</td>
<td>2.92</td>
<td>3.69</td>
<td>2.87</td>
<td>2.92</td>
<td>3.03</td>
<td>2.85</td>
<td>3.00</td>
</tr>
<tr>
<td>\text{H8}</td>
<td>6.06</td>
<td>6.53</td>
<td>5.81</td>
<td>6.03</td>
<td>6.27</td>
<td>5.96</td>
<td>6.24</td>
</tr>
<tr>
<td>\text{H9}</td>
<td>6.17</td>
<td>6.43</td>
<td>5.91</td>
<td>6.21</td>
<td>6.16</td>
<td>6.52</td>
<td>NA</td>
</tr>
<tr>
<td>\text{H10}</td>
<td>5.03</td>
<td>5.52</td>
<td>4.73</td>
<td>5.03</td>
<td>5.22</td>
<td>NA</td>
<td>5.60</td>
</tr>
</tbody>
</table>

\(^a\) Table 4 is a summary of the \(^1\text{H}\) and \(^{13}\text{C}\) NMR chemical shifts for various complexes, including \(\text{Y}_2\text{K}_2-\text{biph}\), \(\text{Sc}_2\text{K}_2-\text{biph}\), \(\text{La}_2\text{K}_2-\text{biph}\), \(\text{Lu}_2\text{K}_2-\text{biph}\), \(\text{Y}_2\text{-biph-K}_2\text{-crown}_2\), \(\text{Y}_2\text{K}_2-\text{terph}\), and \(\text{Lu}_2\text{K}_2-\text{TPB}\). The values are measured at -40 to -50 °C. Table 4 includes the chemical shifts for each complex at these temperatures. The shifts are provided in parts per million (ppm) for both the \(^1\text{H}\) and \(^{13}\text{C}\) nuclei.
### TABLE 5

Comparison of $^{1}H$ and $^{13}C$ chemical shifts (in ppm) for the coordinated biphenyl ring of $M_{2}K_{2}$-biph ($M = Y, Sc, La, and Lu$) and literature values reported on biphenyl dianion species (using the same numbering scheme as Table 4) (Huang et al., 2013).

<table>
<thead>
<tr>
<th></th>
<th>$H(T2, P2)$</th>
<th>$H(T3, P3)$</th>
<th>$H(T4, P4)$</th>
<th>$C1$</th>
<th>$C2$</th>
<th>$C3$</th>
<th>$C4$</th>
<th>$C7$</th>
<th>$C8$</th>
<th>$C9$</th>
<th>$C10$</th>
<th>$T1(P1)$</th>
<th>$T2(P2)$</th>
<th>$T3(P3)$</th>
<th>$T4(P4)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>84.9</td>
<td>68.4</td>
<td>52.1</td>
<td>76.0</td>
<td>138.8</td>
<td>114.3</td>
<td>128.6</td>
<td>103.2</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>88.1</td>
<td>78.1</td>
<td>63.9</td>
<td>79.8</td>
<td>142.3</td>
<td>116.7</td>
<td>128.4</td>
<td>108.5</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>88.1</td>
<td>73.7</td>
<td>61.5</td>
<td>82.0</td>
<td>135.6</td>
<td>113.8</td>
<td>128.5</td>
<td>100.0</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>86.1</td>
<td>72.3</td>
<td>56.9</td>
<td>78.2</td>
<td>137.2</td>
<td>114.2</td>
<td>128.3</td>
<td>102.1</td>
<td>102.1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>78.8</td>
<td>67.4</td>
<td>54.0</td>
<td>74.7</td>
<td>142.4</td>
<td>115.8</td>
<td>127.2</td>
<td>106.5</td>
<td>106.5</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>91.9</td>
<td>70.4</td>
<td>52.4</td>
<td>85.3</td>
<td>131.4</td>
<td>115.1</td>
<td>124.0</td>
<td>110.1</td>
<td>110.1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>87.9</td>
<td>73.1</td>
<td>58.4</td>
<td>81.4</td>
<td>136.7</td>
<td>112.2</td>
<td>140.8</td>
<td>94.5</td>
<td>94.5</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>7.00</th>
<th>6.86</th>
<th>6.42</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
</table>

|       | 7.26        | 7.59        | 7.15        |      |      |      |      |      |      |      |      |         |         |         |         |

$^{a}$ T1-T6 for $p$-terphenyl and P1-P6 for 1,3,5-triphenylbenzene (the other equivalent ring was omitted for clarity). The proton was labelled the same as the carbon attached to it (for example, H1 on C1). The values in purple for proton and in red for carbon are on the phenyl ring coordinated to group 3 metals.
TABLE 6  X-ray structural data for Y2K2-biph, Sc2K2-biph, Lu2K2-biph, Y2-biph-K2-crown2, Y2K2-terph, and Lu2K2-TPB (distances in Å and angles in °) (Huang et al., 2013).
<table>
<thead>
<tr>
<th></th>
<th>Y$_2$K$_2$-biph</th>
<th>Sc$_2$K$_2$-biph</th>
<th>Lu$_2$K$_2$-biph</th>
<th>Y$_2$-biph-K$_2$-biph</th>
<th>Y$_2$K$_2$-terph</th>
<th>Lu$_2$K$_2$-TPB</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C2</td>
<td>1.422</td>
<td>1.436</td>
<td>1.413</td>
<td>1.441</td>
<td>1.420</td>
<td>1.436</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.477</td>
<td>1.474</td>
<td>1.474</td>
<td>1.496</td>
<td>1.476</td>
<td>1.493</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.486</td>
<td>1.481</td>
<td>1.498</td>
<td>1.489</td>
<td>1.484</td>
<td>1.492</td>
</tr>
<tr>
<td>C4-C7</td>
<td>1.414</td>
<td>1.418</td>
<td>1.416</td>
<td>1.477</td>
<td>1.411</td>
<td>1.420</td>
</tr>
<tr>
<td>C7-C8</td>
<td>1.448</td>
<td>1.444</td>
<td>1.438</td>
<td>1.405</td>
<td>1.444</td>
<td>1.439</td>
</tr>
<tr>
<td>C8-C9</td>
<td>1.391</td>
<td>1.390</td>
<td>1.390</td>
<td>1.405</td>
<td>1.372</td>
<td>1.391</td>
</tr>
<tr>
<td>C9-C10</td>
<td>1.402</td>
<td>1.405</td>
<td>1.399</td>
<td>1.329$^a$</td>
<td>1.423</td>
<td>1.420</td>
</tr>
<tr>
<td>M-C1</td>
<td>2.547</td>
<td>2.367</td>
<td>2.512</td>
<td>2.536</td>
<td>2.569</td>
<td>2.511</td>
</tr>
<tr>
<td>M-C2</td>
<td>2.606</td>
<td>2.448</td>
<td>2.599</td>
<td>2.604</td>
<td>2.613</td>
<td>2.599</td>
</tr>
<tr>
<td>M-C3</td>
<td>2.487</td>
<td>2.319</td>
<td>2.395</td>
<td>2.453</td>
<td>2.502</td>
<td>2.403</td>
</tr>
<tr>
<td>M-C4</td>
<td>2.565</td>
<td>2.516</td>
<td>2.535</td>
<td>2.522</td>
<td>2.568</td>
<td>2.553</td>
</tr>
<tr>
<td>C10-T1(P1)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>1.465</td>
<td>1.493</td>
</tr>
<tr>
<td>T1(P1)-T2(P2)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>1.412</td>
<td>1.382</td>
</tr>
<tr>
<td>T2(P2)-T3(P3)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>1.381</td>
<td>1.394</td>
</tr>
<tr>
<td>T3(P3)-T4(P4)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>1.376</td>
<td>1.379</td>
</tr>
<tr>
<td>C8-C7-C12</td>
<td>115</td>
<td>114</td>
<td>115</td>
<td>117</td>
<td>113</td>
<td>115</td>
</tr>
<tr>
<td>C3-C4-C7-C8</td>
<td>-5</td>
<td>-8</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>-5</td>
</tr>
</tbody>
</table>

$^a$ This value contains large errors due to the disorder of C9 and C10 atoms in Y$_2$-biph-K$_2$-crown$_2$.

**TABLE 7** Comparison of C-C distances with reported examples (unit in Å).$^a$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C2</td>
<td>1.429</td>
<td>1.415</td>
<td>1.404</td>
<td>1.459</td>
<td>1.45-1.47</td>
<td>1.422</td>
<td>av.</td>
<td>1.440</td>
<td>1.507</td>
<td>1.46</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.482</td>
<td>1.378</td>
<td>1.508</td>
<td>1.348</td>
<td>1.35-1.36</td>
<td>1.433</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.489</td>
<td>1.453</td>
<td>1.416</td>
<td>1.468</td>
<td>1.44-1.46</td>
<td>1.467</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C4-C7</td>
<td>1.417</td>
<td>1.393</td>
<td>1.481</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>C7-C8</td>
<td>1.447</td>
<td>av.</td>
<td>1.384</td>
<td></td>
<td>1.404</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C8-C9</td>
<td>1.388</td>
<td></td>
<td></td>
<td>1.400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C9-C10</td>
<td>1.428</td>
<td></td>
<td></td>
<td>1.358</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Angle in C₁₆ ring</td>
<td>118-122</td>
<td>NA</td>
<td>NA</td>
<td>110-124</td>
<td>112-124</td>
<td>NA</td>
<td>NA</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
</tbody>
</table>

*Average is for Y₂K₂-biph, Sc₂K₂-biph, Lu₂K₂-biph, Y₂K₂-terph, and Lu₂K₂-TPB. Y-biph-Y and Y₂-biph are from reference (Fryzuk et al., 1997). Cp₂La(C₆H₆)K is [(Cp₄La)(µ-η⁶,η⁶-C₆H₆)]⁻ (Cassani et al., 1998); (Cp₂Ln)₂(C₆H₆)K represents [K(18-crown-6)][(Cp₄Ln)(C₆H₆)] (Ln = La, Ce, and Nd) (Cassani et al., 1999). U₂-biph is from reference (Diaconescu and Cummins, 2012). U₂-tol is from reference (Evans et al., 2004). Calcd. C₆H₆⁺⁺⁺ value is from reference (Li et al., 1993). Calcd. Ba₂(C₆H₆) value is from reference (Diefenbach and Schwarz, 2005).
**FIGURE 19** Thermal-ellipsoid (50% probability) representation of $\text{Y}_2\text{K}_2$-terph (left) and $\text{Lu}_2\text{K}_2$-TPB (right). Hydrogen and solvent atoms are omitted for clarity. Details of structural parameters are presented in Table 6. Adapted from Huang et al. (2013).

**FIGURE 20** Metrical parameters for the biphenyl ligand in $\text{Y}_2\text{K}_2$-biph (a) and $\text{Y}_2$-biph-$\text{K}_2$-crown$_2$ (b). Distances are in [Å] and angles in [°], with errors showed in parentheses. Adapted from Huang et al. (2013). Copyright © 2013, Rights Managed by Nature Publishing Group.
Density functional theory calculations showed that the optimized structures for the model dianion $2\text{-}Y^2^-$ (Si'BuMe2 was replaced by SiMe3; potassium counter cations were omitted) of $Y_2K_2\text{-biph}$ or $Y_2\text{-biph-K}_2\text{-crown}_2$ were in excellent agreement with the experimental findings, with average C-C distances of 1.472-1.479 Å for the coordinated phenyl ring (Huang et al., 2013). The ground state was found to be a singlet, with no unpaired electrons on the yttrium ions and an iron(II) electronic configuration, in agreement with the oxidation states derived from XANES measurements. Kohn-Sham frontier molecular orbitals (Figure 21) also confirmed the presence of a benzene unit reduced by four electrons and that the highest occupied molecular orbital (HOMO) and HOMO-1 clearly resulted from the population of the two $e_{2u}$ vacant orbitals ($\pi_4$ and $\pi_5$) of the benzene motif. In addition, the calculated natural bond orbital (NBO) charges for the coordinated benzene ring (-1.90 to -1.95) and the uncoordinated phenyl group (-0.26 to -0.27) were significantly different. The putative complex in which each yttrium ion is coordinated to a different phenyl ring, could also be investigated computationally for comparison and it was shown to have a 20.7 kcal/mol higher energy than the more stable aromatic isomer $2\text{-}Y^2^-$, in agreement with the absence of fluxionality established experimentally (Huang et al., 2013).
The aromatic character of the tetraanionic biphenyl ligand was further probed by $^{89}$Y NMR spectroscopy (Huang et al., 2013). A series of compounds containing different groups, including halide, alkyl, and the aromatic anion Cp: (NN$^{TBS}$)YI(THF)$_2$ (Y-I), (NN$^{TBS}$)Y(CH$_2$C$_6$H$_5$)(THF)$_2$ (Y-Bn), and (NN$^{TBS}$)Y(Cp)(THF) (Y-Cp) together with $\text{Y}_2\text{K}_2$-biph and $\text{Y}_2\text{K}_2$-terph were investigated. It was found that the value (in ppm) of the $^{89}$Y chemical shift decreased in the series: Y-Bn (+436), Y-I (+370), Y$_2$K$_2$-terph (+213), Y$_2$K$_2$-biph (+189), Y-Cp (+69). These results confirmed the presence of a significant aromatic ring current in the phenyl ring coordinating to yttrium in $\text{Y}_2\text{K}_2$-biph and $\text{Y}_2\text{K}_2$-terph since $^{89}$Y chemical shifts in $\text{Y}_2\text{K}_2$-biph and $\text{Y}_2\text{K}_2$-terph were different from Y-Bn and Y-I, but closer to Y-Cp, which contains the aromatic ligand Cp. The values obtained experimentally were matched by the corresponding calculated values as well.
The isolation of tetraanionic, substituted benzenes was possible because of their coordination to rare earth ions. In addition to the group 3 metals, the phenyl substituents of the reduced benzene ring also have a stabilizing influence on the four-electron reduction state of the arene ligands (Huang et al., 2013).

6. GROUP 3 METAL STILBENE COMPLEXES

As described earlier, the metal naphthalene complexes with the general formula \([(NN^{\text{TBS}})M(\text{THF})_x]([\mu-\eta^4:\eta^4-C_{10}H_8]) (\text{M}_2\text{-naph}, M = Sc, x = 0; M = Y, La, Lu, x = 1)\] contain a naphthalene dianion bridging the two metal centers through different phenyl rings. On the other hand, the metal biphenyl complexes with the general formula \([(NN^{\text{TBS}})M][\mu-\eta^6:\eta^6-C_6H_5Ph)](\text{K(solvent)})_2 (\text{M}_2\text{K}_2\text{-biph}, M = Sc, Y, La, Lu, solvent = toluene, tetrahydrofuran, diethyl ether, or 18-crown-6)\] contain a biphenyl tetraanion bridging the two rare earth centers through the same phenyl ring. While the negative charges in \text{M}_2\text{-naph} are equally distributed over the entire naphthalene fragment, as observed with previously reported complexes, the four-electron reduction is mainly localized on the coordinating phenyl ring in \text{M}_2\text{K}_2\text{-biph} and results in a 6C, 10\pi-electron aromatic system. DFT calculations on the naphthalene and biphenyl complexes showed \pi overlap for the former and \delta overlap for the latter between the metal orbitals and arene \pi^* orbitals.

The divergence in bonding modes observed for the bridged arene group 3 metal complexes supported by \text{NN}^{\text{TBS}} is unlike the situation described for diuranium inverse sandwich arene complexes of biphenyl, \text{p}-terphenyl, naphthalene, and \text{(E)}-stilbene supported by a ketimide ligand.(Diaconescu and Cummins, 2012) In the case of uranium all reduced arene complexes had an analogous electronic structure, featuring \delta overlap between LUMOs of one phenyl ring and the
two uranium centers. Other related diuranium inverse sandwich benzene or toluene complexes that were synthesized with different supporting ligands adhere to similar bonding considerations (Arnold et al., 2012; Diaconescu et al., 2000; Evans et al., 2004; Monreal et al., 2011; Mougel et al., 2012; Patel et al., 2011).

Stilbene is an unusual arene as a ligand in that it offers the possibility of coordination to an arene ring or to the double bond. In spite of the abundance of rare earth naphthalene complexes in literature (Bochkarev et al., 1997; Bochkarev, 2002; Fryzuk et al., 2000), (E)-stilbene complexes are rare. Evans et al. reported the synthesis of \([(C_5Me_5)_2Sm]\]2((E)-stilbene) from the direct reaction of \((C_5Me_5)_2Sm\) and (E)-stilbene (Chart 6-1) (Evans et al., 1990). Due to the poor quality of the crystal, the structure of the molecule could not be unambiguously determined but the authors suggested an asymmetric coordination mode based on connectivity. The analogous samarium styrene and butadiene complexes (styrene complex shown in Chart 23) showed two electron reduction of the C=C bond and concomitant oxidation of Sm(II) to Sm(III) (Evans et al., 2001). Related yttrium and lutetium complexes of the readily available tetraphenylethylene dianion have been reported with similar structural features (Chart 23) (Roitershtein et al., 1998; Roitershtein et al., 2004).
Compound \([(\text{NN}^{\text{TBS}})\text{Y}(\text{THF})]_2(\mu-\eta^3:\eta^3-(E)-\text{stilbene})\) (Y\textsubscript{2-stilbene}) was obtained by KC\textsubscript{8} reduction of \((\text{NN}^{\text{TBS}})\text{YI}(\text{THF})_2\) in the presence of 0.5 equiv. \((E)-\text{stilbene}\) (Scheme 9) and its structure (Figure 22) determined by single-crystal X-ray diffraction (Huang et al., 2014). The analogous lanthanum complex was synthesized following the same protocol and structurally characterized. A heterobimetallic complex, \([(\text{NN}^{\text{TBS}})\text{Y}(\text{THF})][(E)-\text{stilbene}][\text{K(THF)}]\) (Y\textsubscript{-stilbene-K}) was obtained in the presence of excess KC\textsubscript{8} (Scheme 9). The ion-separated pair \([(\text{NN}^{\text{TBS}})\text{Y(THF)}](E-\text{stilbene})[\text{K(18-crown-6)}]\) (Y\textsubscript{-stilbene-K-crown}) could also be structurally characterized (Figure 22).
SCHEME 9  Synthesis of $\text{M}_2$-stilbene, $\text{Y}$-stilbene-$\text{K}$, and transformation of $\text{Y}_2$-stilbene to $\text{Y}$-stilbene-$\text{K}$. Adapted with permission from The Royal Society of Chemistry from Huang et al. (2014).

In both molecular structures of $\text{M}_2$-stilbene ($M = \text{Y, La}$), the central C-C bond was flipped and disordered over two symmetrical positions (Huang et al., 2014). The bridging (E)-stilbene ligand is coordinated equally to the two yttrium centers in an $\eta^3$-fashion through the central C-C bond and one ipso-carbon, with Y-C distances of 2.60, 2.58, and 2.74 Å, respectively. This symmetrical coordination mode is different from the asymmetrical coordination mode suggested for $\[(\text{C}_5\text{Me}_5)\text{Sm}]_2((E)$-stilbene) (Evans et al., 1990). The C-C distance corresponding to the original double bond was found to be 1.52 Å, consistent with single bond character.
FIGURE 22 Molecular structure of Y<sub>2</sub>-stilbene (left) and Y-stilbene-K-crown (right). Adapted from Huang et al. (2014).

Arene exchange experiments (Scheme 10) were employed to compare the reducing power of Y<sub>2</sub>-stilbene with that of its dianionic arene analogues (Huang et al., 2014). It was found that Y<sub>2</sub>-naph is the strongest reducing agent while Y<sub>2</sub>-anth is the weakest, with Y<sub>2</sub>-stilbene being in the middle of the series. This series parallels the reduction potential of the bridging arenes in the free form (Abdul-Rahim et al., 2013; Connelly and Geiger, 1996). Consequently, the reaction of Y<sub>2</sub>-stilbene and 2,2'-bipyridine (bipy) or phenylacetylene (PhCCH) resembled the reactivity of Sc<sub>2</sub>-naph and yielded (NN<sup>TBS</sup>)Y(THF)(bipy) and [(NN<sup>TBS</sup>)Y(THF)][(NN<sup>TBS</sup>)Y](CCPh)<sub>2</sub> with the concomitant formation of (E)-stilbene and bibenzyl, respectively, while the addition of excess pyridine did not yield the corresponding C-C coupled complex.
As remarked in this section, group 3 metals prefer binding to the central C-C bond rather than an aromatic ring as observed for uranium (Diaconescu and Cummins, 2012). This difference in the binding mode was also probed by DFT calculations for the stilbene complexes described here (Huang et al., 2014). The HOMOs of M_2-stilbene were found to be comprised of the π* orbitals of the central C-C bond and are stabilized by a π interaction with the metal ions and delocalization to adjacent phenyl rings (Figure 23). This contrasts the case of uranium and substantiates different binding preferences for rare earths that are similar to those of transition metals and not actinides with respect to arene binding.
7. CONCLUSIONS AND OUTLOOK

Rare earth organometallic chemistry enjoyed a rapid growth after the introduction of cyclopentadienyl and its derivatives as ancillary ligands in the 1970s. Metallocene (Cp₂MX) and half-sandwich complexes (CpMX₂) constituted the main body of this area for a long time. Recently, supporting ligands other than cyclopentadienyls have been developed and introduced, resulting in uncovering chemistry that has not been previously observed with metallocene or half-sandwich complexes.

The present review summarized recent advances in the reduction chemistry of rare earth metals, and described our own efforts in synthesizing inverse sandwiches of rare earth arene complexes using ferrocene-based diamide ligands. Unprecedented molecules were synthesized and their unusual electronic structures were studied. Highlights included the synthesis of the first scandium naphthalene complex and its reactivity toward P₄ activation, and the isolation and characterization of a 6-carbon, 10π-electron aromatic system stabilized by coordination to rare earth metals. The reactivity of those complexes was also discussed.
New developments in the chemistry of reduced arene rare earth complexes show that although this is a relatively mature field, there are still plenty of surprising results at the horizon. Aside from the synthesis of unusual or long-sought molecules, the reduction chemistry of rare earths has the advantage of combining the high Lewis acidity of the metal with storing electrons on a reactive ligand in order to obtain unusual reactivity. Although most of these complexes are air and water sensitive, they can still teach the scientific community important lessons about what is necessary in order to achieve “extreme” reactivity, and advance our fundamental knowledge of structure and bonding.

It is likely that the future will see the isolation of other interesting bonding motifs, some predicted and others maybe not even imagined. Their characterization will benefit greatly from theoretical calculations and advanced spectroscopy techniques, as is becoming more and more the case in the present. And, although lanthanides are considered to form mostly ionic compounds, a detailed and subtle understanding of covalent contributions to bonding will likely emerge as new molecules are reported.

**ACRONYMS AND ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>18-crown-6</td>
<td>1,4,7,10,13,16-hexaoxacyclooctadecane</td>
</tr>
<tr>
<td>2.2.2-cryptand</td>
<td>4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane</td>
</tr>
<tr>
<td>anth</td>
<td>anthracene</td>
</tr>
<tr>
<td>bipy</td>
<td>2,2′-bipyridine</td>
</tr>
<tr>
<td>biph</td>
<td>biphenyl</td>
</tr>
<tr>
<td>Bn</td>
<td>benzyl</td>
</tr>
<tr>
<td>COT²⁻</td>
<td>cyclooctatetraene dianion, (η⁸-C₈H₈)²⁻</td>
</tr>
<tr>
<td>Cp⁻</td>
<td>cyclopentadienyl anion, (η⁵-C₅H₅)⁻</td>
</tr>
<tr>
<td>Cp*⁻</td>
<td>pentamethylcyclopentadienyl anion, (η⁵-C₅Me₅)⁻</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-dimethoxyethane</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>Et₂O</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>fc</td>
<td>1,1'-ferrocenediyi</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>'Pr</td>
<td>iso-propyl</td>
</tr>
<tr>
<td>IR</td>
<td>infra-red</td>
</tr>
<tr>
<td>KC₈</td>
<td>potassium graphite</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>N₂Npy</td>
<td>2,6-bis(2,6-di-iso-propylanilidomethyl)pyridine</td>
</tr>
<tr>
<td>nacnac</td>
<td>β-diketiminato</td>
</tr>
<tr>
<td>naph</td>
<td>naphthalene</td>
</tr>
<tr>
<td>NBO</td>
<td>natural bond orbital</td>
</tr>
<tr>
<td>NHC</td>
<td>N-heterocyclic carbene</td>
</tr>
<tr>
<td>NICS</td>
<td>nuclear-independent chemical shift</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance (spectroscopy)</td>
</tr>
<tr>
<td>NNfc</td>
<td>see NN TBS</td>
</tr>
<tr>
<td>NN TBS</td>
<td>[fc(NSi'BuMe₂)₂]₂⁻</td>
</tr>
<tr>
<td>NN TMS</td>
<td>[fc(NSiMe₃)₂]₂⁻</td>
</tr>
<tr>
<td>OEP</td>
<td>octamethylporphrin</td>
</tr>
<tr>
<td>TACN</td>
<td>1,4,7-triazacyclononane</td>
</tr>
<tr>
<td>'Bu</td>
<td>tert-butyl</td>
</tr>
<tr>
<td>terph</td>
<td>p-terphenyl</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMTAC</td>
<td>1,3,5-trimethyl-1,3,5-triazacyclocexane</td>
</tr>
<tr>
<td>TPB</td>
<td>1,3,5-triphenylbenzene</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
</tr>
</tbody>
</table>
REFERENCES

Marks, T. J. 2013. Organometallics, 32, 1133-1136.


(E)-stilbene, 1
1,1′-ferrocenediyli diamide, 1
6-carbon, 10-π electron aromatic system, 1
activation of white phosphorus, 2
Arene-bridged, 1
donor-acceptor interaction, 37
fused arenes, 1
heterometallic, 12

low-valent, 3
non-cyclopentadienyl ancillary ligands, 3
polyphosphide, 2
Potassium graphite, 45
Rare Earth, 1
Reduction, 1
π ligands, 4