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Huang, W
Diaconescu, PL

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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.

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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 ($(\eta^5\text{-C}_5\text{H}_5)^-$, 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, Cp_3M ($\text{M} = \text{Sc}, \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{and Gd}$), were first synthesized by Wilkinson (Wilkinson and Birmingham, 1954), followed by the metallocenes Cp_2MCl ($\text{M} = \text{Sm}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}, \text{Lu}$) and $(\text{Me-Cp})_2\text{MCl}$ ($\text{M} = \text{Gd}, \text{Er}, \text{Yb}$) (Maginn et al., 1963) and half-sandwich CpMCl_2 ($\text{M} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}, \text{Lu}$) (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 ($(\eta^5\text{-C}_5\text{Me}_5)^-$, 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), $\text{Li}[\text{Cp}^*\text{MX}_3]$ and $[\text{Cp}^*_2\text{MX}_2]$, $\text{M} = \text{Yb}, \text{Lu}$, $\text{X} = \text{Cl}, \text{I}$ (Watson et al., 1981), as well as $[\text{M}'(\text{solvent})][\text{Cp}^*_2\text{MCl}_2]$, $\text{M}' = \text{Li}, \text{Na}$, $\text{M} = \text{Nd}, \text{Sm}, \text{Yb}$; $\text{Cp}^*_2\text{NdCl}(\text{THF})$, $\text{Cp}^*_2\text{Nd}(\text{N}[\text{SiMe}_3]_2)$, $\text{Cp}^*_2\text{YbCl}(\text{THF})$; $[\text{Na}(\text{OEt})_2][\text{Cp}^*\text{NdCl}_3]$, and $\text{Cp}^*\text{Nd}(\text{N}[\text{SiMe}_3]_2)_2$ (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, $(\eta^8\text{-C}_8\text{H}_8)^{2-}$, 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 $\text{Ln}(\text{COT})$ 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 ($\eta^6\text{-C}_5\text{H}_5\text{BR}$)⁻, (first reported rare earth examples: (C₅H₅B-Ph)ScPh₂(THF) and (C₅H₅B-Ph)₂ScPh(THF)) (Putzer et al., 1999), tetramethylphospholyl ($\eta^5\text{-C}_4\text{Me}_4\text{P}$)⁻ (first reported rare earth examples: [Yb($\mu\text{-Cl}$)($\eta^5\text{-C}_4\text{Me}_4\text{P}$)(THF)₂]₂ and [Yb($\mu\text{-SPh}$)($\eta^5\text{-C}_4\text{Me}_4\text{P}$)(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 Hultzs, 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 $[\text{N}(\text{SiMe}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2]^-$ (P_2N) in $(\text{P}_2\text{N})\text{ScR}_2$ ($\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{SiMe}_3$) (Fryzuk et al., 1996), tetradentate $(\text{PhP}[\text{CH}_2(\text{SiMe}_2)\text{N}(\text{SiMe}_2)\text{CH}_2]_2\text{PPh})^{2-}$ (P_2N_2) in $(\text{P}_2\text{N}_2)\text{Y}[\text{CH}(\text{SiMe}_3)_2]$ (Fryzuk et al., 1997), and, recently, the tetradentate $\text{fc}(\text{NP}^i\text{Pr}_2)_2$ in $[(\text{fc}(\text{NP}^i\text{Pr}_2)_2)\text{Sc}(\text{THF})(\mu\text{-H})]_2$ (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 H_2 (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 $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3$ (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).

CHART 2 Non-cyclopentadienyl rare earth complexes reported by various groups (abbreviations are the same as in text).

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-PⁱPr₂-4-methylphenyl)₂, on scandium and isolated rare scandium methylenide 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 tripodal 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, bode 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).

CHART 4 Examples of rare earth carbene complexes reported by various groups (abbreviations are the same as in text).

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, $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_2 \cdot \text{MeCN}$ (Deng and Shore, 1991) and $\text{Cp}_2\text{Lu}(\text{THF})\text{-RuCp}(\text{CO})_2$ (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 $[\text{O}(\text{SiMe}_2\text{N-2-C}_5\text{H}_3\text{N-4-Me})_2]_2\text{NdRh}(\eta^2\text{-C}_2\text{H}_4)$ and $[\text{O}(\text{SiMe}_2\text{N-2-C}_5\text{H}_3\text{N-4-Me})_2]_2\text{Nd}(\text{THF})\text{PdMe}$ in 1998 (Chart 5) (Spannenberg et al., 1998). Probably the most thought-provoking molecule reported in this area is $\text{Sm}(\text{ReCp}_2)_3$, 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 $\text{Sm}(\text{ReCp})_3$ 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, $[(C_5Me_4SiMe_3)Ln(\mu-H)]_4(THF)_n$ ($Ln = Lu, Y, n = 0-2$) (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 CO₂ (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 $Cp_2M(\mu-Me)_2AlR_2$ ($R = Me$ and $M = Sc, Gd, Dy, Ho, Er, Tm$, or Yb ; $R = Et$ and $M = Sc$ or Y) (Ballard and Pearce, 1975; Holton et al., 1976), and were continued by Anwender (Fischbach and

Anwander, 2006), who developed homoleptic tetraalkylaluminate rare earth complexes (Dietrich et al., 2011; Occhipinti et al., 2011) and bridging methylenes (Dietrich et al., 2006b) and methylidynes (Dietrich et al., 2006a) as part of rare earth aluminum small clusters. Interestingly, the crystal structures of isostructural bridging hexacoordinate carbides, $[(\text{TMTAC})\text{M}][\text{M}_2(\mu\text{-CH}_3)][((\mu_6\text{-C})[\text{Al}(\mu\text{-CH}_3)_2(\text{CH}_3)]_3)((\mu_3\text{-CH}_2)(\mu\text{-CH}_3)\text{Al}(\text{CH}_3)_2)_2]$ (TMTAC = 1,3,5-trimethyl-1,3,5-triazacyclohexane, M = Y, Sm), were also reported (Venugopal et al., 2009).

CHART 7 Selected examples of rare earth organoaluminum heterometallic complexes.

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 $\text{fc}(\text{NR})_2$; the system studied the most by us has $\text{R} = \text{Si}^t\text{BuMe}_2$ (Carver et al., 2008), while other versions, such as $\text{R} = \text{SiMe}_3$ (Monreal et al., 2007), SiPhMe_2 (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 ($\text{N}_2\text{N}^{\text{py}}$) (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).

Element	r (Å)	$E^0(M^{3+}/M^{2+})$ (V)
Sc	0.74	NA
Y	0.90	NA
La	1.03	-3.1
Ce	1.02	-3.2
Pr	0.99	-2.7
Nd	0.98	-2.6
Pm	0.97	-2.6
Sm	0.96	-1.6 (-1.55)
Eu	0.95	-0.3 (-0.35)
Gd	0.94	-3.9
Tb	0.92	-3.7
Dy	0.91	-2.6
Ho	0.90	-2.9

Er	0.89	-3.1
Tm	0.88	-2.3 (-2.2)
Yb	0.87	-1.1 (-1.1)
Lu	0.86	NA

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 $[\text{Xe}]d^0f^n$ configuration and those with a $[\text{Xe}]d^1f^{n-1}$ configuration (Meyer et al., 2004). The former (including NdI_2 , SmI_2 , EuI_2 , DyI_2 , TmI_2 , and YbI_2) are genuine $[\text{M}^{2+}][\text{I}^-]_2$ salts, while the latter (the rest of LnI_2) should be viewed as $[\text{M}^{3+}][\text{I}^-]_2[\text{e}^-]$ 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 $\text{M}^{3+/2+}$: the salt-like LnI_2 are those of rare earths having smaller values for the $\text{M}^{3+/2+}$ reduction potential, while the metallic LnI_2 are those with a $\text{M}^{3+/2+}$ reduction potential close to or lower than -3.0 V (the alkali metals have $\text{M}^{1+/0}$ 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 Anwender, 2010). Indeed, no homoleptic Eu(III) alkyl complexes have been reported yet (Zimmermann and Anwender, 2010), likely because the alkyl group is readily oxidized by Eu(III). Yb(II) is also common (Bombieri and Paolucci, 1998; Zimmermann and Anwender, 2010). A major breakthrough in this field was the isolation of organosamarium(II) complexes. Divalent samarium complexes, such as Cp^*_2Sm , are strong reductants. For example, Cp^*_2Sm could reduce N_2 to form the first dinitrogen complex of an f element, $(\text{Cp}^*_2\text{Sm})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ (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-^tBu₃C₅H₂)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).

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 LnZ_3/KC_8 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 $(\text{N}_2)^{2-}$ (Evans et al., 2005; Evans, 2007). Recently, lanthanide complexes of the radical trianion $(\text{N}_2)^{3-}$ 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 $(\text{N}_2)^{3-}$ complexes behave as single molecule magnets due to the spin exchange between the lanthanide ions and $(\text{N}_2)^{3-}$ (Rinehart et al., 2011a), and one of them, $[\text{K}(\text{18-crown-6})(\text{THF})_2][[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Tb}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$ (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: $[\text{K}(\text{18-crown-6})(\text{Et}_2\text{O})][[\text{1,3-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3]_3\text{La}]$ (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 $[\text{Xe}]4f^n5d^16s^0$ configuration, which is the same as that of solid state LnI_2 salts. As mentioned earlier, the latter are considered to be $(\text{Ln}^{3+})(\text{I})_2(\text{e}^-)$ (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 $[\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3]_3\text{M}$ 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 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 π and π^* 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 C_6Me_6 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 π^* 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): $[K([18]\text{-crown-6})][Ln(C_5H_3(SiMe_3)_2\text{-}1,3)_2(C_6H_6)]$ ($Ln = La, Ce, Pr, Nd$) and $[K([18]\text{-crown-6})(C_6H_6)_2][Ln(C_5H_3(t\text{-}Bu)_2\text{-}1,3)_2(C_6H_6)]$ (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 ($SiMe_3$ 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-diyl 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 $[K(18\text{-crown-6})]_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_6\text{H}_6\text{-C}_6\text{H}_6)$ was isolated. It was suggested that the dimer readily dissociated to $\text{C}_6\text{H}_6^{\bullet-}$ 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-diyl 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-diyl (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 P_2N_2 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 $[\text{Tm}(\text{DME})_2(\eta^2\text{-C}_{10}\text{H}_8)_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_{10}\text{H}_8)]$ 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 $[\text{LaI}_2(\text{THF})_3]_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_{10}\text{H}_8)$ and

$[\text{EuI}(\text{DME})_2]_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_{10}\text{H}_8)$ (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 $[\text{Tm}(\text{DME})]_2(\eta^2\text{-C}_{10}\text{H}_8)_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_{10}\text{H}_8)$ (Figure 2) was also isolated from the reaction of TmI_2 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 $\mu\text{-}\eta^4\text{:}\eta^4$ 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 P_2N_2 ligand ($[(\text{P}_2\text{N}_2)\text{Ln}]_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_{10}\text{H}_8)$, $\text{Ln} = \text{Y}, \text{Lu}$, Figure 3) from the reduction with KC_8 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 $[(Cp^*Lu)_3(C_{10}H_8)(C_{10}H_7)(H)][Na(THF)_3]_2[C_{10}H_8]$, which was isolated from the reaction of $[Cp^*LuCl_2]NaCl$ with $C_{10}H_8Na$ (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 η^6 coordination to Lu_2), while the other is a trianion that coordinates η^4 to Lu_3 and η^1 to Lu_2 . 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).

CHART 15 Proposed structure of a bridging naphthalene hydride trilutetium complex reported by Bochkarev's group (Protchenko et al., 1997).

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 $\mu\text{-}\eta^3\text{:}\eta^3$ coordination mode was observed for $(\text{Cp}^*\text{Ln})_2(\text{C}_{14}\text{H}_{10})$ ($\text{Ln} = \text{Sm}, \text{La}$) (Evans et al., 1994; Thiele et al., 1996), in which the two lanthanides bind symmetrically to a terminal and the middle ring, while a $\mu\text{-}\eta^4\text{:}\eta^4$ coordination mode was observed for $[(\text{P}_2\text{N}_2)\text{Ln}]_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_{14}\text{H}_{10})$ ($\text{Ln} = \text{Y}, \text{Lu}$) (Fryzuk et al., 2000), akin to that of naphthalene in the analogous complexes. The solid-state molecular structures of $[(\text{P}_2\text{N}_2)\text{Ln}]_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_{14}\text{H}_{10})$ (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 16 Bridging dianionic anthracene rare earth complexes.

FIGURE 4 Molecular structure of $[(P_2N_2)Y]_2(\mu-\eta^4:\eta^4-C_{14}H_{10})$ 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 $(\text{Cp}^*\text{Sm})_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_{16}\text{H}_{10})$ (Evans et al., 1994) to $[(\text{Cp}^*\text{La})_3(\mu\text{-Cl})_3(\text{THF})(\mu\text{-}\eta^2\text{:}\eta^6\text{:}\eta^6\text{-C}_{16}\text{H}_{10})]$ (Thiele et al., 1998) in pyrene compounds and $(\text{Cp}^*\text{Sm})_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_{18}\text{H}_{12})$ (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 $\text{fc}(\text{NHSiMe}_3)_2$ ($\text{H}_2(\text{NN}^{\text{TMS}})$) to group 4 metals, titanium and zirconium, to afford metal dimethyl and dibenzyl complexes $(\text{NN}^{\text{TMS}})\text{TiMe}_2$ and $(\text{NN}^{\text{TMS}})\text{ZrBn}_2$ ($\text{Bn} = \text{CH}_2\text{Ph}$) (Chart 3-1) (Shafir et al., 2001). $[(\text{NN}^{\text{TMS}})\text{ZrBn}][(\mu\text{-Bn})\text{B}(\text{C}_6\text{F}_5)_3]$ could be obtained by treating $(\text{NN}^{\text{TMS}})\text{ZrBn}_2$ with 1 equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ 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 $(\text{NN}^{\text{TBS}})_2\text{U}$ ($\text{NN}^{\text{TBS}} = 1,1'\text{-fc}(\text{NSi}^t\text{BuMe}_2)_2$) and its one electron oxidation product $[(\text{NN}^{\text{TBS}})_2\text{U}][\text{BPh}_4]$ 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, $[(\text{NN}^{\text{TBS}})_2\text{U}][\text{BPh}_4]$ (Monreal et al., 2007). At the time, it was also observed that the *tert*-butyldimethylsilyl version, $1,1'\text{-fc}(\text{NHSi}^t\text{BuMe}_2)_2$ ($\text{H}_2(\text{NN}^{\text{TBS}})$), 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 $(\text{NN}^{\text{TBS}})\text{M}(\text{CH}_2\text{Ar})(\text{THF})$ ($\text{M} = \text{Sc}$ (Carver et al., 2008) and Lu (Carver et al., 2009), $\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$; $\text{M} = \text{Y}$ (Carver and Diaconescu, 2008) and La (Miller et al., 2009), $\text{Ar} = \text{C}_6\text{H}_5$) and the uranium dialkyl complex $(\text{NN}^{\text{TBS}})\text{UBn}_2$ (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 NN^{TBS} as the ancillary ligand for d^0f^n 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 $(\text{NN}^{\text{TBS}})\text{Sc}(\text{CH}_2\text{Ar})(\text{THF})$ ($\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$). 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 $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{S})_2]\text{Pd}(\text{PPh}_3)$ (Seyferth et al., 1983); Akabori later provided a comprehensive study based on $[\text{M}(\eta^5\text{-C}_5\text{H}_4\text{O})_2]\text{M}'(\text{PPh}_3)$ ($\text{M} = \text{Fe}$ or Ru , $\text{M}' = \text{Pd}$ 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)metallocenes (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 $([(\text{NN}^{\text{TMS}})\text{Ti}(\mu\text{-Cl})_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$ (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^{TMS} ligand varied according to the electrophilicity of the titanium center: Fe-Ti distance is 3.32 Å in the neutral dialkyl complex $(\text{NN}^{\text{TMS}})\text{TiMe}_2$, but it shortens to 3.07 Å in the Lewis adduct $[(\text{NN}^{\text{TMS}})\text{TiMe}][(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ and reaches the shortest value, 2.49 Å, in the chloride-bridged dicationic complex $[(\text{NN}^{\text{TMS}})\text{Ti}(\mu\text{-Cl})_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$. Our group observed a similar trend for group 3 metal complexes supported by the NN^{TBS} ligand: the Fe-Sc distance is 3.16 and 2.80 Å in $(\text{NN}^{\text{TBS}})\text{Sc}(\text{CH}_2\text{C}_6\text{H}_3\text{Me}_2\text{-3,5})(\text{THF})$ (Figure 5) and $[(\text{NN}^{\text{TBS}})\text{Sc}(\mu\text{-Cl})_2]$ (Figure 6), respectively (Carver et al., 2008). Recently, our group also reported a dative Fe-Ru interaction in $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{NH})_2]\text{Ru}(\text{PPh}_3)_2$ and characterized it by spectroscopic methods and DFT calculations (Green et al., 2013).

CHART 19 Metallocene complexes containing dative iron-metal bonds (indicated as red dashed lines).

FIGURE 6 Molecular structure of $[(\text{NN}^{\text{TBS}})\text{Sc}(\mu\text{-Cl})]_2$. Figure was adapted from Carver et al. (2008).

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 d^0f^n 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 $(\text{NN}^{\text{TBS}})\text{ScI}(\text{THF})_2$, which crystallized in the space group $C2/c$, all other $(\text{NN}^{\text{TBS}})\text{MI}(\text{THF})_2$ crystallized in the same space group, $P-1$, and differed only slightly in their structural parameters (Figure 8). In all $(\text{NN}^{\text{TBS}})\text{MI}(\text{THF})_2$ 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.

SCHEME 1 Synthesis of $(\text{NN}^{\text{TBS}})\text{MI}(\text{THF})_2$ (M = Sc, Y, La, and Lu).

FIGURE 8 Molecular structure of $(\text{NN}^{\text{TBS}})\text{ScI}(\text{THF})_2$ (left) and $(\text{NN}^{\text{TBS}})\text{YI}(\text{THF})_2$ (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 π^* orbital of the ferrocene backbone; however, for $(\text{NN}^{\text{TBS}})\text{YI}(\text{THF})_2$, both the LUMO and LUMO+1 were the π^* 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.

FIGURE 9 Selected molecular orbitals for $(\text{NN}^{\text{TBS}})\text{ScI}(\text{THF})_2$ and $(\text{NN}^{\text{TBS}})\text{YI}(\text{THF})_2$. Top: $(\text{NN}^{\text{TBS}})\text{ScI}(\text{THF})_2$; bottom: $(\text{NN}^{\text{TBS}})\text{YI}(\text{THF})_2$. Hydrogen atoms were omitted for clarity.

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, KC_8 forms a suspension in common organic solvents such as *n*-pentane, Et_2O , and THF (Bergbreiter and Killough, 1978). However, the reaction of KC_8 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 KC_8 in *n*-pentane and Et_2O are not as well dispersed as those formed in THF (Bergbreiter and Killough, 1978).

FIGURE 10 Space-filling model of KC_8 : left, side view; right, top view. Use granted by Ben Mills from the Wikimedia Commons.

Potassium graphite (commonly referred to as KC_8) is the most potassium rich form of a series of graphite intercalation compounds with potassium (Rüdorff and Schulze, 1954). A space-filling model of KC_8 is shown in Figure 10. KC_8 is probably the most widely used reductant in organometallic rare earth chemistry (Nief, 2010). The system composed of trivalent lanthanide precursors LnZ_3 (Z represents a monoanionic ligand) and KC_8 developed by Evans proved successful in reducing dinitrogen to form stable lanthanide dinitrogen complexes with the general formula $(\text{Z}_2\text{Ln})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ (Evans et al., 2005). In addition, KC_8 was used in obtaining a series of divalent lanthanide complexes $[\text{K}(2.2.2\text{-cryptand})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Ln}]$ (Chart 10) (MacDonald et al., 2013a). The strategy of using KC_8 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) ($L = :C[N(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)CH]_2$), 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; Ungureanu 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 Anwender, 2010). This is best illustrated by the product from the co-condensation of scandium metal and 1,3,5-*t*-Bu₃C₆H₃ (Cloke et al., 1991). While other rare earths gave the formally zero-valent sandwich complexes (1,3,5-*t*-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^{TBS} ligand proved to be the right choice for supporting inverse sandwiches of reduced arene scandium complexes: the reaction between (NN^{TBS})ScI(THF)₂ (NN^{TBS} = 1,1'-fc(NHSi^{*i*}BuMe₂)₂) and 0.5 equiv naphthalene (Scheme 2a) led to the first scandium naphthalene complex, [(NN^{TBS})Sc]₂(μ-η⁴:η⁴-C₁₀H₈) (**Sc₂-naph**) (Figure 11) (Huang et al., 2011). The

analogous anthracene complex, $[(\text{NN}^{\text{TBS}})\text{Sc}]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{10})$ (**Sc₂-anth**), could be obtained by following a similar protocol (Scheme 2b) and was also crystallographically characterized (Figure 11).

SCHEME 2 a) Synthesis of **Sc₂-naph**; b) synthesis of **Sc₂-anth**; c) conversion of **Sc₂-naph** to **Sc₂-anth**. Adapted with permission from Huang et al. (2011). Copyright © 2011, American Chemical Society.

FIGURE 11 Molecular structures of **Sc₂-naph** (left) and **Sc₂-anth** (right). Thermal ellipsoids are drawn at the 50% probability level. Adapted from Huang et al. (2011).

The molecular structure of **Sc₂-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, 8 π -electron system for the six co-planar center carbon atoms. Each scandium ion binds η^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 [Li(TMEDA)]₂(μ - η^4 : η^4 -C₁₀H₈) (TMEDA = tetramethylethylenediamine) (Melero et al., 2009).

Besides common structural parameters with previously reported rare earth or alkali metal naphthalene dianion complexes, **Sc₂-naph** featured a short Fe-Sc distance of 2.83 Å, which was significantly shorter than that of (NN^{TBS})ScI(THF)₂ (3.12 Å) and among the shortest Fe-Sc distances observed by our group with the NN^{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 **Sc₂-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 **Sc₂-anth**. When using a non-ferrocene-based amide complex, [(Me₃Si)₂N]₂ScI(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 **Sc₂-anth** (Figure 11) was similar to that of ((P₂N₂)₂Y)₂(μ-C₁₄H₁₀) (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. ¹H NMR spectroscopy, however, indicated that the solution structure of **Sc₂-anth** was symmetrical at 25 °C in C₆D₆. A variable temperature NMR experiment conducted with a toluene-*d*₈ solution of **Sc₂-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 ((P₂N₂)₂Y)₂(μ-C₁₄H₁₀) (Fryzuk et al., 2000).

FIGURE 12 Variable temperature ^1H NMR spectra of **Sc₂-anth** in aromatic solvents (209 K to 298 K in C_7D_8 ; 326 K to 359 K in C_6D_6). $\text{NN}^{\text{fc}} = \text{NN}^{\text{TBS}}$. 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 **Sc₂-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 η^4 coordination mode observed in the solid state. The nearly degenerate HOMO-1 and HOMO-2 (HOMO-5 for **Sc₂-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 **Sc₂-anth**.

FIGURE 13 Top: Selected molecular orbitals of **Sc₂-naph**: HOMO (left); HOMO-1 (right). Bottom: HOMO-5 of **Sc₂-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 **Sc₂-naph** to **Sc₂-anth** could be achieved by heating a 1:1 mixture of **Sc₂-naph** and anthracene at 50 °C in C₆D₆ for five days (Scheme 2c),

indicating that the naphthalene ligand in **Sc₂-naph** is more reducing than the anthracene ligand in **Sc₂-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 C₆D₆ solution of **Sc₂-naph** (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 **Sc₂-naph** with 2,2'-bipyridine to form (NN^{TBS})Sc(2,2'-bipyridine) with the elimination of free naphthalene; b) reaction of **Sc₂-naph** with pyridine to form [(NN^{TBS})Sc(NC₅H₅)]₂[μ-(NC₅H₅-C₅H₅N)] with the elimination of free naphthalene; c) reaction of **Sc₂-naph** with phenylacetylene to form [(NN^{TBS})Sc(μ-CCPh)]₂ with the elimination of dihydronaphthalene. Reproduced with permission from Huang et al. (2011). Copyright © 2011, American Chemical Society.

The reaction of **Sc₂-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(NC₅H₅)]₂[μ-(NC₅H₅-C₅H₅N)]. 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 **Sc₂-naph** with 2 equivalents of phenylacetylene led to the immediate formation of [(NN^{TBS})Sc(μ-CCPh)]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 phenylacetylide bridging dimer with a short Fe-Sc (2.89 Å) distance.

4.2 P₄ Activation by Rare Earth Arene Complexes

4.2.1 P₄ Activation by Scandium Arene Complexes

White phosphorous (P_4) 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 P_n -containing early transition metal complexes formed from direct P_4 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 P_4 activation had involved low-valent metal complexes prior to our reports. For example, $(Cp^*_2Sm)_4P_8$ was obtained by vapor transfer of P_4 to a toluene solution of Cp^*_2Sm over the course of a week in a low yield (ca. 10%). The heterometallic Sm-Fe P_5 complex was obtained by reacting $Cp^*Fe(\eta^5-P_5)$ with samarium reagents. It is worth noting that late transition metal arene complexes have also been used for P_4 activation recently (Schnöckelborg et al., 2011).

CHART 22 Examples of rare earth P_n -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 [(NN^{TBS})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 [(NN^{TBS})Sc] fragments were equivalent in solution on the NMR timescale. The ³¹P NMR spectrum featured an AA'A''A'''MM'M''M''' spin system.

SCHEME 4 Reactions of **Sc₂-naph** and **Sc₂-anth** with P₄ to form [(NN^{TBS})Sc]₄(μ₄-η²:η²:η²:η²-P₈) (**Sc₄P₈**) and [(NN^{TBS})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 **Sc₄P₈** (Figure 14) has a realgar-type P₈ unit in the center and four [(NN^{TBS})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 **Sc₄P₈**. The P₈ unit showed local C_{2v} symmetry, with two distinct types of P-atoms: P_{inner} (three neighboring P atoms) and P_{corner} (two neighboring P atoms). The average P_{inner}-P_{inner} distance is 2.31 Å, 0.11 Å longer than that of P_{inner}-P_{corner}. The average P_{inner}-P_{corner} distance of 2.20 Å is close to the P-P interatomic distance in P₄ (2.21 Å) (Corbridge and Lowe, 1952) or a recent updated gas phase value 2.1994(3) Å (Cossairt et al., 2010a). The structure of the P₈ unit resembled that of (Cp*₂Sm)₄P₈ (Konchenko et al., 2009). The P₈ unit had been previously observed in some late transition metal complexes, which were obtained from the photolysis reaction of P₄ 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 $[(\text{NN}^{\text{TBS}})\text{Sc}]_4(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-P}_8)$ (left) and $[(\text{NN}^{\text{TBS}})\text{Sc}]_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-P}_7)$ (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 **Sc₂-naph** and P₄ and was isolated based on its solubility properties, different from those of **Sc₄P₈**. X-ray crystallography indicated it to be the first early transition metal P₇ compound, $[(\text{NN}^{\text{TBS}})\text{Sc}]_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-P}_7)$ (**Sc₃P₇**) (Figure 14). It was also found that the product distribution could be tuned by either changing the stoichiometry of P₄ or using a different scandium arene starting material: employing 1.0 equivalent or a sub-stoichiometric amount of P₄ favored the formation of **Sc₄P₈**, while using excess P₄ or the less reactive but more labile **Sc₂-anth** (as indicated by its fluxional behavior in solution) favored the formation of **Sc₃P₇**.

Sc₃P₇ was the first example of a Zintl-type P₇³⁻ compound formed directly from 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 **Sc₃P₇**: P_{apex}, P_{edge}, and P_{bottom}. The difference in P-P distances was smaller than that observed in **Sc₄P₈**, with almost identical P_{apex}-P_{edge} and P_{edge}-P_{bottom} distances of 2.20 Å and a slightly longer P_{bottom}-P_{bottom} distance of 2.23 Å. The P₇³⁻ unit in **Sc₃P₇** resembles that of the solid-state structure of Li₃P₇, although in the latter case, the difference in P-P distances is larger. Similarly to **Sc₄P₈**, **Sc₃P₇** also bears a short Fe-Sc distance of 2.80 Å. The ³¹P NMR spectrum showed three sets of peaks, at δ = +23.1 -118.9, and -131.4 ppm, in a 3:1:3 ratio, featuring an AA'A"MM'M"X spin system similar to the previously reported Li₃P₇, Fe₃P₇ and P₇R₃ (R = silyl or alkyl) cases (Ahlrichs et al., 1996; Fritz and Härer, 1983).

DFT calculations on model molecules of **Sc₄P₈** and **Sc₃P₇** indicated that the two polyphosphide complexes exhibit mostly ionic interactions between the metal and the polyphosphide anion as described for (Cp^{*}₂Sm)₄P₈ (Konchenko et al., 2009). The examination of bonding orbitals with the same symmetry, HOMO-15 for **Sc₄P₈** and HOMO-18 for **Sc₃P₇** (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 **Sc₄P₈** and **Sc₃P₇**, 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 **Sc₄P₈** and **Sc₃P₇**, respectively.

FIGURE 15 Selected molecular orbitals of **Sc₄P₈** and **Sc₃P₇**. Top: HOMO-12 (left) and HOMO-15 (right) for **Sc₄P₈**. Bottom: HOMO-17 (left) and HOMO-18 (right) for **Sc₃P₇**. 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 P₄ Activation

The success of direct P₄ 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 **Sc₂-naph** (Scheme 5). Different from **Sc₂-naph**, which did not coordinate THF, the other rare earth naphthalene complexes were synthesized with the general formula of [(NN^{TBS})M(THF)]₂(μ-η⁴:η⁴-C₁₀H₈) (**M₂-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 NN^{TBS} ligand, it was possible to compare their physical properties. **Sc₂-naph** is a black solid barely soluble in hexanes but soluble in aromatic solvents. However, **Y₂-naph** is a dark-red solid barely soluble in hexanes, aromatic solvents, and diethyl ether, but only soluble in

THF. While **Lu₂-naph** has similar physical properties to **Y₂-naph**, **La₂-naph**, with the largest ionic radius of all rare earths and same molecular formula as **Y₂-naph** and **Lu₂-naph**, has physical properties similar to **Sc₂-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 **M₂-naph** (M = Y, La, and Lu); (b) exclusive formation of $[(\text{NN}^{\text{TBS}}\text{M})(\text{THF})]_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-P}_7)$ (**M₃P₇**) from P_4 activation by employing **M₂-naph**. Adapted with permission from Huang and Diaconescu (2013). Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

All **M₂-naph** were characterized by ^1H 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 **La₂-naph** were shifted significantly upfield compared to the other three complexes (Table 2). However, it was found that the ¹³C chemical shifts for **La₂-naph** were similar to those of other rare earth naphthalene complexes (Huang and Diaconescu, 2013).

TABLE 2 Summary of ¹H and ¹³C NMR chemical shifts (unit in ppm) of (C₁₀H₈)²⁻ unit and structural parameters (distance in Å) for **M₂-naph** (M = Sc, Y, La, and Lu).

	Sc₂-naph	Y₂-naph	La₂-naph	Lu₂-naph
α -CH and β -CH	5.06, 4.02	5.09, 3.94	4.28, 2.73	5.17, 4.23
<i>ipso</i> -C, α -C, β -C	158, 120, 95	158, 118, 94	157, 122, 100	155, 118, 95
C $_{\alpha}$ -C $_{\beta}$	1.428(7)	1.441(6)	1.433(4)	1.444(6)
C $_{\beta}$ -C $_{\beta}$	1.368(7)	1.376(7)	1.374(4)	1.374(6)
C _{<i>ipso</i>} -C $_{\alpha}$	1.421(6)	1.423(6)	1.418(3)	1.424(6)
C _{<i>ipso</i>} -C _{<i>ipso</i>}	1.445(9)	1.450(6)	1.451(5)	1.452(6)

Although **M₂-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 **Y₂-naph** is shown in Figure 16 as a representative for **M₂-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 **M₂-naph** were found to contain the usual μ - η^4, η^4 coordination motif of the bridging naphthalene ligand.

Lu₃P₇ were barely soluble in hexanes and slightly soluble in aromatic solvents. While the solubility of **Lu₃P₇** was similar to that of the previously reported **Y₃P₇**, the solubility of **La₃P₇** was different but similar to that of the THF free compound **Sc₃P₇**. The unexpected solubility properties of **M₃P₇** (M = Sc, Y, La, Lu) echoed the different solubilities of **M₂-naph** described above.

The molecular structure of **Y₃P₇** is shown in Figure 16 as a representative for **M₃P₇**. While **Lu₃P₇** is isostructural to **Y₃P₇**, **La₃P₇** 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 **La₃P₇** showed different ratios between THF and diethyl ether as a coordinating solvent. Similarly to **La₃P₇**, some batches of **La₂-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 **M₃P₇** (unit: Å, error in brackets, all are average values).

M₃P₇	P _{apex} -P _{edge}	P _{edge} -P _{bottom}	P _{bottom} -P _{bottom}
Sc₃P₇ ^[a]	2.201(2)	2.197(2)	2.229(2)
Lu₃P₇	2.183(2)	2.181(2)	2.233(2)
Y₃P₇	2.188(2)	2.176(3)	2.238(2)
La₃P₇	2.191(2)	2.161(2)	2.258(2)

[a] Unlike other **M₃P₇**, **Sc₃P₇** has no solvent molecule coordinated to scandium.

All **M₃P₇** structures feature a central Zintl-type polyphosphide P₇³⁻ anion surrounded by three [(NN^{TBS})M(solvent)] fragments (Huang and Diaconescu, 2013). Except for **Sc₃P₇**, which does not coordinate any THF, all the other **M₃P₇** 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 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 La_3P_7 , the difference among the P-P distances is comparable to those of alkali earth P_7^{3-} binary complexes; for Sc_3P_7 , the difference among the P-P distances is at the minimum and is close to that observed for silyl substituted $P_7\text{R}_3$ compounds. For instance, in $P_7(\text{SiMe}_3)_3$, $P_{\text{apex}}-P_{\text{edge}}$, $P_{\text{edge}}-P_{\text{bottom}}$, 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, 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 Li_3P_7 in $\text{THF-}d_8$ is temperature dependent: at low temperature ($-60\text{ }^\circ\text{C}$), 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_{edge} atoms right next to the two P_{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_3P_7 and Cs_3P_7 (Kraus et al., 2003); no tautomerization was observed for silyl substituted P_7R_3 compounds (Baudler and Glinka, 1993).

The ^{31}P NMR spectra of **Sc₃P₇**, **Y₃P₇**, and **Lu₃P₇**, 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 **La₃P₇** showed only one, broad signal centered at -75 ppm, similarly to Li_3P_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 **La₃P₇** and a coalescence temperature comparable to that of Li_3P_7 .

FIGURE 17 Left: Overlay of ^{31}P NMR spectra (toluene- d_8) of La_3P_7 at different temperatures. Right: Proposed mechanism for valence tautomerization of P_7^{3-} in La_3P_7 . NN^{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 La_3P_7 , while for Li_3P_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, Li_3P_7 decomposed. This difference was explained by the migration

of the (NN^{TBS})La(THF) fragment from one phosphorous atom to another, allowing the valence tautomerization to occur (Huang and Diaconescu, 2013). This mechanism for P₇³⁻ tautomerization in **La₃P₇** requires the simultaneous breaking and formation of four La-P bonds (Figure 17 right). The tautomerization involves one of the five-member rings of P₇³⁻: a P_{bottom}-P_{bottom} bond breaks while a P_{edge}-P_{edge} bond forms; at the same time, the lanthanum fragment coordinated to that face migrates from two P_{edge} atoms to two P_{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_{edge} atoms and two neighbouring P_{bottom} atoms. To support this hypothesis, the average La-P_{edge} distance is 3.10 Å, while the average La-P_{bottom} distance is 3.54 Å. The 0.44 Å difference is smaller than the corresponding distance difference in the other **M₃P₇** (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 **La₃P₇** than for **Y₃P₇** > **Lu₃P₇** > **Sc₃P₇**. Consequently, it was found that the tautomerization also took place in **Y₃P₇** but at a high temperature (coalescence temperature higher than 75 °C). Unfortunately, the low solubility of **Y₃P₇** in aromatic solvents and the high coalescence temperature prevented a detailed variable temperature ³¹P NMR spectroscopy study for this complex (Huang and Diaconescu, 2013).

4.5 Synthesis of Organic P-containing Compounds from P₄

Transferring the activated polyphosphide is essential to generate organophosphorus compounds (Cossairt et al., 2010b). The reaction of **Sc₃P₇** or **Y₃P₇** (Scheme 6) with 3 equiv Me₃SiI led to the formation of the corresponding rare earth iodide and P₇(SiMe₃)₃ (Huang and Diaconescu, 2012), as confirmed by ³¹P NMR spectroscopy (Fritz and Härer, 1983).

SCHEME 6 Reaction of M_3P_7 with Me_3SiI . 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 π -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 π -electron system. The calculated nuclear-independent chemical shift (NICS) confirmed the $(\text{C}_6\text{H}_6)^{4-}$ formulation. The report suggested some suitable metal centers, such as thorium, to stabilize the highly electron-rich $(\text{C}_6\text{H}_6)^{4-}$. 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 $[\text{toluene}]^{4-}$ ligand in $[\text{U}(\text{Ts}^{\text{Xy}})]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_5\text{Me})$ ($\text{Ts}^{\text{Xy}} = \text{HC}(\text{SiMe}_2\text{NAr})_3$; $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$) (Patel et al., 2011; Patel et al., 2013); however, XANES spectroscopy studies have not been reported for this or the other uranium examples, $[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_7\text{H}_8)$, $\text{K}[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_7\text{H}_8)$, $\text{K}_2[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_7\text{H}_8)$ (Camp et al., 2013), with proposed $[\text{toluene}]^{4-}$ ligands.

Compound $[(\text{NN}^{\text{TBS}})\text{Y}]_2[\text{K}(\text{toluene})]_2(\mu\text{-biphenyl})$ (**Y₂K₂-biph**) was obtained by addition of potassium graphite to a pre-mixed tetrahydrofuran (THF) solution of $(\text{NN}^{\text{TBS}})\text{YI}(\text{THF})_2$ 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 η^6 fashion, while the two potassium ions coordinate to the other biphenyl ring in an η^6 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 **M₂K₂-biph** (M = Sc, Y, La, and Lu), **Y₂K₂-terph**, and **Lu₂K₂-TPB**. Adapted from Huang et al. (2013). Copyright © 2013, Rights Managed by Nature Publishing Group.

FIGURE 18 Thermal-ellipsoid (50% probability) representation of **Y₂K₂-biph** (left) and the anion of **[K(18-crown-6)(THF)_{1.5}]₂[[(NN^{TBS})Y]₂(μ-biphenyl)]** (**Y₂-biph-K₂-crown₂**) (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 **Y₂K₂-biph** with yttrium and potassium coordinating to different rings was maintained in solution. The ¹H NMR spectra of **Y₂K₂-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 ¹H 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 ¹H, ¹³C chemical shifts is summarized in Table 4). In addition, ¹³C[¹H] NMR spectroscopy showed that the signals for the *ortho*- and *meta*-carbon atoms of the ring coordinating to yttrium were

triplets due to coupling to ^{89}Y ; the *para*- and *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 **Y₂K₂-biph**, no fluxional behavior was observed in solution. In addition, the isolation of the 18-crown-6 version of **Y₂K₂-biph**, $[\text{K}(\text{18-crown-6})(\text{THF})_{1.5}]_2[[(\text{NN}^{\text{TBS}})\text{Y}]_2(\mu\text{-biphenyl})]$ (**Y₂-biph-K₂-crown₂**, 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, **Y₂K₂-biph** was formed exclusively even when sub-stoichiometric amounts of KC_8 were used and the comproportionation reaction between $(\text{NN}^{\text{TBS}})\text{YI}(\text{THF})_2$ and **Y₂K₂-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 **Y₂K₂-biph** and **Y₂-biph-K₂-crown₂**. Adapted from Huang et al. (2013). Copyright © 2013, Rights Managed by Nature Publishing Group.

The structural motif of **Y₂K₂-biph** was not restricted to yttrium and/or biphenyl: other group 3 metals, namely, scandium, lanthanum, and lutetium formed **Sc₂K₂-biph**, **La₂K₂-biph**, and **Lu₂K₂-biph**, respectively, following a synthetic protocol analogous to that for **Y₂K₂-biph** (Figure 18). These compounds show ¹H and ¹³C NMR spectra and solid-state molecular structures similar to **Y₂K₂-biph**. Other non-fused arenes (Scheme 7) such as *p*-terphenyl or 1,3,5-triphenylbenzene

(TPB) led to $[(\text{NN}^{\text{TBS}})\text{Y}]_2[\text{K}(\text{THF})_2]_2[\mu-(p\text{-terphenyl})]$ (**Y₂K₂-terph**) and $[(\text{NN}^{\text{TBS}})\text{Lu}]_2[\text{K}(\text{THF})_2]_2[\mu\text{-}1,3,5\text{-C}_6\text{H}_3\text{Ph}_3]$ (**Lu₂K₂-TPB**, Ph = C₆H₅), respectively (Figure 19) (Huang et al., 2013). Table 4 summarizes the ¹H and ¹³C NMR chemical shifts of related substituted bridging benzene complexes. Table 5 compares the ¹H and ¹³C NMR chemical shifts with literature values for anionic biphenyl species. Table 6 summarizes the representative structural parameters for **M₂K₂-arene** complexes; while Table 7 compares those values with literature examples of anionic biphenyl or benzene species.

TABLE 4 Summary of ¹H and ¹³C NMR chemical shifts (in ppm) for **M₂K₂-biph** (M = Sc, Y, La, and Lu), and **Y₂K₂-terph**, **Lu₂K₂-TPB**, and **Y₂-biph-K₂-crown₂** (all measured at -40 to -50 °C) (Huang et al., 2013).^a

	Y₂K₂-biph	Sc₂K₂-biph	La₂K₂-biph	Lu₂K₂-biph	Y₂-biph-K₂-crown₂	Y₂K₂-terph	Lu₂K₂-TPB
H1	4.02	4.23	4.20	3.76	3.83	4.13	3.77
H2	3.85	4.17	3.89	3.59	3.76	3.82	3.77
H3	2.92	3.69	2.87	2.92	3.03	2.85	3.00
H8	6.06	6.53	5.81	6.03	6.27	5.96	6.24
H9	6.17	6.43	5.91	6.21	6.16	6.52	NA
H10	5.03	5.52	4.73	5.03	5.22	NA	5.60

H(T2, P2)	NA	NA	NA	NA	NA	7.00	7.26
H(T3, P3)	NA	NA	NA	NA	NA	6.86	7.59
H(T4, P4)	NA	NA	NA	NA	NA	6.42	7.15
C1	84.9	88.1	88.1	86.1	78.8	91.9	87.9
C2	68.4	78.1	73.7	72.3	67.4	70.4	73.1
C3	52.1	63.9	61.5	56.9	54.0	52.4	58.4
C4	76.0	79.8	82.0	78.2	74.7	85.3	81.4
C7	138.8	142.3	135.6	137.2	142.4	131.4	136.7
C8	114.3	116.7	113.8	114.2	115.8	115.1	112.2
C9	128.6	128.4	128.5	128.3	127.2	124.0	140.8
C10	103.2	108.5	100.0	102.1	106.5	110.1	94.5
T1(P1)	NA	NA	NA	NA	NA	140.6	144.2
T2(P2)	NA	NA	NA	NA	NA	119.6	126.0
T3(P3)	NA	NA	NA	NA	NA	128.5	128.5
T4(P4)	NA	NA	NA	NA	NA	118.4	126.4

^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 5 Comparison of ¹H and ¹³C chemical shifts (in ppm) for the coordinated biphenyl ring of **M₂K₂-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).^a

	Average for M₂K₂-biph	(biphenyl)²⁻	Y₂-biph	Y-biph-Y
H1	4.05	2.96	NA	4.2
H2	3.88	5.28	4.2	5.1

H3	3.10	3.96	4.2	4.5
H8	6.11	3.96	4.2	4.5
H9	6.18	5.28	4.2	5.1
H10	5.08	2.96		4.2
C1	86.8	74.2		
C2	73.1	128.5	110.5	
C3	58.6	104.6	104.0	
C4	79.0	102.3	136.8	
C7	138.5	102.3	136.8	
C8	114.8	104.6	104.0	
C9	128.5	128.5	110.5	
C10	103.5	74.2		

^a (biphenyl)²⁻ values are from reference (Huber et al., 1981); **Y₂-biph** and **Y-biph-Y** values were adopted from reference (Fryzuk et al., 1997), in which **Y₂-biph** had two yttrium ions coordinated to the same ring of the 4,4'-dimethylbiphenyl dianion and **Y-biph-Y** had two yttrium ions on different rings of the biphenyl dianion.

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).

	Y₂K₂- biph	Sc₂K₂- biph	Lu₂K₂- biph	Y₂-biph- K₂-biph	Y₂K₂- terph	Lu₂K₂- TPB
C1-C2	1.422	1.436	1.413	1.441	1.420	1.436
C2-C3	1.477	1.474	1.474	1.496	1.476	1.493
C3-C4	1.486	1.481	1.498	1.489	1.484	1.492
C4-C7	1.414	1.418	1.416	1.477	1.411	1.420
C7-C8	1.448	1.444	1.438	1.405	1.444	1.439
C8-C9	1.391	1.390	1.390	1.405	1.372	1.391
C9-C10	1.402	1.405	1.399	1.329 ^a	1.423	1.420
M-C1	2.547	2.367	2.512	2.536	2.569	2.511
M-C2	2.606	2.448	2.599	2.604	2.613	2.599
M-C3	2.487	2.319	2.395	2.453	2.502	2.403
M-C4	2.565	2.516	2.535	2.522	2.568	2.553
K-C(7-12)	3.066 - 3.189	3.064 - 3.344	3.079 - 3.205	NA	3.099 - 3.231	3.156 - 3.279
C10-T1(P1)	NA	NA	NA	NA	1.465	1.493
T1(P1)-T2(P2)	NA	NA	NA	NA	1.412	1.382
T2(P2)-T3(P3)	NA	NA	NA	NA	1.381	1.394
T3(P3)-T4(P4)	NA	NA	NA	NA	1.376	1.379
C8-C7-C12	115	114	115	117	113	115
C3-C4-C7-C8	-5	-8	3	1	4	-5

^a This value contains large errors due to the disorder of C9 and C10 atoms in **Y₂-biph-K₂-crown₂**.

TABLE 7 Comparison of C-C distances with reported examples (unit in Å).^a

	Average	Y-biph-Y	Y ₂ -biph	Cp ₂ La(C ₆ H ₆)K	(Cp ₂ Ln) ₂ (C ₆ H ₆)K	U ₂ -biph	U ₂ -tol	Calcd. C ₆ H ₆ ⁴⁻	Calcd. Ba ₂ (C ₆ H ₆)	C ₆ H ₆
C1-C2	1.429	1.415	1.404	1.459	1.45-1.47	1.422	av. 1.440	1.507	1.46	1.39
C2-C3	1.482	1.378	1.508	1.348	1.35-1.36	1.433				
C3-C4	1.489	1.453	1.416	1.468	1.44-1.46	1.467				
C4-C7	1.417	1.393	1.481	NA	NA	NA	NA	NA		NA
C7-C8	1.447		av. 1.384			1.404				
C8-C9	1.388					1.400				
C9-C10	1.428					1.358				
Angle in C₁₋₆ ring	118-122	NA	NA	110-124	112-124	NA	NA	120	120	120

^a 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 [(Cp[†]₂La)₂(μ-η⁶,η⁶-C₆H₆)]⁻ (Cassani et al., 1998); **(Cp₂Ln)₂(C₆H₆)K** represents [K(18-crown-6)][(Cp[†]₂Ln)(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. C₆H₆⁴⁻ 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 $\text{Y}_2\text{K}_2\text{-terph}$ (left) and $\text{Lu}_2\text{K}_2\text{-TPB}$ (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 $\text{Y}_2\text{K}_2\text{-biph}$ (a) and $\text{Y}_2\text{-biph-K}_2\text{-crown}_2$ (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-Y²⁻** (Si^tBuMe₂ was replaced by SiMe₃; potassium counter cations were omitted) of **Y₂K₂-biph** or **Y₂-biph-K₂-crown₂** 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 (π_4 and π_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-Y²⁻**, in agreement with the absence of fluxionality established experimentally (Huang et al., 2013).

FIGURE 21 HOMO and HOMO-1 of anion **2-Y²⁻** (C_2 symmetry) and frontier molecular orbitals in free biphenyl. Adapted from Huang et al. (2013). Copyright © 2013, Rights Managed by Nature Publishing Group.

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: $(\text{NN}^{\text{TBS}})\text{Y}(\text{THF})_2$ (**Y-I**), $(\text{NN}^{\text{TBS}})\text{Y}(\text{CH}_2\text{C}_6\text{H}_5)(\text{THF})_2$ (**Y-Bn**), and $(\text{NN}^{\text{TBS}})\text{Y}(\text{Cp})(\text{THF})$ (**Y-Cp**) together with **Y₂K₂-biph** and **Y₂K₂-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), **Y₂K₂-terph** (+213), **Y₂K₂-biph** (+189), **Y-Cp** (+69). These results confirmed the presence of a significant aromatic ring current in the phenyl ring coordinating to yttrium in **Y₂K₂-biph** and **Y₂K₂-terph** since ^{89}Y chemical shifts in **Y₂K₂-biph** and **Y₂K₂-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 $[(\text{NN}^{\text{TBS}})\text{M}(\text{THF})_x](\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_{10}\text{H}_8)$ (**M₂-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 $[(\text{NN}^{\text{TBS}})\text{M}](\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_5\text{Ph})[\text{K}(\text{solvent})]_2$ (**M₂K₂-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 **M₂-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 **M₂K₂-biph** and results in a 6C, 10 π -electron aromatic system. DFT calculations on the naphthalene and biphenyl complexes showed π overlap for the former and δ overlap for the latter between the metal orbitals and arene π^* orbitals.

The divergence in bonding modes observed for the bridged arene group 3 metal complexes supported by NN^{TBS} is unlike the situation described for diuranium inverse sandwich arene complexes of biphenyl, *p*-terphenyl, naphthalene, and (*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 δ 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; Mougél 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 $[(C_5Me_5)_2Sm]_2((E)\text{-stilbene})$ 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).

CHART 23 Rare earth alkene complexes reported by Evans's group.

Compound $[(\text{NN}^{\text{TBS}})\text{Y}(\text{THF})]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}(E)\text{-stilbene})$ (**Y₂-stilbene**) was obtained by KC_8 reduction of $(\text{NN}^{\text{TBS}})\text{YI}(\text{THF})_2$ in the presence of 0.5 equiv. (E) -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, $[(\text{NN}^{\text{TBS}})\text{Y}(\text{THF})][(E)\text{-stilbene}][\text{K}(\text{THF})]$ (**Y-stilbene-K**) was obtained in the presence of excess KC_8 (Scheme 9). The ion-separated pair $[(\text{NN}^{\text{TBS}})\text{Y}(\text{THF})](E\text{-stilbene})[\text{K}(18\text{-crown-6})]$ (**Y-stilbene-K-crown**) could also be structurally characterized (Figure 22).

SCHEME 9 Synthesis of **M₂-stilbene**, **Y-stilbene-K**, and transformation of **Y₂-stilbene** to **Y-stilbene-K**. Adapted with permission from The Royal Society of Chemistry from Huang et al. (2014).

In both molecular structures of **M₂-stilbene** (M = 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 η^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 $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2((E)\text{-stilbene})$ (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 **Y₂-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 **Y₂-stilbene** with that of its dianionic arene analogues (Huang et al., 2014). It was found that **Y₂-naph** is the strongest reducing agent while **Y₂-anth** is the weakest, with **Y₂-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 **Y₂-stilbene** and 2,2'-bipyridine (bipy) or phenylacetylene (PhCCH) resembled the reactivity of **Sc₂-naph** and yielded (NN^{TBS})Y(THF)(bipy) and [(NN^{TBS})Y(THF)][(NN^{TBS})Y](CCPh)₂ 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.

SCHEME 10 Relative reducing strength of **Y₂-stilbene**. Adapted with permission from The Royal Society of Chemistry from Huang et al. (2014).

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 **M₂-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.

FIGURE 23 HOMO (left) and HOMO-1 (right) for **Y₂-stilbene**. Reproduced with permission from The Royal Society of Chemistry from Huang et al. (2014).

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, 10 π -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

18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
2.2.2-cryptand	4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane
anth	anthracene
bipy	2,2'-bipyridine
biph	biphenyl
Bn	benzyl
COT ²⁻	cyclooctatetraene dianion, (η^8 -C ₈ H ₈) ²⁻
Cp ⁻	cyclopentadienyl anion, (η^5 -C ₅ H ₅) ⁻
Cp ^{*-}	pentamethylcyclopentadienyl anion, (η^5 -C ₅ Me ₅) ⁻
DME	1,2-dimethoxyethane

DFT	density functional theory
Et ₂ O	diethyl ether
fc	1,1'-ferrocenediyl
HOMO	highest occupied molecular orbital
<i>i</i> Pr	<i>iso</i> -propyl
IR	infra-red
KC ₈	potassium graphite
LUMO	lowest unoccupied molecular orbital
N ₂ N ^{py}	2,6-bis(2,6-di- <i>iso</i> -propylanilidomethyl)pyridine
nacnac	β-diketiminato
naph	naphthalene
NBO	natural bond orbital
NHC	N-heterocyclic carbene
NICS	nuclear-independent chemical shift
NMR	nuclear magnetic resonance (spectroscopy)
NN ^{fc}	see NN ^{TBS}
NN ^{TBS}	[fc(NSi ^{<i>i</i>} BuMe ₂) ₂] ²⁻
NN ^{TMS}	[fc(NSiMe ₃) ₂] ²⁻
OEP	octamethylporphrin
TACN	1,4,7-triazacyclononane
^{<i>t</i>} Bu	<i>tert</i> -butyl
terph	<i>p</i> -terphenyl
THF	tetrahydrofuran
TMTAC	1,3,5-trimethyl-1,3,5-triazacyclohexane
TPB	1,3,5-triphenylbenzene
XANES	X-ray absorption near edge structure

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(*E*)-stilbene, **1**
1,1' -ferrocenediyl 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**