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Advances in f element reductive reactivity as a paradigm for expanding lanthanide and actinide science and technology☆

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ABSTRACT

Although f element chemistry has progressed enormously since the time when it was investigated by F.H. Spedding, much still remains to be discovered in this area. This address will describe some recent developments in a fundamental type of f element reaction, reduction, that show just how much new chemistry is still to be discovered in a heavily studied area of f element chemistry that was thought to be mature. This lecture should serve to encourage new efforts to challenge conventional ideas in other "mature" areas of f element science and technology.

For 90 years, lanthanide-based reduction chemistry was accomplished with just three divalent ions, Eu^{2+}, Yb^{2+}, and Sm^{2+}. Now there are many new ways to accomplish molecular reductive chemistry equivalent to that of the traditional Ln^{2+} ions, but with all the metals in the lanthanide series, La–Lu. Several years ago such an idea would have been unthinkable. This lecture will describe the development of these new types of reduction and their implications in both lanthanide and actinide chemistry.

1. Introduction

The purpose of this Spedding Award Address and written summary is to stimulate *all* researchers to be highly ambitious in their efforts to expand their respective fields of activity. As research advances, there is a tendency to think that some fields are mature and that most of the major discoveries in these areas have already been made [1,2]. We need to remind ourselves that major breakthrough discoveries are always awaiting us and we must not complacently think that we are restricted only to incremental advances in knowledge in "mature" fields.

To illustrate this point, the major changes that have occurred in recent years in a fundamental type of reaction long studied in f element chemistry, namely reduction chemistry, will be described. Redox reactions along with acid–base reactions are the two most common types of processes in chemistry. They have been heavily studied and well developed. Consistent with this, the area of f element reduction chemistry was considered to be mature. However, as we shall see, many advances were waiting to be discovered.

These recent advances are even more surprising considering the surge of development in f element chemistry in recent years. As background for the discussion on recent reduction chemistry, it will be beneficial to examine the development of f element chemistry in a broader historical context. This will be presented in two parts: advances during the research career of Frank Spedding from 1929 to 1972 and developments from the early 1970s until the late 1990s, the point at which the discussion of recent developments in f element reduction chemistry will start. These historical perspectives have some important lessons for us as researchers. As I was preparing this address, I talked with a student who had not known that there was a time when most organometallic lanthanide chemistry was limited primarily to the smaller metals later in the series. They were surprised to learn that there was a time when working with a metal as large as samarium was pushing the outer limits of what was possible in organolanthanide chemistry. Since this type of information rarely gets published, it seemed worthwhile to consider the status of rare earth chemistry in some earlier times and to examine how our vision of the field has changed. Hopefully, this will encourage us to experiment boldly as we pursue the next wave of major advances in this field.

2. Background

It is difficult to imagine the state of f element chemistry when Spedding began his research career in 1929. Only a few points

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are presented here, but full details are available in a fascinating description of Spedding's research written by the 11th Spedding Awardee, John Corbett [3]. Spedding began his academic career just as the Great Depression hit. There were few jobs and little money for academic salaries. However, the major challenge in pursuing rare earth research in the 1930s was acquiring samples of lanthanide compounds. Spedding's first lanthanide research sample was obtained as a loan with the promise that it would not be consumed in any way! In the 1940s obtaining pure f element starting materials was a major goal. As part of the Manhattan project, Spedding's research involved the preparation of large amounts of pure uranium and later cerium and yttrium for nuclear applications. The following titles of papers illustrate how basic the f element chemistry was at that time; these were papers published from patents written in the 1940s that were later declassified.

> "The Preparation of Samarium and Yttrium Metals" J. Am. Chem. Soc. 75 (1953) 2272.
>
> "The Separation of Adjacent Rare Earths with Ethylenediaminetetra-acetic Acid by Elution from an Ion-exchange Resin" J. Am. Chem. Soc. 76 (1954) 612.
>
> "Vapor Pressure of Thulium Metal" J. Am. Chem. Soc. 79 (1957) 5160.

So much was unknown and awaited discovery in the f element area at that time. So many frontiers were available, that discovering new results retrospectively seemed easy.

From the start of Spedding's career in 1929 until 1972 when he retired, enormous development of the basic chemistry of the lanthanides occurred. Once the metals could be separated and obtained in pure form, the classical coordination chemistry of these metals could be explored. Tremendous progress was made in establishing the chemistry of these elements, primarily in aqueous solution, and many aspects appeared to be fully explored and mature. The chemistry was dominated by oxygen donor atom ligands and it appeared that the limits of metal ligand chemistry were well defined. As late as 1964, it was thought that Ln—N bonds were not very stable [4] and hence ligands with donor atoms other than oxygen were expected to contribute little additional chemistry to this area.

Given the dominance of oxygen ligands for the electropositive ionic lanthanides, the prospects for organometallic chemistry looked bleak. Despite major advances in the organometallic chemistry of the transition metals, only a few types of organolanthanide complexes were known. Review articles from that period in the early 1970s [5,6] focused only on the compounds in Scheme 1.

Tris(cyclopentadienyl) lanthanide complexes, $(C_5H_5)_3Ln$, had been made by Wilkinson in the 1950s [7,8] and by Fischer in the 1960s [9] as part of research programs focused not on the rare earths, but on the $(C_5H_5)^{1-}$ ligand. Some years later, Tsutsui made six (tris)indenyl analogs, $Ln(C_9H_7)_3$ [10]. Researchers at Ethyl Corporation, then in Detroit, reported $(C_5H_5)_3Eu$ [11] as well as complexes formulated as $(C_5H_5)_2LnCl$ [12] and $(C_5H_5)LnCl_2$ [13] as part of a project to find octane enhancing additives for gasoline. However, the bis- and mono-cyclopentadienyl complexes were available only for the smaller lanthanides, later in the series, specifically Sm–Lu. Bis(cyclopentadienyl) complexes of divalent Eu and Yb were synthesized by Fischer and Fischer [14] and the THF-insoluble samarium analog was later reported by Watt and Gillow [15]. Streitwieser's synthesis of uranocene, $(C_8H_8)_2U$, in 1968 [16] stimulated the field and cyclooctatetraenyl complexes of both trivalent [17–19] and divalent [20] lanthanides were subsequently reported. The only crystal structure of an organolanthanide with a Ln—C single bond was that of the aryl "ate" salt, $[Lu(2,6\text{-}Me_2C_6H_3)_4][Li(THF)_4]$, which was reported in 1972 [21].

In the early 1970s when Spedding retired and when I was starting my independent academic career (April 1, 1975), organolanthanide chemistry was limited to the few classes of compounds described above. There were no hydrides, no alkyls, and no catalysis. Retrospectively, there was much to be discovered, but at the time, the limits appeared to have been reached. For example, there was a pervasive view that the lanthanides early in the series were so large and so prone to ligand redistribution reactions, that only ligand sets involving three cyclopentadienyl ligands or cyclooctatetraenyl ligands would provide tractable compounds with the large lanthanides. The following quotes show that little organolanthanide chemistry was expected from with these early lanthanides.

Regarding the synthesis of $(C_5H_5)_2LnCl$ complexes [5]:

> "Any lanthanide from samarium through lutetium may be used in these reactions, but the light lanthanides, from lanthanum through neodymium, will not react....The compounds of the light lanthanides do not form."

1954-1956 $LnCl_3 + 3\,NaC_5H_5 \longrightarrow 3\,NaCl + \underline{(C_5H_5)_3Ln}$

Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

1963 $LnCl_3 + 2\,NaC_5H_5 \longrightarrow 2\,NaCl + \underline{(C_5H_5)_2LnCl}$ Ln = Sm, Eu, Gd, Dy, Ho, Yb

1963 $LnCl_3 + NaC_5H_5 \longrightarrow NaCl + \underline{(C_5H_5)LnCl_2}$ Ln = Sm, Gd, Dy, Ho, Er, Yb, Lu

1965 $Ln + 3\,C_5H_6 \longrightarrow C_5H_8 + \underline{(C_5H_5)_2Ln}$ Ln = Eu, Yb

1969 $LnCl_3 + 3\,NaC_9H_7 \longrightarrow 3\,NaCl + \underline{(C_9H_7)_3Ln}$ Ln = La, Sm, Gd, Tb, Dy, Yb

1969 $(C_5H_5)_3Sm + KC_{10}H_8 \longrightarrow KC_5H_5 + C_{10}H_8 + \underline{(C_5H_5)_2Sm(THF)}$

1969 $Ln + C_8H_8 \longrightarrow \underline{Ln(C_8H_8)}$ Ln = Eu, Yb

1970 $LnCl_3 + 2\,K_2C_8H_8 \longrightarrow 3\,KCl + \underline{[(C_8H_8)_2Ln]K}$ Ln = Ce, Pr, Nd, Sm, Tb

1971 $2\,LnCl_3 + 2\,K_2C_8H_8 \longrightarrow 4\,KCl + \underline{[(C_8H_8)LnCl(THF)_2]_2}$ Ln = Ce, Pr, Nd, Sm

1972 $LuCl_3 + 4\,LiC_6H_3Me_2\text{-}2,6 \longrightarrow 3\,LiCl + \underline{[(2,6\text{-}Me_2C_6H_3)_4Lu][Li(THF)_4]}$

Scheme 1. Organolanthanide complexes in the early 1970s.

$$2\,(C_5H_5)_3Ln + 3\,FeCl_2 \longrightarrow 3\,(C_5H_5)_2Fe + 2\,LnCl_3$$

$$[(C_8H_8)_2Ce]K + UCl_4 \longrightarrow (C_8H_8)_2U + CeCl_3 + KCl$$

Scheme 2. Organolanthanides act as alkali metal reagents with other metal halides.

Regarding the synthesis of $(C_5H_5)LnCl_2$ *complexes* [6]:

> "As was observed in the $(C_5H_5)_2MCl$ series, the compounds below samarium cannot be prepared."

Regarding $[Lu(2,6\text{-}Me_2\text{-}C_6H_3)_4]^{1-}$ [21]:

> "Our attempts to prepare analogous compounds of lighter lanthanides have so far failed."

In addition, both Wilkinson and Streitwieser had shown the cyclopentadienyl and cyclooctatetraenyl lanthanide complexes would react like alkali metal reagents and give up their organic ligands to other metals, Scheme 2. Hence their chemistry was thought to be analogous to alkali or alkaline earth metal chemistry and consequently quite limited.

Think about this situation! Organolanthanide chemistry was thought to be an area with limited potential. The complexes were considered to be highly reactive and difficult to handle due to high air and water sensitivity and a propensity to undergo ligand redistribution. The early metals did not form analogous complexes and samarium was the limit of what you could obtain in many cases. Lutetium was the limit in complexes with Ln—C single bonds.

Today we take for granted that we can use all of the lanthanides large and small for any type of organometallic chemistry we want. The chemistry is almost unlimited in terms of what ligands and donor atoms we can use. Certainly the introduction of the permethylated cyclopentadienyl ligand, $(C_5Me_5)^{1-}$, to lanthanide chemistry in the early 1980s [22–24] helped in this regard, but the organometallic chemistry of cyclopentadienyl-free metal complexes is now a major successful endeavor with many groups. In the early 1970s, it would have been inconceivable to build ancillary ligand platforms with nitrogen donor ligands, to do hydride much less polyhydride chemistry, to have a broad variety of alkyl complexes, and to have many varieties of organometallic catalysis.

Retrospectively, it is clear that there was much to discover in the 1970s. During Spedding's career, basic separation and purification was developed as well as aqueous and oxygen donor chemistry. Since Spedding's retirement, the non-aqueous and organometallic chemistry of the f elements flourished.

One can now ask, "Are there any major new developments still to be found in f element chemistry?" I will argue that the answer to that question is an emphatic "Yes!" I expect that there are just as many new opportunities waiting to be developed now as there were when Spedding started in 1929 or when I started in 1975. I predict that in 10 years the f element community will look back, just as we are now, and say "In 2008, the whole community thought this. . .but they did not realize that this whole new set of options was waiting to be discovered."

I can make that prediction because of what has happened in f element reduction chemistry in the past 10 years just in my own lab. This is the main topic described in the remainder of this article.

3. f element reduction chemistry before 1997

My view of lanthanide chemistry when I started research in this area can be summarized by the following statement from an early paper [25]:

Table 1

Properties of the most common divalent lanthanide ions traditionally available in solution as molecular species.

	$Ln^{3+} + e^{1-} \rightarrow Ln^{2+}$ ($E_{1/2}$ vs. NHE)	Electron configuration of Ln^{2+}	Ionic radius of eight coordinate Ln^{2+}
Eu^{2+}	−0.35 V	$[Xe]4f^7$	1.25
Yb^{2+}	−1.15 V	$[Xe]4f^{14}$	1.14
Sm^{2+}	−1.55 V	$[Xe]4f^6$	1.27

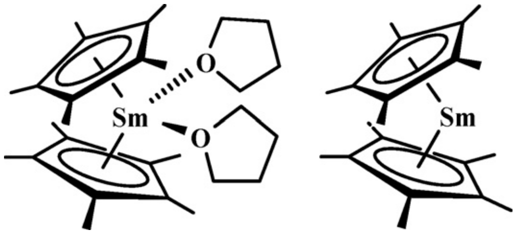


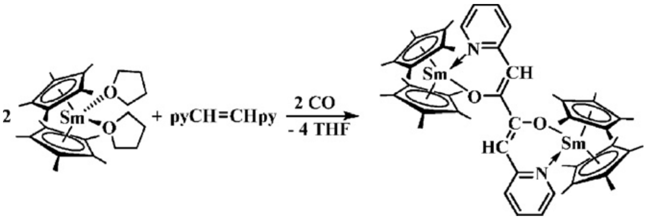
Fig. 1. $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$.

> "Although the lanthanide metals at times have been regarded as trivalent versions of the alkali and alkaline earth metals, and at other times have been compared to the transition metals, in fact, the lanthanides are unique. The radial properties, electronic properties, ionization potentials, and electron affinities of the lanthanide metals clearly distinguish them from any other metals. The challenge in the lanthanide area, therefore, is to place the lanthanide metals in chemical environments which allow exploitation of their chemical uniqueness."

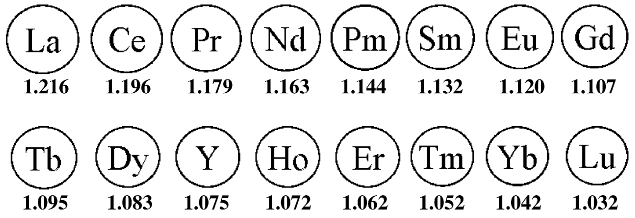
To develop the new chemical environments, my group and I focused on reductive lanthanide chemistry [26–30]. The three divalent ions that were available in solution when I started my career were Eu^{2+}, Yb^{2+}, and Sm^{2+} as shown in Table 1 [31].

We sought to develop the chemistry of the most reactive of those three ions, Sm^{2+}, and this proved to very productive. We were able to synthesize the first soluble, crystallographically characterizable, metallocene of Sm^{2+}, namely the solvated $(C_5Me_5)_2Sm(THF)_2$, [32,33] and subsequently, the surprisingly bent, unsolvated decamethylsamarocene, $(C_5Me_5)_2Sm$, Fig. 1 [34,35]. A wealth of new chemistry was provided to the f elements from just these two divalent compounds [28–30].

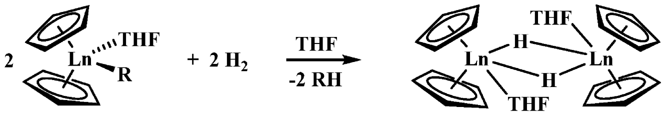
To illustrate the capacity of these compounds to open up new f element chemistry and to show the importance of reductive chemistry to the f element field, two examples of Sm^{2+} reactivity are shown in Eqs. (1) [36] and (2) [37]. The first reaction is unusual in



(1)

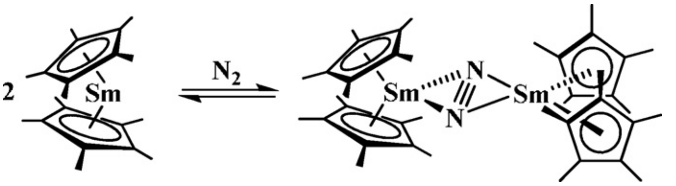


Scheme 3. Ionic radii (Å) for 9-coordinate trivalent lanthanide ions (circles drawn to scale to show the relative size of each ion).



	Metal Radius	Yield of Hydride Product	Reaction Time
$(C_5H_5)_2ErMe(THF)$	1.004 Å	55%	24 h
$(C_5H_5)_2YbMe(THF)$	0.985 Å	trace	24 h

Scheme 4. Sensitivity of hydrogenolysis reactivity to metal radius.



(2)

that the alkene and carbon monoxide substrates were not expected to have significant reactivity with the ionic lanthanides at the time this reaction was discovered. Due to the limited radial extension of the 4f orbitals [38], little backbonding was expected between π acceptor ligands like these and the lanthanides. Consequently, little reactivity was expected. The transformation shown is a unique way to effect a double homologation of a C=C double bond.

Eq. (2) shows how Sm^{2+} reductive chemistry provided the first dinitrogen complex of an f element [37]. Again, due to the limited radial extension of the 4f orbitals, such dinitrogen complexes were unexpected. Of broader importance was the fact that this was the first example of a new coordination mode between dinitrogen and metals of any kind. The $M_2(\mu-\eta^2:\eta^2-N_2)$ co-planar arrangement of two metals and the two nitrogens had never been observed before in metal dinitrogen chemistry [39].

$(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ also provided distinctive chemistry with CO [40], CO_2 [41], azobenzene [42], and alkynes [43,44] among others [30,45]. We expected that compounds of this type and Sm^{2+} would continue to define the leading edge of f element reduction chemistry. However, there were also many reactions involving these compounds in which fully definable products were not obtainable. Although neither Sm^{2+} nor Sm^{3+} are highly paramagnetic ($\mu = 3.5$ and 1.7 BM, respectively [46]), this paramagnetism limited the amount of definitive information that could be obtained from NMR spectroscopy. Unless crystals suitable for X-ray crystallography could be grown, it was often not possible to define the new reduction chemistry. A common solution to this problem in trivalent lanthanide chemistry is to change the size of the metal to get quality single crystals. Frequently, the size of a given ligand set does not match the size of all the metals in the series to give high quality crystals for each metal. Choosing from among the many options shown in Scheme 3 [47] can provide such crystals. However, this option is not available for Sm^{2+} reductive chemistry. Only two other divalent ions, Eu^{2+} and Yb^{2+}, were available and they were significantly less reducing than Sm^{2+}, Table 1.

This metal size optimization is important not only for obtaining crystals, but it often can determine the success or failure of a reaction. Scheme 4 [48] shows one of many examples in the literature [49–51]. In this case, an erbium alkyl is readily hydrogenolyzed to a hydride, but the analogous reactions fails for the slightly smaller ytterbium, even though the hydride product is known and accessible by other routes.

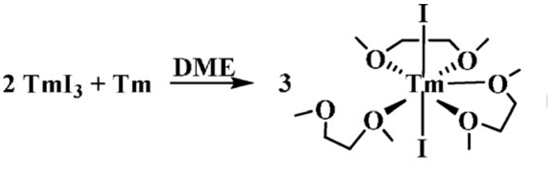
Hence, one of the limitations of Sm^{2+} reductive chemistry is that it could not be size optimized based on the metal. Prior to 1997, this problem seemed insurmountable. The outlook for reductive Sm^{2+} chemistry in 1997 was that it was a productive area that would continue to grow by variation of substrate, reaction conditions, and ligands on the Sm^{2+} complexes. Since it was well established that Nature had provided only three divalent ions that were accessible in solution and since Sm^{2+} was the most reactive, this was the only option.

The following sections show that this narrow view of lanthanide reduction chemistry was far too limited. The assumption that reductive lanthanide chemistry was restricted only to Eu^{2+}, Yb^{2+}, and Sm^{2+} has been overturned by the discovery of *five* different ways of accomplishing the equivalent of this Ln^{2+} reductive reactivity.

4. New molecular divalent oxidation states in solution

The first development involved the discovery that divalent ions besides Eu^{2+}, Yb^{2+}, and Sm^{2+} were available in solution for reaction chemistry. The first example involves Tm^{2+}. This $4f^{13}$ ion is the next most likely divalent ion to be accessible based on its calculated redox potential of −2.3 V [31]. However, since it was much more reducing than Sm^{2+} and all previous reports on Tm^{2+} described highly colored solutions that had only transient existence [52–55], it was assumed that it was too reactive to use in solution reaction chemistry.

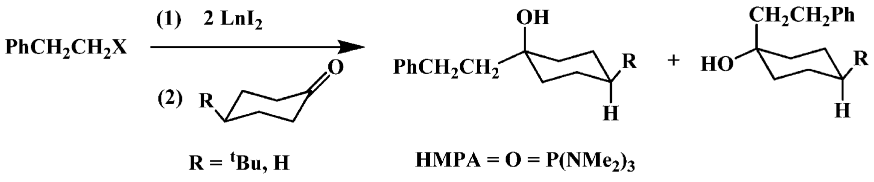
When Professor Mikhail N. Bochkarev of Nizhny Novgorod, Russia suggested to me that we collaborate to obtain structural information on what he thought was the first example of an isolable molecular Tm^{2+} complex, I was skeptical. Although initial attempts to obtain crystallographic data on samples of “TmI_2″ were unsuccessful, preparation of a fresh sample made in our lab by the Bochkarev method [56], provided the first example of a molecular divalent thulium complex, $TmI_2(DME)_3$, Eq. (3) [57].



$TmI_2(DME)_3$

(3)

This was a very exciting development since Tm^{2+} was more reactive than the Sm^{2+} ion that had given a broad range of new chemistry to the lanthanide area. However, for the next three years neither my lab nor the Bochkarev lab obtained any significant new reductive reactivity from this Tm^{2+} complex [56,58–60,61]. The intensely colored green compound reacted quickly with many substrates to give colorless Tm^{3+} products, but TmI_3 was the only product readily identified. These results suggested that Tm^{2+} might be too reactive to provide useful divalent lanthanide chemistry as had been assumed prior to the discovery of $TmI_2(DME)_3$ and the latter complex might be just an anomaly.

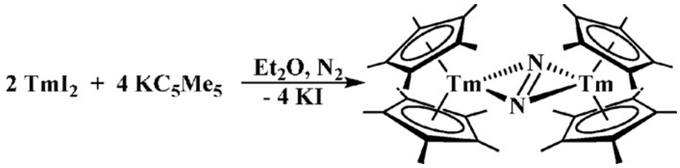


Reagent	X	Time	Isolated Yield
SmI_2/HMPA	I	<1 min	92%
TmI_2	I	<1 min	99%
SmI_2/HMPA	Br	15 min	65%
TmI_2	Br	<1 min	92%
SmI_2/HMPA	Cl	18 h	(no reaction)
TmI_2	Cl	<3 min	95%

Scheme 5. *In situ* $TmI_2(DME)_x$ reactivity with alkyl halides relative to SmI_2/HMPA.

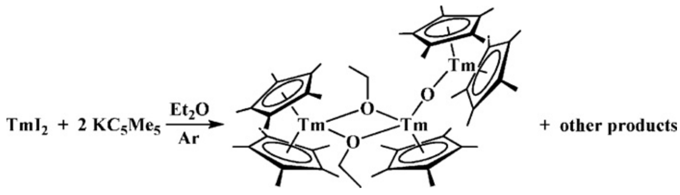
However, a breakthrough in Tm^{2+} chemistry occurred when attempts were made to use it *in situ* [62]. Examination of alkyl halide ketone coupling reactions effective with SmI_2/HMPA (HMPA = hexamethylphosphoramide), Scheme 5, *in situ* showed that TmI_2 could effect equivalent results without the carcinogenic HMPA additive. Moreover, TmI_2 could couple alkyl chlorides that were unreactive with SmI_2/HMPA [62].

Subsequent attempts to use the *in situ* method to accomplish organometallic chemistry with Tm^{2+} revealed the reason that Tm^{2+} chemistry previously had been so intractable. Efforts to make the thulium analog of $(C_5Me_5)_2Sm$ for *in situ* reactions by addition of two equivalents of KC_5Me_5 to a TmI_2 solution resulted in a reduction reaction before a substrate could be added! The addition of KC_5Me_5 to TmI_2 resulted in the reduction of the dinitrogen atmosphere that had been assumed to be inert, Eq. (4) [63]. As described later, the reduction of dinitrogen by addition of ligands to TmI_2 is quite general. Hence, the rapid fading of the intense color of Tm^{2+} solutions observed in previous attempts to make Tm^{2+} derivatives presumably occurred because dinitrogen was being reduced.



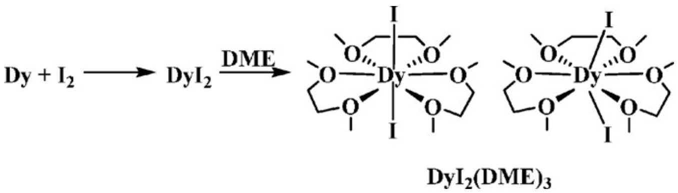
(4)

Examination of Tm^{2+}, *in situ*, under argon instead of the reactive dinitrogen, demonstrated the high reactivity of this ion. Eq. (5) shows that Tm^{2+} can cleave diethyl ether to make ethoxide and oxide ligands [63].



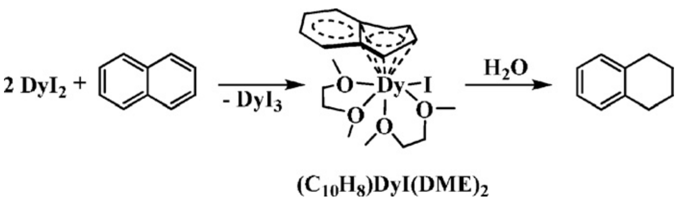
(5)

Once it was established that Tm^{2+} could be accessed in solution, the assumptions that Dy and Nd were too unstable to be isolated as molecular species were suspect. It should be noted that TmX_2, DyX_2 and NdX_2 (X = Cl, Br, I) had all been identified previously in the solid state and had been shown to contain divalent ions [64,65]. Encouraged by the Tm^{2+} result, the synthetic method of Bochkarev and Fagin [56] was used in our lab to obtain crystallographic data on the first molecular complex of Dy^{2+}, Eq. (6) [66]. Both linear and bent DyI_2 components were observed in the same single crystal as had previously been found with the isomorphous samarium analog [61].



(6)

Like TmI_2, DyI_2 in the presence of cyclopentadienyl salts reduces dinitrogen in analogy to Eq. (4) above [67]. However, the more reducing Dy^{2+} is also capable of reducing naphthalene as shown in Eq. (7) [66]. Hydrolysis of the $(C_{10}H_8)^{2-}$ product to dihydronaphthalene parallels the type of reactivity found in Birch reductions [68]. However, with Dy^{2+}, an ether soluble molecular species can be used instead of an alkali metal in liquid ammonia.



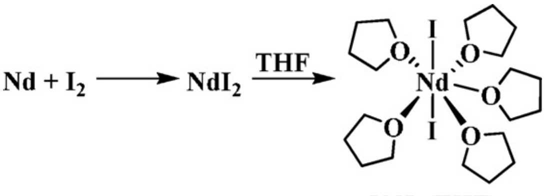
(7)

The first molecular complex of Nd^{2+} was subsequently identified by Professor Bochkarev and Professor Schumann of the Technical

Table 2
Properties of the most common divalent lanthanide ions available in solution as molecular species.

	$Ln^{3+} + e^{1-} \rightarrow Ln^{2+}$ ($E_{1/2}$ vs. NHE)	Electron configuration of Ln^{2+}	Ionic radius of eight coordinate Ln^{2+}
Eu^{2+}	−0.35 V	$[Xe]4f^7$	1.25
Yb^{2+}	−1.15 V	$[Xe]4f^{14}$	1.14
Sm^{2+}	−1.55 V	$[Xe]4f^6$	1.27
Tm^{2+}	−2.3 V	$[Xe]4f^{13}$	1.09
Dy^{2+}	−2.5 V	$[Xe]4f^{10}$	1.19
Nd^{2+}	−2.6 V	$[Xe]4f^4$	1.29

University of Berlin, Eq. (8) [69].



NdI$_2$(THF)$_5$ (8)

Taken all together this meant that the number of divalent ions available in soluble form for lanthanide-based reductions had doubled from 1997 to 2001. After some 90 years of using Table 1, Table 2 became the appropriate list of divalent ions for which fully characterized molecular compounds were available. Imagine if someone suggested that in the next few years the number of oxidation states you commonly use would double. This seems impossible. However, it happened in lanthanide chemistry.

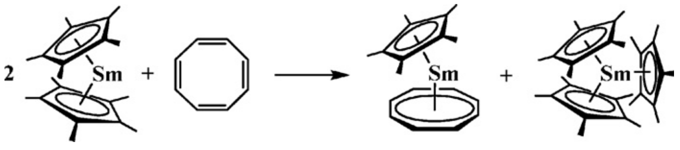
Although the number of divalent oxidation states accessible in solution had doubled, size optimization of the Sm^{2+} reductive chemistry was still not possible. Although six divalent ions were now available and had different sizes, the Ln^{2+} ions also had significantly different reaction chemistry. Size optimization of Sm^{2+}-like chemistry awaited further advances in reductive lanthanide chemistry.

5. Sterically induced reduction

A second major development in reductive lanthanide chemistry arose from a series of sterically crowded complexes that we have termed “long bond organometallics.” This class of complexes was discovered in the course of defining the reductive chemistry of $(C_5Me_5)_2Sm$ [34,35]. Reactions of $(C_5Me_5)_2Sm$ with unsaturated hydrocarbons of known redox potentials were being studied to define the reductive capacity indirectly since solution electrochemistry with these species was so challenging [70]. The reaction of $(C_5Me_5)_2Sm$ with 1,3,5,7-cyclooctatetraene was investigated because it was anticipated that two equivalents of $(C_5Me_5)_2Sm$ would reduce C_8H_8 to a dianion, Eq. (9), and the resulting “$[(C_5Me_5)_2Sm]_2(C_8H_8)$” composition would be very crowded and could display unusual structure or reactivity.

$$C_8H_8 + 2e^{1-} \rightarrow (C_8H_8)^{2-} \qquad (9)$$

As shown in Eq. (10), C_8H_8 is reduced in this reaction to $(C_8H_8)^{2-}$ but a monometallic product, $(C_8H_8)Sm(C_5Me_5)$, is isolated not the bimetallic composition cited above. The components remaining after the stable $(C_8H_8)Sm(C_5Me_5)$ compound forms are three $(C_5Me_5)^{1-}$ ligands and Sm^{3+}. With no better way to satisfy their electrostatic needs these assemble to generate the first structurally characterized tris(pentamethylcyclopentadienyl) complex, $(C_5Me_5)_3Sm$, Fig. 2 [71].



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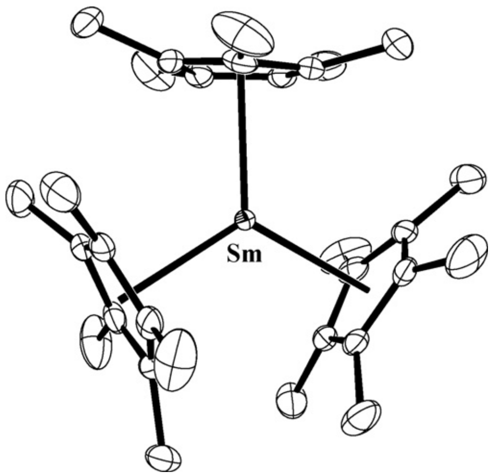


Fig. 2. Tris(pentamethylcyclopentadienyl) samarium, $(C_5Me_5)_3Sm$.

This was surprising since for decades it was assumed that it was impossible to put three of these large ligands around one metal center. As the cone angle of a $(C_5Me_5)^{1-}$ ring was estimated to be approximately 142° [72–74], $(C_5Me_5)_3M$ compounds seemed inaccessible because the sum of the cone angles would exceed 360°. Decades of studies on $(C_5Me_5)^{1-}$ chemistry by numerous research groups had not generated any $(C_5Me_5)_3M$ complexes.

However, the synthesis of $(C_5Me_5)_3Sm$ showed that the cone angle of a $(C_5Me_5)^{1-}$ ligand could be 120° in some cases. How was this possible? One way to reduce the cone angle of a ligand is to move it further away from the metal as shown in Fig. 3. Indeed, the Sm–C(C_5Me_5) distances in $(C_5Me_5)_3Sm$ [71] were significantly longer than those observed in previously characterized Sm^{3+} complexes of $(C_5Me_5)^{1-}$. The 2.82 (5) Å average was larger than the typical averages, 2.71 (2)–2.75 (2) Å [75], and the three crystallographically independent Sm-C(C_5Me_5) distances displayed the larger than normal values of 2.782 (2), 2.817 (2), and 2.910 (3) Å. Bending the methyl substituents back out of the plane of the $(C_5Me_5)^{1-}$ ring would also reduce the cone angle. Subsequent analyses have shown that this is a complicated situation in these long bond organometallics in which only one of the three crystallographically unique methyl groups has unusual bending out of the plane [76].

Since the $(C_5Me_5)^{1-}$ rings are much further from the Sm^{3+} cation than in conventional complexes, the electrostatic stabilization of the rings is not optimal. Consequently, the rings are much

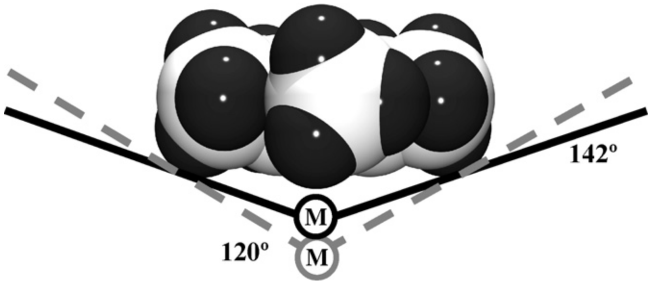
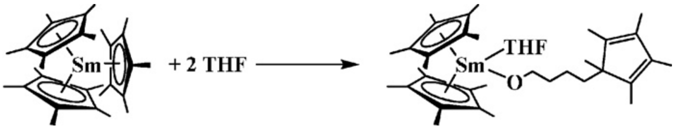
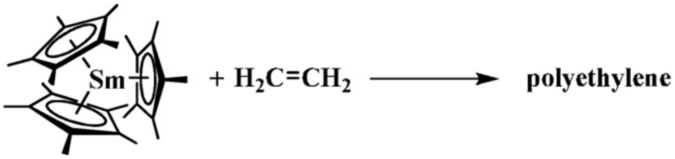


Fig. 3. Effect of changing the metal cyclopentadienyl distance on cone angle.

more reactive than those in “sterically normal” complexes. This enhanced reactivity is observed in several types of unusual reactions. Eqs. (11)–(14) show that the $(C_5Me_5)^{1-}$ rings in $(C_5Me_5)_3Sm$ can ring open THF [77], initiate the polymerization of ethylene [77], engage in the first example of insertion chemistry between CO and $(C_5Me_5)^{1-}$ ligands [78], and undergo hydrogenolysis [77].



(11)



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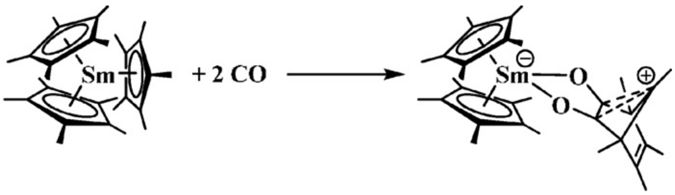
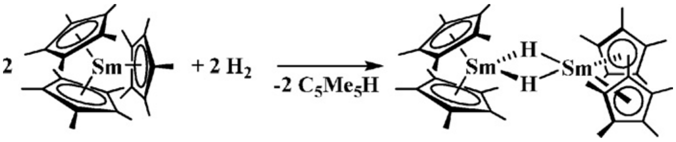
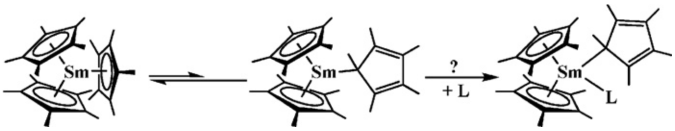


(13)



(14)

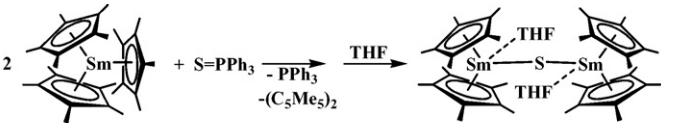
Eqs. (11)–(14) can be rationalized if an η^1-intermediate such as $(\eta^5\text{-}C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)$ is accessible, Eq. (15), since the reactivity is consistent with that of a Ln—C single bond.



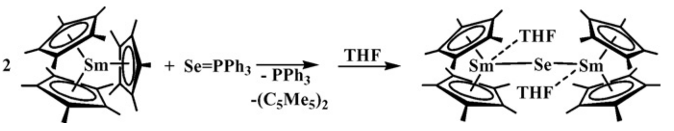
(15)

In efforts to obtain structural evidence for an η^1-complex such as $(C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)L$, $(C_5Me_5)_3Sm$ was reacted with numerous ligands, L. This revealed a new type of reduction chemistry.

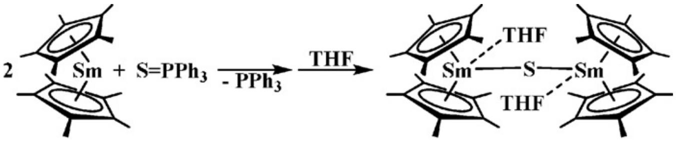
When ligands such as $O{=}PPh_3$, $S{=}PPh_3$, and $Se{=}PPh_3$ were added to $(C_5Me_5)_3Sm$, the ligands were reduced [77]. Eqs. (16) and (17) show that $S{=}PPh_3$ and $Se{=}PPh_3$ are reduced to PPh_3 and $(S)^{2-}$ or $(Se)^{2-}$ complexes previously synthesized by reduction of $S{=}PPh_3$ and $Se{=}PPh_3$ with the divalent $(C_5Me_5)_2Sm$, Eqs. (18) and (19) [79].



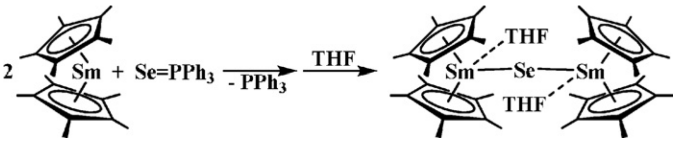
(16)



(17)



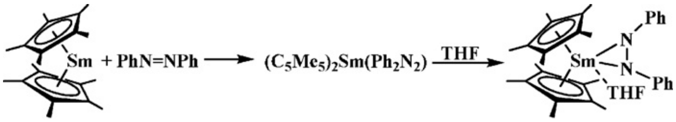
(18)



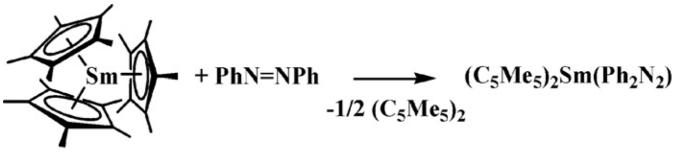
(19)

Reactions (16) and (17) are analogous to reactions (18) and (19), respectively, with identical stoichiometries and samarium products. The difference is that the reductions in Eqs. (16) and (17) are accomplished with a trivalent samarium complex, not the divalent complex of Eqs. (18) and (19).

The parallel reaction chemistry of trivalent $(C_5Me_5)_3Sm$ and divalent $(C_5Me_5)_2Sm$ was also observed with other types of substrates. Eqs. (20) and (21) show that $(C_5Me_5)_3Sm$ reduces azobenzene [77] to the same product obtained by the reaction of one equivalent of $(C_5Me_5)_2Sm$ with azobenzene [42].

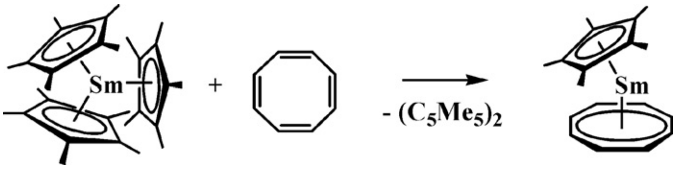


(20)



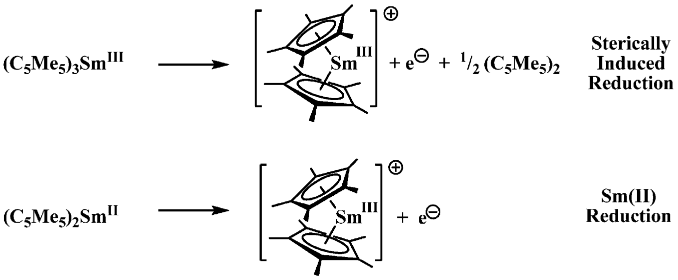
(21)

1,3,5,7-C_8H_8 is also reduced similarly. Hence, $(C_5Me_5)_3Sm$ reduces C_8H_8 to form a $(C_8H_8)^{2-}$ dianion, Eq. (22) [77], in a reaction parallel to that originally used to make $(C_5Me_5)_3Sm$ from C_8H_8 and $(C_5Me_5)_2Sm$, Eq. (10) [71].



(22)

Since the reductions in Eqs. (16), (17), (21) and (22) were occurring without a change in the metal oxidation state, i.e. both



Scheme 6. Comparison of sterically induced reduction (SIR) vs. traditional divalent Sm^{2+} reduction.

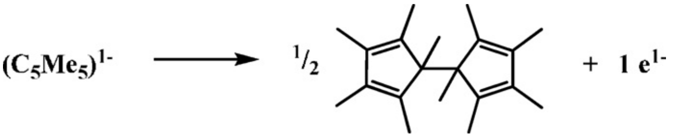
reactants and products contained Sm^{3+}, this meant that the formal reducing agent must be the ligand, $(C_5Me_5)^{1-}$. Consistent with this, $(C_5Me_5)_2$ is found as a byproduct of the above reactions and the fully balanced transformations are shown in Eqs. (23)–(26). If the $(C_5Me_5)^{1-}$ ligand acted as a one-electron reductant to generate an electron and a C_5Me_5 radical, the dimerized product $(C_5Me_5)_2$ would be expected, Eq. (27).

$$2(C_5Me_5)_3Sm + S{=}PPh_3 \xrightarrow[-PPh_3]{THF} [(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}S) + (C_5Me_5)_2 \tag{23}$$

$$2(C_5Me_5)_3Sm + Se{=}PPh_3 \xrightarrow[-PPh_3]{THF} [(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}Se) + (C_5Me_5)_2 \tag{24}$$

$$(C_5Me_5)_3Sm + PhN{=}NPh \rightarrow (C_5Me_5)_2Sm[\eta^2\text{-}(N,N')\text{-}(PhNNPh) + \tfrac{1}{2}(C_5Me_5)_2 \tag{25}$$

$$2(C_5Me_5)_3Sm + 1,3,5,7\text{-}C_8H_8 \rightarrow (C_5Me_5)Sm(C_8H_8)] + (C_5Me_5)_3Sm + (C_5Me_5)_2 \tag{26}$$

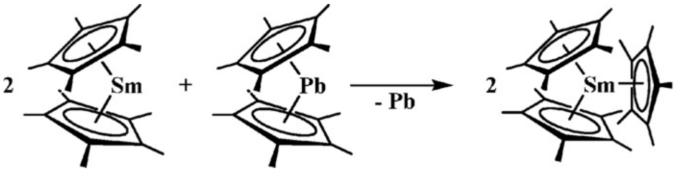


(27)

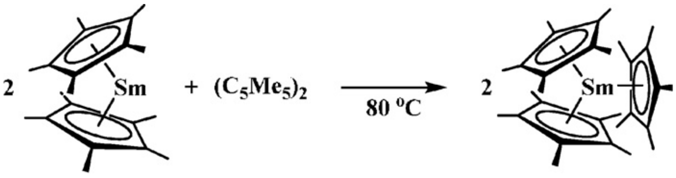
The reason that $(C_5Me_5)_3Sm$ effects reduction analogous to $(C_5Me_5)_2Sm$ is that both reagents provide one electron and form a $[(C_5Me_5)_2Sm]^{1+}$ cation that can complex the reduced substrate, Scheme 6. Since the $(C_5Me_5)^{1-}$ reduction reaction, Eq. (27), has only been observed in sterically crowded molecules, it has been termed sterically induced reduction (SIR) [30].

The sterically induced reduction observed with $(C_5Me_5)_3Sm$ suggested that with the right amount of steric crowding, reduction could be accomplished without the need for a divalent metal ion. If $(C_5Me_5)_3Sm$ is a reductant only because of the steric crowding, then other $(C_5Me_5)_3Ln$ complexes could also be reductants. If $(C_5Me_5)_3Ln$ complexes could be made and had reduction chemistry analogous to $(C_5Me_5)_2Sm$, this would allow size optimization of this $(C_5Me_5)_2Sm$ chemistry for the first time. Sm^{2+} reductive reactivity would be available to all of the lanthanides and the metal could be selected, not because it had a divalent ion, but because it had the desired crystallizability or optical and magnetic properties.

The extension of SIR to the other lanthanides initially was problematic since the only routes to $(C_5Me_5)_3Sm$ involved the special reactivity of Sm^{2+} precursors, i.e. Eq. (10) [71] above and Eq. (28) [80] and 29 [81].

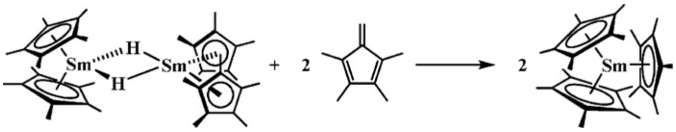


(28)



(29)

However, this synthetic barrier was overcome by identifying two additional synthetic routes to $(C_5Me_5)_3Sm$ that started with trivalent precursors, $[(C_5Me_5)_2SmH]_2$ [82] and $(C_5Me_5)_2Sm(\mu\text{-}Ph_2BPh_2)$ [83], Eqs. (30) [84] and (31) [83], respectively. In both of these reactions, as in Eqs. (10), (28) and (29), and virtually all the syntheses subsequently discovered for $(C_5Me_5)_3M$ complexes (vide infra), a stable byproduct is made that leaves three $(C_5Me_5)^{1-}$ rings and the M^{3+} with no better alternative than to form a sterically crowded $(C_5Me_5)_3M$ complex. In Eq. (30), the combination of a hydride ligand and tetramethylfulvene makes a stable $(C_5Me_5)^{1-}$ entity and leaves the $[(C_5Me_5)_2Sm]^{1+}$ ion and the $(C_5Me_5)^{1-}$ product [84]. In Eq. (31), $KBPh_4$ forms leaving $[(C_5Me_5)_2Sm]^{1+}$ and $(C_5Me_5)^{1-}$ [83].



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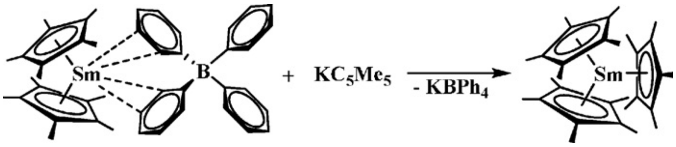
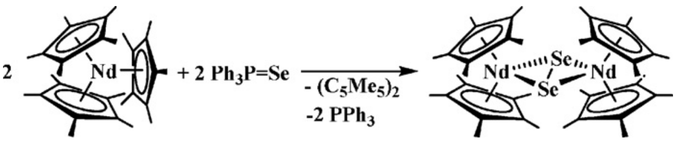


(31)

The metallocene cation route in Eq. (31) was initially used to generate $(C_5Me_5)_3Nd$ [83], which allowed an examination of sterically induced reduction with a metal other than samarium. Although SIR appeared to be based on steric crowding, with $(C_5Me_5)_3Sm$, there was the possibility that the reaction was occurring via an undetected Sm^{2+} intermediate.

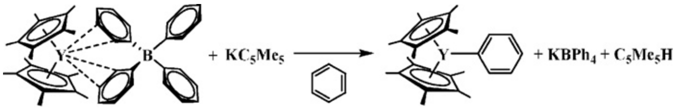
Trivalent $(C_5Me_5)_3Nd$ is in fact a reducing agent as shown with $Se{=}PPh_3$ in Eq. (32) [85], but it does not generate a reduction product analogous to that in the $(C_5Me_5)_3Sm$ reaction, Eq. (17).



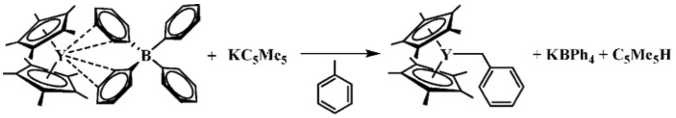
(32)

Along with $(C_5Me_5)_2$ and PPh_3, a $(Se_2)^{2-}$ organolanthanide product is formed instead of the $(Se)^{2-}$ product in Eq. (17). This indicated that $(C_5Me_5)_3Nd$ was a reductant, but was not as powerful as $(C_5Me_5)_3Sm$. Since $(C_5Me_5)_3Nd$ is not as sterically crowded as $(C_5Me_5)_3Sm$, this suggested that SIR could be moderated by the degree of steric crowding. This meant that metal size optimization could be used to control the reducing capacity of these sterically crowded complexes. Subsequent syntheses of $(C_5Me_5)_3Ln$ complexes of La, Ce, Pr, and Gd via Eq. (31) allowed this aspect to be examined further and the data indicate that reduction capacity can be modulated by varying the size of the metal and consequently the amount of steric crowding [81].

Extension of Eq. (31) to the larger metals, La and Ce, which have less crowded $(C_5Me_5)_3Ln$ complexes was surprisingly more difficult than the syntheses of $(C_5Me_5)_3Nd$ and $(C_5Me_5)_3Sm$. It was essential to use silylated glassware and freshly recrystallized $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ with the larger metals [81,86]. Synthesis of $(C_5Me_5)_3Ln$ complexes of the smaller metals, proved to be even more challenging. Application of Eq. (31) to yttrium did not yield $(C_5Me_5)_3Y$, but instead formed $(C_5Me_5)_2YPh$ in benzene, Eq. (33), and $(C_5Me_5)_2YCH_2Ph$ in toluene, Eq. (34) [87]. C_5Me_5H was the byproduct.

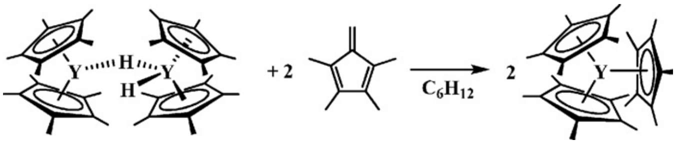


(33)

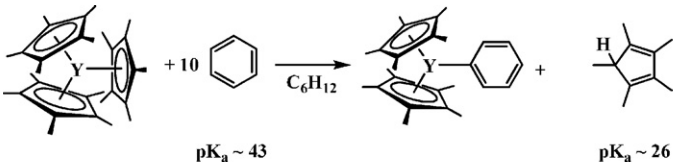


(34)

Formation of C_5Me_5H (pK_a = 26) from benzene (pK_a = 43) and toluene (pK_a = 40) was surprising. To avoid the use of arene solvents, the synthesis of $(C_5Me_5)_3Y$ was attempted from the hydride $[(C_5Me_5)_2YH]_2$ and tetramethylfulvene according to Eq. (35). This provided $(C_5Me_5)_3Y$, the most crowded $(C_5Me_5)_3M$ isolated to date. Subsequent reaction of pure, isolated $(C_5Me_5)_3Y$ with benzene generated $(C_5Me_5)_2YPh$ and C_5Me_5H, Eq. (36), and demonstrated that the steric crowding was severe enough to allow $(C_5Me_5)^{1-}$ to engage in C—H bond activation of benzene. Attempts to isolate $(C_5Me_5)_3Lu$ have not yet been successful, but have led to additional unusual C—H bond activation chemistry [88].



(35)



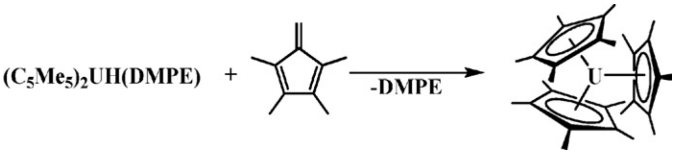
(36)

The results obtained with the $(C_5Me_5)_3Ln$ complexes show that the one-electron reduction chemistry of divalent $(C_5Me_5)_2Sm$ can be extended across the lanthanide series from La to Y by synthesizing sterically crowded tris(pentamethylcyclopentadienyl) complexes. In addition, the reduction capacity appears to be tunable by varying the amount of steric crowding. Hence, the powerful aspect of metal size optimization can be applied to reduction chemistry.

The results obtained with the $(C_5Me_5)_3Ln$ complexes show more generally that new ligand reactivity can be accessed by making sterically crowded complexes. It seems that this result should not be limited only to $(C_5Me_5)_3M$ complexes and could be quite general for ligands with reducing capacity. An example of SIR with a $(C_5Me_5)_2M$(large ligand) is described below and it is expected that complexes such as (large ligand)$_2M(C_5Me_5)$ and even (large ligand)$_xM$ could also display sterically induced reduction if the ligands are sufficiently reducing. In fact it seems plausible that sterically induced reduction reactivity has been observed before, but perhaps was not recognized. Attempts to synthesize sterically crowded complexes that gave unexpected reduction products or C—H bond activation products or ring-opened products, might have remained unpublished because the results did not make sense. It is possible that the sterically crowded product did form in these reactions and then went on to do unexpected chemistry.

6. Multi-electron reduction by combining SIR with metal based reduction

The synthesis of $(C_5Me_5)_3U$ via Eq. (37) [84] provided an opportunity to determine if sterically induced reduction could be combined with metal based reduction. $(C_5Me_5)_3U$ has U–C(C_5Me_5) distances that are much longer than those in previously observed $(C_5Me_5)^{1-}$ complexes of U^{3+} and is sterically crowded enough to do SIR. However, the U^{3+} ion is redox active on its own [89]. Hence, $(C_5Me_5)_3U$ could function as a two-electron reductant that converts a U^{3+} precursor to a U^{4+} product. It should be noted that once it was determined that $(C_5Me_5)_3U$ could exist, four other syntheses of were subsequently identified [90].



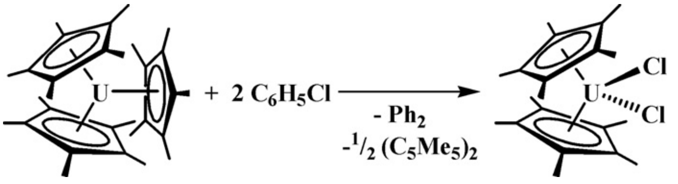
(37)

To examine the reductive capacity of $(C_5Me_5)_3U$, the 1:1 reaction of $(C_5Me_5)_3U$ and 1,3,5,7-C_8H_8 was studied since cyclooctatetraene can be reduced by two electrons, Eq. (9), that $(C_5Me_5)_3U$ could provide. A reaction occurred and formed $(C_5Me_5)_2$, the signature byproduct of sterically induced reduction, as well as a new uranium product, but some $(C_5Me_5)_3U$ starting material was left over. A clean reaction was obtained with a 2:3 $(C_5Me_5)_3U$:C_8H_8 ratio and the unusual mixed ligand product, $[(C_5Me_5)(C_8H_8)U]_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_8H_8)$, was isolated, Scheme 7 [91]. This product is structurally unique in that the $(C_8H_8)^{2-}$ ligand is not planar and is bound in a bis(allyl) mode in which one carbon is part of each coordinating allyl moiety.

The transformation in Scheme 7 is also unusual in terms of the reaction stoichiometry. Three equivalents of C_8H_8 are reduced to form the three $(C_8H_8)^{2-}$ ligands in the U^{4+} product, an overall six-electron reduction, but this was accomplished with just two equivalents of trivalent $(C_5Me_5)_3U$. Hence, this sterically crowded U^{3+} functions as a three-electron reductant to make U^{4+} complexes rather than acting as the two-electron reductant originally expected. Each $(C_5Me_5)_3U$ formally provides one electron from U^{3+}

and two electrons from sterically induced reduction involving two $(C_5Me_5)^{1-}$ ligands per uranium.

The fact that SIR could be combined with U^{3+} reduction raised the question of which redox process occurred first. Although most $(C_5Me_5)_3U$ reactions are too rapid to obtain this information, the reaction of $(C_5Me_5)_3U$ with chlorobenzene allowed the sequence to be determined [92]. $(C_5Me_5)_3U$ reacts with C_6H_5Cl primarily as a two-electron reductant to form $(C_5Me_5)_2UCl_2$, $(C_5Me_5)_2$, and biphenyl as primary products, Eq. (38).



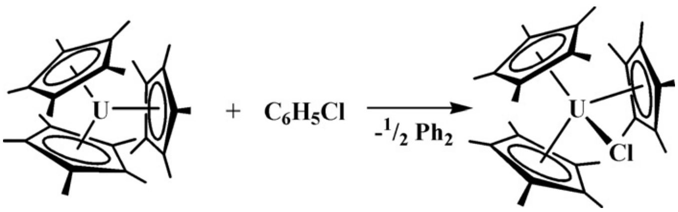
(38)

This reaction occurs in a stepwise fashion in which one equivalent of C_6H_5Cl reacts quickly to make an isolable intermediate, whereas the second equivalent reacts slowly to form $(C_5Me_5)_2UCl_2$ from the intermediate in Eq. (39). If the first reduction occurred

$$(C_5Me_5)_3U + C_6H_5Cl \rightarrow [\text{intermediate}] \xrightarrow{C_6H_5Cl} (C_5Me_5)_2UCl_2 \qquad (39)$$

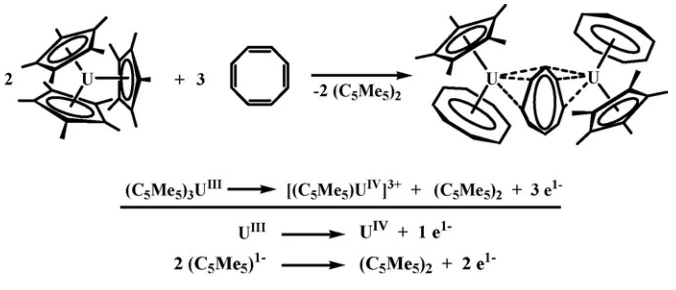
via SIR, the metal would stay at the +3 oxidation state, a $(C_5Me_5)^{1-}$ would be lost, the reduction product, Cl^{1-}, would be added, and the intermediate would be the known complex $[(C_5Me_5)_2UCl]_3$ [93]. If U^{3+} reduction occurred first, the intermediate would be a U^{4+} complex that still has three $(C_5Me_5)^{1-}$ rings and possibly the Cl^{1-} product. This product, "$(C_5Me_5)_3UCl$," would be much more crowded than the $(C_5Me_5)_3U$ starting material. Hence, it seemed most likely that SIR would occur first to make $[(C_5Me_5)_2UCl]_3$ as the intermediate.

As shown in Eq. (40), the isolated intermediate is $(C_5Me_5)_3UCl$

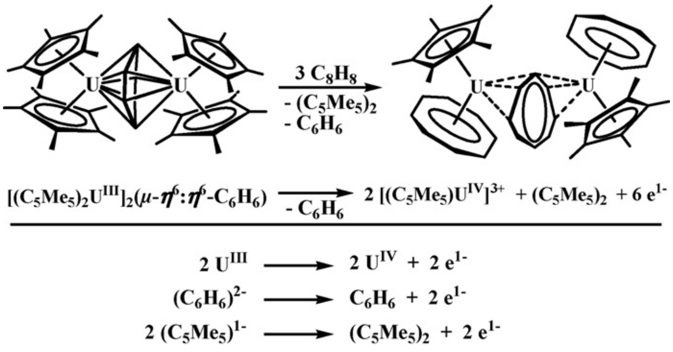


(40)

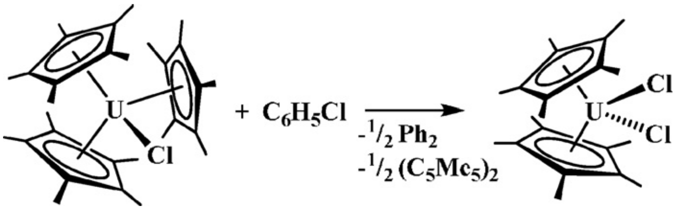
[92]. This indicated that U^{3+} reduction occurred first, but more importantly it showed that it was possible to add another ligand to the already sterically crowded $(C_5Me_5)_3$ ligand set. The limits of steric crowding in $(C_5Me_5)_3M$ complexes had evidently not been reached. As expected from the overall reaction, Eq. (38), the U^{4+} intermediate, $(C_5Me_5)_3UCl$, reacts with a second equivalent of C_6H_5Cl to make the U^{4+} product, $(C_5Me_5)_2UCl_2$, via SIR, Eq. (41).



Scheme 7. $(C_5Me_5)_3U$ as a three-electron reductant.



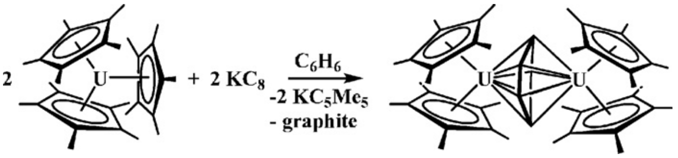
Scheme 8. Six-electron reduction via both metal and ligand based reduction.



(41)

As in the case of $(C_5Me_5)_3Sm$ and $(C_5Me_5)_3U$, once it was known that $(C_5Me_5)_3UCl$ could be synthesized, four additional new syntheses were discovered [92].

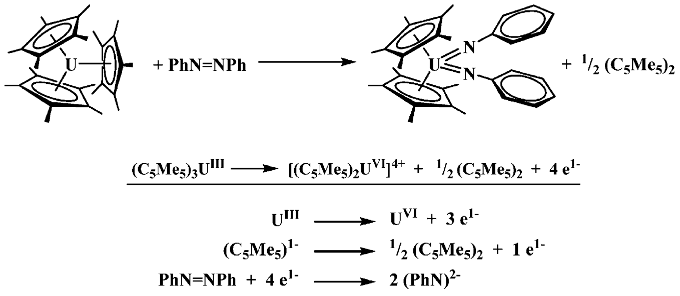
Another example of combining SIR with metal based reduction and the first example of sterically induced reduction with a bis(pentamethylcyclopentadienyl) complex was discovered with $[(C_5Me_5)_2U]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$. This compound, obtained via Eq. (42) [94], has a non-planar C_6H_6 ligand derived from benzene sandwiched between two uranium metallocenes. This complex, as well as the analogs previously reported in which a ligand derived from toluene is sandwiched between two bis(arylamide) uranium units, $[(ArRN)_2U]_2(C_6H_5CH_3)$ (R = CMe$_3$, Ar = $C_6H_3Me_2$-3,5) [95], are interesting in that there are several ways to assign oxidation states. $[(C_5Me_5)_2U]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$ is considered to be a U^{3+} complex of a $(C_6H_6)^{2-}$ dianion on the basis of its structure and reactivity. In addition to the reduction capacity of the U^{3+} and $(C_6H_6)^{2-}$ components, the U–C(C_5Me_5) distances in $[(C_5Me_5)_2U]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$ are in the long bond range appropriate for sterically induced reduction chemistry.



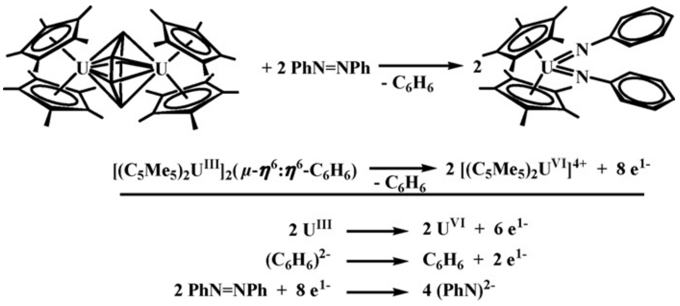
(42)

The reaction chemistry of $[(C_5Me_5)_2U]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$ with cyclooctatetraene showed that all of these sources of reduction reactivity could combine to make this complex a six-electron reductant, Scheme 8. Formally, two electrons are obtained from two U^{3+} centers, two electrons from $(C_6H_6)^{2-}$, and two from sterically induced reduction from two $(C_5Me_5)^{1-}$ ligands. This reaction showed that SIR can be combined with both metal and ligand reduction reactivity to accomplish multi-electron reduction [94].

In addition to the two, three, and six-electron reduction reactions shown above, examples of four and eight-electron reductions were obtained by examining reactions of azobenzene with



Scheme 9. Four-electron reduction via both metal and ligand-based reduction.



Scheme 10. Eight-electron reduction via both metal and ligand based reduction.

$(C_5Me_5)_3U$ and $[(C_5Me_5)_2U]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$, respectively [96]. As shown in Schemes 9 and 10, both reactions generate the U^{6+} bis(imido) complex $(C_5Me_5)_2U(=NPh)_2$ previously reported by Burns and coworkers [97]. In Scheme 9, a one-electron SIR process is combined with the U^{3+} to U^{6+} transformation. In Scheme 10, the uranium redox chemistry combines with reduction from the $(C_6H_6)^{2-}$ ligand.

The growing list of sterically crowded complexes shown in Table 3 demonstrates that it is possible to make an entire class of new complexes that have bond distances significantly longer than those previously observed. Once the first example of these so-called "long bond organometallics" was discovered as part of the investigation of $(C_5Me_5)_2Sm$ reduction chemistry, researchers had the confidence to try to make such complexes in other ways. Subsequently, at least 19 different reactions have been discovered that lead to $(C_5Me_5)_3M$ compounds. All of these retrospectively look reasonable, but none had been attempted because it was believed that the product could not exist.

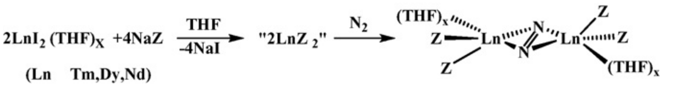
The long bond organometallics are not only structurally interesting, but they also display enhanced ligand reactivity due to the long metal ligand distances. It is surprising that these sterically crowded complexes generate new reductive chemistry since redox chemistry of metal complexes is usually manipulated by controlling the electronic, not steric, aspects of the complexes. In this case, redox reactivity is generated with normally inert ligands via steric crowding.

Table 3
Long-bond organometallics in approximate order of discovery.

$(C_5Me_5)_3Sm$
$(C_5Me_5)_3U$
$(C_5Me_5)_3Nd$
$(C_5Me_5)_3UCl$, $(C_5Me_5)_3UF$
$(C_5Me_5)_3La$, $(C_5Me_4R)_3La$ R = Et, ^{i}Pr, $SiMe_3$, $(C_5Me_4Et)_3Sm$
$(C_5Me_5)_3ThH$
$(C_5Me_5)_3Ce$, $(C_5Me_5)_3Pr$
$[(C_5Me_5)_2U]_2(C_6H_6)$
$(C_5Me_5)_3UMe$,
$(C_5Me_5)_3Gd$, $(C_5Me_5)_3Y$

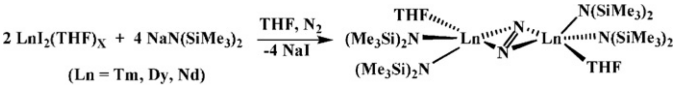
7. Divalent reduction chemistry from trivalent reagents and alkali metals, "LnZ_3/M"

A third new option in reductive f element chemistry arose from investigations of the reduced dinitrogen complexes accessible via the recently discovered molecular complexes of Nd^{2+}, Dy^{2+}, and Tm^{2+} discussed above. The reaction exemplified by the synthesis of $[(C_5R_5)_2Tm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, $\{C_5R_5 = [1,3\text{-}(Me_3Si)_2C_5H_3]$ and $(C_5H_4SiMe_3)\}$, in Eq. (4) [63] is quite general. As shown in Eq. (43), a variety of anionic ligands, Z^{1-}, can be added to the diiodides of Tm^{2+}, Dy^{2+}, and Nd^{2+} under nitrogen to generate



(43)

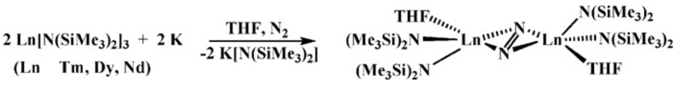
$[Z_2Ln(THF)_x]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ products. The applicable ancillary anionic ligands are $(Z)^{1-} = [1,3\text{-}(Me_3Si)_2C_5H_3]^{1-}$ and $(C_5H_4SiMe_3)^{1-}$ [63,67], $[N(SiMe_3)_2]^{1-}$ [98], and $(OC_6H_3{}^tBu_2\text{-}2,6)^{1-}$ [98]. Eq. (44) specifically shows the bis(trimethylsilylamide)



(44)

example. In each of these reactions it was assumed that ionic metathesis between the added ligand salt and LnI_2 reagent generated a reactive divalent intermediate of formula "LnZ_2", i.e. "$Ln[N(SiMe_3)_2]_2$" in the case of Eq. (44), that reduced dinitrogen. The only case in which we could isolate an intermediate, however, was $[1,3\text{-}(Me_3Si)_2\text{-}C_5H_3]_2Tm(THF)$ [67,99,100].

In efforts to find alternative routes to these reactive "LnZ_2" intermediates, the reduction of $Ln[N(SiMe_3)_2]_3$ with potassium metal was investigated [101,102]. Bradley showed in the 1970s that these $Ln[N(SiMe_3)_2]_3$ complexes can be readily synthesized from $LnCl_3$ and $[N(SiMe_3)_2]^{1-}$ salts [103]. As shown in Eq. (45), $\{[(Me_3Si)_2N]_2Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ complexes of Tm, Dy, and Nd can be made in this way. Since the precursor complexes, $Ln[N(SiMe_3)_2]_3$,



(45)

are easier to synthesize and handle than the LnI_2 reagents, this was an important synthetic breakthrough.

Eq. (44) was also mechanistically interesting because no evidence for the anticipated divalent intermediates was observed during the reactions. Since divalent lanthanide complexes are intensely colored, color changes were expected during these reactions. It was possible that the divalent intermediates were so short lived that they could not be observed, but it was also possible that the reaction did not proceed through the anticipated intermediate.

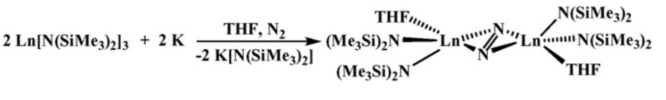
To examine this point, Eq. (45) was conducted with $Ho[N(SiMe_3)_2]_3$. Holmium had no previously identified molecular divalent oxidation state chemistry in solution. Holmium was chosen because it had a size similar to Dy and Tm and its calculated reduction potential was closer to the known divalent ions than many of the other lanthanides of that size, Table 4 [31]. Surprisingly, dinitrogen is reduced in this holmium reaction, Eq. (46), Ln = Ho,

Table 4
Calculated values of the $Ln^{3+} + e^{1-} \rightarrow Ln^{2+}$ half reaction vs. NHE and electronic configurations.[31].

Ln	Ln(III)/Ln(II) vs. NHE	Ln(II) electron configuration	Ln	Ln(III)/Ln(II) vs. NHE	Ln(II) electron configuration
Eu	−0.35 V	$[Xe]4f^7$	Er	−3.1 V	$[Xe]4f^{12}$
Yb	−1.15 V	$[Xe]4f^{14}$	La	−3.1 V	$[Xe]4f^1$
Sm	−1.55 V	$[Xe]4f^6$	Ce	−3.2 V	$[Xe]4f^2$
Tm	−2.3 V	$[Xe]4f^{13}$	Tb	−3.7 V	$[Xe]4f^9$
Dy	−2.5 V	$[Xe]4f^{10}$	Gd	−3.9 V	$[Xe]4f^8$
Nd	−2.6 V	$[Xe]4f^4$	Lu	[a]	$[Xe]4f^{14}5d^1$
Pr	−2.7 V	$[Xe]4f^3$	Y	[a]	$[Kr]4d^1$
Ho	−2.9 V	$[Xe]4f^{11}$			

[a] No calculated value.

and examination of all the other lanthanides began. Dinitrogen



(46)

is also reduced according to Eq. (46) for Ln = Er, Tb, Gd, Y, and Lu [101]. Er, Tb, and Gd have calculated Ln^{3+}/Ln^{2+} reduction potentials (Table 4) more negative than the reduction potential of the potassium reductant, −2.9 V vs. NHE! A comparison with potassium cannot be made for Y and Lu, since there are no calculated values for the Y^{2+} or Lu^{2+}. These ions had never been observed either in solution or the solid state [65].

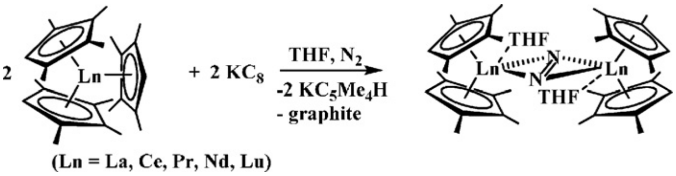
The results in Eq. (46) suggested that divalent-like lanthanide reduction can be obtained by combining a trivalent precursor with potassium. This LnZ_3/M combination in which M is an alkali metal generates "LnZ_2" reactivity. This is almost arithmetically trivial, a +3 metal plus a reagent that delivers a −1 electron generates +2 metal reactivity [65]. However, with many of these metals, this is the first time +2 reactivity has been observed in solution. Alkali metal reductions of metal complexes are common in the literature, but they generally involve intermediates of lower valent ions that are isolable. The reactions most closely related to Eq. (46) in the literature are Lappert's alkali metal reductions of $(C_5H_3R_2)_3Ln$ complexes (Ln = La, Ce; R = CMe_3, $SiMe_3$) [104–107].

If the dinitrogen reductions in Eqs. (45) and (46) involve divalent "$Ln[N(SiMe_3)_2]_2$" intermediates, this would be the first evidence of soluble, molecular species containing Ho^{2+}, Er^{2+}, Tb^{2+}, Gd^{2+}, Y^{2+}, and Lu^{2+}. If the reactions did not involve a "$Ln[N(SiMe_3)_2]_2$" pathway, then alternative methods of dinitrogen reduction involving trivalent intermediates like "$(\eta^1\text{-}N_2)Ln[N(SiMe_3)_2]_3$" would have to be considered. Although species such as $(\eta^1\text{-}N_2)M(NR_2)_3$ are well known in transition metal chemistry [108,109], they are much less likely with the lanthanides particularly in THF solution. The only fully characterized, monometallic, end-on dinitrogen complex of an f element, $(C_5Me_5)_3U(\eta^1\text{-}N_2)$, is stable only under dinitrogen pressure in non-coordinating solvents [110]. The THF solvent of Eqs. (45) and (46) would be expected to bind the lanthanide centers before N_2 both because of lanthanide preferences for polar ligands and the higher concentration of the solvent.

Although the mechanisms of Eqs. (45) and (46) remain to be determined, the LnZ_3/K reaction constitutes another method to accomplish divalent "LnZ_2" chemistry. This also provides an additional route to size optimization of Ln^{2+}-like reductive chemistry and allows reduction chemistry with diamagnetic Y and Lu.

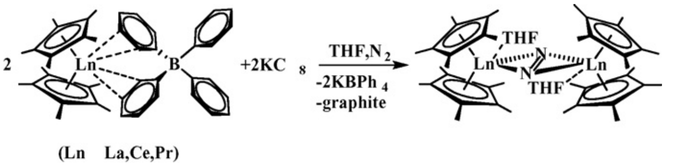
Although Eq. (46) was successful with most of the lanthanides, crystals of $\{[(Me_3Si)_2N]_2Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ products were not obtainable for Ln = La, Ce, and Pr [102]. Examination of Table 4 shows that this does not correlate with calculated reduction potentials, i.e. these ions are not the most difficult to reduce. On the other hand, since these are the three largest lanthanides in the series, a size correlation was suggested.

If Eq. (46) was not successful with La, Ce, and Pr because size of the metals was not commensurate with this ligand set for crystal formation, it should be possible to change the size of the ligand and achieve successful dinitrogen reduction with these metals. This was achieved with $Ln(C_5Me_4H)_3$ complexes [111–113]. These are desirable precursors since they can be synthesized directly from $LnCl_3$ and KC_5Me_4H for most of the lanthanides [51]. The LnZ_3/K reaction is successful with $(Z)^{1-} = (C_5Me_4H)^{1-}$ for the largest lanthanide, La, as well as the smallest, Lu, Eq. (47). Examples with Ln = Ce, Pr, and Nd were also identified and the reaction presumably is general for the entire series.



(47)

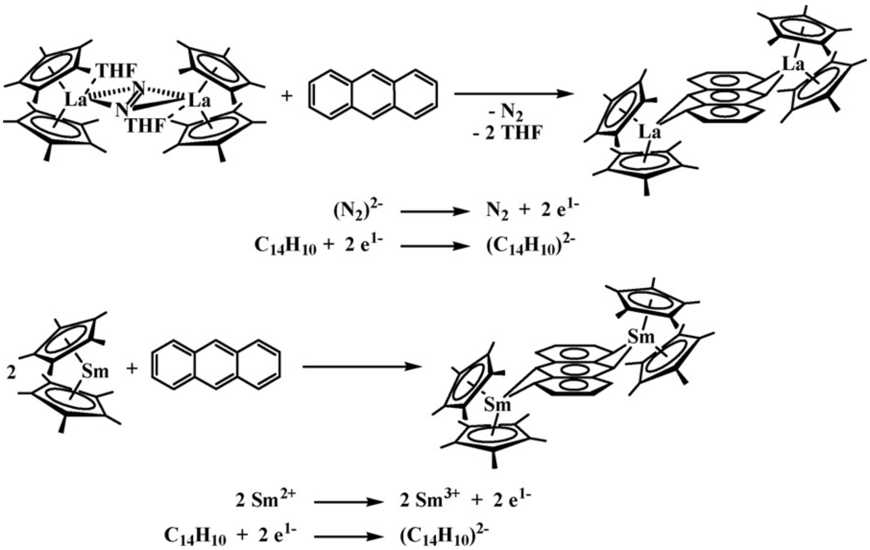
Accessing "LnZ_2" reactivity via LnZ_3/K with $Z^{1-} = (C_5Me_5)^{1-}$ was desirable due to the large amount of information already in the literature on bis(pentamethylcyclopentadienyl) complexes. However, as described in Section 5, synthesis of the $(C_5Me_5)_3Ln$ precursors is challenging and the diamagnetic Ln = Lu complex has not yet been isolated [88]. As an alternative, the reduction chemistry of the tetraphenylborate salts, $(C_5Me_5)_2Ln(\mu\text{-}Ph_2BPh_2)$ [83], that are precursors to $(C_5Me_5)_3Ln$ according to Eq. (31) was examined. These tetraphenylborate salts also can be used as precursors to the dinitrogen complexes, Eq. (48) [111], and this established that heteroleptic LnZ_2Z'/K reactions as well as homoleptic LnZ_3/K reactions can provide "LnZ_2"-like reactivity.



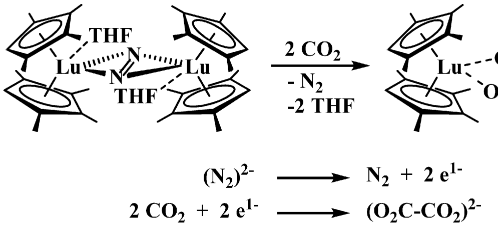
(48)

8. Divalent reduction chemistry from reduced dinitrogen complexes, "$(Z_2LnL_x)_2N_2$"

A fourth method of effecting Ln^{2+}-like reductive reactivity was discovered while examining the reactivity of the $[Z_2(THF)Ln]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes broadly obtainable from LnZ_3/M and LnZ_2Z'/M reactions. Since these compounds contain a reduced dinitrogen ligand, $(N_2)^{2-}$, they have considerable reductive capacity on their own. Accordingly their reactivity with reducible substrates was examined for comparison with the other reduction systems described above.



Scheme 11. Similarity of $[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ and $(C_5Me_5)_2Sm$ in reduction of anthracene.



Scheme 12. Reduction of CO_2 by $[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$.

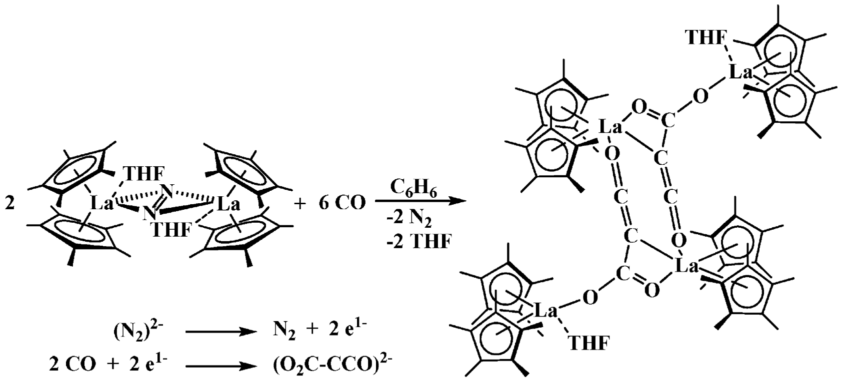
As shown in Scheme 11 [114], the trivalent lanthanum complex, $[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, reduces anthracene to make a $(C_{14}H_{10})^{2-}$ complex analogous to that obtained previously with $(C_5Me_5)_2Sm$ [70]. Carbon dioxide can be reductively coupled to form an oxalate as shown in Scheme 12 by an analogous tetramethylcyclopentadienyl lutetium complex, $[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ [115].

The reducing capacity of $[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ is best shown in its reaction with CO [114]. This involves a complicated two-electron reductive homologation of three molecules of carbon monoxide to a carboxylic acid derivative of ketene. The product is obtained as a dimer, Scheme 13. This remarkable transformation involves complete cleavage of CO triple bonds since each $(O_2CC{=}C{=}O)^{2-}$ ligand contains one carbon free of oxygen. A similar reaction had previously been observed with $(C_5Me_5)_2Sm(THF)_2$ [40], but the product was too insoluble to obtain full NMR characterization. By size optimizing the metal via the "Ln_2N_2" reductive system, full ^1H and ^{13}C NMR characterization of the ^{12}CO and ^{13}CO products was possible.

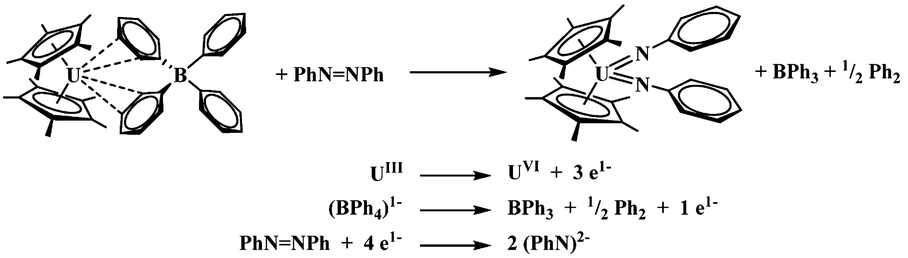
Since the $(N_2)^{2-}$ ligand delivers two electrons as it reverts to N_2 in these reactions, the trivalent bimetallic $[Z_2(THF)Ln]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes effectively react to generate two equivalents of "LnZ_2". Since the Ln_2N_2 reduction system involves a single molecular species, it is experimentally simpler than the two-component LnZ_3/M method. In some cases, the Ln_2N_2 method is complementary to LnZ_3/M reduction in that it can generate products not readily obtainable from any other currently available reductive lanthanide metal system. For example, reductions of CO and CO_2 via $(C_5Me_5)_2Ln[(\mu\text{-}Ph)_2BPh_2]$/K reactions are not as clean as those in Schemes 12 and 13.

9. Reduction chemistry from "innocent" ligands

In the course of examining "control" reactions to evaluate sterically induced reduction, yet another type of reduction option was identified, namely the use of common ligands to effect reduction. This can be viewed as an outgrowth of the SIR reaction that uses $(C_5Me_5)^{1-}$ ligands for reduction and the Ln_2N_2 method that uses $(N_2)^{2-}$ ligands, but it involves neither sterically crowded complexes nor ligands that are clearly in a highly reduced state.



Scheme 13. Reductive homologation of CO by $[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$.



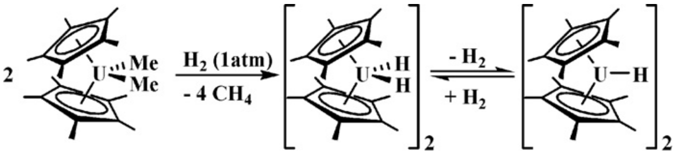
Scheme 14. Reduction by a tetraphenylborate complex.

This fifth approach to f element reduction chemistry was identified by examining a blank reaction for comparison with the reduction of azobenzene with $(C_5Me_5)_3U$, Scheme 9 [96]. To determine how a "sterically normal" U^{3+} metallocene would react with PhN=NPh in the absence of steric crowding, the reaction with $(C_5Me_5)_2U[(\mu\text{-Ph})_2BPh_2]$ was examined. Surprisingly, $(C_5Me_5)_2U[(\mu\text{-Ph})_2BPh_2]$ was found to reduce azobenzene to the same organoactinide product as $(C_5Me_5)_3U$, i.e. the U^{6+} bis(imido) complex, $(C_5Me_5)_2U({=}NPh)_2$, Scheme 14. This involves a four-electron reduction of azobenzene. Although it was anticipated that three electrons could come from a U^{3+}/U^{6+} couple, the origin of the fourth electron was not clear. In $(C_5Me_5)_3U$, this came from a $(C_5Me_5)^{1-}$ ligand via SIR. As shown in Scheme 14, the fourth electron arises from the $(BPh_4)^{1-}$ ligand. Although this $(BPh_4)^{1-}$ redox couple has been known for a long time [116], this was the first time, to our knowledge, that it was used in conjunction with a metal based reduction to accomplish a multi-electron reduction. It is interesting to note that $(BPh_4)^{1-}$ is often avoided as the counteranion in olefin polymerization reactions involving cationic metal alkyl complexes. One reason is that it is presumed to give poor catalyst performance by blocking the incoming olefin substrates. However, if reduction reactions occur as shown in Scheme 14 during these polymerization reactions, this would be another reason that other counteranions are preferred.

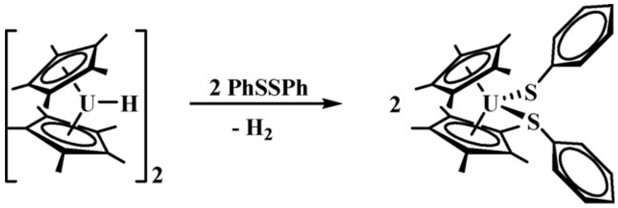
In light of the $(BPh_4)^{1-}$ result we wondered what other "innocent" ligands common in f element chemistry could act as reductants. One obvious choice is the hydride ligand. This is a well known reductant, although it usually adds to substrates as reduction occurs and does not simply provide an electron and an inert byproduct as observed for $(C_5Me_5)^{1-}$ in sterically crowded complexes, $(N_2)^{2-}$, and $(BPh_4)^{1-}$ as described above. Moreover with f element hydrides, sigma bond metathesis is a common reaction in addition to reductive addition to unsaturated substrates [117]. Nonetheless, we opted to examine the possibility that hydride ligands could provide reduction according to Eq. (49).

$$2H^{1-} \rightarrow H_2 + 2e^{1-} \tag{49}$$

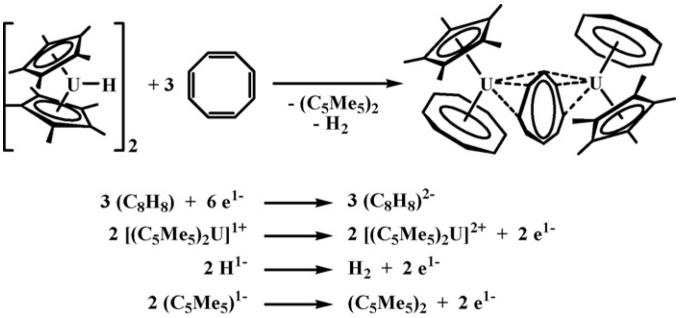
Comparison of hydride reductive reactivity with the $(C_5Me_5)^{1-}$ and $(BPh_4)^{1-}$ reactions described above was complicated by the fact that the relevant uranium hydrides exist as an equilibrium mixture of trivalent and tetravalent species as shown in Eq. (50) [118,119]. Fortunately, conditions were found to obtain relatively pure examples of both the U^{3+} and U^{4+} hydrides so their reduction chemistry could be examined [119].



(50)

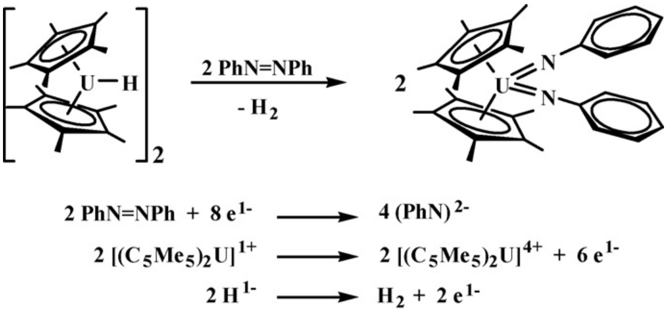


Scheme 15. Uranium hydride reduction of diphenyldisulfide.

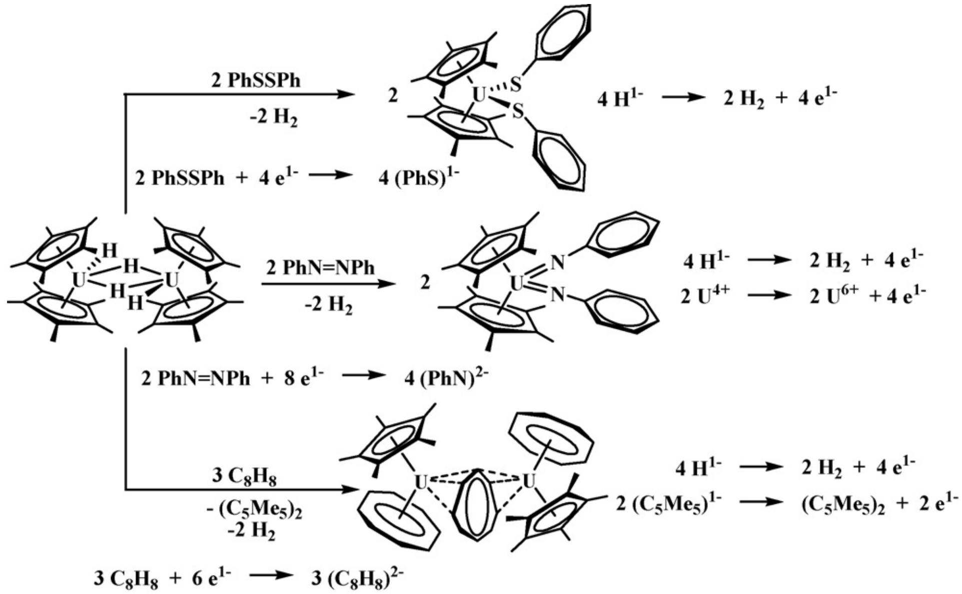


Scheme 16. Uranium hydride reduction of cyclooctatetraene.

As shown in Scheme 15, $[(C_5Me_5)_2UH]_2$ effects a four-electron reduction of two equivalents of PhSSPh to form two equivalents of $(C_5Me_5)_2U(SPh)_2$ [119]. The reductive capacity formally derives from two U^{3+}/U^{4+} redox couples and two H^{1-}/H processes. In Scheme 16, $[(C_5Me_5)_2UH]_2$ reduces three equivalents of C_8H_8 to make $[(C_5Me_5)(C_8H_8)U]_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_8H_8)$, in a reaction analogous to Scheme 7 above. In this case, hydride reduction according to Eq. (49) is combined with U^{3+}/U^{4+} redox couples and SIR. Scheme 17 shows that $[(C_5Me_5)_2UH]_2$ can function as an eight-electron reduc-



Scheme 17. Uranium hydride reduction of azobenzene.



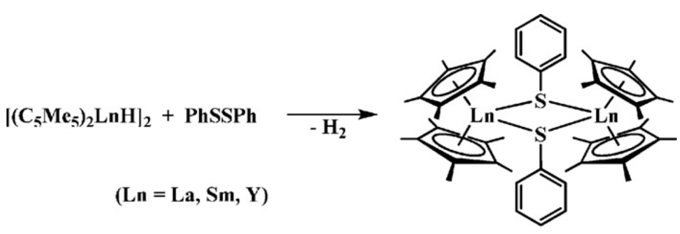
Scheme 18. Reduction chemistry of tetravalent $[(C_5Me_5)_2UH_2]_2$.

tant with PhN=NPh. In this case the hydride reductive reactivity is combined with a U^{3+}/U^{6+} redox couple [119].

Scheme 18 shows that the analogous transformations can be accomplished starting from the U^{4+} hydride $[(C_5Me_5)_2UH_2]_2$ [119]. Although it is possible that all of these reactions go through $[(C_5Me_5)_2UH]_2$, via the equilibrium in Eq. (50), the half reactions shown indicate the hydride origin of the reducing equivalents.

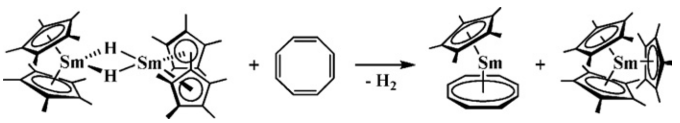
The reductive reactivity of $[(C_5Me_5)_2ThH_2]_2$ was examined since thorium does not have a readily accessible trivalent state and reduction from the hydride ligands alone would be better defined. Indeed, as shown in Scheme 19, $[(C_5Me_5)_2ThH_2]$ also reduces PhSSPh and C_8H_8 in analogy to the uranium reactions above [119]. In the four-electron PhSSPh reaction, all the reduction arises from hydride ligands. In the six-electron reduction of C_8H_8, four electrons arise from the hydrides and two from SIR. This provided the thorium analog of $[(C_5Me_5)(C_8H_8)U]_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_8H_8)$, for the first time. Since $[(C_5Me_5)(C_8H_8)U]_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_8H_8)$, was made from U^{3+} precursors for which there were no Th^{3+} analogs, there was no obvious route to $[(C_5Me_5)(C_8H_8)Th]_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_8H_8)$. However, these reactions show that $An^{4+}–H^{1-}$ hydrides can provide reactivity equivalent to An^{3+}.

Examination of the analogous hydride reductive chemistry with lanthanides has shown that although $Ln^{3+}–H^{1-}$ units can deliver reductive reactivity equivalent to Ln^{2+}, i.e. this "Z_2LnH" is another approach to "LnZ_2", there are additional side reactions that occur [120]. Hence, the $[(C_5Me_5)_2LnH]_x$ complexes with Ln = La, Sm, and Y cleanly reduce PhSSPh to $[(C_5Me_5)_2LnSPh]_2$ products, Eq. (51). $[(C_5Me_5)_2SmSPh]_2$ was previously accessible from divalent $(C_5Me_5)_2Sm$, but there was no analogous route for the lanthanum and yttrium complexes.



(51)

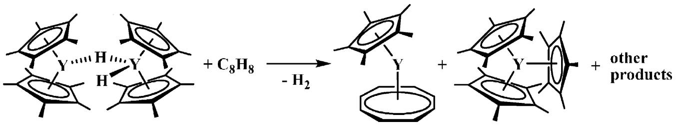
Although the PhSSPh reactions with the $[(C_5Me_5)_2LnH]_x$ complexes were straightforward, reactions with C_8H_8 and PhN=NPh are more complicated with the metals larger and smaller than samarium. $[(C_5Me_5)_2SmH]_2$ reacts with C_8H_8 according to Eq. (52).



(52)

This is equivalent to the $(C_5Me_5)_2Sm$ reaction with C_8H_8, Eq. (10), that was the original synthesis of $(C_5Me_5)_3Sm$. Hence, $(C_5Me_5)_3Sm$ could have been discovered via $Sm^{3+}–H^{1-}$ chemistry rather than by Sm^{2+} chemistry.

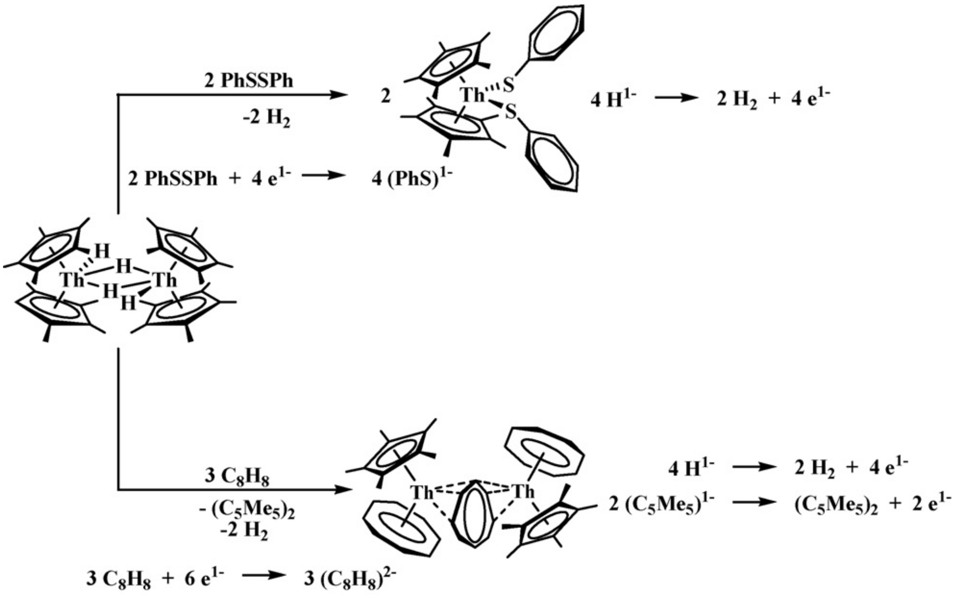
The reactions of $[(C_5Me_5)_2YH]_x$ with C_8H_8 are more complicated and have provided some insight into opportunities for expanding f element metallocene chemistry in new directions [120]. The main reaction between $[(C_5Me_5)_2YH]_x$ and C_8H_8 is a reduction analogous to that shown above with $(C_5Me_5)_2Sm$ in Eq. (10). Hence $[(C_5Me_5)_2YH]_x$ provides divalent-like reactivity and the equivalent of "$(C_5Me_5)_2Y$" to form $(C_5Me_5)Y(C_8H_8)$ and $(C_5Me_5)_3Y$, Eq. (53).



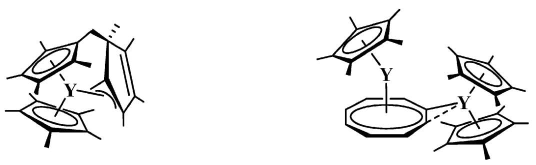
(53)

However, two unusual byproducts have been isolated from this reaction that show the capacity for future possibilities in f element metallocene chemistry, Scheme 20. In benzene, a $(C_5Me_5)Y[(\eta^5\text{-}C_5Me_4CH_2\text{-}C_5Me_4CH_2\text{-}\eta^3)]$ complex forms in which two $(C_5Me_5)^{1-}$ rings are linked to make a new type of *ansa*-allyl-cyclopentadienyl dianion that binds as a pentahapto–trihapto chelate. In cyclohexane, a $(C_5Me_5)_2Y(\mu\text{-}\eta^8{:}\eta^1\text{-}C_8H_7)Y(C_5Me_5)$ complex forms in which a $(C_8H_8)^{2-}$ ring is metalated to form the first example of a bridging $(C_8H_7)^{3-}$ trianion [120].

Collectively, the $(BPh_4)^{1-}$ and H^{1-} reactions suggest that a wider variety of ligands common in f element chemistry should be inves-



Scheme 19. Reduction chemistry of tetravalent $[(C_5Me_5)_2ThH_2]_2$.



$(C_5Me_5)Y[(\eta^5\text{-}C_5Me_4CH_2\text{-}C_5Me_4CH_2\text{-}\eta^3)]$ $(C_5Me_5)_2Y(\mu\text{-}\eta^8{:}\eta^1\text{-}C_8H_7)Y(C_5Me_5)$

Scheme 20. Unusual byproducts from $[(C_5Me_5)_2YH]_2$ reduction of C_8H_8.

tigated for their ability to deliver electrons and provide access to lower oxidation state reactivity.

10. Conclusion

For over 90 years, reductive lanthanide chemistry via Ln^{2+} ions was limited to just three elements, Eu^{2+}, Yb^{2+}, and Sm^{2+}. Extensive experimental research as well as thermodynamic and spectroscopic analyses suggested that these were the only divalent species available for reductive chemistry in solution.

During the past 10 years, five new options for accessing Ln^{2+}-like reactivity have become available. The number of fully characterized divalent lanthanides available in solution has doubled. Reductive chemistry has been found in “long bond organometallics” that were thought to be too sterically crowded to exist. The combination of an alkali metal with a trivalent lanthanide complex has provided access to Ln^{2+}-like reactivity even with elements for which no divalent ions are known in solution. Reduced dinitrogen complexes containing $(N_2)^{2-}$ ligands made by the LnZ_3/M and LnZ_2Z'/M reduction methods provide yet another class of effective and powerful reducing agents. This type of ligand based reduction chemistry has also been identified in sterically normal lanthanide complexes with “innocent ligands” like hydrides and tetraphenylborates. These methods extend options for productive lanthanide reduction chemistry beyond Eu^{2+}, Yb^{2+}, and Sm^{2+} to all the other elements in the series including complexes of diamagnetic La^{3+}, Y^{3+}, and Lu^{3+}.

The reductive chemistry of the 5f elements has also been expanded in the course of these lanthanide studies. Sterically induced reduction and the reductive chemistry of traditional ligands like hydride and tetraphenylborate in sterically normal compounds have been exceptionally valuable in uranium and thorium chemistry. These approaches have provided access to the equivalent of reduced oxidation states for these actinides that are not normally accessible. This has expanded the reductive reactivity possible and led to new types of organoactinides.

The results demonstrate that it is possible to access the reactivity of “virtual” divalent oxidation states, even if they have never been isolated under the reaction conditions. This research also provides methods to access multi-electron redox reactivity with f elements including examples with two, three, four, six, and eight-electron reductions. Multi-electron reductions with mono- and bimetallic complexes of this type are unusual not only in f element chemistry, but in chemistry in general. These studies have also shown that traditional assumptions about the distances of stable bond lengths in f element chemistry were limited.

Considering that reduction chemistry is such a fundamental reaction and has been studied so long and thoroughly, it is remarkable that this many new options were waiting to be discovered. The fact that this heavily studied area can provide fertile ground for new types of reaction chemistry suggests that similar advances are awaiting us in many other areas of f element research. Just as there was much to be discovered during Spedding’s four decade research career, during the 1970–1997 period, and during the past decade, it is likely that we now are on the brink of many equally incredible discoveries in f element science and technology. The recent developments in reductive chemistry should be used as an example of the benefits of moving beyond traditional assumptions and should be used to stimulate us to attempt *major* breakthroughs in each of the areas that we currently do our research. As stated by John Corbett in his 11th Spedding Award Address, “It is always difficult to predict the unimaginable.” We must use our imagination to try to push the limits of our fields no matter how much has been discovered to date. History suggests that advances as fundamental as those described here are just waiting to be discovered.

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