

The Importance of Questioning Scientific Assumptions: Some Lessons from f Element Chemistry†

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As scientists, we know that we should constantly question the assumptions upon which our research is based. We also know that we do not do this often enough. The recent results in f element chemistry described here should serve to remind us not to take the traditional boundaries of any area of chemistry for granted including topics as fundamental as redox chemistry and bond-length generalizations. New ways of doing reductive chemistry in the f element area as well as the synthesis of “long bond organometallics” that have unconventional bond distances and reactivity demonstrate how the “rules” in this area, thought to be true for decades, have been recently overturned. The synthetic chemistry that made these advances possible has generated additional unexpected opportunities in f element chemistry that are also described here. Overall, these results should stimulate researchers in all areas to challenge their assumptions.

Introduction

The importance of questioning scientific assumptions has been known to scientists for hundreds of years. The following quotes show only a small part of this history:

“Do not acknowledge as true anything that is not obvious.” —Descartes quoted by Santiago Ramón y Cajal in *Advice to a Young Investigator*, 1916¹

“Michael Faraday warned against the tendency of the mind ‘to rest on an assumption’ and when it appears to fit in with other knowledge to forget that it has not been proved.” —quoted by W. I. B. Beveridge in *The Art of Scientific Investigation*, 1957²

“The main thing you need to learn is doubt. Don’t believe anything you’re told without good reason and argument. Doubt underpins science.” —Nobel Prize winner Richard Smalley, in *Chem. Eng. News* **2002**, July 15, 2002, p. 3³

Given this long tradition of questioning assumptions, one can ask why there should be a lecture or topic with such a title. The answer lies in the fact that *all too often scientific*

assumptions are not questioned thoroughly or often enough. It is too easy to become comfortable with the fundamental bases upon which scientific results are interpreted. Certain assumptions are so well established after many years that they seem irrefutable.

The purpose of this paper is to stimulate researchers in any area of science to make advances by thinking beyond the traditional assumptions currently made in their areas. The summary presented here shows how much new chemistry can become available if one can push through the barriers of conventional assumptions. As scientists, we know this is true, but we do not act on this principle with appropriate frequency.

In recent years, several basic assumptions in the f element area have been overturned. These involve concepts as fundamental as how reductive chemistry is accomplished with these elements and what constitutes a stable metal–ligand bond length. These new discoveries are almost unbelievable to me because this is my area of science and I thought I knew the rules, boundaries, and limitations that defined the chemistry of these elements. This is especially surprising because the new results were discovered in the “straightforward” areas of redox chemistry and bond-length analysis that seemed well established for decades. The advances described here provide an excellent lesson in how much new chemistry is awaiting discovery when the old traditional principles are overturned. This paper focuses on our efforts in this area, but it should be realized that other groups around the world are also challenging these assumptions.

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William Evans was born in 1947 in Madison, WI. He received a B.S. degree from the University of Wisconsin, where he did undergraduate research with Professor Donald F. Gaines, and a Ph.D. from the University of California, Los Angeles, under the direction of Professor M. Frederick Hawthorne. He did postdoctoral research with the late Professor Earl L. Muetterties at Cornell University. He joined the Faculty of the University of Chicago in 1975, was promoted to Associate Professor with tenure in 1982, and moved to the University of California, Irvine, where he has been a Professor since 1983. He was a Camille and Henry Dreyfus Teacher Scholar, an Alfred P. Sloan Foundation Research Fellow, the Reilly Lecturer at the University of Notre Dame, the Fishel Lecturer at Vanderbilt University, and a Frontiers in Chemical Research Lecturer at Texas A&M University. He was the Chair of the Gordon Research Conference on Inorganic Chemistry in 1993. He received the American Chemical Society Award in Inorganic Chemistry in 2005 and the UCI Distinguished Faculty Award for Research in 2006.

Background: Questioning Assumptions To Get the f Element Field Moving

To present this information properly, it is appropriate to present some background information on f element chemistry. This material will be presented anecdotally to indicate how scientific assumptions were overturned to initiate investigations in this area of science. This is a well-established modus operandi in science.¹ Typically, young investigators seek to overturn previously held assumptions to establish themselves in the area. Although challenging assumptions in this way is common, it is much less common to question the assumptions once the area and the investigator are established.

For many years, lanthanide chemistry was deemed to be an area of little interest and importance. The unfortunate

Table 1. Abundance of the “Rare-Earth” Elements in the Earth’s Crust in Comparison with Other Metallic Elements (ppm)⁴

iron	43200	ytterbium	2.0
chromium	126	europium	1.3
cerium	60	molybdenum	1.1
nickel	56	tungsten	1.0
lanthanum	30	holmium	0.80
neodymium	27	terbium	0.65
cobalt	24	lutetium	0.35
lead	14.8	thulium	0.30
praseodymium	6.7	silver	0.07
samarium	5.3	mercury	0.040
gadolinium	4.0	gold	0.0025
dysprosium	3.8	platinum	0.0004
erbium	2.1	rhodium	0.00006

name of “rare-earth” elements for the lanthanides implied that these metals were uncommon, esoteric, and probably expensive. The assumption of terrestrial scarcity, like many of the early assumptions, was incorrect. As shown in Table 1, many of the lanthanides are as common as cobalt and lead. The least common lanthanide, thulium, is more common than silver, mercury, and the precious metals.⁴ The “rare-earth” name arose not based on crustal abundance but because historically these metal oxides were among the last to be discovered.

A more serious assumption that initially limited the chemistry of these elements was the belief that these elements lacked the proper orbitals to have effective metal-based chemistry. For example, in the area of organometallic chemistry, some textbooks did not include f element chemistry because these metals lacked the orbital interaction and back-bonding capacity that is so important in transition-metal reactivity.⁵

Indeed, theoretical, spectroscopic, magnetic, synthetic, structural, and reactivity studies all indicated that the 4f orbitals of the lanthanides had a limited radial extension compared to the d orbitals of the transition metals.^{6–13} For example, Wilkinson’s early studies in organolanthanide chemistry showed that there was no 18-electron rule for the cyclopentadienyl complexes of these metals.¹⁴ As shown in Scheme 1, (C₅H₅)₃Ln complexes could be made for all of the lanthanides with electron counts ranging from 18 for (C₅H₅)₃La to 32 for (C₅H₅)₃Lu. Despite the variable electron counts and 4fⁿ configurations, all of the tetrahydrofuran (THF) adducts of these complexes had similar structures and their reactivities were also similar.¹¹ This is very different from the d metal metallocenes; e.g., ferrocene and cobaltocene display very different modes of reactivity.

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Importance of Questioning Scientific Assumptions

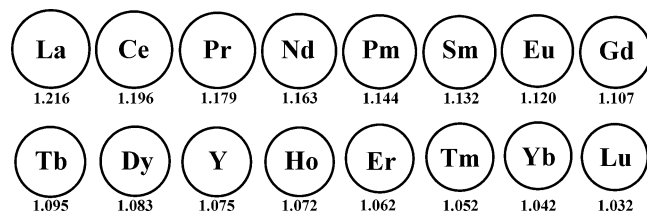
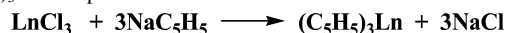


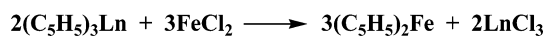
Figure 1. Ionic radii (Å) for nine-coordinate trivalent lanthanide ions (circles drawn to scale to show the relative size of each ion).

Scheme 1. Synthesis, Valence Electron Count, and Reactivity of $(C_5H_5)_3Ln$ Complexes



Valence Electrons

$(C_5H_5)_3La$	18	$(C_5H_5)_3Tb$	26
$(C_5H_5)_3Ce$	19	$(C_5H_5)_3Dy$	27
$(C_5H_5)_3Pr$	20	$(C_5H_5)_3Ho$	28
$(C_5H_5)_3Nd$	21	$(C_5H_5)_3Er$	29
$(C_5H_5)_3Sm$	23	$(C_5H_5)_3Tm$	30
$(C_5H_5)_3Eu$	24	$(C_5H_5)_3Yb$	31
$(C_5H_5)_3Gd$	25	$(C_5H_5)_3Lu$	32



Wilkinson also showed that organolanthanides give up their ligands to iron halides much like alkali metal or alkaline-earth metal cyclopentadienyl reagents (Scheme 1).^{15,16} In this sense, the lanthanides appeared to be more like trivalent extensions of the ionic alkali metals and alkaline-earth metals than transition-metal analogues. Associated with this comparison, they were assumed to have little interesting chemistry.

From the early studies of organolanthanide chemistry, a few simple rules for reactivity developed:¹²

1. The limited radial extension of the 4f valence orbitals results in minimal orbital effects.

a. Reactivity is not strongly dependent on the 4fⁿ electron configuration.

b. Ligand geometries simply need to optimize electrostatic interactions.

2. Reactivity can be strongly affected by steric factors ("sterically saturated" complexes are the most stable).

One might assume that such minimalistic rules would not generate interesting reaction chemistry. However, this combination actually offers the lanthanides some unique opportunities for steric control over reactivity. This is based on the lanthanide contraction, the gradual reduction in the size of the metals from lanthanum to lutetium. For example, the nine-coordinate radii of these ions change from 1.216 Å for La³⁺ to 1.032 Å for Lu³⁺, a 0.18-Å change over 16 metals (including yttrium; Figure 1).¹⁷

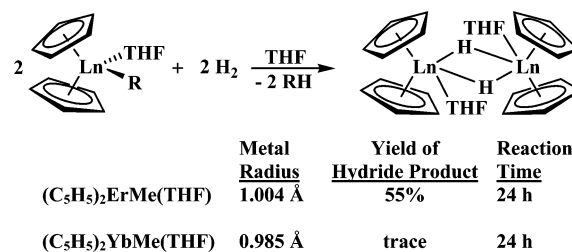
Because the reactivities of these ions are not strongly affected by the 4fⁿ configuration and because steric factors control the chemistry, it is possible to fine-tune the reactivity by changing the size of the metals. Steric control can generally be manipulated by changing the ligand size.

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Scheme 2. Sensitivity of Hydrogenolysis Reactivity to the Metal Radius¹⁷



However, with the lanthanides and a given set of ligands, the size of the metal can also be changed to further adjust the reactivity. This precise size optimization option based on the metals is not available anywhere else in the periodic table. The lanthanides are the only large set of chemically similar metals that have a gradually changing size.

The power of size optimization with lanthanides is shown in Scheme 2. In this case, changing the size of the metal by just 0.02 Å from erbium to ytterbium changes a successful hydrogenolysis to one with a very low yield.¹⁸ There are many examples of size optimization in the lanthanide literature.^{11,19–22}

In addition to the assumption that the lanthanides have an orbital limitation to their chemistry, it was assumed that the lack of variable oxidation states for these metals would also inhibit their utility. The most stable oxidation state for all of the lanthanides is 3+ and, traditionally, few other oxidation states were commonly available. For over 90 years, the only non-trivalent states considered accessible were Ce⁴⁺, Eu²⁺, Yb²⁺, and Sm²⁺.²³ Because the 4+ and 2+ oxidation states were not found on a single metal, the two-electron redox processes so common for the transition metals, e.g., oxidative addition and reductive elimination, could not occur on a single lanthanide metal center.

These aspects of lanthanide chemistry led researchers to assume that this part of the periodic table would not generate interesting chemistry. However, an alternative view was that, because these metals are different, they have the potential to accomplish unique chemistry not possible with the transition metals. Indeed, the special combination of the physical properties of the lanthanides as large, highly electropositive metals with gradually changing size and limited orbital extension, provided the basis for proposing unique chemistry for these elements.²⁴

The Importance of Reductive Chemistry

When we started our efforts to overturn the assumptions about the limited nature of lanthanide chemistry, one option we pursued was to expand the reductive chemistry of these elements. Only three divalent states were available at that

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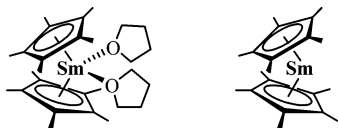
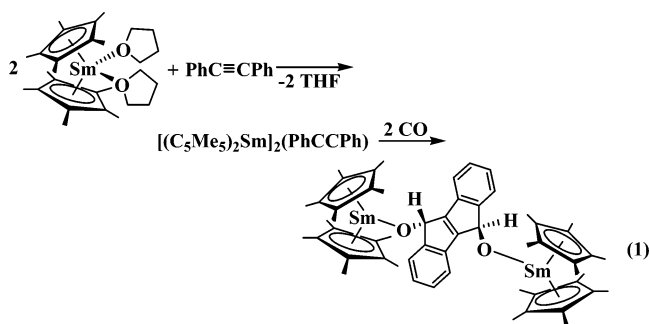


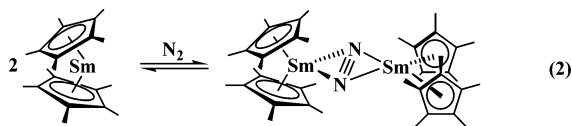
Figure 2. $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$.

time and we sought to develop the chemistry of the most reactive of those three, Sm^{2+} . The first soluble, crystallographically characterizable, metallocene of Sm^{2+} was synthesized, namely, the solvated $(C_5Me_5)_2Sm(THF)_2$ (Figure 2).^{25,26} Subsequently, the surprisingly bent, desolvated decamethylsamarocene, $(C_5Me_5)_2Sm$,^{27,28} was discovered (Figure 2). These two compounds alone provided a wealth of new chemistry to the f elements.^{12,29–31}

Only two examples of this Sm^{2+} reactivity will be shown here for the purpose of demonstrating the importance of reductive chemistry in the lanthanide field. Equation 1^{32,33} was unusual in that neither the alkyne nor the CO substrate were expected to have significant chemistry with the lanthanides because these metals could not effectively back-bond like transition metals as a result of the limited radial extension of the 4f orbitals. This reaction generated directly from simple reagents a tetracyclic hydrocarbon not accessible by other means of organic synthesis.



Equation 2 shows how decamethylsamarocene was used to synthesize the first dinitrogen complex of an f element.³⁴ More importantly, this was the first example of coplanar coordination of two metals to dinitrogen; i.e., the $M_2(\mu-\eta^2:\eta^2-N_2)$ structural feature had not been previously observed in all of the years of studying dinitrogen transition-metal chemistry.³⁵ Again, dinitrogen was a substrate not expected to have extensive chemistry with the lanthanides as a result of the limited radial extension of the 4f valence orbitals.



Although Sm^{2+} provided many interesting new options for f element reactivity, there were also many Sm^{2+} -based

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Table 2. Properties of the Most Common Divalent Lanthanide Ions Available in Solution as Molecular Species^{17,36}

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

reactions that did not give fully definable products. Because both Sm^{2+} and Sm^{3+} are paramagnetic, NMR spectroscopy was often not definitive. If crystals suitable for X-ray crystallography could not be grown, it was often not possible to definitively identify the reaction product. Ordinarily in lanthanide chemistry, a problem of this type would be addressed by size optimization of the metal. However, size optimization of the reductive chemistry was not possible. The only other divalent ions available were Eu^{2+} and Yb^{2+} , and they were significantly less reactive reductants (Table 2).^{17,36}

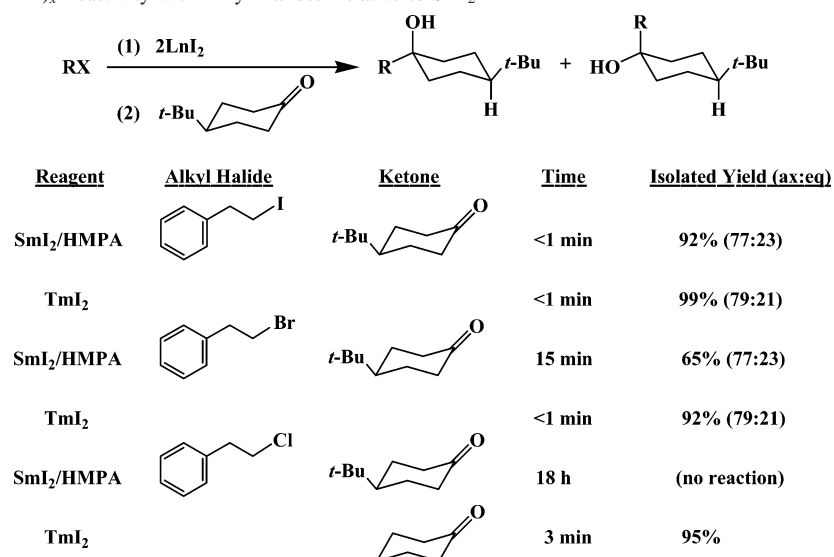
Hence, the view of the future of reductive divalent lanthanide chemistry in the late 1990s was that it was a productive area that would continue to grow by changing the ligand set to optimize the reactivity of the divalent reagent and stabilize the trivalent product. Because the redox chemistry of the lanthanides was well established, the only available option was to optimize the chemistry of the known oxidation states.

The assumption that this was the limit of divalent reductive chemistry was completely wrong! As shown in the following sections, at least three different ways of expanding this area were waiting to be discovered.

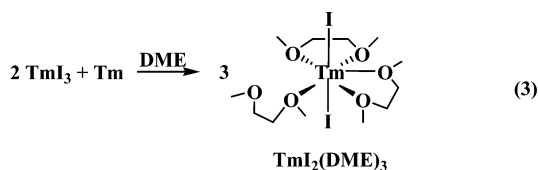
New Molecular Divalent Oxidation States

Tm^{2+} . In 1996, Professor Mikhail N. Bochkarev of Nizhny Novgorod, Russia, contacted me to suggest a collaboration to obtain structural information on what he thought was the first example of an isolable molecular Tm^{2+} complex. I assumed this was wrong because the calculated redox potential for Tm^{3+}/Tm^{2+} was -2.3 V,³⁶ i.e., much more reducing than Sm^{2+} , and all previous reports on Tm^{2+} described highly colored solutions that had only a transient existence.^{37–42} It was assumed that Tm^{2+} was sufficiently reducing to destroy any solvent. Nonetheless, I agreed to collaborate. When the material arrived in our laboratory and did not diffract X-rays, I was not surprised because I assumed it must be something other than a molecular Tm^{2+} complex. Subsequent attempts to recrystallize the material also failed.

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Scheme 3. In Situ $\text{TmI}_2(\text{DME})_3$ Reactivity with Alkyl Halides Relative to SmI_2/HMPA


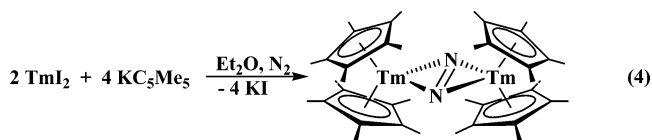
However, when a fresh sample was made in our laboratory via the Bochkaev method,⁴¹ it diffracted. Much to my surprise, the first molecular divalent thulium complex was crystallographically identified, $\text{TmI}_2(\text{DME})_3$ (eq 3).⁴²



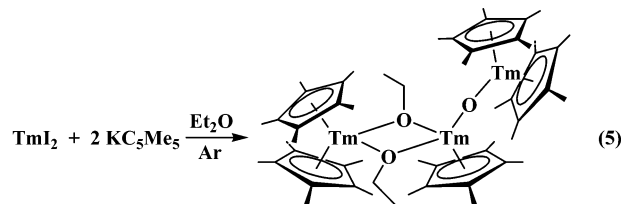
Given the importance of Sm^{2+} to the lanthanide field, the isolation of a new, more reactive divalent ion like Tm^{2+} was very exciting. However, for the next 3 years neither the Bochkaev laboratory nor my laboratory could obtain any significant new divalent lanthanide reactivity from the Tm^{2+} species.^{43–47} Reactions of this intensely colored green species quickly gave colorless Tm^{3+} salts, e.g., TmI_3 , but new reductive chemistry was not identified. At this point, the assumption that the limit of useful divalent lanthanide chemistry was restricted to Sm^{2+} seemed reasonable.

However, a breakthrough in using Tm^{2+} came about when it was decided to use it in situ.^{48,49} A study that compared TmI_2 to SmI_2/HMPA (HMPA = hexamethylphosphoramide) in situ in alkyl halide ketone coupling reactions (Scheme 3) showed that TmI_2 was equivalent to SmI_2/HMPA with iodides and bromides without the use of carcinogenic HMPA.⁴⁸ Moreover, TmI_2 achieved this coupling even with alkyl chlorides, substrates that were unreactive with SmI_2/HMPA .

Once the in situ value of Tm^{2+} in organic synthesis was established, attempts to use Tm^{2+} in situ in organometallic chemistry were made.⁴⁹ This revealed the reason that Tm^{2+} had been so difficult to isolate. When 2 equiv of KC_5Me_5 were added to a TmI_2 solution to make the thulium analogue of the divalent samarium metallocene, $(\text{C}_5\text{Me}_5)_2\text{Sm}$, for in situ reactions, reduction was observed before a substrate could be added! Reduction of the supposedly inert dinitrogen atmosphere occurred to make the $(\text{N}_2)^{2-}$ complex shown in eq 4.⁴⁹ Apparently, the addition of KC_5Me_5 to Tm^{2+} generated a species sufficiently reactive to reduce dinitrogen. Dinitrogen reduction also proceeds with the less electron-donating cyclopentadienyl ligand, $(\text{C}_5\text{H}_4\text{SiMe}_3)^-$.⁴⁹ Presumably, the intense color of Tm^{2+} solutions generated in previous studies faded so rapidly because dinitrogen was being reduced.

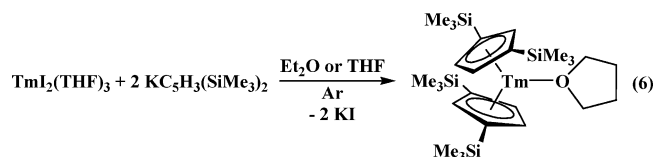


Because dinitrogen does not provide an inert atmosphere to Tm^{2+} , in situ reactions under argon were examined. As shown in eq 5, under these conditions, Tm^{2+} was sufficiently reactive to destroy diethyl ether to make ethoxide and oxide complexes.⁴⁹ At this point, it could be assumed that a

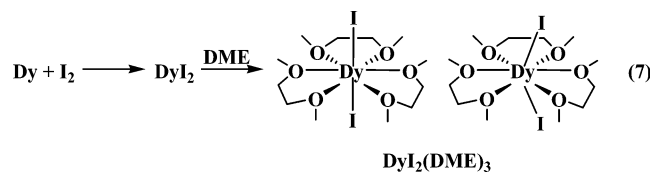


metallocene of Tm^{2+} would be too reactive to be isolable. However, by careful choices of the ligand, solvent, and inert atmosphere, the first metallocene of Tm^{2+} was isolated, $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Tm}(\text{THF})$ (eq 6).⁵⁰

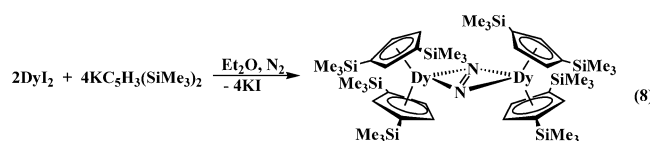
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 (46) Bochkaev, M. N.; Fagin, A. A. *Chem.—Eur. J.* **1999**, 5, 2990.
 (47) Evans, W. J.; Broomall-Dillard, R. N. R.; Ziller, J. W. *Polyhedron* **1998**, 17, 3361.
 (48) Evans, W. J.; Allen, N. T. *J. Am. Chem. Soc.* **2000**, 122, 2118.
 (49) Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, 123, 7927.



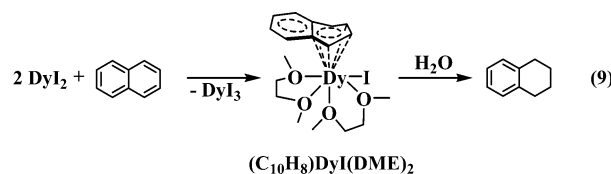
Dy²⁺. Once the divalent chemistry of Tm²⁺ was established, the assumptions about the inaccessibility of the other oxidation states were suspect. Indeed, using the synthetic method of Bochkarev,⁴¹ we were able to obtain crystallographic data on the first molecular complex of Dy²⁺ (eq 7).⁵¹ This complex crystallizes with both linear and bent DyI₂ components in the same single crystal. The crystals are isomorphous with the samarium analogue.⁵²



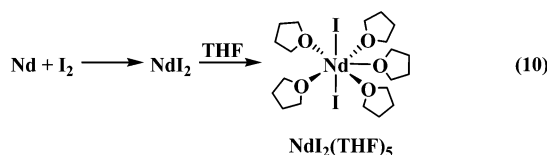
On the basis of the Tm²⁺ chemistry, it would be expected that DyI₂ would also reduce dinitrogen in the presence of cyclopentadienyl salts. Indeed, analogous dysprosium complexes can be made according to eq 8.⁵⁰ However, Dy²⁺ is



more reducing and is capable of reducing naphthalene, as shown in eq 9.⁵¹ Because this product can subsequently be hydrolyzed to dihydronaphthalene, this reactivity is starting to approach Birch reduction reactivity⁵³ but with a soluble molecular species in an ether solution rather than an alkali metal in liquid ammonia.



Nd²⁺. While this Tm²⁺ and Dy²⁺ chemistry was being developed, yet another divalent ion was isolated for the first time in a molecular species: Professor Bochkarev and Professor Schumann of the Technical University of Berlin reported the first molecular complex of Nd²⁺ (eq 10).⁵⁴ Neodymium has a calculated Nd³⁺/Nd²⁺ reduction potential of -2.6 V vs NHE .³⁶



Impact of Tm²⁺, Dy²⁺, and Nd²⁺. The isolation of molecular species of Tm²⁺, Dy²⁺, and Nd²⁺ constituted a

Table 3. Properties of the Most Common Divalent Lanthanide Ions Available in Solution as Molecular Species^{17,36}

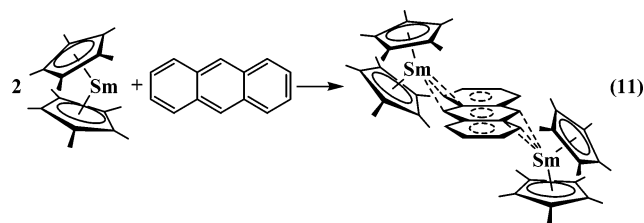
	$E_{1/2}$ (V) vs NHE for $\text{Ln}^{3+} + \text{e}^- \rightarrow \text{Ln}^{2+}$	electron configuration of Ln^{2+}	ionic radius of eight-coordinate Ln^{2+}
Eu ²⁺	-0.35	[Xe]4f ⁷	1.25
Yb ²⁺	-1.15	[Xe]4f ¹⁴	1.14
Sm ²⁺	-1.55	[Xe]4f ⁶	1.27
Tm ²⁺	-2.3	[Xe]4f ¹³	1.09
Dy ²⁺	-2.5	[Xe]4f ¹⁰	1.19
Nd ²⁺	-2.6	[Xe]4f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

doubling of the number of divalent ions available in soluble form for lanthanide-based reductions. Table 3, not the former Table 2, shows the fully characterized divalent ions now available for molecular chemistry. Imagine the possibility that the number of oxidation states with which you are working could be doubled! One would assume this is impossible. However, it happened in lanthanide chemistry.

Although the number of divalent oxidation states accessible in well-defined molecular species had doubled, size optimization of the reductive Sm²⁺-like chemistry was still not possible. More divalent ions and a wider variety of sizes were available, but the six molecular divalent species had significantly different reaction chemistry. Hence, the size optimization based on metals of similar reactivity was still not possible for the divalent ions as it was for the trivalent ions. To achieve this size optimization of Sm²⁺-like chemistry, further advances in reductive lanthanide chemistry were necessary.

Sterically Induced Reduction

A second recent advance in reductive lanthanide chemistry arose from an exploratory study of the reductive chemistry of (C₅Me₅)₂Sm. The reactivity of this complex with unsaturated hydrocarbons of known redox potential was being studied to define its reductive capacity. The reaction of (C₅Me₅)₂Sm with anthracene gave the 2:1 Sm/substrate reaction product [(C₅Me₅)₂Sm]₂(μ-η³:η³-C₁₄H₁₀) (eq 11). The formation of such 2:1 products was typical for (C₅Me₅)₂Sm⁵⁵ and allowed this one-electron reductant to accomplish two-electron reductions.



Although the reduction reaction was not unusual, the structure of the anthracene dianion was unexpected because it remained planar. In contrast, the reduction of anthracene by magnesium generates a dianion with a nonplanar central

(51) Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11749.

(52) Evans, W. J.; Broomhall-Dillard, R. N. R.; Ziller, J. W. *Polyhedron* **1998**, *17*, 3361.

(53) Rabideau, P. W.; Marcinow, Z. *Org. React.* **1992**, *42*, 1.

(54) Bochkarev, M. N.; Fedushkin, I. L.; Dechert, S.; Fagin, A. A.; Schumann, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 3176.

(50) Evans, W. J.; Allen, N. T.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 359.

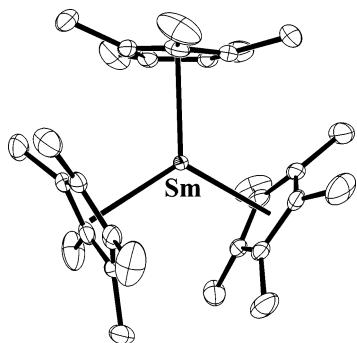
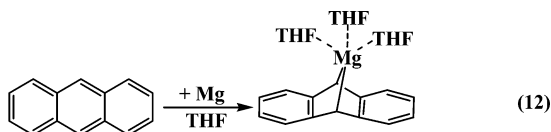


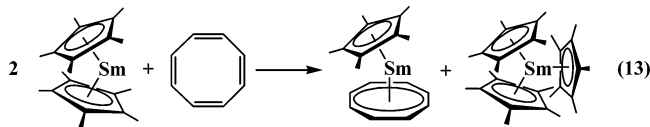
Figure 3. Tris(pentamethylcyclopentadienyl)samarium, $(C_5Me_5)_3Sm$.

ring (eq 12),⁵⁶ as is expected when electrons are added to a planar aromatic system.



To examine further the capacity of $(C_5Me_5)_2Sm$ to make organic anions of unusual structure and perhaps reactivity, the reaction of $(C_5Me_5)_2Sm$ with 1,3,5,7-cyclooctatetraene was investigated. It was expected that 2 equiv of $(C_5Me_5)_2Sm$ would reduce C_8H_8 to a dianion that would normally be planar. However, the steric crowding that could result from complexing the $(C_8H_8)^{2-}$ dianion to two $[(C_5Me_5)_2Sm]^+$ cations could distort the ring to a nonplanar form that might have unusual reactivity. The formation of a nonplanar dianion of cyclooctatetraene would be the reverse type of distortion seen in eq 11, in which a nonplanar dianion was expected but a planar dianion was obtained.

As shown in eq 13, the reduction of C_8H_8 does occur, but the $(C_8H_8)^{2-}$ dianion forms a monometallic product, $(C_8H_8)Sm(C_5Me_5)$, not the bimetallic analogue of eq 11. This



leaves as byproducts three $(C_5Me_5)^-$ rings and Sm^{3+} . The surprising result was that they come together to form the first structurally characterized tris(pentamethylcyclopentadienyl) complex, $(C_5Me_5)_3Sm$ (Figure 3).⁵⁷

For decades it had been assumed by the many groups studying $(C_5Me_5)^-$ chemistry that it was impossible to put three of these large rings around one metal center. Statements such as “only two pentamethylcyclopentadienyl groups can be attached to a metal atom even for large metals atoms such as uranium and thorium” could be found in the literature. These were unquestioned because the cone angle of a $(C_5Me_5)^-$ ring was estimated to be about 142° ^{58–60} and three of these would exceed 360° . However, in the case of

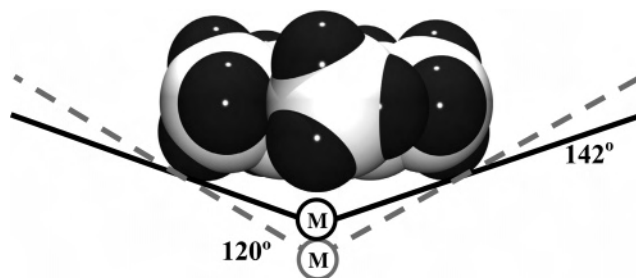


Figure 4. Change in the metal–ligand distance to accommodate three $(C_5Me_5)^-$ ligands around a metal center. The “normal” cone angle of 142° (solid line) results when the metal–ring centroid distance is normal. A smaller cone angle (dashed line) results when the metal is located further away from the ring.

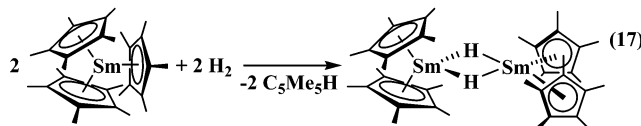
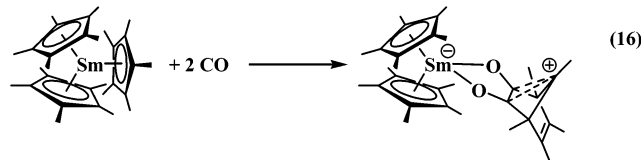
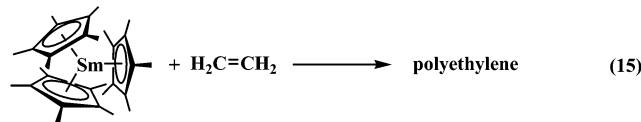
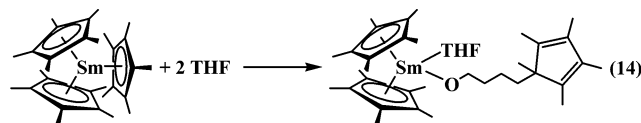
Table 4. Previously Observed $Sm-C(C_5Me_5)$ Distances Compared to Those in $(C_5Me_5)_3Sm$ ⁶²

	Sm–C(C_5Me_5) Distances (Å)
typical averages	2.71(2)–2.75(2)
range of averages	2.68(1)–2.80(1)
$(C_5Me_5)_3Sm$ average	2.82(5)
$(C_5Me_5)_3Sm$ distances	2.782(2), 2.817(2), 2.910(3)

$(C_5Me_5)_3Sm$, the cone angles of the $(C_5Me_5)^-$ ligands were each 120° !

How can the cone angle of a ligand be substantially reduced? One way is to move the ligand further away from the metal, as shown in Figure 4. Indeed, the $Sm-C(C_5Me_5)$ distances in $(C_5Me_5)_3Sm$ were significantly longer than those observed in previously characterized Sm^{3+} complexes of $(C_5Me_5)^-$ (Table 4).^{61,62}

Although the extreme steric crowding in $(C_5Me_5)_3Sm$ could have limited its reactivity because substrates could not approach the metal, the long $Sm-C(C_5Me_5)$ distances caused by the crowding actually provided a basis for high reactivity. As shown in eqs 14–17, $(C_5Me_5)_3Sm$ decomposes in the presence of THF to form a ring-opened product,⁶³ it polymerizes ethylene,⁶³ it undergoes the first insertion chemistry ever observed with $(C_5Me_5)^-$ ligands and CO,⁶⁴



(55) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2600.

(56) Engelhardt, L. M.; Harvey, S.; Raston, C. L.; White, A. H. *J. Organomet. Chem.* **1988**, 341.

(57) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 7423.

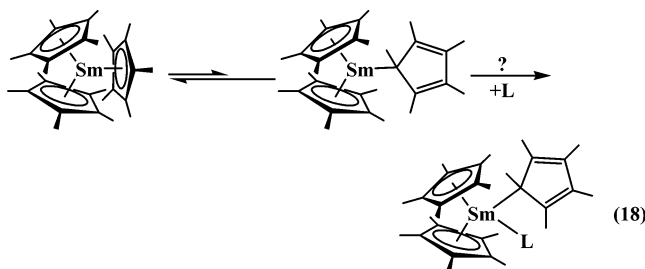
(58) White, D.; Taverner, B. C.; Leach, P. G. L.; Coville, N. J. *J. Comput. Chem.* **1993**, *14*, 1042.

(59) Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 5673.

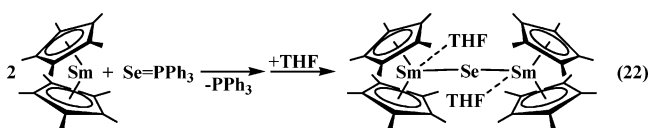
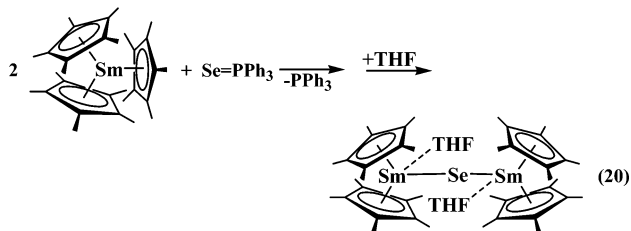
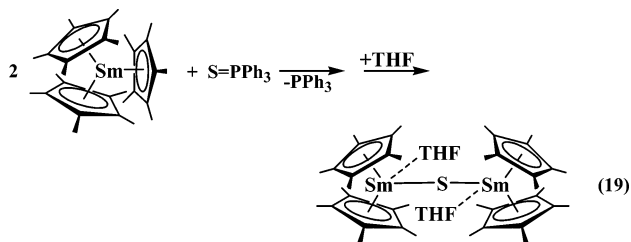
(60) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424.

and it undergoes hydrogenolysis, an uncommon reaction for $(C_5Me_5)^-$ ligands.⁶³

All of these reactions can be understood by invoking the accessibility of an intermediate that contains a mono-hapto ring, $(\eta^5-C_5Me_5)_2Sm(\eta^1-C_5Me_5)$, as shown in eq 18. In search of structural evidence for this mono-hapto form, numerous ligands, L, were added to $(C_5Me_5)_3Sm$ to make a crystallographically characterizable $(C_5Me_5)_2Sm(\eta^1-C_5Me_5)L$ complex. This led to the discovery of a new type of reduction chemistry.



When $(C_5Me_5)_3Sm$ was reacted with ligands such as $O=PPh_3$, $S=PPh_3$, and $Se=PPh_3$, these ligands were reduced.⁶³ As shown in eqs 19 and 20, $S=PPh_3$ and $Se=PPh_3$ are reduced by $(C_5Me_5)_3Sm$ to form PPh_3 and $(S)^{2-}$ or $(Se)^{2-}$



complexes previously made from the reduction of $S=PPh_3$ and $Se=PPh_3$ by the divalent $(C_5Me_5)_2Sm$ (eqs 21 and 22).

(61) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119.

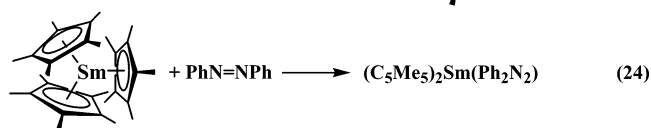
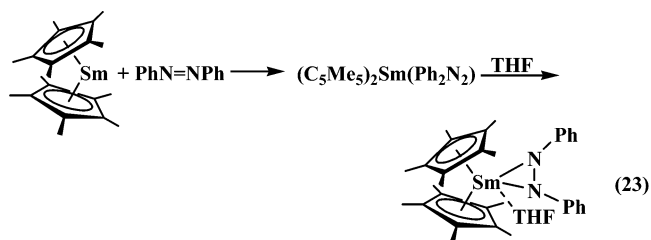
(62) Evans, W. J.; Foster, S. E. *J. Organomet. Chem.* **1992**, *433*, 79.

(63) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 9273.

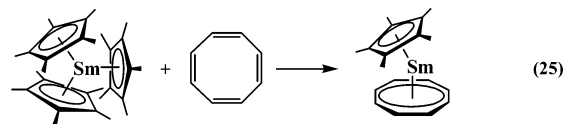
(64) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 12635.

Equation 19 is parallel to eq 21, and eq 20 is parallel to eq 22. The stoichiometries and samarium products are identical. This was surprising because a trivalent complex was effecting the same reduction chemistry as a divalent complex.

Because a wide range of $(C_5Me_5)_2Sm$ reactions were known, it was possible to examine this unusual parallel reduction reactivity with other types of substrates. As shown in eqs 23 and 24, $(C_5Me_5)_3Sm$ reduces azobenzene just like the reaction of 1 equiv of $(C_5Me_5)_2Sm$ with azobenzene.

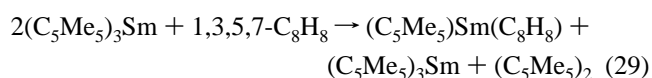
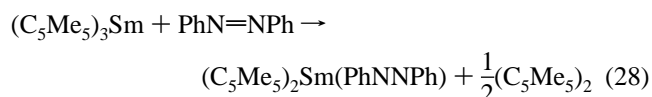
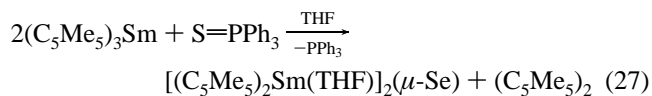
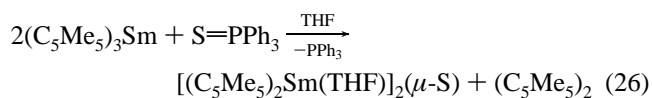


With yet another type of substrate, 1,3,5,7- C_8H_8 , a parallel result was once again observed. $(C_5Me_5)_3Sm$ reduces C_8H_8 to form a $(C_8H_8)^{2-}$ dianion (eq 25) in a reaction analogous to that originally used to make $(C_5Me_5)_3Sm$ from C_8H_8 and $(C_5Me_5)_2Sm$ (eq 13).



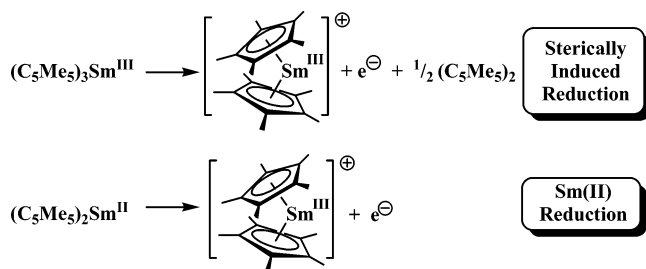
Equations 19, 20, 24, and 25 were puzzling because a sterically crowded trivalent complex, $(C_5Me_5)_3Sm$, was accomplishing the same reductions as the sterically open divalent reducing agent, $(C_5Me_5)_2Sm$. Because in no case were Sm^{4+} products observed, the reduction was not arising from the Sm^{3+} .

If the metal is not doing the reduction, this means the effective reducing agent must be the ligand. Indeed, in each of the $(C_5Me_5)_3Sm$ reactions above, examination of the organic byproducts revealed the presence of $(C_5Me_5)_2$. Equations 26–29 show the fully balanced versions of eqs 19, 20, 24, and 25. $(C_5Me_5)_2$ is the product expected if a

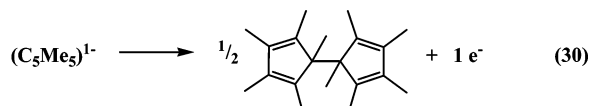


Importance of Questioning Scientific Assumptions

Scheme 4. Comparison of SIR vs Traditional Divalent Sm^{2+} Reduction



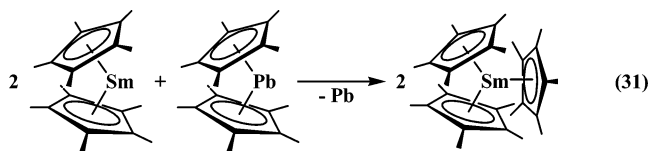
$(\text{C}_5\text{Me}_5)^-$ ligand gave up an electron and formed C_5Me_5 radicals, which dimerized according to eq 30.



This explained why $(\text{C}_5\text{Me}_5)_3\text{Sm}$ displays reductive reactivity analogous to that of $(\text{C}_5\text{Me}_5)_2\text{Sm}$. Both reagents give up one electron, leaving the $[(\text{C}_5\text{Me}_5)_2\text{Sm}]^+$ cation, which can complex the reduced substrate (Scheme 4). The $(\text{C}_5\text{Me}_5)_3\text{Sm}$ reaction has been termed sterically induced reduction (SIR)²⁹ to differentiate it from traditional metal-based reduction and because it has only been observed in sterically crowded molecules.

The discovery of SIR was exciting not because it provided a new way to do samarium reduction chemistry but because it offered a way to extend Sm^{2+} reduction chemistry to the other lanthanides and effect the size optimization of the reduction chemistry. If $(\text{C}_5\text{Me}_5)_3\text{Sm}$ is a reductant only because of steric crowding, then other $(\text{C}_5\text{Me}_5)_3\text{Ln}$ complexes could also be reductants. This would bring Sm^{2+} reductive chemistry to all of the lanthanides. Size optimization of Sm^{2+} reduction chemistry would be possible and reductive reactions previously accessible only with samarium could be carried out to give products with a variety of electronic and magnetic properties.

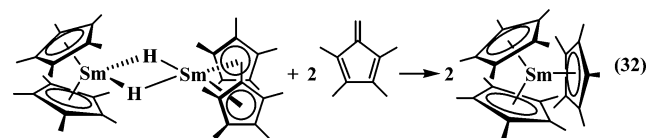
To test these ideas, the initial target was $(\text{C}_5\text{Me}_5)_3\text{Nd}$. Neodymium was selected because it is larger than samarium. If $(\text{C}_5\text{Me}_5)_3\text{Sm}$ exists, so should the less crowded $(\text{C}_5\text{Me}_5)_3\text{Nd}$ provided a synthetic pathway is available. One obstacle to using SIR to extend reduction chemistry to all of the lanthanides was that the only available syntheses of $(\text{C}_5\text{Me}_5)_3\text{Sm}$ required Sm^{2+} precursors (eqs 13⁵⁷ and 31⁶⁵). Only for $\text{Ln} = \text{Sm}$ were $(\text{C}_5\text{Me}_5)_3\text{Ln}$ syntheses known. To extend SIR to the other lanthanides, new syntheses of $(\text{C}_5\text{Me}_5)_3\text{Sm}$ from trivalent precursors were necessary. This was challenging because $(\text{C}_5\text{Me}_5)_3\text{Sm}$ was a complex that was not supposed to exist!



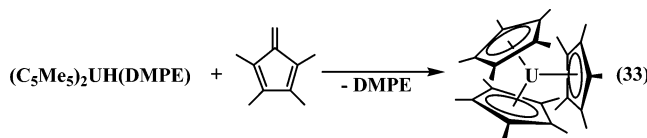
The first synthetic breakthrough came when considering the reactivity of $(\text{C}_5\text{Me}_5)_3\text{Sm}$ in its $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\eta^1\text{-C}_5\text{Me}_5)$

(65) Evans, W. J.; Forrestal, K. J.; Leman, J. T.; Ziller, J. W. *Organometallics* **1996**, *15*, 527.

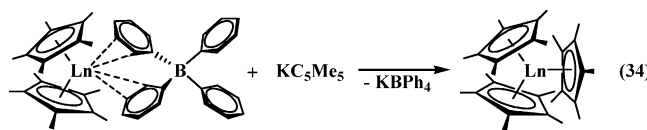
form. In this form, the complex has β -hydrogen atoms and could β -hydrogen eliminate to form the known hydride $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-H})_2]$ ⁶⁶ and tetramethylfulvene. When it was realized that this reaction was not favored, the reverse was examined and provided for the first time a route to $(\text{C}_5\text{Me}_5)_3\text{Ln}$ complexes from trivalent precursors (eq 32).⁶⁷ When this



reaction was not immediately successful with neodymium, it was applied to show that the method worked with a metal other than samarium (eq 33).⁶⁷ The chemistry of $(\text{C}_5\text{Me}_5)_3\text{U}$ is discussed later.



The second critical synthetic advance came from the realization that unsolvated cations of the formula $(\text{C}_5\text{Me}_5)_2\text{-Ln}(\text{BPh}_4)$ could be isolated and were soluble in benzene.⁶⁸ Previous efforts suggested that they were not soluble in anything but coordinating solvents. These complexes are unusual in that they have a higher degree of solubility in benzene than toluene. These tetraphenylborate salts have $(\text{C}_5\text{Me}_5)_2\text{Ln}[(\mu\text{-Ph})_2\text{BPh}_2]$ structures that contain the $(\text{BPh}_4)^-$ anions loosely ligated to the metal via long metal aryl linkages. These are excellent precursors because the $(\text{BPh}_4)^-$ anions can be easily displaced. KC_5Me_5 displaces the $(\text{BPh}_4)^-$ anion to make a stable byproduct, KBPh_4 , and $(\text{C}_5\text{Me}_5)_3\text{Ln}$ (eq 34).⁶⁸



Equation 34 provided $(\text{C}_5\text{Me}_5)_3\text{Nd}$ and the opportunity to see if SIR would occur with a metal other than samarium. In the SIR reactions of $(\text{C}_5\text{Me}_5)_3\text{Sm}$, there was always residual concern that the reaction was occurring via undetected Sm^{2+} intermediates.

As shown in eq 35, $(\text{C}_5\text{Me}_5)_3\text{Nd}$ does reduce $\text{Se}=\text{PPh}_3$ ⁶⁹ but not in the same way as $(\text{C}_5\text{Me}_5)_3\text{Sm}$. Instead of forming a $(\text{Se})^{2-}$ product analogous to the one shown in eq 20 above, a $(\text{Se}_2)^{2-}$ product forms. Hence, $(\text{C}_5\text{Me}_5)_3\text{Nd}$ is a reductant but not as strong a reductant as $(\text{C}_5\text{Me}_5)_3\text{Sm}$. This result is reasonable considering that $(\text{C}_5\text{Me}_5)_3\text{Nd}$ is not as sterically crowded as $(\text{C}_5\text{Me}_5)_3\text{Sm}$. Equations 20 and 35 suggested that the reducing capacity could be modulated by the amount of

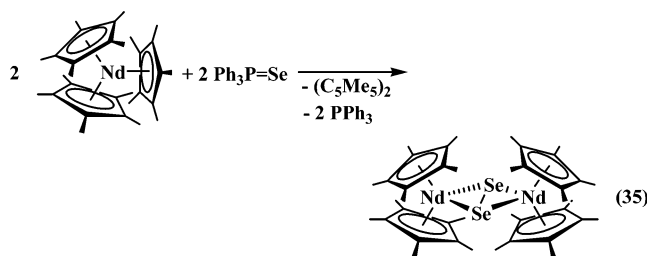
(66) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401.

(67) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 774.

(68) Evans, W. J.; Seibel, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 6745.

(69) Evans, W. J.; Nyce, G. W.; Clark, R. D.; Doedens, R. J.; Ziller, J. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 1801.

steric crowding. Subsequent studies have been consistent with that analysis.⁷⁰



Implications of SIR in Lanthanide Chemistry. The results obtained with $(C_5Me_5)_3Sm$ and $(C_5Me_5)_3Nd$ indicate that the one-electron reduction chemistry of divalent $(C_5Me_5)_2Sm$ can be extended to lanthanides beyond samarium by synthesizing sterically crowded tris(pentamethylcyclopentadienyl) complexes. Moreover, the reduction capacity appears to be tunable by varying the amount of steric crowding. Because the lanthanides offer a large range of metal sizes and a variety of substituted peralkylcyclopentadienyl ligands are available, including $(C_5Me_4R)^-$ ($R = Et, iPr, SiMe_3$),⁷¹ the amount of steric crowding should be precisely controllable. The challenge will be in synthesizing the highly reactive sterically crowded species.

More broadly, these results suggest that new ligand reactivity can be developed by making sterically crowded complexes. The reactivity displayed by $(C_5Me_5)^-$ ligands in $(C_5Me_5)_3Ln$ could also occur in complexes of other compositions such as $(C_5Me_5)_2M(\text{large ligand})$ and $(\text{large ligand})_2M(C_5Me_5)$. In fact, sterically crowded complexes of composition $(\text{large ligand})_xM$ could also display SIR chemistry if the ligands are sufficiently reducing.

This raises the general possibility that SIR reactivity has been observed before but was not recognized. Attempted syntheses of sterically crowded complexes that “failed”, in that they did not provide the target complex but instead gave unexpected reduction products, might not be published in the literature. Yet, it is possible that sterically crowded complexes had formed and SIR occurred. It seems quite likely that the SIR chemistry observed here is not restricted to only f elements and $(C_5Me_5)^-$ ligands. Because many anions can affect reduction without steric crowding, the steric aspect can often be difficult to detect.

Combining SIR with Metal-Based Reduction To Make Multielectron Reductants

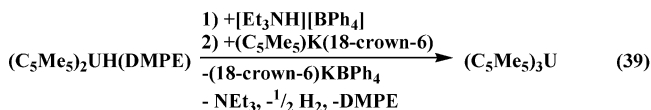
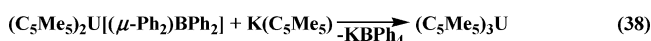
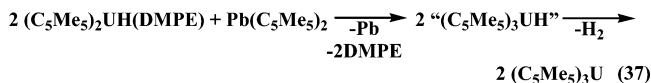
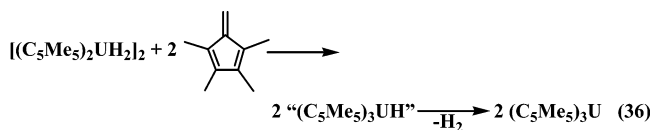
The synthesis of $(C_5Me_5)_3U$ described above⁶⁷ provided an opportunity to combine SIR with metal-based reduction. $(C_5Me_5)_3U$ is sterically crowded enough to do SIR; i.e., its $U-C(C_5Me_5)$ distances are much longer than normal $U^{3+}(C_5Me_5)^-$ complexes. However, it also has a redox-active U^{3+} component that typically reacts as a one-electron reductant to make U^{4+} products.⁷² To determine if $(C_5Me_5)_3U$ would function as a two-electron reductant, its reactivity with 1,3,5,7-cyclooctatetraene was examined.

(70) Evans, W. J.; Perotti, J. M.; Davis, B. L.; Kozimor, S. A.; Nyce, G. W.; Fujimoto, C. H.; Clark, R. D.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 3916.

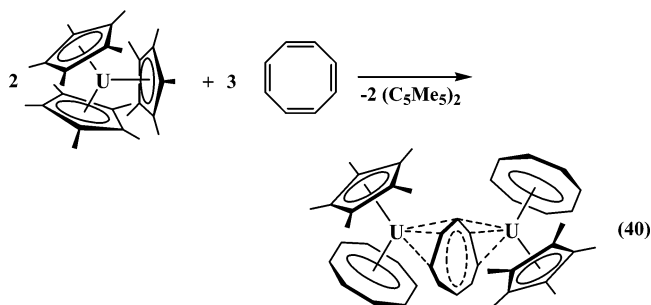
(71) Evans, W. J.; Davis, B. L.; Ziller, J. W. *Inorg. Chem.* **2001**, *40*, 6341.

(72) Evans, W. J.; Kozimor, S. A. *Coord. Chem. Rev.* **2006**, *250*, 911.

Before the reactivity is discussed, it should be mentioned that once it was established that $(C_5Me_5)_3U$ could exist, four additional synthetic routes were identified (eqs 36–39).⁷³

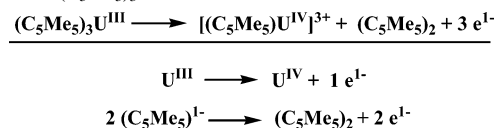


The 1:1 reaction of $(C_5Me_5)_3U$ and 1,3,5,7- C_8H_8 was examined because cyclooctatetraene can be reduced by two electrons and $(C_5Me_5)_3U$ was expected to be a two-electron reductant. This reaction gave a new uranium product and $(C_5Me_5)_2$, the signature byproduct of SIR, but the stoichiometry was not correct because some $(C_5Me_5)_3U$ was left over. A 2:3 $(C_5Me_5)_3U/C_8H_8$ ratio gave a clean reaction, and as shown in eq 40,⁷⁴ an unusual mixed-ligand product, $[(C_5Me_5)(C_8H_8)U]_2(\mu-\eta^3:\eta^3-C_8H_8)$, was isolated. This reaction actually achieved the original goal that stimulated the reaction of $(C_5Me_5)_2Sm$ with C_8H_8 (eq 13), i.e., it generated a complex containing a bridging $(C_8H_8)^{2-}$ ligand sandwiched between two metallocene units such that it adopts an unusual nonplanar geometry! In this case, the metallocenes are the mixed-ligand tetravalent uranium $[(C_8H_8)(C_5Me_5)U]^+$ units, and they bind to the $(C_8H_8)^{2-}$ ligand in a bis(allyl) mode in which one carbon is part of each allyl coordination.



Equation 40 is unusual not only for the structure of the product but also for the stoichiometry. The 2:3 stoichiometry was needed because 3 equiv of C_8H_8 were reduced to form the three $(C_8H_8)^{2-}$ ligands in the product. This overall six-electron reduction was done by just 2 equiv of $(C_5Me_5)_3U$; i.e., it is functioning as a three-electron reductant rather than the two-electron reductant originally expected. As shown in Scheme 5, each $(C_5Me_5)_3U$ unit is providing one electron

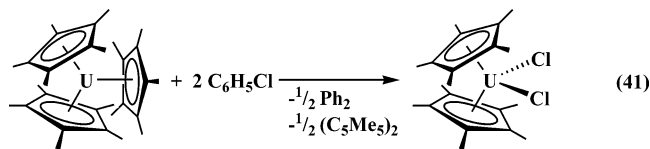
Scheme 5. $(C_5Me_5)_3U$ as a Three-Electron Reductant



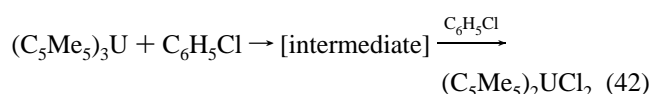
Importance of Questioning Scientific Assumptions

from U^{3+} and two electrons from SIR because the product contains only one $(C_5Me_5)^-$ ligand per uranium.

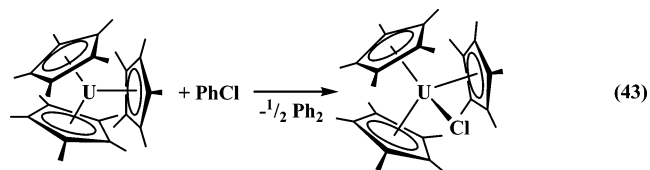
Once it was known that SIR could be combined with U^{3+} reduction, it was of interest to determine which redox process occurred first. Because these reactions are rapid, this seemed difficult. However, the reaction of $(C_5Me_5)_3U$ with chlorobenzene gave an answer. $(C_5Me_5)_3U$ reacts with C_6H_5Cl primarily as a two-electron reducing agent forming $(C_5Me_5)_2UCl_2$ and biphenyl (eq 41).



Interestingly, eq 41 goes stepwise. The first equivalent of C_6H_5Cl reacts quickly to make an isolable intermediate that slowly reacts with a second equivalent, forming $(C_5Me_5)_2UCl_2$ (eq 42). If SIR occurred first, $(C_5Me_5)^-$ would be lost,



the metal would stay at the $3+$ oxidation state, the reduction product, Cl^- , would be added, and the intermediate would be $[(C_5Me_5)_2UCl]_3$, a complex crystallographically characterized many years ago.⁷⁵ If U^{3+} reduction occurred first, the product would retain all of the $(C_5Me_5)^-$ rings and it would contain a smaller U^{4+} metal center. If the Cl^- product was present, the product would be $(C_5Me_5)_3UCl$, a compound more crowded than the $(C_5Me_5)_3U$ starting material. Hence, it was assumed that SIR occurred first to make the known $[(C_5Me_5)_2UCl]_3$ as the intermediate.



Surprisingly, the intermediate is $(C_5Me_5)_3UCl$ (eq 43).⁷⁶ This showed that the limit of steric crowding in $(C_5Me_5)_3M$ complexes has not been reached. Complexes with three $(C_5Me_5)^-$ rings and an additional ligand are also sterically and synthetically accessible. Hence, U^{3+} reduction occurs first in eq 41, and the U^{4+} intermediate, $(C_5Me_5)_3UCl$, reacts with another equivalent of C_6H_5Cl to make the U^{4+} product, $(C_5Me_5)_2UCl_2$, by SIR (eq 44).

(73) Evans, W. J.; Nyce, G. W.; Ziller, J. W. *Organometallics* **2002**, *21*, 1050.

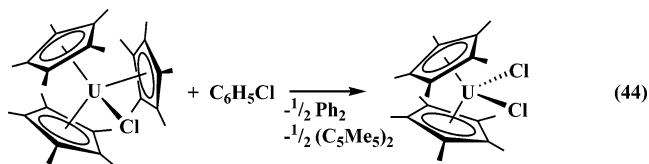
(74) Evans, W. J.; Nyce, G. W.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 240.

(75) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S.; Day, V. W. *Organometallics* **1982**, *1*, 170.

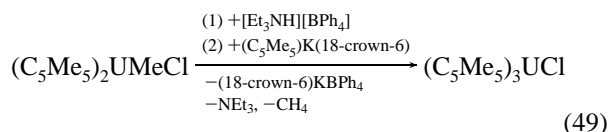
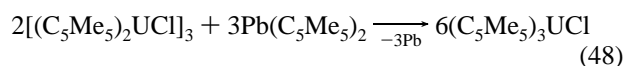
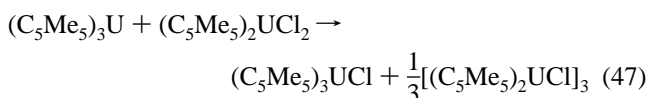
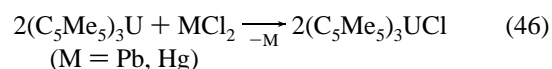
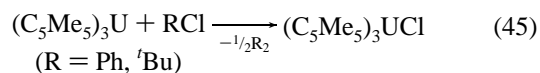
(76) Evans, W. J.; Nyce, G. W.; Johnston, M. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 12019.

(77) Evans, W. J.; Kozimor, S. A.; Ziller, J. W.; Kaltsoyannis, N. *J. Am. Chem. Soc.* **2004**, *126*, 14533.

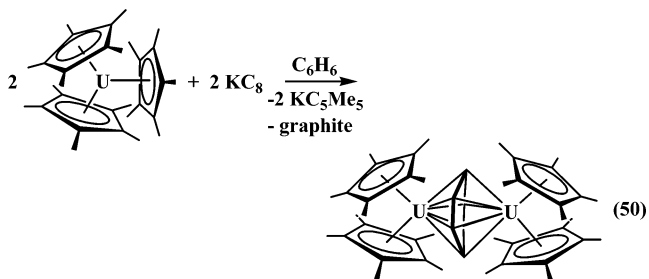
(78) Diaconescu, P. L.; Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C. *J. Am. Chem. Soc.* **2000**, *122*, 6108.



As in the case of $(C_5Me_5)_3U$ above, once the existence of $(C_5Me_5)_3UCl$ was established, several new synthetic routes were discovered (eqs 45–49).⁷⁶



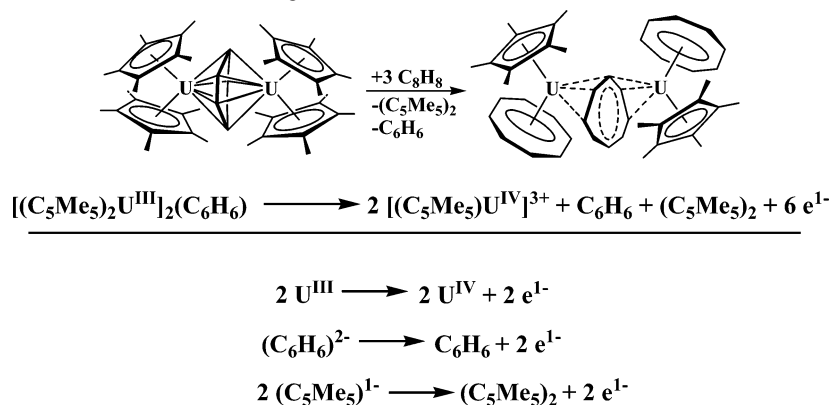
In the course of examining the chemistry of $(C_5Me_5)_3U$, an unusual complex derived from benzene was obtained as shown in eq 50.⁷⁷ In this complex, two uranium metallocene



units sandwich a C_6H_6 ligand derived from benzene. The closest complex in the literature was an analogue in which two bis(arylamide)uranium units are located on either side of a ligand derived from toluene to form $[(ArNR)_2U]_2(C_6H_5CH_3)$ (R = CMe₃; Ar = C₆H₃Me₂-3,5).⁷⁸ These complexes are interesting in that there are a variety of ways to assign oxidation states. On the basis of the structure and reactivity of $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, this complex is considered to be a U^{3+} complex of a $(C_6H_6)^{2-}$ dianion. As such, it has considerable reductive capacity. In addition, the U–C(C_5Me_5) distances in $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$ are as long as those in $(C_5Me_5)_3U$. This means that $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$ also has the capacity to do SIR chemistry.

The reaction of $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$ with cyclooctatetraene demonstrated that it could deliver reduction chemistry from all of these sources. The bimetallic complex functions as a six-electron reductant, as shown in Scheme 6. Formally, two electrons come from two U^{3+} centers, two electrons from $(C_6H_6)^{2-}$, and two electrons from SIR from two $(C_5Me_5)^-$ ligands.

Scheme 6. Six-Electron Reduction via Both Metal- and Ligand-Based Reduction



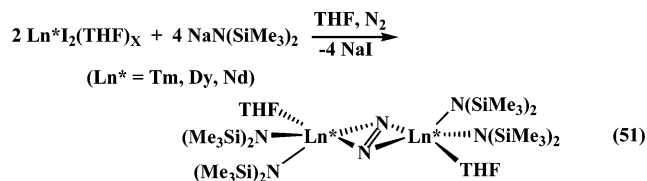
Hence, SIR can be combined with both metal and ligand reduction reactivity to accomplish multielectron reduction. Another significant feature of the reaction in Scheme 6 is that this is the first bis(pentamethylcyclopentadienyl) complex to display SIR. This demonstrates that SIR reactivity is not limited only to $(C_5Me_5)_3M$ complexes.

Lessons from $(C_5Me_5)_3M$ Chemistry. From a straightforward exploratory synthetic study of the chemistry of $(C_5Me_5)_2Sm$, a new class of sterically crowded complexes, the $(C_5Me_5)_3M$ compounds, was discovered. This alone is significant. It demonstrates how an entire class of complexes in which all of the metal–ligand bond lengths are longer than the conventional distances can be accessed. Previously, it was assumed that it would not be possible to make classes of complexes with bond lengths 0.1 Å longer than normal. Equations 13, 31–33, 34, 36–39, and 45–49 demonstrate that this is possible in a variety of ways.

Surprisingly, these sterically crowded complexes generated new reductive chemistry. Generally, redox chemistry of metal complexes is manipulated by controlling the electronic, not steric, aspects of the complexes. In this case, steric factors are generating redox reactivity with normally inert ligands.

A Third Type of Reduction from Studies of Dinitrogen

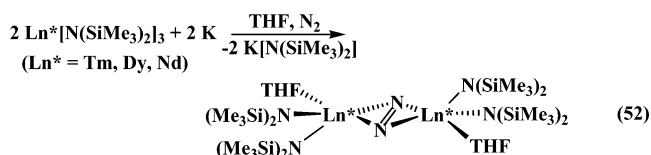
Another new approach to reductive f element chemistry arose from studies of the reduction of dinitrogen by the recently discovered molecular complexes of Nd^{2+} , Dy^{2+} , and Tm^{2+} discussed above. As shown in eqs 4 and 8, the addition of cyclopentadienyl salts to Ln^*I_2 reagents ($Ln^* = Nd^{2+}$, Dy^{2+} , Tm^{2+}) generated $[(C_5R_5)_2Ln^*]_2(\mu-\eta^2:\eta^2-N_2)$ complexes.^{49,50} It was subsequently found that a variety of anionic ligands, Z^- , when added to the Ln^*I_2 reagents under nitrogen would generate $[Z_2Ln^*]_2(\mu-\eta^2:\eta^2-N_2)$ products including $(Z)^- = [N(SiMe_3)_2]^-$ and $(OC_6H_3tBu_2)^-$, e.g., eq 51.⁷⁹ These



reactions were all thought to occur by ionic metathesis between the added ligand salt and Ln^*I_2 to form a reactive divalent intermediate of formula “ Ln^*Z_2 ”, which was the

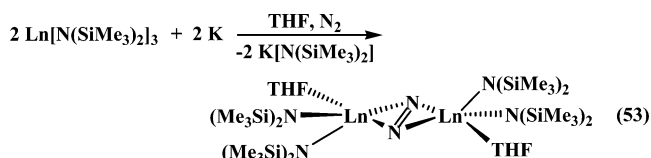
active agent in reducing dinitrogen. Only in the case of $[C_5H_3-(SiMe_3)_2]_2Tm(THF)$ was a divalent intermediate isolated, however (eq 6).

In an attempt to discover alternative synthetic routes to these presumably reactive “ Ln^*Z_2 ” intermediates, the reduction of $Ln^*[N(SiMe_3)_2]_3$ with potassium metal was investigated.^{80,81} $Ln[N(SiMe_3)_2]_3$ complexes have been known since the studies of Bradley in the 1970s and are readily synthesized from $LnCl_3$ precursors. As shown in eq 52, this approach to $[Z_2Ln^*]_2(\mu-\eta^2:\eta^2-N_2)$ complexes was successful and $\{[(Me_3Si)_2N]_2Ln\}_2(\mu-\eta^2:\eta^2-N_2)$ complexes of thulium, dysprosium, and neodymium could be made in this way. This was advantageous because the precursor complexes, $Ln^*[N(SiMe_3)_2]_3$, are easier to synthesize and handle than Ln^*I_2 .



Interestingly, no evidence for divalent intermediates was observed during the reactions shown in eq 52. It was expected that divalent intermediates would form and be intensely colored, as is typical for divalent lanthanide complexes. No such colors were seen, but it was possible that the divalent intermediates had only a transitory existence and would not be detectable.

To test these ideas, a reaction analogous to eq 52 was conducted with $Ln = Ho$. Holmium had no known molecular divalent oxidation state chemistry. Holmium was chosen because, as shown in Table 5,³⁶ its calculated reduction potential was closer to the known divalent ions than many of the other lanthanides and it had a size similar to those of dysprosium and thulium. To our surprise, $Ln = Ho$ also gives successful dinitrogen reduction according to eq 53.⁸⁰



(80) Evans, W. J.; Lee, D. S.; Ziller, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 454.

(81) Evans, W. J.; Lee, D. S.; Rego, D. B.; Perotti, J. M.; Kozimor, S. A.; Moore, E. K.; Ziller, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 14574.

(79) Evans, W. J.; Zucchi, G.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 10.

Table 5. Calculated Values of the $\text{Ln}^{3+} + \text{e}^- \rightarrow \text{Ln}^{2+}$ Half-Reaction vs NHE³⁶ and Electronic Configurations

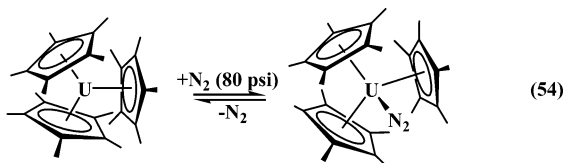
Ln	$\text{Ln}^{3+}/\text{Ln}^{2+}$ vs NHE (V)	Ln^{2+} electron configuration	Ln	$\text{Ln}^{3+}/\text{Ln}^{2+}$ vs NHE (V)	Ln^{2+} electron configuration
Eu	-0.35	[Xe]4f ⁷	Er	-3.1	[Xe]4f ¹²
Yb	-1.15	[Xe]4f ¹⁴	La	-3.1	[Xe]4f ¹
Sm	-1.55	[Xe]4f ⁶	Ce	-3.2	[Xe]4f ²
Tm	-2.3	[Xe]4f ¹³	Tb	-3.7	[Xe]4f ⁹
Dy	-2.5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

^a No calculated value.

Encouraged by these results, we began to examine all of the other lanthanides for this dinitrogen reduction reactivity. Equation 53 proved to be successful not only for $\text{Ln} = \text{Ho}$ but also for $\text{Ln} = \text{Er}, \text{Tb}, \text{Gd}, \text{Y},$ and Lu .⁸¹ As shown in Table 5, these metals have calculated $\text{Ln}^{3+}/\text{Ln}^{2+}$ reduction potentials³⁶ more negative than the -2.9 V vs NHE reduction potential of the potassium reductant! In the case of yttrium and lutetium, no calculated values are available for the formation of divalent Y^{2+} or Lu^{2+} ions because they had never been observed either in solution or in the solid state.²³

The success of all of these metals in eq 53 suggested that there was another way of achieving divalent lanthanide reduction by combining a trivalent precursor with potassium. The LnZ_3/K combination in which $(\text{Z})^- = [\text{N}(\text{SiMe}_3)_2]^-$ gave chemistry equivalent to “ LnZ_2 ”. The closest related reactions in the literature were those of Lappert et al., who used alkali metal reductions of $(\text{C}_5\text{H}_3\text{R}_2)_3\text{Ln}$ complexes of lanthanum and cerium ($\text{R} = \text{CMe}_3, \text{SiMe}_3$) to effect the reduction of arenes.^{82–85}

If eqs 52 and 53 proceeded through divalent “ $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_2$ ” intermediates, then this would be the first evidence of soluble, molecular species containing $\text{Ho}^{2+}, \text{Er}^{2+}, \text{Tb}^{2+}, \text{Gd}^{2+}, \text{Y}^{2+},$ and Lu^{2+} . If the reactions did not proceed through “ $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_2$ ” intermediates, then activation of dinitrogen via trivalent intermediates such as “ $(\text{N}_2)\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ ” would have to be considered. Although $(\text{N}_2)\text{M}(\text{NR}_2)_3$ species are quite reasonable in transition-metal chemistry,^{86,87} they are not known in lanthanide chemistry. For example, the simple monometallic end-on dinitrogen complex of uranium, $(\text{C}_5\text{Me}_5)_3\text{U}(\eta^1\text{-N}_2)$ (eq 54), is stable only



under dinitrogen pressure.⁸⁸ The existence of such $\text{Ln}-\text{N}_2$ intermediates in eqs 52 and 53 would be unusual because

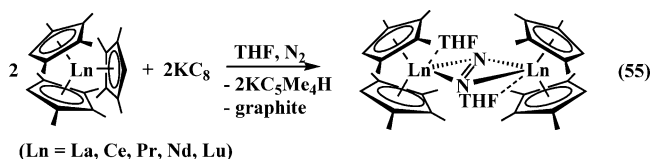
- (82) Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1996**, 1987.
 (83) Cassani, M. C.; Duncalf, D. J.; Lappert, M. F. *J. Am. Chem. Soc.* **1998**, *120*, 12958.
 (84) Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F.; Laschi, F. *Organometallics* **1999**, *18*, 5539.
 (85) Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **2000**, *19*, 2832.
 (86) Peters, J. C.; Cherry, J. F.; Thomas, J. C.; Baraldo, L.; Mindiola, D. J.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1999**, *121*, 10053.
 (87) O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R.; Reiff, W. M. *Inorg. Chem.* **1999**, *38*, 243.

the reactions are conducted in THF, a much better ligand for the oxophilic lanthanide that is present in higher concentration.

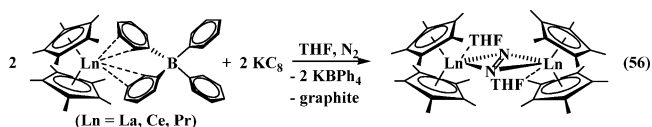
Regardless of the mechanism of eqs 52 and 53, the LnZ_3/K reaction appears to be another alternative to accessing divalent “ LnZ_2 ” chemistry. Moreover, it extends the divalent chemistry to a wider range of lanthanides, allowing for size optimization and the extension of reduction chemistry to diamagnetic systems such as yttrium and lutetium.

Although eq 53 was successful with many of the lanthanides, crystals of $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ln}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ were not isolable with $\text{Ln} = \text{La}, \text{Ce},$ and Pr . As shown in Table 5, this did not seem to correlate with calculated reduction potentials. Ions much more difficult to reduce than these gave reduced dinitrogen products via eq 53.

Because size effects can be so important in lanthanide chemistry, it was conceivable that the lanthanum, cerium, and praseodymium systems failed to give crystals of $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ln}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ complexes because of a less than optimal ligand/metal combination. To test this and to test the generality of the LnZ_3/K system, reactions involving another Z were examined. Reactions with $(\text{Z})^- = (\text{C}_5\text{Me}_4\text{H})^-$ were selected because the $\text{Ln}(\text{C}_5\text{Me}_4\text{H})_3$ complexes can be obtained directly from LnCl_3 and $\text{KC}_5\text{Me}_4\text{H}$ for most of the lanthanides. As shown in eq 55, the LnZ_3/K reaction is successful with the largest lanthanide, lanthanum, as well as with cerium, praseodymium, neodymium, and lutetium.^{89–91}



It was also desirable to be able to do “ LnZ_2 ” chemistry via LnZ_3/K with $\text{Z}^- = (\text{C}_5\text{Me}_5)^-$ because extensive background information is already available on pentamethylcyclopentadienyl lanthanide chemistry. However, as described above, the $(\text{C}_5\text{Me}_5)_3\text{Ln}$ precursors necessary for such LnZ_3/K reactions are challenging to make.^{61,70} To circumvent this problem, a $\text{LnZ}_2\text{Z}'/\text{K}$ reaction was examined with the precursors to $(\text{C}_5\text{Me}_5)_3\text{Ln}$, namely, the tetraphenylborate salts, $(\text{C}_5\text{Me}_5)_2\text{Ln}[(\mu\text{-Ph})_2\text{BPh}_2]$.⁶⁸ As shown in eq 56, these precursors provide synthetic routes to $[(\text{C}_5\text{Me}_5)_2\text{Ln}]_2(\mu\text{-}\eta^2\text{-N}_2)$ complexes and demonstrate that both heteroleptic $\text{LnZ}_2\text{Z}'/\text{K}$ reactions as well as homoleptic LnZ_3/K reactions are viable.⁸⁹



$\eta^2\text{-N}_2$) complexes and demonstrate that both heteroleptic $\text{LnZ}_2\text{Z}'/\text{K}$ reactions as well as homoleptic LnZ_3/K reactions are viable.⁸⁹

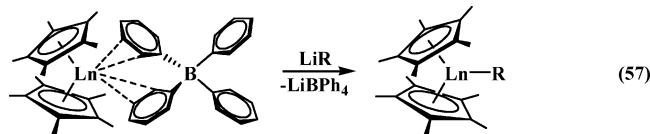
Summary on LnZ_3/K and $\text{LnZ}_2\text{Z}'/\text{K}$ Reactions. This approach to accessing the chemistry of “ LnZ_2 ” reductive divalent chemistry seems quite promising. This method of reduction is successful with both the largest and smallest

- (88) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 14264.
 (89) Evans, W. J.; Lee, D. S.; Lie, C.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 5517.
 (90) Evans, W. J.; Lee, D. S.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 6393.
 (91) Evans, W. J.; Rego, D. B.; Ziller, J. W. *Inorg. Chem.* **2006**, *45*, 10790.

lanthanides, thereby allowing the full range of size optimization for the reductive chemistry. Moreover, these divalent-like reductions can now be done with metals that generate diamagnetic products, i.e., La^{3+} , Y^{3+} , and Lu^{3+} , so that diamagnetic NMR spectroscopy can be applied to study this chemistry. In the past, the reduction chemistry of Eu^{2+} , Yb^{2+} , Sm^{2+} , Tm^{2+} , Dy^{2+} , and Nd^{2+} always involved paramagnetic trivalent products.

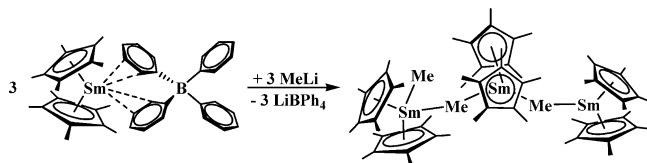
The Importance of Precursors

Precursor molecules are often underappreciated in the development of chemistry because the focus is generally on new reactions and products. It is worth noting the importance of one class of precursors that made much of the above chemistry possible. As described earlier, the tetraphenylborate salts, $(\text{C}_5\text{Me}_5)_2\text{Ln}[(\mu\text{-Ph})_2\text{BPh}_2]$,⁶⁸ were essential for the synthesis of the $(\text{C}_5\text{Me}_5)_3\text{M}$ complexes (eq 34).^{61,70} They also opened up LnZ_3/K chemistry to $(\text{Z})^- = (\text{C}_5\text{Me}_5)^-$ complexes via $\text{LnZ}_2\text{Z}'$, where $(\text{Z}')^- = [(\mu\text{-Ph})_2\text{BPh}_2]^-$ (eq 56).⁸⁹ The following equations show how these precursors are contributing further to organolanthanide chemistry. Equation 57 shows how they provide access to unsolvated lanthanide metallocene alkyls of the larger lanthanides.⁹²



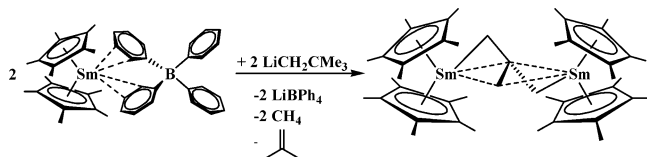
Previously, these types of compounds were laborious to synthesize even for the less reactive later lanthanides, and compounds of this type were inaccessible for the larger metals. The method allowed the isolation of $[(\text{C}_5\text{Me}_5)_2\text{-SmMe}]_3$ (Scheme 7), a compound that has an extensive C–H

Scheme 7. Synthesis of $[(\text{C}_5\text{Me}_5)_2\text{SmMe}]_3$ Utilizing $[(\text{C}_5\text{Me}_5)_2\text{Sm}][(\mu\text{-Ph})_2\text{BPh}_2]$ as a Precursor



bond activation chemistry.⁹² When eq 57 was examined with neopentylolithium, the product was unexpectedly found to contain only a four-carbon unit instead of the five-carbon unit of the organolithium reagent (Scheme 8). This resulted

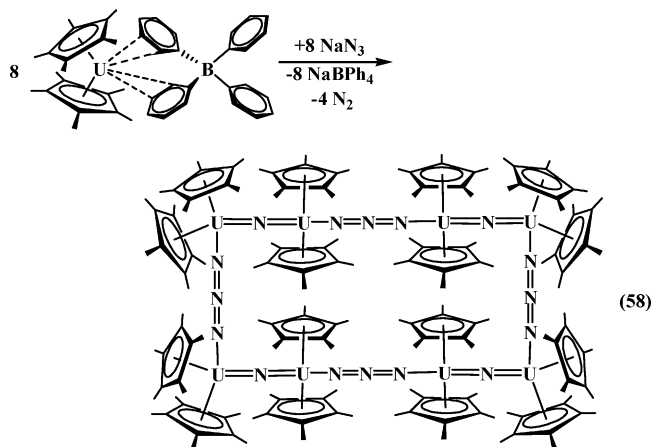
Scheme 8. Formation of the Trimethylenemethane Complex, $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2[\text{C}(\text{CH}_2)_3]$, via β -Methyl Elimination Utilizing $[(\text{C}_5\text{Me}_5)_2\text{Sm}][(\mu\text{-Ph})_2\text{BPh}_2]$ as a Precursor



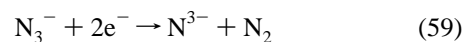
because of an unusual β -methyl elimination reaction at this sterically unsaturated unsolvated metallocene alkyl center.⁹³

Perhaps the most unusual chemistry observed so far with $(\text{C}_5\text{Me}_5)_2\text{M}[(\mu\text{-Ph})_2\text{BPh}_2]$ precursors was found with $\text{M} = \text{U}$ and NaN_3 . It was of interest to see how the combination

of a reducible azide ligand on a reducing U^{3+} metal center in a sterically unsaturated unsolvated metallocene would react. As shown in eq 58, the result is the formation of a 24-membered ring of uranium and nitrogen atoms in a mixed azide nitride complex.⁹⁴ The formation of this complex can



be understood from the perspective of the initial formation of a trivalent “ $(\text{C}_5\text{Me}_5)_2\text{U}(\text{N}_3)$ ” intermediate. Azide to nitride reduction according to eq 59 requires two electrons per azide.



Hence, only one azide per two $(\text{C}_5\text{Me}_5)_2\text{U}(\text{N}_3)$ units can form a nitride. This gives rise to the bimetallic $[(\text{C}_5\text{Me}_5)_2\text{U}(\text{N})\text{U}(\text{C}_5\text{Me}_5)_2(\text{N}_3)]$ building block. Four of these units generate the complex shown.

The resulting complex is unusual from several perspectives. Previously, it had been assumed that f elements would not be ideal for the self-assembly of large polymetallic complexes because they do not have the rigid orbital requirements found with transition metals to make the necessary corners and edges. Evidently, these metallocene units have the necessary rigidity. The complex is also unusual in that it has a near linear $\text{U}=\text{N}=\text{U}$ linkage not previously observed.

Conclusion

For over 90 years, the reductive divalent chemistry of the lanthanides was limited to three ions, Eu^{2+} , Yb^{2+} , and Sm^{2+} . On the basis of extensive experimental research and thermodynamic and spectroscopic analyses, these were the only three ions expected to be accessible in solution and available for reduction. It was assumed that this was the limit of divalent reductive lanthanide chemistry.

The past few years have shown that this assumption was wrong. The number of fully characterized divalent lanthanides has doubled, and new ways of accomplishing divalent reduction chemistry have been developed. In one case, the LnZ_3/K and $\text{LnZ}_2\text{Z}'/\text{K}$ reductions involve the combination of a trivalent complex with an alkali metal. Divalent-like chemistry results even for metals that have no known divalent oxidation states. In the case of SIR, steric factors, not the usual electronic factors, lead to new chemistry

(92) Evans, W. J.; Perotti, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 3894.

(93) Evans, W. J.; Perotti, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 1068.

(94) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Science* **2005**, *309*, 1835.

Importance of Questioning Scientific Assumptions

and divalent-like reduction chemistry in sterically crowded complexes.

This latter reduction method was discovered in a class of complexes that was assumed to be too sterically crowded to exist. This class of "long bond organometallics" is growing and shows that the traditional assumptions about the distances of stable bond lengths in f element chemistry were also too limited. Entire classes of complexes can be synthesized in which all of the bond lengths are longer than expected.

Given that these well-established assumptions in these fundamental areas were wrong, it seems quite likely that basic assumptions in many other areas of chemistry are also waiting to be overturned. The old adage about challenging assumptions continues to be valid. To be effective scientists, we must never stop questioning our scientific assumptions.

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