The Periodic Table as a Career Guide: A Journey to Rare Earths

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Abstract: This chapter describes a personal journey through the periodic table in which an undergraduate starting research in boron hydride chemistry developed into a professorial researcher in rare earth chemistry. The chapter details how the periodic table became a career guide through connections and developments that led the boron chemist into the rare earth field. Also presented is the evolution of reductive rare-earth chemistry which started with just a few +2 lanthanide ions, Eu(II), Yb(II), and Sm(II), and now extends to +2 ions for all the rare earth metals, i.e. Sc, Y, and the lanthanides, La-Lu. The special reactivity of Sm(II), which led to the first lanthanide-based dinitrogen reduction is described, as well as the rare earth dinitrogen reduction that led to the new Ln(II) ions. Periodic trends in these developments are discussed and speculation on the future of the rare-earth elements in terms of periodic properties is also presented.

Key words. Boron, boron hydride, rare-earth, scandium, yttrium, lanthanide, actinide, samarium, bismuth, oxidation state, metal vapor reactor

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1 Introduction

1.1 First Element. All chemists start their research somewhere in the periodic table. Usually, that first entry into chemical research and, therefore, the first element with which we become scientifically involved, arises from random circumstances rather than a deliberate choice. This was certainly the case for me.

As an undergraduate at the University of Wisconsin, I was heavily committed to the rowing program. The crew team practiced year-round with long workouts on a daily basis. When I had a chance to choose an organic research group for undergraduate research in my senior year, I was interested in the group with the minimum time requirements, because I was already heavily obligated with crew practice. I had the opportunity to do research with numerous organic professors who required 12 hours per week in the lab. However, that year the Chemistry Department also allowed one inorganic professor to be part of the options for “organic” research, Professor Donald F. Gaines, a boron chemist. Since Professor Gaines required only 10 hours per week, I chose his group and that set my course in chemistry!

Dropping into the periodic table at boron was wonderful, I fell in love with chemical research through my studies of boron in the Gaines lab and that passion for chemical discovery has never ebbed. After a few weeks in the Gaines lab, I found myself spending 24 hours a week in the lab! The original decision to choose the lab with the lowest time requirement was completely overturned. The research was fascinating even though it involved a colorless gas I never could see: pentaborane. I learned to handle reactive gases using vacuum line techniques and develop glass blowing skills to make the specialized glassware necessary for my studies. These lessons were of lifelong value.

1.2 The Boron Pipeline. Starting my research in a boron lab had even more profound consequences on my career. Professor Gaines introduced me to Professor M. Frederick Hawthorne, a famous boron chemist at UCLA, when he visited Wisconsin for a seminar. As a consequence, I applied to UCLA for graduate school and subsequently joined the Hawthorne group for my graduate research. The focus of my research was the synthesis of metallocarboranes. Four years later, after a most enjoyable PhD experience and some sixteen publications, I continued in the "boron pipeline."

One of Professor Hawthorne's close friends was Dr. Earl L. Muetterties, also a boron chemist and the head of research at DuPont. Dr. Muetterties was moving from DuPont to be a professor at Cornell just as I was finishing my PhD and he was looking for postdoctoral fellows. On the basis of Professor Hawthorne's recommendation, I accepted a postdoctoral appointment in the first Muetterties research group at Cornell. Those were the days when students chose graduate schools and postdoctoral appointments without visiting, without video interviews, and, in my case, without ever meeting the new advisor.

Although Professor Muetterties had made extensive contributions in boron chemistry, his choice of research at Cornell was transition metal cluster chemistry. Indeed, if he had continued doing boron research at Cornell, I would not have joined his group. The boron pipeline connected me with him, but I wanted postdoctoral experience in a new area.

1.3 A Move to Molybdenum. Professor Muetterties took me into a new part of the periodic table. With four new postdoctoral fellows in his group, Professor Muetterties suggested each initiate research in one of the triads of Groups 6, 7, 8 and 9 of the transition series. My assignment was Group 6 and my research concentrated on the chemistry of molybdenum. Although I had made cobalt and iron metallocarboranes in graduate school, my horizons were broadened by this metal-focused research. My project involved the synthesis of molybdenum phosphite analogs of molybdenum carbonyls. It was fascinating to me to do inorganic synthesis in a new part of the Periodic Table.

Soon after starting my postdoctoral studies, I started to think about what part of the periodic table I wanted to study in my independent research if I was lucky enough to secure a faculty position. I realized I loved to synthesize new molecules and began looking around the periodic system for an area that could benefit from an exploratory synthetic effort.

1.4 Reaching the Rare Earths. My choice of independent research area was significantly influenced by three young inorganic chemists who had started research several years before me and were becoming prominent in their fields. Professor John E. Bercaw at Caltech was doing exciting research in Group 4 transition metal chemistry, Dr. Richard R. Schrock at DuPont was doing seminal work on carbene complexes of Group 5 metals, and Professor Tobin J. Marks at Northwestern was opening up organoactinide chemistry beyond that known for uranocene. The trend was clearly to "go West" in the periodic table for exciting new chemistry. One set of metals that was not being explored in the "western" part of the table was the rare earth metals, i.e. scandium, yttrium, and the lanthanides.

2 The Lanthanide Elements

2.1 A Less-studied Part of the Periodic Table. I had been intrigued by the lanthanide elements since graduate school when I did my oral proposal on these metals. The chemistry of the lanthanides had been largely ignored compared to that of the transition metals and actinides. As I read more about these metals, I found out why they had received little attention: the limited radial extension of their 4f orbitals. Unlike any of the other elements in the periodic table, the lanthanides' valence orbitals, the 4f orbitals, do not have a significant radial extension from the nucleus beyond the xenon core of electron density present in each lanthanide metal. Since their valence orbitals were more core-like, they could not participate in covalent bonding and the chemistry was viewed as very limited. The transition metals were obviously more attractive since they had d valence orbitals with good overlap for covalent interaction and activation of substrates such as CO, CO_2, H_2, and N_2. The bonding in lanthanide complexes was primarily ionic because overlap between the 4f orbitals and ligand orbitals was minimal. Evidence for this was found in the optical spectra and magnetic moments of lanthanide complexes which resembled those expected for the "free-ion", i.e. the spectra and magnetism of a given ion were similar from complex to complex regardless of the ligands present. Furthermore, there appeared to be little variation in their reactivities with $4f^n$ electron configuration. Ligands and substrates could not easily differentiate a $4f^3$ ion from a $4f^{12}$ ion because the electrons were inside the xenon core. The following 1970 statement by Pimentel and Sprately [1] was frequently cited when describing the lanthanides: "Lanthanum has only one important oxidation state in aqueous solution, the +3 state. With few exceptions, this tells the whole boring story about the other lanthanides."

The perceived "limited" chemistry of these metals presented a significant challenge to a synthetic chemist since it gave the possibility of overturning the current dogma. This seemed like an area in the periodic table that could benefit from exploratory synthesis. Few people had worked in the area and most of the effort had been in polar solvents such as water and alcohols. If new classes of complexes could be synthesized, new chemistry could develop. This was a big "if," however.

I was excited to work in this part of the periodic table for another reason as I began my career as an assistant professor at the University of Chicago. I had been told that to get tenure at Chicago, you had to be the best in the world in your area. I joked that if I was the only one working in this area, I would naturally be the best. Although I did get tenure, it was not because of a solo effort. Unbeknownst to me, others were simultaneously finding interest in the lanthanides including Professor Richard A. Andersen at UC Berkeley, Professor Herbert Schumann at the Technical University of Berlin, and Professor Michael F. Lappert at Sussex

My decision to investigate synthetic lanthanide chemistry was not viewed positively by my research advisors. They, like most other chemists, thought that there was little new chemistry to be learned in this part of the periodic table. Professors Hawthorne and Muetterties later told me that they had multiple conversations about how to get me my next job, because they were convinced that I would not get tenure at Chicago working with the lanthanides. I am indebted to them for not telling me their fears for my career! I pursued this area without trepidation.

2.2 In a New Part of the Periodic Table with No Prior Experience. When I embarked on my studies of the lanthanides, I knew almost nothing about them. I even had to learn the order of the lanthanide elements in the periodic table! Given the prevalent idea that the lanthanides were all the same, learning their names and electron configurations had not been emphasized in any classes I had taken.

I was not bothered by the fact that I knew so little about this part of the periodic table. On the contrary, I actually thought it was an advantage. With no formal training on these metals, I might try reactions outside the norm and thereby discover new chemistry. It was also not lost on me that I grew up in main group 3 (formally group 13) chemistry with trivalent boron and the new elements I was studying were primarily trivalent and in a group 3. That periodic table coincidence was comforting somehow, although so far this has not had major consequences. I remember that I was particularly excited about this group 3 coincidence when we synthesized $\{[Y(C_5H_5)]_5(\mu\text{-}OCH_3)_4O\}$ [2]. This complex had a square pyramidal structure of five yttrium centers each with a terminal ligand and four doubly-bridging groups along the edges of the bottom square face. This is analogous to the five BH vertices and four (μ-H) groups in pentaborane $\{(BH)_5(\mu\text{-}H)_4\}$ [3], Figure 1.

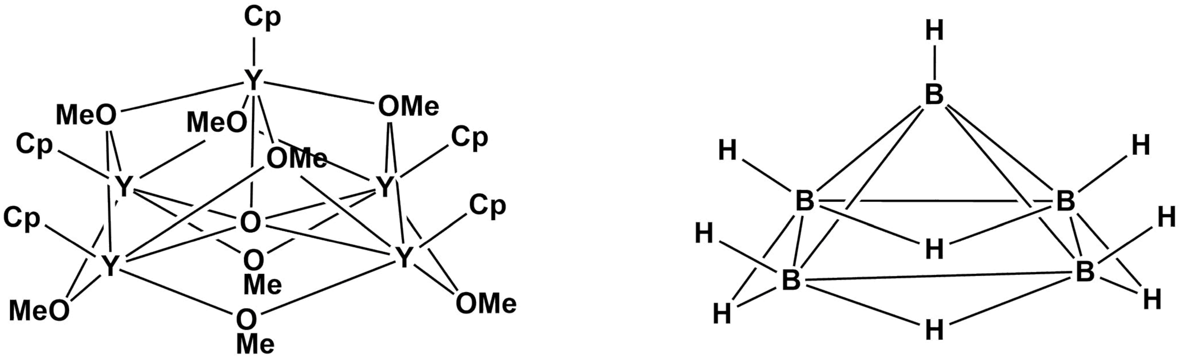


Figure 1. Square pyramidal Group 3 molecules with one terminal ligand/substituent on each of the five vertices and four bridging ligands/substituents along the basal edges (Cp = C_5H_5).

2.3 Early Ideas on Reductive Lanthanide Chemistry. My ideas for pursuing synthetic rare earth chemistry appeared in the early publications from the group. One of the obvious limitations of lanthanide chemistry was that the +3 oxidation state was so stable that the only other oxidation states known in isolable molecular complexes were Ce(IV), Eu(II), Yb(II), and Sm(II). So I decided to try to expand the non-aqueous lower oxidation state chemistry of the lanthanides. In 1978, I wrote:

> "In efforts to demonstrate experimentally a broader chemistry for the lanthanide metals, we have begun an investigation of the non-aqueous reductive chemistry of these elements. Specifically, we wish to determine if lower oxidation states are accessible in isolable complexes or obtainable transiently in solution. We anticipate that the lanthanide metals in lower oxidation states will display unusual and perhaps unique chemistry." [4]

This was further delineated in a subsequent publication citing +1 and 0 oxidation states as targets:

> "In our initial attempts to diversify lanthanide chemistry by studying the non-aqueous reductive chemistry of these metals, we decided to focus on the synthesis

and isolation of complexes in which the lanthanide metal is in the low, formal oxidation states, +1 and 0." [5]

I was basically trying to extend the range of metal oxidation states well known in other parts of the periodic table to the lanthanides. Although there is periodicity in the range of oxidation states found for metals, there was no periodic basis to assume that the lanthanides should have low oxidation states just because other elements do. However, I felt that targeting the synthesis of these low oxidation states could lead to new chemistry:

> "Admittedly, this goal was speculative, and we realized that the attainment of this particular objective was less important than the development of new lanthanide chemistry in the process." [5]

Part of the basis for these targets arose from examining the gas phase atomic spectra of the lanthanides:

> "the atomic spectra of the elements show that in low valence states, the 5d orbitals of the lanthanides are close in energy to the 4f levels. It is possible, therefore, that the valence electrons of a low valent lanthanide would possess some 5d as well as 4f character. Such an electronic situation would be unique…" [5]

The rationale was to find chemistry that was different from both transition metal chemistry and known +3 oxidation state lanthanide chemistry. The overall synthetic goal was summarized thus:

> "The challenge in the lanthanide area, therefore, is to place the lanthanide metals in chemical environments which allow exploitation of their chemical uniqueness." [5]

This was a perfect goal for a synthetic inorganic chemist. This turned out much better than I ever could have imagined!

2.4 Metal Vapor Chemistry. The next periodic trend that influenced my research career involved a popular experimental development that swept the periodic table. When I was starting my independent research, metal vapor reaction chemistry was being explored as a new synthetic technique by a variety of researchers including Professor Peter L. Timms at Bristol, Professor M. L. H. Green at Oxford, Dr. Steven D. Ittel at DuPont, and Professor Kenneth J. Klabunde at Kansas State University [6]. This proved to be an excellent method for making low oxidation state complexes. The method was being investigated across the periodic table…..except for the lanthanides. So, we built both static and rotary metal vapor reactors following the literature designs shown in Figure 2, and began the search for lanthanide complexes with the metal in the zero oxidation state.

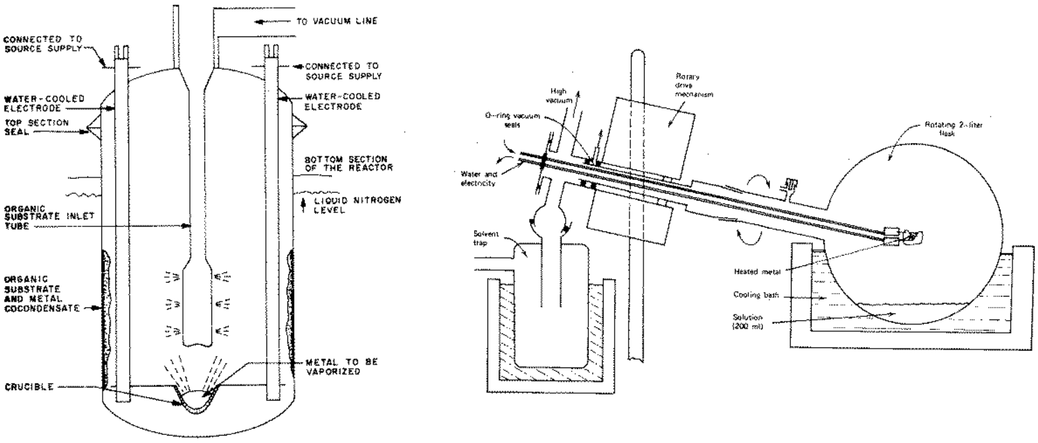
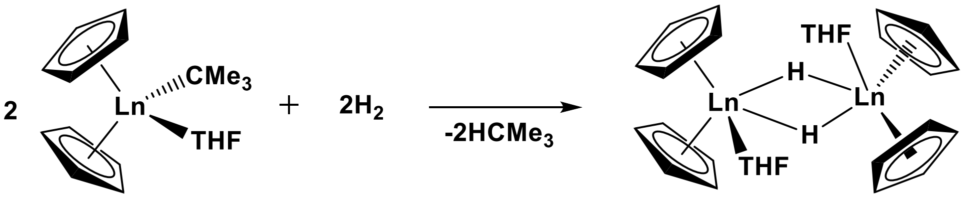


Figure 2. Published diagrams of static (left) and rotary (right) metal vapor reactors from reference 6.

Initial studies of reactions between lanthanide metals and unsaturated hydrocarbons like alkenes, dienes, alkynes, and toluene produced non-crystalline paramagnetic materials that could not be definitively identified. The only characterization methods were elemental analyses and infrared and optical spectroscopy, but these did not give us detailed structural information [4,5,7]. This was not a road to tenure. However, these materials functioned as hydrogenation catalysts [8,9] and we began to pursue the chemistry of lanthanide hydrides.

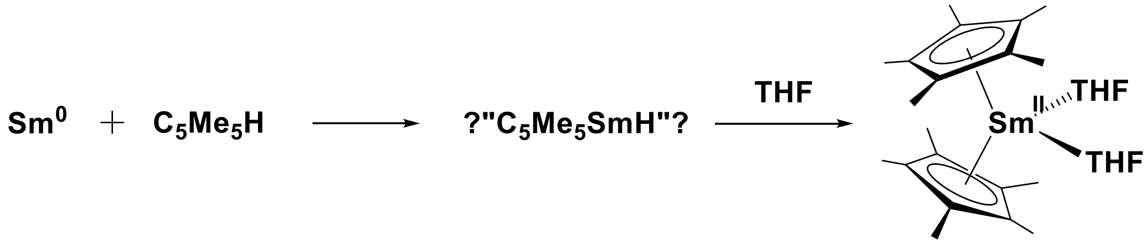
Although hydrogen had been attached to almost every other element in the periodic table, no well-characterized molecular lanthanide hydrides were known. So we decided to use +3 chemistry to deliberately make the first lanthanide hydrides [10]. Equation 1 shows the initial syntheses. Exploring the chemistry of lanthanide hydrides has continued to be a fruitful area of research even to this day [11].



(1)

2.5 The Good Samarium. After we made the first lanthanide hydrides by these hydrogenolysis reactions, we wondered if hydride complexes were also being formed in the metal vapor reactions. This would explain their ability to catalyze hydrogenation reactions. To test this, we examined the reaction of samarium and pentamethylcyclopentadiene to determine if we could isolate a hydride like $(C_5Me_5)SmH$. C_5Me_5 metal chemistry, which had been dormant for years [12], was being investigated across the periodic table due to exciting discoveries of Professor Bercaw in group 4 [13,14]. Initially, I did not want to jump onto the C_5Me_5 bandwagon, because I wanted to do unique chemistry. However, I was glad I did, because the C_5Me_5 ligand has proved to be exceptionally important in developing lanthanide chemistry and this continues into the present day [15]. We used C_5Me_5 hoping that the large steric bulk of the ligand would help stabilize the metal hydride in the absence of other ligands. We chose Sm since it had a known +2 oxidation state and we had made unusual materials with it starting from unsaturated hydrocarbons [7].

The reaction of Sm metal with C_5Me_5H did not make the $(C_5Me_5)SmH$ product we were targeting. However, it did provide a reaction product exceptionally important to my career. The reaction generated $(C_5Me_5)_2Sm(THF)_2$ after extraction of the reaction residue with THF, eq 2 [16].



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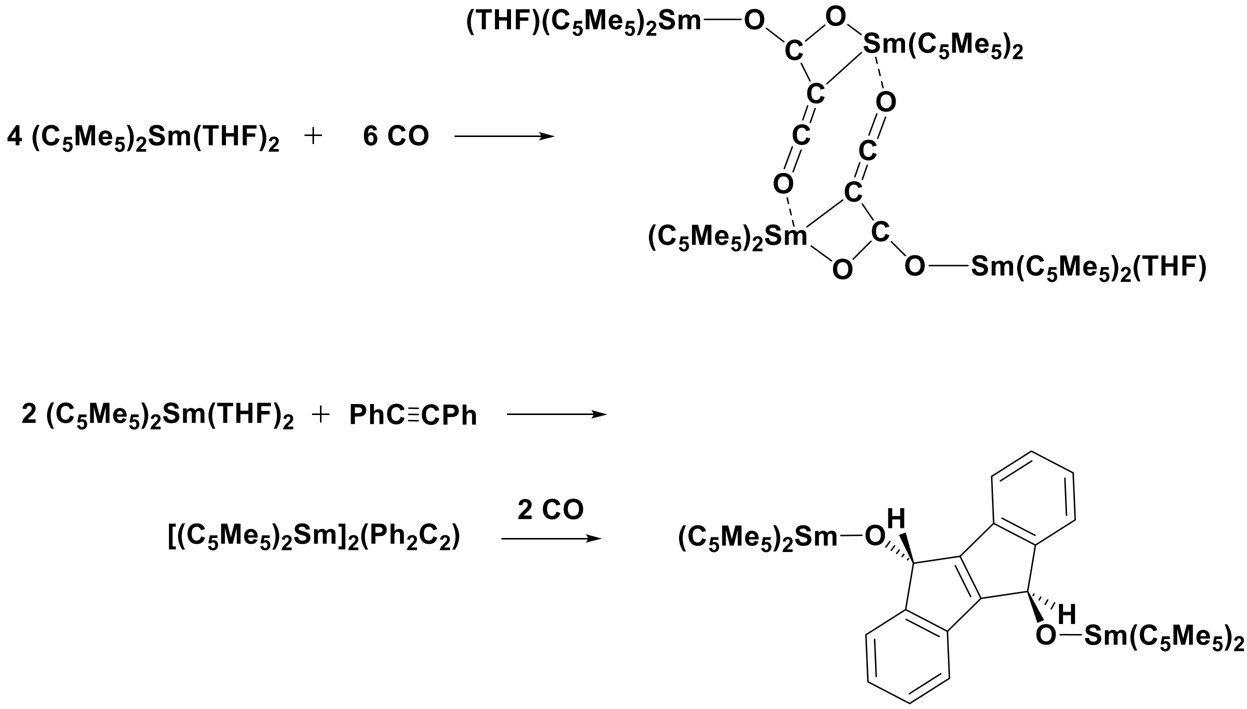
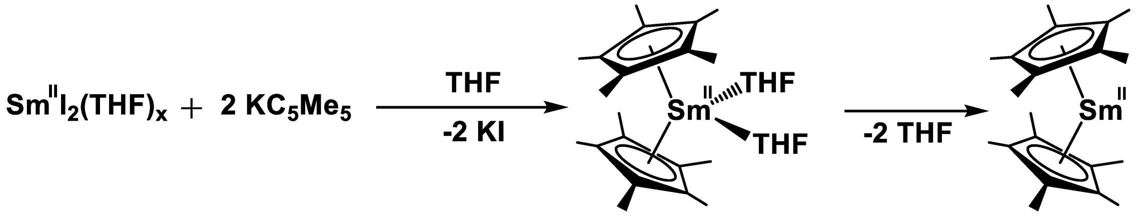
$(C_5Me_5)_2Sm(THF)_2$ proved to be a highly reactive complex that opened up new horizons in lanthanide reaction chemistry. This complex reacted in unusual ways with CO, NO, CO_2, and unsaturated hydrocarbons, i.e. soft unsaturated substrates that were not supposed to react with the ionic lanthanides! Scheme 1 shows two specific examples [17,18]. Reductive coupling of three CO molecules was observed in the first reaction and hydrocarbon reduction and CO insertion occurred in the second reaction. This extensive new Sm(II) chemistry along with the trivalent hydride chemistry provided the results that formed the basis of a positive tenure decision for me at the University of Chicago.



Scheme 1. Reaction chemistry of $(C_5Me_5)_2Sm(THF)_2$ with CO and diphenylacetylene/CO.

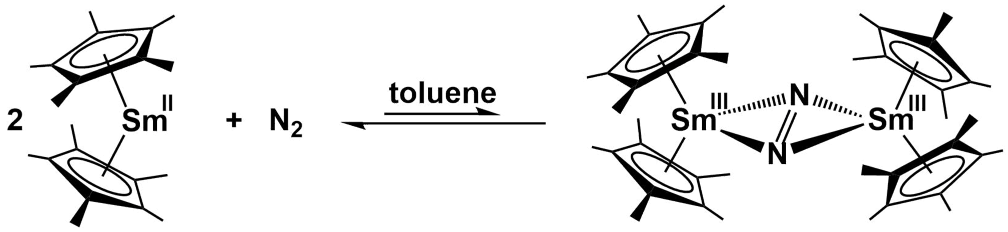
Later, after I was recruited to join the faculty at the University of California, Irvine, we discovered that $(C_5Me_5)_2Sm(THF)_2$ could be desolvated under high vacuum, eq 3, to generate the unsolvated derivative, $(C_5Me_5)_2Sm$, which had even more spectacular reactivity [19]. The isolation of decamethylsamarocene was unusual because it was generally accepted that only larger rings such as cyclo-octatetraenide would form sandwich complexes with the larger lanthanide and actinide metal ions. The name uranocene was coined for $U(C_8H_8)_2$ [20] in analogy with the transition metal sandwich complex, ferrocene, because it was thought that no bis(cyclopentadienyl) lanthanide sandwich complexes, $(C_5R_5)_2Ln$, would ever be isolable. Decamethylsamarocene was also structurally unusual because it had a bent geometry and did not adopt the parallel ring sandwich structure found in ferrocene and related transition metal complexes.



(3)

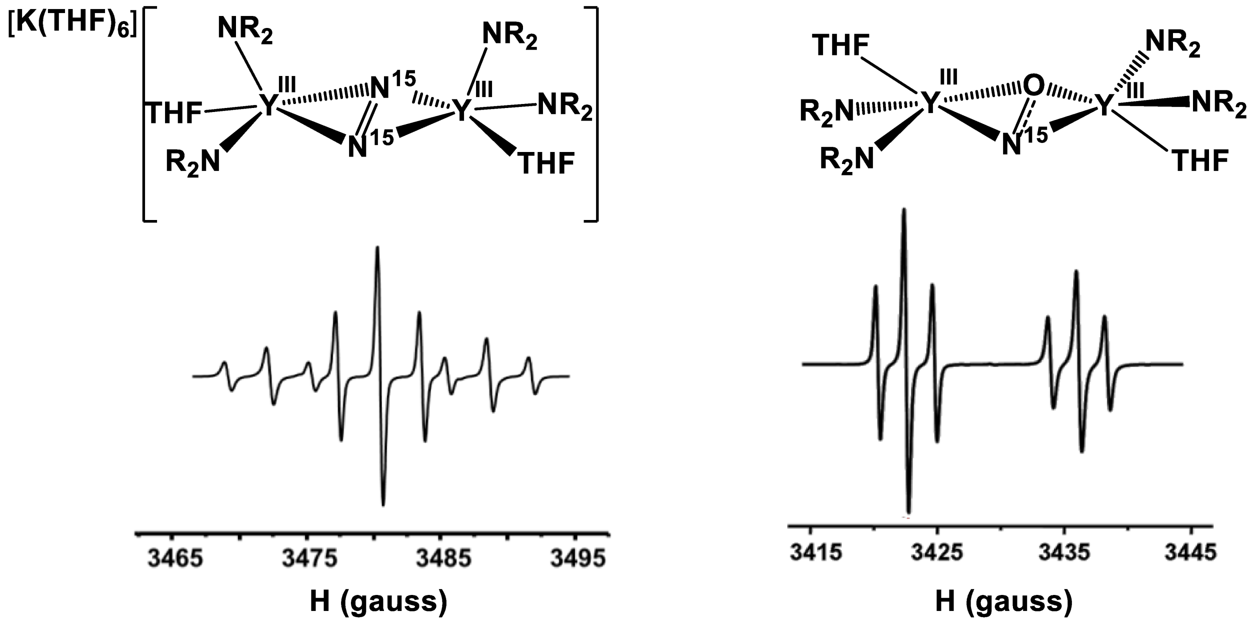
Our efforts with Sm(II) compounds and those of Professor Henri Kagan with SmI_2 [21] suggested that samarium was a very special lanthanide. Neither Eu(II) nor Yb(II) were sufficiently reducing [22,23] to do this unusual chemistry and there were no other Ln(II) ions available in solution (at that time, see below). Our efforts in Sm(II) chemistry were not driven by periodic trends, but rather focused on a single metal. We did use the periodic table to guide us in substrate selection, however.

2.6 Reduction of Dinitrogen. $(C_5Me_5)_2Sm$ reduced N_2 to make the first reduced dinitrogen complex of an f element, eq 4 [24]. This was quite unexpected since the lanthanides were thought to lack the orbitals to interact with small molecules. More importantly, this complex was the first example with any metal of an $M_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ unit with a planar geometry. The study of lanthanide dinitrogen reduction continues to be pursued [25].



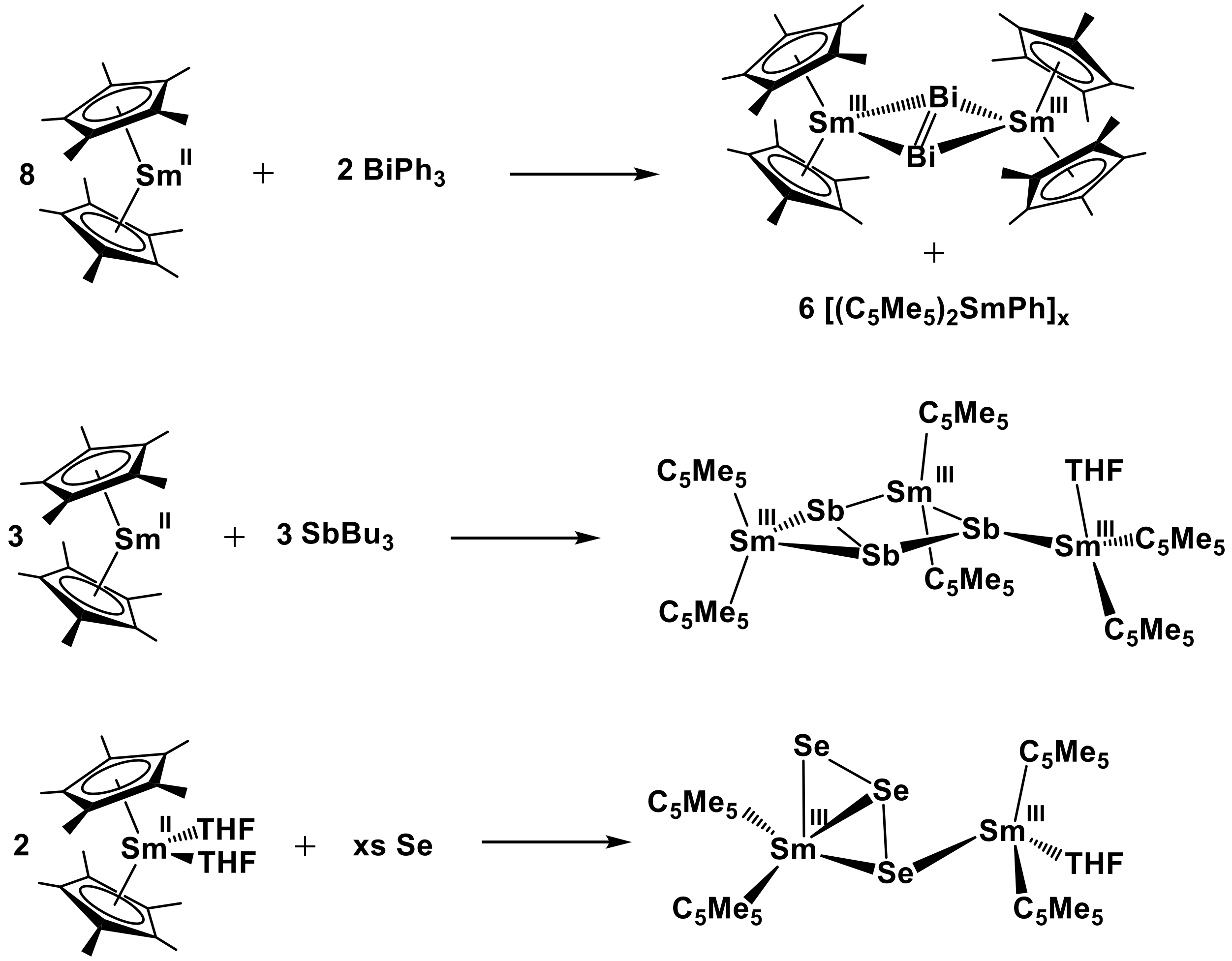
(4)

The dinitrogen reduction studies led to the isolation of the first complexes of the radical trianion $(N_2)^{3-}$ [26] and the radical dianion $(NO)^{2-}$, Scheme 2 [27]. The isolation of new forms of these extensively studied, simple, diatomic molecules demonstrated the broader value of exploratory synthesis in the lanthanide part of the periodic table. The $(N_2)^{3-}$ ion was later used to bridge bimetallic complexes of paramagnetic Dy(III) and Tb(III) ions to make outstanding single-molecule magnets [28,29].



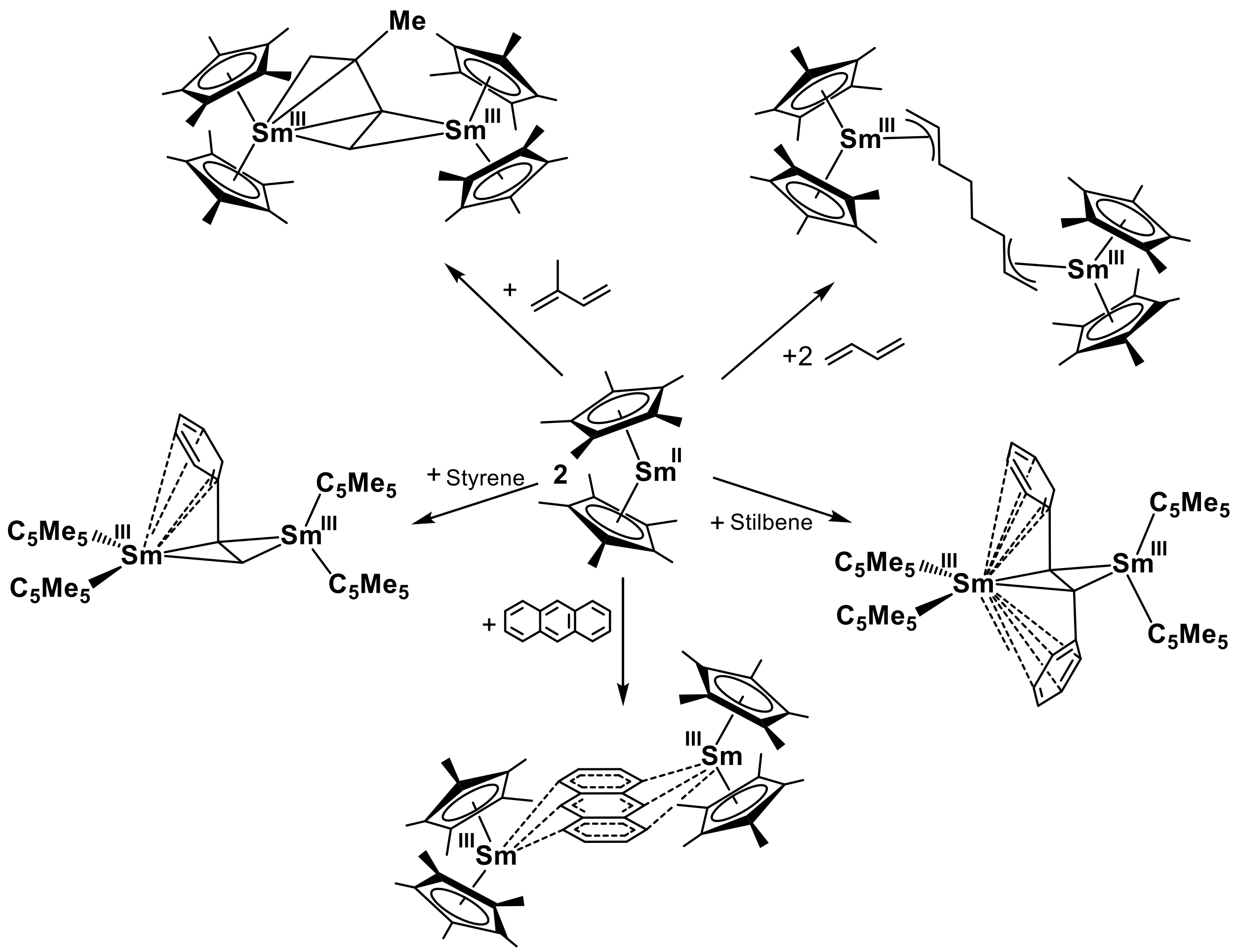
Scheme 2. The first $(N_2)^{3-}$ and $(NO)^{2-}$ complexes shown with the EPR spectra for their ^{15}N isotopomers with splitting due to I = ½ ^{89}Y and ^{15}N nuclei.

We also surveyed the main group section of the periodic table with Sm(II) and made species containing unusual ligands such as $(Bi_2)^{2-}$ [30], $(Sb_3)^{2-}$ [31], and $(Se_3)^{2-}$ [32], Scheme 3. Efforts to synthesize unusual main group species with decamethylsamarocene continue to be made [33].



Scheme 3. Reactivity of Sm(II) with various main group compounds.

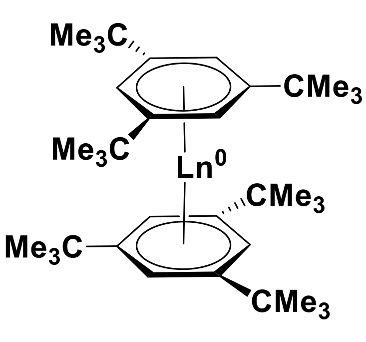
$(C_5Me_5)_2$Sm also also displayed unusual reactions with unsaturated hydrocarbons as shown in Scheme 4.



Scheme 4. Reactivity of $(C_5Me_5)_2Sm$ with unsaturated hydrocarbons.

2.7 Zero Valent Complexes. The dinitrogen and hydride chemistry of the +3 ions as well as the Sm(II) chemistry was sufficiently productive that we stopped doing metal vapor chemistry. However, many years later, this area was pursued by Professor Geoffrey Cloke at the University of Sussex. Professor Cloke showed that our initial ideas on zero valent lanthanides were reasonable, but that we just had not used ligands that had enough steric bulk. Professor Cloke made the first complexes of the lanthanides in the zero oxidation state as the sandwich species $Ln(C_6H_3{}^tBu_3)_2$ with Ln = Nd, Gd, Tb, Dy, Ho, Er, Lu, eq 5 [34]. In doing so, he achieved one of the early goals we had targeted. We were delighted that this goal was finally reached even though it was not accomplished in our laboratory.

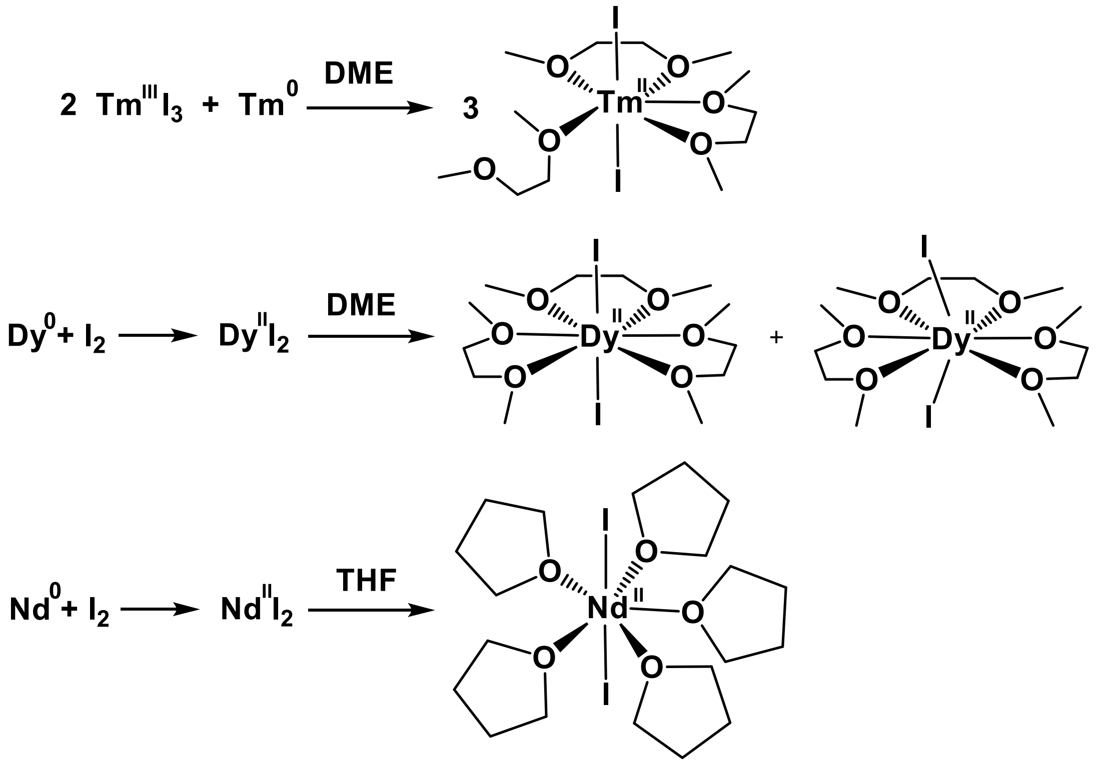
$$Ln^0 + 2\ C_6H_3({}^tBu)_3 \longrightarrow$$



(5)

2.8 Thulium, Dysprosium, and Neodymium. Solid state chemists knew for years that Tm(II), Dy(II), and Nd(II) could be isolated as bulk solids like LnI_2 from reactions of the metals with halogens in sealed tantalum vessels at high temperatures [35,36]. However, it was generally believed that these Ln(II) were so reducing that their compounds would decompose any solvents they would dissolve them [22,23]. The existence of Eu(II) and Yb(II) made periodic sense in that these ions had half-filled and filled shells, $4f^7$ and $4f^{14}$, respectively, that had quantum mechanical stabilization. Since half-filled is more stabilized than filled, it made sense the Yb(II) was more reducing than Eu(II). The existence of $4f^6$ Sm(II) and $4f^{13}$ Tm(II) could be similarly rationalized since they were approaching half-filled and filled shells, respectively. These ions were less stable than the half- and filled-shell species and Tm(II) was more reducing than Sm(II). However, the $4f^{10}$ and $4f^4$ electron configurations of Dy(II) and Nd(II), respectively, did not follow such a periodic pattern.

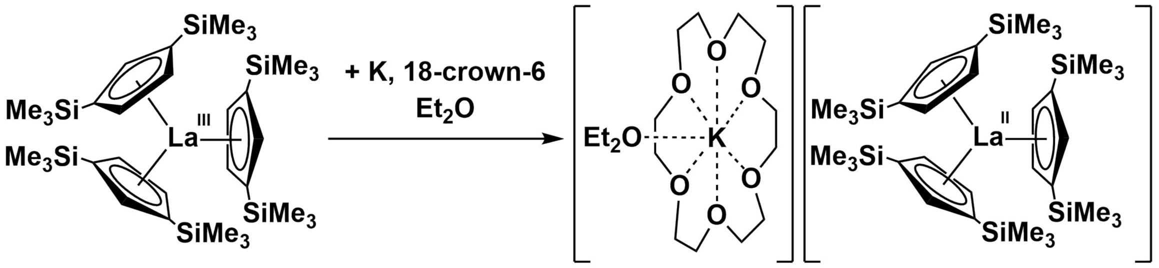
The myth that Tm(II), Dy(II), and Nd(II) could not exist in isolable molecular compounds was overturned by Professor Mikhail Bochkarev in Nizhny Novgorod, Russia. He found conditions under which the molecular species, $TmI_2(DME)_3$ [37], $DyI_2(DME)_3$ [38,39], and $NdI_2(THF)_5$ [40], could be isolated and crystallographically characterized in collaboration with our group and that of Professor Herbert Schumann in Berlin, Scheme 5.



Scheme 5. Molecular complexes of LnI_2 for Ln = Nd, Dy, Tm.

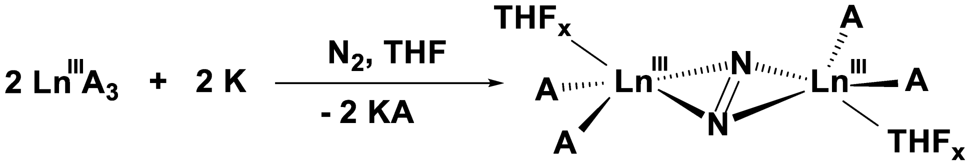
With the isolation of these three additional Ln(II) ions as molecular species, it appeared in 2001 that the +2 oxidation state chemistry of the lanthanides was complete. Solution syntheses matched solid state studies which showed that Ln + I_2 reactions made salts for Ln = Eu, Yb, Sm, Tm, Dy, and Nd (in order of decreasing stability), but would not form complexes of +2 ions for the other metals. With the other lanthanides, the Ln + I_2 reactions generated materials of composition “LnI_2” that were best described as $(Ln^{3+})(I^{1-})_2(e^{1-})$. These compounds were insoluble black materials that were described as having a delocalized electron in a conduction band. This was assumed to form from the 5d orbitals because the limited radial extension of the 4f orbitals would not lead to band formation [35,36].

2.9 The +2 Oxidation State for All of the Lanthanides. The myth that the +2 ion was available for only six lanthanides was overturned in 2008 when Professor Lappert reported the first La(II) complex, $(Cp''_3La)^{1-}$ (Cp” = $C_5H_3(SiMe_3)_2$), eq 6 [41]. This La(II) complex did not have the longer bond distances typically observed for the other Ln(II) complexes vs analogous Ln(III) complexes, but Lappert rationalized this by suggesting that the La(II) ion was a $5d^1$ ion rather than a $4f^1$ species. This was a reasonable argument because the 5d orbitals had energy similar to the 4f orbitals at the beginning of the lanthanide series and transition metals do not show the large change of bond distance with oxidation state that occurs with the ionic lanthanides.



(6)

We were intrigued by Lappert’s La(II) complex and the fact that he reported no dinitrogen reduction with it. We had conducted numerous reduction reactions analogous to eq 6, but under N_2 to make reduced dinitrogen complexes, eq 7 [42-45]. We had never been able to isolate any Ln(II) complexes in the absence of N_2. We called these reactions LnA_3/M reactions (where A is an anion and M an alkali metal) rather than “LnA_2” reactions, since we had no evidence for a Ln(II) intermediate.

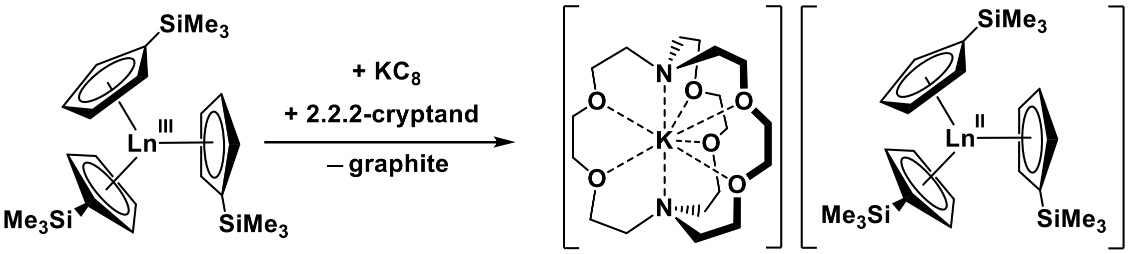


(7)

Ln = Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu
A = $N(SiMe_3)_2$, $OC_6H_3{}^tBu_2$-2,6, C_5Me_5, C_5Me_4H, $C_5H_4SiMe_3$
x = 1, 2

After Professor Lappert retired, we made his La(II) complex to determine if it would react with N_2. We were surprised to find that it did not reduce N_2 and it could be synthesized under an N_2 atmosphere! It was clear that the ligands strongly influence this reductive reactivity. The LaA_3/M reaction with A = Cp” gave a La(II) complex, eq 6 [41], but no N_2 reduction; LnA_3/M reactions with A = C_5Me_5, C_5Me_4H, $N(SiMe_3)_2$, and aryloxide ligands, gave reduced dinitrogen products, but no isolable Ln(II) complexes, eq 7.

We sought to explore more LnA_3/M reactions with silylcyclopentadienyl complexes like Lappert’s Cp''_3Ln species. To access the bis(silyl) Cp”H precursor, the mono(silyl) species, Cp’H (Cp’ = $C_5H_4SiMe_3$) must be synthesized first. Graduate student Matthew MacDonald cleverly decided to examine Cp'_3Ln reduction to save a step in ligand synthesis. This turned out to be a wonderful choice of ligand as Cp'_3Ln/M reactions allowed us to synthesize crystallographically-characterizable molecular complexes of +2 ions of all the other lanthanides except radioactive promethium, eq 8 [46,47]! This could not be accomplished with the larger bis(silyl) ligand, Cp”, due to problems of steric crowding: to date, Cp''_3Ln/M reductions have only given isolable Ln(II) complexes for the larger metals earlier in the series, Ln = La-Pr [41,48]. We also made the first molecular Y(II) complex [49], since Y is similar in size to Ho and Er and the +3 chemistry of yttrium is often indistinguishable from that of the late lanthanides.



(8)

Ln = Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu

Hence by 2013, +2 oxidation states were known in molecular species for all the lanthanides and yttrium. These oxidation states were always available in the periodic table! However, no one pressed hard enough experimentally to get them since it was generally assumed they were too reducing to isolate [50,51]. A key aspect of the experimental discovery was that the syntheses were all initially done at –35 °C and completed in less than a minute to avoid decomposition in solution [52]. These are highly reactive species that would not easily be “uncovered” in conventional syntheses and this is why it took so long to identify them.

A second surprise, beyond the fact that complexes of these Ln(II) ions could be isolated, was revealed by the density functional theory (DFT) studies by the group of our colleague Professor Filipp Furche. The calculations showed that reduction of the $4f^n$ Ln(III) Cp'_3Ln precursors did not form $4f^{n+1}$ Ln(II) ions as previously observed for Eu, Yb, Sm, Tm, Dy, and Nd, but the new ions had $4f^n5d^1$ electron configurations [46,47,53]. Apparently in the trigonal coordination environment of three Cp’ rings, the $5dz^2$ orbital becomes close in energy to the 4f orbitals such that $4f^n5d^1$ configurations are the ground state. Hence, Lappert’s assessment of La(II) as a $5d^1$ ion was correct not only for lanthanum, but across the whole series. This was a most pleasing result for me personally since as quoted above, I had mused about a d orbital contribution to low oxidation state chemistry of the lanthanides: “it is possible, therefore, that the valence electrons of a low valent lanthanide would possess some 5d as well as 4f character. Such an electronic situation would be unique…"[5]. This was realized in the $(Cp'_3Ln)^{1-}$ and $(Cp''_3Ln)^{1-}$ series.

3 Periodic Properties of Ln(III) vs Ln(II) Rare Earth Ions.

The rare earth elements are defined as Sc, Y, and the lanthanides. The most commonly described periodic property of the lanthanides is the gradual decrease in radial size, i.e. the lanthanide contraction. Each metal has an ionic radius about 0.013 Å smaller than the metal preceding it in the periodic table. For complexes of +3 ions, the ionic radii can be used to predict bond distances from one complex to its analog with another metal just by considering the difference in ionic radii [54].

Since yttrium is similar in size to Ho and Er, its complexes have structures and metrical parameters very similar to those of the late lanthanides. The chemistry of yttrium had been associated with the lanthanides since Birmingham and Wilkinson made Cp_3Y ($Cp = C_5H_5$) along with Cp_3Ln complexes of the other lanthanides in 1954 [55]. Professor Lappert used Y(III) most effectively to model late lanthanide chemistry as early as 1973 [56]. NMR studies could be done with complexes of the diamagnetic Y(III) and its 100% naturally abundant $I = \frac{1}{2}$ nuclear spin provided added structural information. In contrast, complexes of the similarly-sized Ho(III) and Er(III) ions, which had magnetic moments of $10.6\ \mu_B$ and $9.57\ \mu_B$, were not amenable to NMR characterization.

Although yttrium was a valuable mimic of lanthanide chemistry, scandium was not. It often formed complexes of different composition and structure because it was so much smaller than the other rare earth elements. Scandium would be the "23rd" lanthanide according to size based on the decrease of about 0.013 Å per element.

The bond distances of yttrium and lanthanide complexes in the +2 oxidation state also decrease across the series, but there are two different groups of metals. The distances of the traditional $4f^{n+1}$ Ln(II) ions of Sm, Eu, Tm, and Yb decrease following the radii of those ions and are 0.1 to 0.2 Å larger than those of their Ln(III) analogs. The distances in complexes of new $4f^n5d^1$ Ln(II) ions also decrease across the series, but they are within 0.03 to 0.05 Å of the Ln(III) distances and form a different series than the traditional ions, Figure 3.

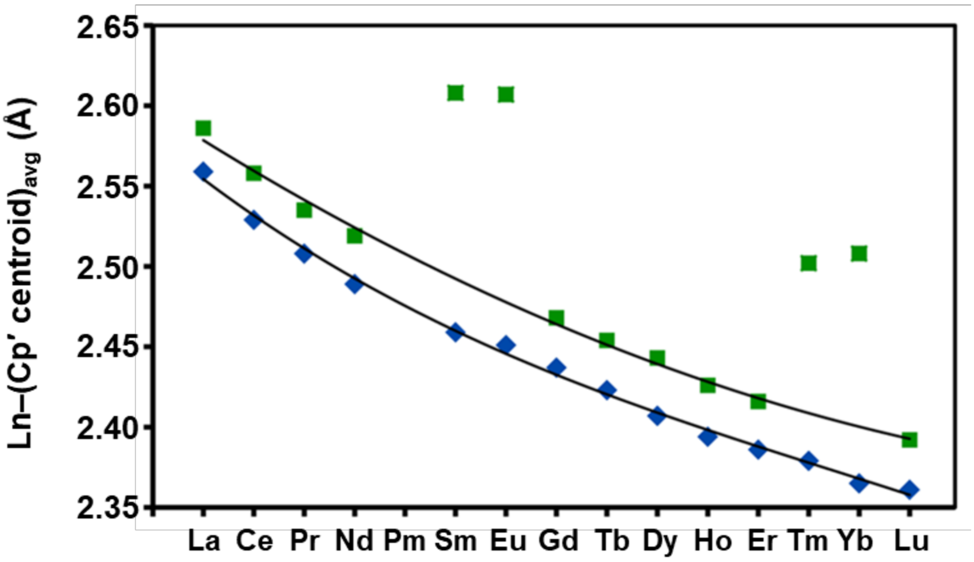
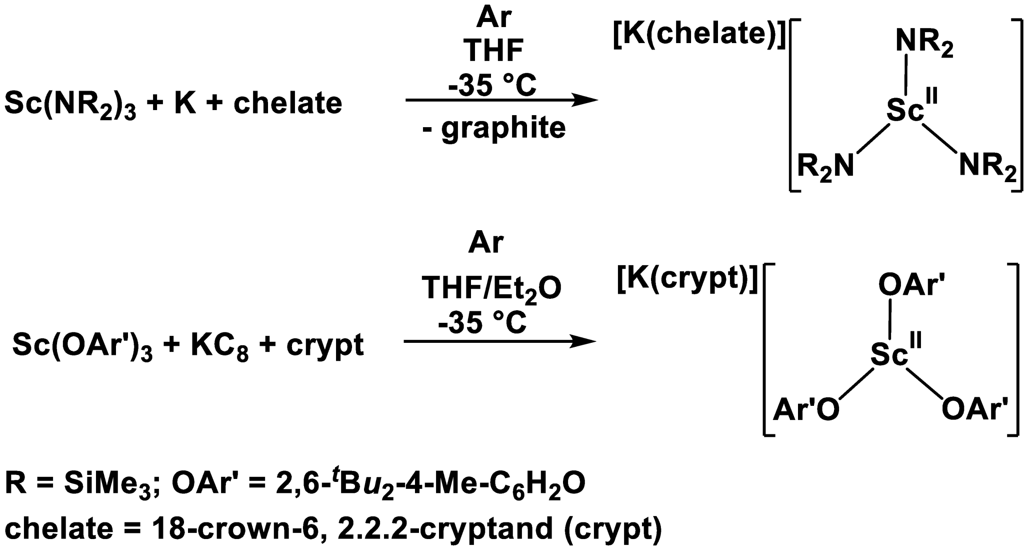


Figure 3. Change in Ln-(Cp' ring centroid) distance with atomic number in the lanthanide series. The blue diamonds are for trivalent Cp'_3Ln^{III} complexes. The green squares are for divalent $(Cp'_3Ln^{II})^{1-}$ complexes. This shows the difference between the traditional $4f^{n+1}$ ions of Sm, Eu, Tm, and Yb and the new Ln(II) ions with $4f^n5d^1$ electron configurations.

Efforts to isolate a Sc(II) complex were not initially made since Sc(II) compounds were reported in the 1990's by Cloke and co-workers via metal vapor chemistry [57,58]. However, no crystal structures of Sc(II) complexes were obtainable at that time. Subsequently, we have found that LnA_3/M reactions can provide crystallographically characterizable Sc(II) complexes with amide and aryloxide ligands, Scheme 6 [51,59].

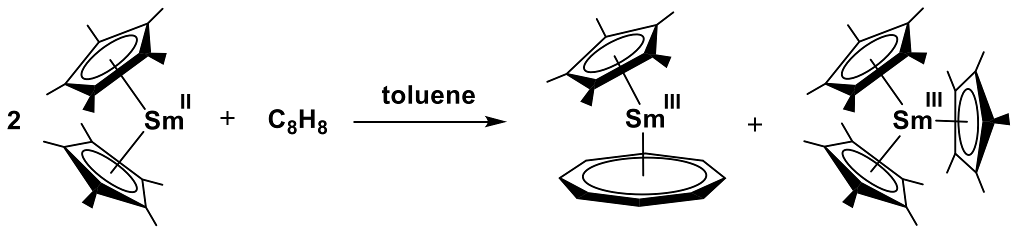


Scheme 6. Synthesis of crystallographically-characterized Sc(II) complexes utilizing amide and aryloxide ligands.

Surprisingly, the Y(II) analogs of the Sc(II) compounds in Scheme 6 are much more reactive. Neither $[Y(NR_2)_3]^{1-}$ (R = $SiMe_3$) nor $[Y(OAr')_3]^{1-}$ (OAr'=$OC_6H_2{}^tBu_2$-2,6-Me-4) can be isolated under similar conditions. In contrast, $[Ho(NR_2)_3]^{1-}$ and $[Er(NR_2)_3]^{1-}$ are isolable [60]. So the periodic similarity of yttrium with the late lanthanides, so well-known in +3 chemistry since the early studies of Lappert [56], is not evident in the Ln(II) complexes. Moreover, it seems there are more similarities between Sc(II) and the late lanthanides such as Ho(II) and Er(II) than with Y(II). Since these complexes of the new Ln(II) ions have only recently been synthesized, it is too early to make long-term conclusions about the periodicity of the Ln(II) chemistry. *This shows that elaboration of all the properties of the periodic system is continuing to evolve.*

4 Expanding into Actinide Chemistry.

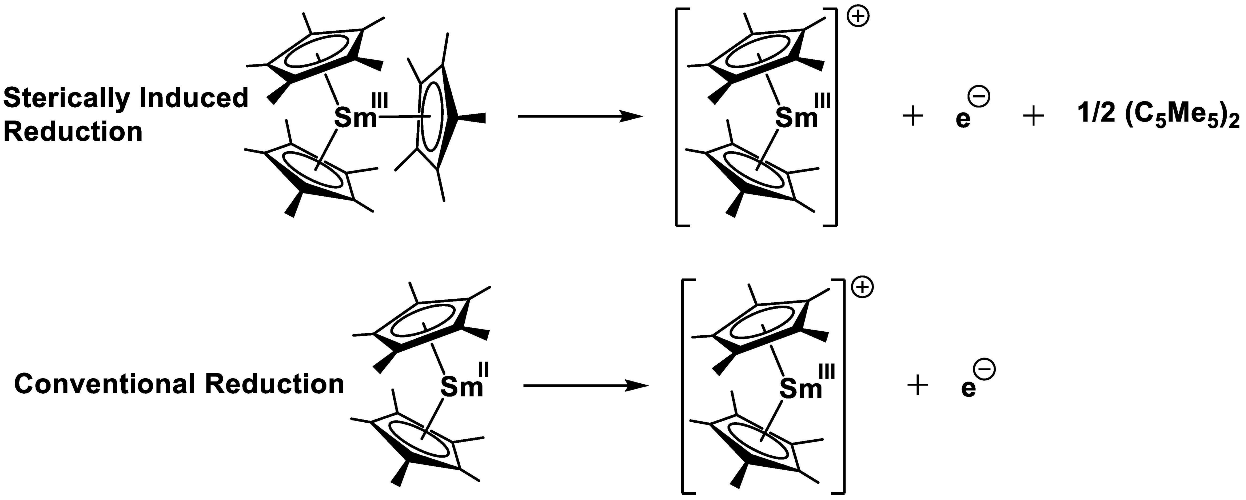
4.1 Exploring 5f Elements due to Sterically Induced Reduction. For many years our efforts focused primarily on the rare earth elements because Professor Marks and others were adequately exploring the related 5f elements, thorium and uranium. However, a desire to explore more of the periodic table and a reaction initiated by $(C_5Me_5)_2Sm$ led us into the actinide series. The reaction of $(C_5Me_5)_2Sm$ with cyclooctatetraene was expected to be a straightforward reaction based on the reduction potentials of Sm(II) and C_8H_8. However, the reaction provided a big surprise when it was found that the components of the byproducts came together to make the first tris(pentamethylcyclopentadienyl) complex, $(C_5Me_5)_3Sm$, eq 9 [61].



(9)

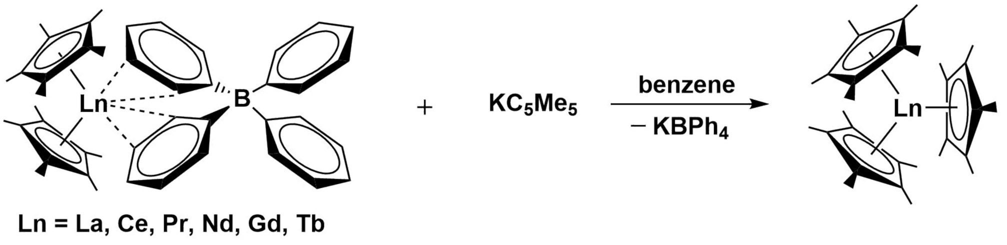
$(C_5Me_5)_3M$ complexes were not supposed to exist since the cone angle of a C_5Me_5 ring was estimated to be 142°. Three of these would exceed 360°. However, $(C_5Me_5)_3Sm$ could be crystallographically identified and the ligands had 120° cone angles in this compound. This large change in cone angle was possible because the ligands were located further from the metal than ever observed in C_5Me_5 complexes of Sm: all 15 Sm−C bonds in $(C_5Me_5)_3Sm$ were about 0.1 Å longer than ever seen before! It was very surprising to be able to synthesize a molecule in which all of the metal ligand distances are so much larger than ever previously observed.

The long bond distances in $(C_5Me_5)_3Sm$ had important consequences. The complex was highly reactive since the C_5Me_5 ligands were not effectively stabilized because of the longer M-C distances. In this complex, C_5Me_5 does not behave just as a stabilizing ancillary ligand: it is reactive. $(C_5Me_5)_3Sm$ reacts like an alkyl complex, $(C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)$ with substrates such as hydrogen, ethylene, THF, CO, nitriles, and isocyanates [62]. With other substrates, it functions as a one electron reducing agent. These reactions involved one $(C_5Me_5)^{1-}$ anion delivering an electron and forming the C_5Me_5 radical which was observed as the dimer, $(C_5Me_5)_2$, Scheme 7. Hence, this Sm(III) complex was functioning like a Sm(II) complex. Since the reduction was caused by the steric crowding, we called this sterically induced reduction (SIR) [62]. This was particularly unusual since redox properties are normally modulated by electronic factors rather than steric factors.



Scheme 7. Sterically induced reduction (SIR) with $(C_5Me_5)_3Sm^{III}$ vs conventional reduction with $(C_5Me_5)_2Sm^{II}$.

Since $(C_5Me_5)_3Sm$ had been made from a Sm(II) precursor and Sm(II) was special, extension of SIR to other metals was not immediately possible. However, synthetic advances in other parts of our research program led to the metallocene cations, $[(C_5Me_5)_2Ln]^{1+}$, in the tetraphenylborate complexes $(C_5Me_5)_2Ln(\mu\text{-}Ph)_2BPh_2$ [63]. The loosely-bound $(BPh_4)^{1-}$ anion was easily displaced and these species readily reacted with KC_5Me_5 to make $(C_5Me_5)_3Ln$ complexes across the series, eq 10 [64,65,15].

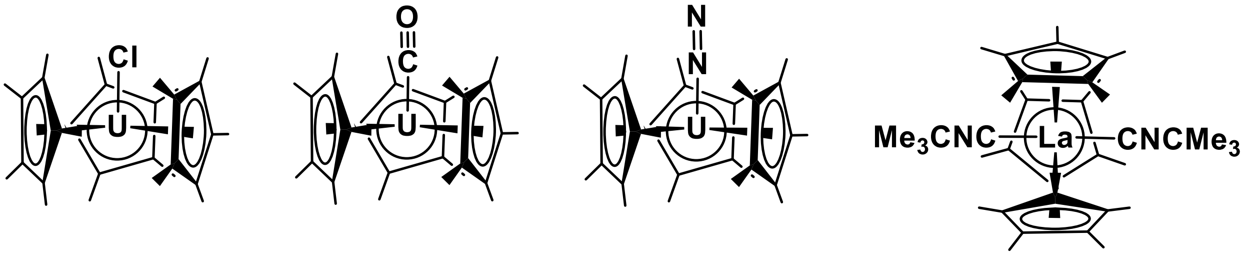


(10)

Our entry into actinide chemistry occurred because we wanted to determine if SIR chemistry was applicable in other parts of the periodic table. $(C_5Me_5)_3U$ was a particularly attractive target since it could effect one electron SIR chemistry, but it also had the redox active U(III) ion which could form U(IV), U(V), and U(VI) products. We expanded our 4f chemistry to the 5f series with the synthesis of $(C_5Me_5)_3U$, eq 11 [66]. This proved to be a wonderful development for our continued exploration of the western part of the periodic table.

(11)

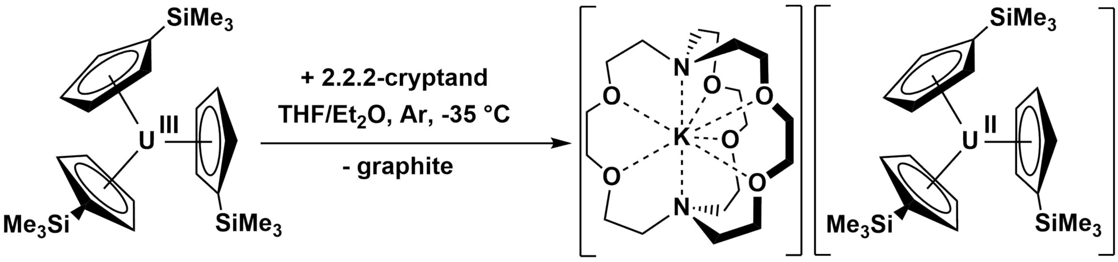
$(C_5Me_5)_3U$ allowed us to make even more crowded tris(pentamethylcyclopentadienyl) complexes. We found we could make $(C_5Me_5)_3UX$ complexes with conventional f element ligands like X = halide, Scheme 8 [67]. We also found that we could make $(C_5Me_5)_3UL$ complexes with L = CO [68] and N_2 [69], i.e. ligands that were traditionally limited to the transition metals. The actinide research encouraged us to synthesize even more crowded lanthanide complexes and examples with two additional ligands, $(C_5Me_5)_3LnL_2$, were isolated with L = nitriles and isocyanides, Scheme 8 [70,71]. The pentamethylcyclopentadienyl actinide chemistry continues into the present as exemplified by the recent synthesis of $(C_5Me_5)_3Th$ [72].



Scheme 8. Complexes of $(C_5Me_5)_3UX$, $(C_5Me_5)_3UL$, and $(C_5Me_5)_3La(CNCMe_3)_2$.

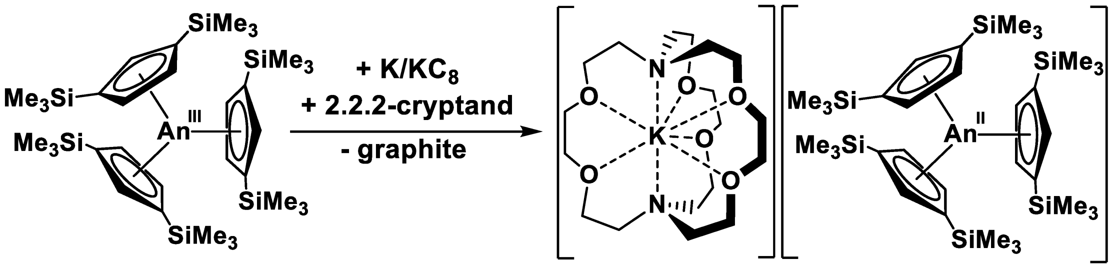
4.2 Sterically Induced Reduction and Bismuth. To further explore SIR chemistry in the periodic table, we sought to synthesize $(C_5Me_5)_3Bi$. The rationale was that bismuth forms a +3 ion with a size similar to that of the rare earths. However, this project was not as productive as the expansion of $(C_5Me_5)_3M$ chemistry to the actinides, because bismuth has a higher electronegativity than the rare earths and actinides. Chemistry analogous to that of the f elements does not occur for bismuth with cyclopentadienyl ligands because it is in a different part of the periodic table. Periodic properties matter! However, this study of bismuth drew our attention to this under-developed metal, just as the lanthanides were under-studied when we started working on them. We have subsequently explored new bismuth chemistry [73,74] and expect there is much more to discover in this part of the periodic table.

4.3 Low Valent Actinides Including Transuranics. Although our initial plans did not involve the study of low oxidation state actinide species, our experience with $(C_5Me_5)_3U$ primed our interest in the actinide series. However, when the new +2 oxidation states of Y, Pr, Gd, Tb, Ho, Er, and Lu were discovered in our laboratory by reducing Cp'_3Ln complexes (Cp' = $C_5H_4SiMe_3$), we did not immediately try reduction of the known uranium analog, Cp'_3U [75]. We reasoned that uranium had multiple higher oxidation states not known with the rare earths and would not necessarily have analogous low oxidation state chemistry. In addition, Cp'_3U had been known since 1986 [75] and someone must have tried to reduce it. We eventually attempted the reduction of this complex and, to my surprise, we made the first molecular complex of U(II), eq 12 [76]. This proved to be isomorphous with the rare earth complexes and even had a mixed $5f^36d^1$ electron configuration. It turned out to be analogous to its congener, $(Cp'_3Nd)^{1-}$, another triumph for Mendeleev's table.



(12)

Extension of the +2 chemistry to thorium seemed unreasonable because it was already difficult to make complexes of the highly reducing 6d^1 Th(III) ion. Less than ten Th(III) complexes had been crystallographically characterized. In fact, since Cp'$_3$Th was not known, it was not possible to do a reaction analogous to equations 8 and 12. Moreover, I did not think it appropriate to ask any student to try the reduction of the known bis(silyl) analog, Cp”$_3$Th [77], in a reaction analogous to eq 7, since this seemed like a low probability project. Fortunately, graduate student Ryan Langeslay was not afraid of challenges and showed that Th(II) complexes were accessible by this route, eq 13 [78]. DFT studies of product, $(Cp''_3Th)^{1-}$, revealed that it had a 6d^2 electron configuration consistent with its diamagnetic NMR spectrum. This complex is the first ion with this configuration, a ground state expected for *fourth* row transition metals. This is what would be expected for superheavy ions like Rf(II) and Db(III). Hence, our low valent chemistry ended up taking us to the frontiers of the periodic table as it continues to develop.



An = Th, U, Np, Pu

(13)

In collaboration with researchers at Los Alamos National Laboratory, we were able to go even further along the actinide series and find new oxidation states for neptunium and plutonium. Hence the first examples of crystallographically-characterizable complexes Np(II) and Pu(II) were synthesized as shown in eq 13 [79]. A key feature in discovering these new oxidation states was the prior research done with Th, U, and the large lanthanides of size similar to Np and Pu [80]. Hence, the periodic properties of these metals were used to make these breakthroughs with the transuranic elements.

5 Future Opportunities for the Rare-Earth Metals Based on the Periodic Table.

5.1 New Oxidation States. With the knowledge that the +2 oxidation state is available in molecular complexes across the series and the existence of zero oxidation state complexes of Sc, Y, Nd, Gd, Tb, Dy, Ho, Er, Lu [34], the availability of isolable Ln(I) complexes seems like an obvious synthetic target. Indeed, Sc(I) complexes have already been crystallographically characterized [57,81,82]. Hence, Ln(I) species should be isolable under some conditions. It is unclear if half-filled shell ions will be favored, e.g. $4f^7$ Sm(I) or $4f^75d^1$ Eu(I), or if f^nd^2 configurations will be favored, e.g. $4f^75d^2$ for Gd(I). As described above, a $6d^2$ ion is known for Th(II) [78].

The unexpected isolation of the +2 ions also raises the question of the possibility of isolating more Ln(IV) ions than the three currently known, Ce(IV), Pr(IV), and Tb(IV). Looking further west in the periodic table from the rare earths, the existence of $5d^1$ La(II) raises the possibility of complexes of a $5d^1$ Ba(I) ion.

5.2. Dichotomies: La or Lu Under Y?

Commonly displayed periodic tables locate the lanthanide and actinide blocks below the other elements presumably to save space. One of the interesting features of this arrangement is a question of which element, La or Lu, should be displayed in group 3 under Sc and Y. In terms of periodic trends in size there are *two reasonable answers that give opposite conclusions!*

(1) La should be under Y since it is most similar in size to barium on the left and
(2) Lu should be under Y since it is most similar in size to hafnium on the right.

The lanthanides are sometimes called the “inner” transitional elements because they form a transition between the alkali and alkaline earth metals to the “regular” transition metals that form a bridge to the main group elements. The developments of the +2 oxidation state chemistry of the rare earths described in this paper indicate that the lanthanides can be more “transition-metal-like” by adopting electron configurations with d orbital character.

Dichotomies are always interesting because they can suggest two different periodic trends. The dual placement of hydrogen in both main group 1 and main group 7 in some periodic tables is a good example of that. Hydrogen is unique since it can act like an alkali metal and lose an electron to form a +1 cation and it can act like a halide and gain an electron to form a –1 anion. I expect there are more discoveries to be made in lanthanide chemistry from exploiting the dual character of the lanthanides as both alkaline earth and early transition metal analogs.

One aspect of this dual nature of the lanthanides involves configurational crossover ions [53]. One of the details of the isolation of the $(Cp'_3Ln)^{1-}$ ions not mentioned above is that two ions, Dy(II) and Nd(II), have $4f^n5d^1$ electron configurations when surrounded by three silylcyclopentadienyl rings, but they have $4f^{n+1}$ electron configurations in other coordination environments. These configurational crossover ions have the capacity to be like ionic lanthanides more similar to the alkaline earths or like d^1 ions more similar to the early transition metals depending on the ligands. Previously, it was not possible to change the ground state of f element ions by changing the ligands since the 4f valence orbitals are shielded by the inert gas core. Interestingly, U(II) is also a configurational crossover ion like its Nd(II) congener. Hence, the Mendeleev periodicity carries over to this special aspect of the M(II) ions of the f elements.

The identification of the two configurational crossover ions means that there are three classes of Ln(II) ions, i.e. the traditional $4f^{n+1}$ ions of Eu(II), Yb(II), Sm(II), and

Tm(II), the configurational crossover ions of Dy(II) and Nd(II), and the new $4f^n5d^1$ ions of Pr(II), Gd(II), Tb(II), Ho(II), Er(II), and Lu(II). The traditional ions are more like Ba(II). The new ions are more like $5d^1$ Hf(III). This is not the same dichotomy as H^{1+} and H^{1-}, but it should lead to differences in reactivity depending on the electron configuration. One future development that is likely to occur along these lines is that the borderlines between these three groups may change as new ligands environments are developed that change the relative stabilities of the 4f and 5d orbitals. High pressure experiments should also cause the crossover [83].

6 Summary.

The periodic table has guided my entire career in chemistry. Although my entry into the periodic table at boron was random, boron connections and friendships developed my interest to become a synthetic inorganic chemist. Developments in early transition metal and actinide chemistry led me to an under-developed part of the periodic table, the lanthanides. The desire to expand newly-found lanthanide chemistry took me to the other rare earths, yttrium and scandium, as well as to the actinides and bismuth. Hence, the fascinating system developed long ago by Mendeleev and others has been a constant guide in my career in chemistry.

I expect the periodic table to continue to guide us in the future. I anticipate considerable future development of the oxidation state chemistry of the rare earths, since they have not been studied as intensively as the other metals in the periodic table. As the new discoveries appear, it seems likely that valuable connections will be made with elements in the other parts of the periodic table that will deepen our understanding and lead to new perspectives. Hence the visionary periodic table of Mendeleev continues to help us organize chemistry and to aspire to new goals.

7 Acknowledgments. We thank the National Science Foundation (CHE-1565776) and the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy (DE-SC0004739) for support of the rare-earth metal and actinide metal parts of this review, respectively.

8 References.

1. Pimentel GC, Spratley RD (1971) Understanding chemistry. Holden-Day, San Francisco
2. Evans WJ, Sollberger MS (1986) Synthesis and x-ray crystal structure of a soluble pentametallic organoyttrium alkoxide oxide complex,$(C_5H_5)_5Y_5(\mu\text{-}OCH_3)_4(\mu^5\text{-}O)$. J Am Chem Soc 108 (19):6095-6096
3. Gaines DF, Iorns TV (1971) 1-Silyl derivatives of pentaborane (9). Inorg Chem 10 (5):1094-1095
4. Evans WJ, Engerer SC, Neville AC (1978) Nonaqueous reductive lanthanide chemistry. 1. Reaction of lanthanide atoms with 1, 3-butadienes. J Am Chem Soc 100 (1):331-333
5. Evans W, Engerer S, Piliero P, Wayda A (1979) Organometallic Chemistry of the Lanthanides under Reductive Conditions. In: Fundamental Research in Homogeneous Catalysis. Springer, pp 941-952

6. Klabunde K (1980) Chemistry of free atoms and particles. Academic Press, New York
7. Evans WJ, Coleson KM, Engerer SC (1981) Reactivity of lanthanide metal vapor with unsaturated hydrocarbons. Reactions with ethene, propene, and 1, 2-propadiene. Inorg Chem 20 (12):4320-4325
8. Evans WJ, Engerer SC, Piliero PA, Wayda AL (1979) Homogeneous catalytic activation of molecular hydrogen by lanthanoid metal complexes. J Chem Soc, Chem Commun (22):1007-1008
9. Evans WJ, Bloom I, Engerer SC (1983) Catalytic activation of molecular hydrogen in alkyne hydrogenation reactions by lanthanide metal vapor reaction products. J Catal 84 (2):468-476
10. Evans WJ, Meadows JH, Wayda AL, Hunter WE, Atwood JL (1982) Organolanthanide hydride chemistry. 1. Synthesis and x-ray crystallographic characterization of dimeric organolanthanide and organoyttrium hydride complexes. J Am Chem Soc 104 (7):2008-2014
11. Fieser ME, Palumbo CT, La Pierre HS, Halter DP, Voora VK, Ziller JW, Furche F, Meyer K, Evans WJ (2017) Comparisons of lanthanide/actinide +2 ions in a tris (aryloxide) arene coordination environment. Chem Sci 8 (11):7424-7433
12. King RB, Bisnette MB (1967) Organometallic chemistry of the transition metals XXI. Some π-pentamethylcyclopentadienyl derivatives of various transition metals. J Organomet Chem 8 (2):287-297
13. Brintzinger H, Bercaw JE (1971) Bis (pentamethylcyclopentadienyl) titanium (II). Isolation and reactions with hydrogen, nitrogen, and carbon monoxide. J Am Chem Soc 93 (8):2045-2046
14. Manriquez JM, Bercaw JE (1974) Preparation of a dinitrogen complex of bis (pentamethylcyclopentadienyl) zirconium (II). Isolation and protonation leading to stoichiometric reduction of dinitrogen to hydrazine. J Am Chem Soc 96 (19):6229-6230
15. Woen DH, Kotyk CM, Mueller TJ, Ziller JW, Evans WJ (2017) Tris(pentamethylcyclopentadienyl) Complexes of Late Lanthanides Tb, Dy, Ho, and Er: Solution and Mechanochemical Syntheses and Structural Comparisons. Organometallics 36 (23):4558-4563
16. Evans WJ, Bloom I, Hunter WE, Atwood JL (1981) Synthesis and x-ray crystal structure of a soluble divalent organosamarium complex. J Am Chem Soc 103 (21):6507-6508
17. Evans WJ, Grate JW, Hughes LA, Zhang H, Atwood JL (1985) Reductive homologation of carbon monoxide to a ketenecarboxylate by a low-valent organolanthanide complex: synthesis and x-ray crystal structure of $[(C_5Me_5)_4Sm_2(O_2CCCO)(THF)]_2$. J Am Chem Soc 107 (12):3728-3730
18. Evans WJ, Hughes LA, Drummond DK, Zhang H, Atwood JL (1986) Facile stereospecific synthesis of a dihydroxyindenoindene unit from an alkyne and carbon monoxide via samarium-mediated carbon monoxide and CH activation. J Am Chem Soc 108 (7):1722-1723
19. Evans WJ, Hughes LA, Hanusa TP (1984) Synthesis and crystallographic characterization of an unsolvated, monomeric samarium bis (pentamethylcyclopentadienyl) organolanthanide complex,$(C_5Me_5)_2Sm$. J Am Chem Soc 106 (15):4270-4272
20. Streitwieser Jr A, Mueller-Westerhoff U (1968) Bis (cyclooctatetraenyl) uranium (uranocene). A new class of sandwich complexes that utilize atomic f orbitals. J Am Chem Soc 90 (26):7364-7364

21. Kagan H, Namy J (1986) Tetrahedron report number 213: Lanthanides in organic synthesis. Tetrahedron 42 (24):6573-6614
22. Morss LR (1976) Thermochemical properties of yttrium, lanthanum, and the lanthanide elements and ions. Chem Rev 76 (6):827-841
23. Morss LR (1994) Comparative thermochemical and oxidation-reduction properties of lanthanides and actinides. Handbook on the Physics and Chemistry of Rare Earths 18:239-291
24. Evans WJ, Ulibarri TA, Ziller JW (1988) Isolation and X-ray crystal structure of the first dinitrogen complex of an f-element metal,$[(C_5Me_5)_2Sm]_2N_2$. J Am Chem Soc 110 (20):6877-6879
25. Woen DH, Chen GP, Ziller JW, Boyle TJ, Furche F, Evans WJ (2017) End-On Bridging Dinitrogen Complex of Scandium. J Am Chem Soc 139 (42):14861-14864
26. Evans WJ, Fang M, Zucchi G, Furche F, Ziller JW, Hoekstra RM, Zink JI (2009) Isolation of dysprosium and yttrium complexes of a three-electron reduction product in the activation of dinitrogen, the $(N_2)^{3-}$ radical. J Am Chem Soc 131 (31):11195-11202
27. Evans WJ, Fang M, Bates JE, Furche F, Ziller JW, Kiesz MD, Zink JI (2010) Isolation of a radical dianion of nitrogen oxide $(NO)^{2-}$. Nat Chem 2 (8):644
28. Rinehart JD, Fang M, Evans WJ, Long JR (2011) A N_2^{3-} Radical-Bridged Terbium Complex Exhibiting Magnetic Hysteresis at 14 K. J Am Chem Soc 133 (36):14236-14239. doi:10.1021/ja206286h
29. Rinehart JD, Fang M, Evans WJ, Long JR (2011) Strong exchange and magnetic blocking in N_2^{3-}-radical-bridged lanthanide complexes. Nat Chem 3 (7):538-542
30. Evans WJ, Gonzales SL, Ziller JW (1991) Organosamarium-mediated synthesis of bismuth-bismuth bonds: x-ray crystal structure of the first dibismuth complex containing a planar $M_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Bi_2)$ unit. J Am Chem Soc 113 (26):9880-9882
31. Evans WJ, Gonzales SL, Ziller JW (1992) The utility of $(C_5Me_5)_2Sm$ in isolating crystallographically characterizable zintl ions. X-Ray crystal structure of a complex of $(Sb_3)^{3-}$. J Chem Soc, Chem Commun (16):1138-1139
32. Evans WJ, Rabe GW, Ziller JW, Doedens RJ (1994) Utility of organosamarium (II) reagents in the formation of polyatomic group 16 element anions: synthesis and structure of $[(C_5Me_5)_2Sm]_2(E_3)(THF)$,$[(C_5Me_5)_2Sm(THF)]_2(E)$, and related species (E= S, Se, Te). Inorg Chem 33 (13):2719-2726
33. Schoo C, Bestgen S, Egeberg A, Seibert J, Konchenko SN, Feldmann C, Roesky PW (2019) Samarium Polyarsenides Derived from Nanoscale Arsenic. Angew Chem Int Ed Engl 58 (13):4386-4389
34. Cloke FGN (1993) Zero oxidation state compounds of scandium, yttrium, and the lanthanides. Chem Soc Rev 22 (1):17-24
35. Corbett J (1973) Reduced halides of rare-earth elements. Revue de Chimie Minerale 10 (1-2):239-257
36. Meyer G (2013) The divalent state in solid rare earth metal halides. In: Atwood DA (ed) The rare earth elements: fundamentals and applications. John Wiley & Sons, New York, pp 161-173
37. Bochkarev MN, Fedushkin IL, Fagin AA, Petrovskaya TV, Ziller JW, Broomhall-Dillard RNR, Evans WJ (1997) Synthesis and Structure of the First Molecular Thulium(II) Complex: $[TmI_2(MeOCH_2CH_2OMe)_3]$. Angewandte Chemie International Edition in English 36 (1-2):133-135
38. Bochkarev MN, Fagin AA (1999) A New Route to Neodymium(II) and Dysprosium(II) Iodides. Chemistry – A European Journal 5 (10):2990-2992

39. Evans WJ, Allen NT, Ziller JW (2000) The Availability of Dysprosium Diiodide as a Powerful Reducing Agent in Organic Synthesis: Reactivity Studies and Structural Analysis of $DyI_2(DME)_3$ and Its Naphthalene Reduction Product. J Am Chem Soc 122 (47):11749-11750
40. Bochkarev MN, Fedushkin IL, Dechert S, Fagin AA, Schumann H (2001) $[NdI_2(thf)_5]$, the First Crystallographically Authenticated Neodymium(II) Complex. Angew Chem Int Ed 40 (17):3176-3178
41. Hitchcock PB, Lappert MF, Maron L, Protchenko AV (2008) Lanthanum Does Form Stable Molecular Compounds in the +2 Oxidation State. Angew Chem Int Ed 47 (8):1488-1491
42. Evans WJ, Lee DS, Ziller JW (2004) Reduction of Dinitrogen to Planar Bimetallic $M_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ Complexes of Y, Ho, Tm, and Lu Using the $K/Ln[N(SiMe_3)_2]_3$ Reduction System. J Am Chem Soc 126 (2):454-455
43. Evans WJ, Lee DS, Lie C, Ziller JW (2004) Expanding the LnZ_3/Alkali-Metal Reduction System to Organometallic and Heteroleptic Precursors: Formation of Dinitrogen Derivatives of Lanthanum. Angew Chem Int Ed 43 (41):5517-5519
44. Evans WJ, Lee DS, Rego DB, Perotti JM, Kozimor SA, Moore EK, Ziller JW (2004) Expanding Dinitrogen Reduction Chemistry to Trivalent Lanthanides via the LnZ_3/Alkali Metal Reduction System: Evaluation of the Generality of Forming $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ Complexes via LnZ_3/K. J Am Chem Soc 126 (44):14574-14582
45. Evans WJ, Lee DS, Johnston MA, Ziller JW (2005) The Elusive $(C_5Me_4H)_3Lu$: Its Synthesis and $LnZ_3/K/N_2$ Reactivity. Organometallics 24 (26):6393-6397
46. MacDonald MR, Bates JE, Fieser ME, Ziller JW, Furche F, Evans WJ (2012) Expanding Rare-Earth Oxidation State Chemistry to Molecular Complexes of Holmium(II) and Erbium(II). J Am Chem Soc 134 (20):8420-8423
47. MacDonald MR, Bates JE, Ziller JW, Furche F, Evans WJ (2013) Completing the Series of +2 Ions for the Lanthanide Elements: Synthesis of Molecular Complexes of Pr^{2+}, Gd^{2+}, Tb^{2+}, and Lu^{2+}. J Am Chem Soc 135 (26):9857-9868
48. Palumbo CT, Darago LE, Windorff CJ, Ziller JW, Evans WJ (2018) Trimethylsilyl versus Bis(trimethylsilyl) Substitution in Tris(cyclopentadienyl) Complexes of La, Ce, and Pr: Comparison of Structure, Magnetic Properties, and Reactivity. Organometallics 37 (6):900-905. doi:10.1021/acs.organomet.7b00881
49. MacDonald MR, Ziller JW, Evans WJ (2011) Synthesis of a Crystalline Molecular Complex of Y^{2+}, $[(18\text{-crown-}6)K][(C_5H_4SiMe_3)_3Y]$. J Am Chem Soc 133 (40):15914-15917
50. Evans WJ (2016) Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States. Organometallics 35 (18):3088-3100
51. Woen DH, Evans WJ (2016) Expanding the+ 2 Oxidation State of the Rare-Earth Metals, Uranium, and Thorium in Molecular Complexes. Handbook on the Physics and Chemistry of Rare Earths 50:337-394
52. MacDonald MR (2013) New Reaction Overturns Periodic Table Assumptions. CEN Online. https://www.youtube.com/watch?v=CoGFF4YReFo.
53. Fieser ME, MacDonald MR, Krull BT, Bates JE, Ziller JW, Furche F, Evans WJ (2015) Structural, Spectroscopic, and Theoretical Comparison of Traditional vs Recently Discovered Ln^{2+} Ions in the $[K(2.2.2\text{-cryptand})][(C_5H_4SiMe_3)_3Ln]$ Complexes: The Variable Nature of Dy^{2+} and Nd^{2+}. J Am Chem Soc 137 (1):369-382
54. Shannon R (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica Section A 32 (5):751-767

55. Wilkinson G, Birmingham JM (1954) Cyclopentadienyl compounds of Sc, Y, La, Ce and some lanthanide elements. J Am Chem Soc 76 (23):6210-6210

56. Holton J, Lappert MF, Ballard DGH, Pearce R, Atwood JL, Hunter WE (1979) Alkyl-bridged complexes of the d- and f-block elements. Part 1. Di-μ-alkyl-bis(η-cyclopentadienyl)metal(III)dialkylaluminium(III) complexes and the crystal and molecular structure of the ytterbium methyl species. J Chem Soc, Dalton Trans (1):45-53

57. Arnold PL, Cloke FGN, Hitchcock PB, Nixon JF (1996) The First Example of a Formal Scandium(I) Complex: Synthesis and Molecular Structure of a 22-Electron Scandium Triple Decker Incorporating the Novel 1,3,5-Triphosphabenzene Ring. J Am Chem Soc 118 (32):7630-7631

58. Arnold PL, Cloke FGN, Nixon JF (1998) The first stable scandocene: synthesis and characterisation of bis(η-2,4,5-tri-tert-butyl-1,3-diphosphacyclopentadienyl)scandium(II). Chem Commun (7):797-798

59. Moehring SA, Beltrán-Leiva MJ, Páez-Hernández D, Arratia-Pérez R, Ziller JW, Evans WJ (2018) Rare-Earth Metal(II) Aryloxides: Structure, Synthesis, and EPR Spectroscopy of [K(2.2.2-cryptand)][Sc($OC_6H_2{}^tBu_2$-2,6-Me-4)$_3$]. Chemistry – A European Journal 24 (68):18059-18067

60. Ryan AJ, Darago LE, Balasubramani SG, Chen GP, Ziller JW, Furche F, Long JR, Evans WJ (2018) Synthesis, Structure, and Magnetism of Tris(amide) [Ln{N($SiMe_3$)$_2$}$_3$]$^{1-}$ Complexes of the Non-traditional+ 2 Lanthanide Ions. Chemistry–A European Journal 24 (30):7702-7709

61. Evans WJ, Gonzales SL, Ziller JW (1991) Synthesis and x-ray crystal structure of the first tris(pentamethylcyclopentadienyl)metal complex: (η^5-C_5Me_5)$_3$Sm. J Am Chem Soc 113 (19):7423-7424

62. Evans WJ, Davis BL (2002) Chemistry of Tris(pentamethylcyclopentadienyl) f-Element Complexes, (C_5Me_5)$_3$M. Chem Rev 102 (6):2119-2136

63. Evans WJ, Seibel CA, Ziller JW (1998) Unsolvated Lanthanide Metallocene Cations [(C_5Me_5)$_2$Ln][BPh_4]: Multiple Syntheses, Structural Characterization, and Reactivity Including the Formation of (C_5Me_5)$_3$Nd. J Am Chem Soc 120 (27):6745-6752. doi:10.1021/ja980534o

64. Evans WJ, Perotti JM, Kozimor SA, Champagne TM, Davis BL, Nyce GW, Fujimoto CH, Clark RD, Johnston MA, Ziller JW (2005) Synthesis and Comparative η^1-Alkyl and Sterically Induced Reduction Reactivity of (C_5Me_5)$_3$Ln Complexes of La, Ce, Pr, Nd, and Sm. Organometallics 24 (16):3916-3931

65. Evans WJ, Davis BL, Champagne TM, Ziller JW (2006) C–H bond activation through steric crowding of normally inert ligands in the sterically crowded gadolinium and yttrium (C_5Me_5)$_3$M complexes. Proceedings of the National Academy of Sciences 103 (34):12678

66. Evans WJ, Forrestal KJ, Ziller JW (1997) Activity of [Sm(C_5Me_5)$_3$] in Ethylene Polymerization and Synthesis of [U(C_5Me_5)$_3$], the First Tris(pentamethylcyclopentadienyl) 5f-Element Complex. Angewandte Chemie International Edition in English 36 (7):774-776

67. Evans WJ, Nyce GW, Johnston MA, Ziller JW (2000) How Much Steric Crowding Is Possible in Tris(η^5-pentamethylcyclopentadienyl) Complexes? Synthesis and Structure of (C_5Me_5)$_3$UCl and (C_5Me_5)$_3$UF. J Am Chem Soc 122 (48):12019-12020

68. Evans WJ, Kozimor SA, Nyce GW, Ziller JW (2003) Comparative Reactivity of Sterically Crowded nf^3 (C_5Me_5)$_3$Nd and (C_5Me_5)$_3$U Complexes with CO: Formation of a Nonclassical Carbonium Ion versus an f Element Metal Carbonyl Complex. J Am Chem Soc 125 (45):13831-13835

69. Evans WJ, Kozimor SA, Ziller JW (2003) A Monometallic f Element Complex of Dinitrogen: $(C_5Me_5)_3U(\eta\text{-}N_2)$. J Am Chem Soc 125 (47):14264-14265. doi:10.1021/ja037647e

70. Evans WJ, Mueller TJ, Ziller JW (2009) Reactivity of $(C_5Me_5)_3LaL_x$ Complexes: Synthesis of a Tris(pentamethylcyclopentadienyl) Complex with Two Additional Ligands, $(C_5Me_5)_3La(NCCMe_3)_2$. J Am Chem Soc 131 (7):2678-2686

71. Evans WJ, Mueller TJ, Ziller JW (2010) Lanthanide versus Actinide Reactivity in the Formation of Sterically Crowded $[(C_5Me_5)_3ML_n]$ Nitrile and Isocyanide Complexes. Chem Eur J 16 (3):964-975

72. Langeslay RR, Chen GP, Windorff CJ, Chan AK, Ziller JW, Furche F, Evans WJ (2017) Synthesis, Structure, and Reactivity of the Sterically Crowded Th_{3+} Complex $(C_5Me_5)_3Th$ Including Formation of the Thorium Carbonyl, $[(C_5Me_5)_3Th(CO)][BPh_4]$. J Am Chem Soc 139 (9):3387-3398

73. Casely IJ, Ziller JW, Fang M, Furche F, Evans WJ (2011) Facile Bismuth−Oxygen Bond Cleavage, C−H Activation, and Formation of a Monodentate Carbon-Bound Oxyaryl Dianion, $(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)^{2-}$. J Am Chem Soc 133 (14):5244-5247

74. Kindra DR, Casely IJ, Fieser ME, Ziller JW, Furche F, Evans WJ (2013) Insertion of CO_2 and COS into Bi–C Bonds: Reactivity of a Bismuth NCN Pincer Complex of an Oxyaryl Dianionic Ligand, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(C_6H_2tBu_2O)$. J Am Chem Soc 135 (20):7777-7787

75. Brennan JG, Andersen RA, Zalkin A (1986) Chemistry of trivalent uranium metallocenes: electron-transfer reactions with carbon disulfide. Formation of $[(RC_5H_4)_3U]_2[\mu\text{-}\eta^1\ \eta^2\text{-}CS_2]$. Inorg Chem 25 (11):1756-1760

76. MacDonald MR, Fieser ME, Bates JE, Ziller JW, Furche F, Evans WJ (2013) Identification of the +2 Oxidation State for Uranium in a Crystalline Molecular Complex, $[K(2.2.2\text{-}cryptand)][(C_5H_4SiMe_3)_3U]$. J Am Chem Soc 135 (36):13310-13313

77. Blake PC, Lappert MF, Atwood JL, Zhang H (1986) The synthesis and characterisation, including X-ray diffraction study, of $[Th\{\eta\text{-}C_5H_3(SiMe_3)_2\}_3]$; the first thorium(III) crystal structure. J Chem Soc, Chem Commun (15):1148-1149

78. Langeslay RR, Fieser ME, Ziller JW, Furche F, Evans WJ (2015) Synthesis, structure, and reactivity of crystalline molecular complexes of the $\{[C_5H_3(SiMe_3)_2]_3Th\}^{1-}$ anion containing thorium in the formal+ 2 oxidation state. Chemical science 6 (1):517-521

79. Windorff CJ, Chen GP, Cross JN, Evans WJ, Furche F, Gaunt AJ, Janicke MT, Kozimor SA, Scott BL (2017) Identification of the formal +2 oxidation state of plutonium: synthesis and characterization of $\{Pu^{II}[C_5H_3(SiMe_3)_2]_3\}^{1-}$. J Am Chem Soc 139 (11):3970-3973

80. Su J, Windorff CJ, Batista ER, Evans WJ, Gaunt AJ, Janicke MT, Kozimor SA, Scott BL, Woen DH, Yang P (2018) Identification of the Formal +2 Oxidation State of Neptunium: Synthesis and Structural Characterization of $\{Np^{II}[C_5H_3(SiMe_3)_2]_3\}^{1-}$. J Am Chem Soc 140 (24):7425-7428

81. Neculai AM, Neculai D, Roesky HW, Magull J, Baldus M, Andronesi O, Jansen M (2002) Stabilization of a Diamagnetic Sc^IBr Molecule in a Sandwich-Like Structure. Organometallics 21 (13):2590-2592

82. Clentsmith GKB, Cloke FGN, Green JC, Hanks J, Hitchcock PB, Nixon JF (2003) Stabilization of Low-Oxidation-State Early Transition-Metal Complexes Bearing 1,2,4-Triphosphacyclopentadienyl Ligands: Structure of $[\{Sc(P_3C_2{}^tBu_2)_2\}_2]$; Sc^{II} or Mixed Oxidation State? Angew Chem Int Ed 42 (9):1038-1041

83. Beck, HP (1976) NdI_2, a Metallic High Pressure Modification. Z.Naturforsh.B 31b, 1548-1549.