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Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States[†]

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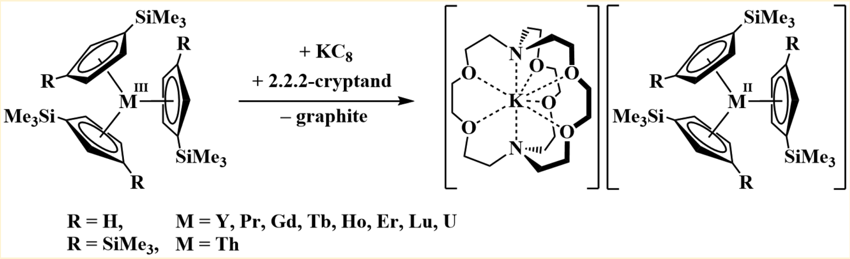

ABSTRACT: A fundamental aspect of any element is the range of oxidation states accessible for useful chemistry. This tutorial describes the recent expansion of the number of oxidation states available to the rare-earth and actinide metals in molecular complexes that has resulted through organometallic chemistry involving the cyclopentadienyl ligand. These discoveries demonstrate that the cyclopentadienyl ligand, which has been a key component in the development of organometallic chemistry since the seminal discovery of ferrocene in the 1950s, continues to contribute to the advancement of science. Background information on the rare-earth and actinide elements is presented, as well as the sequence of events that led to these unexpected developments in the oxidation state chemistry of these metals.

INTRODUCTION

Since the discovery of ferrocene six decades ago,[1] organometallic chemistry has provided an extensive series of breakthroughs that have advanced science and technology in many areas.[2] One of the key ligands that has supported this development is the cyclopentadienyl ligand. From the early involvement of the $(C_5H_5)^-$ ligand in the discovery of the first organometallic sandwich compound, ferrocene, $(C_5H_5)_2Fe$,[1] to the highly substituted cyclopentadienyl variants that led to sophisticated catalysts,[3] the cyclopentadienyl ligand has been of central importance in organometallic chemistry.[2] Although extensive efforts have been made to develop ancillary ligands beyond cyclopentadienyl in the "postmetallocene era",[4] cyclopentadienyl ligands continue to make significant contributions.

This tutorial describes another type of chemical advance made accessible using the cyclopentadienyl ligand: the discovery of new oxidation states in the periodic table. A fundamental aspect of the chemistry of any element is the number of formal oxidation states available in molecules for chemical reactions. The range of accessible oxidation states for all of the elements is so important to reactivity that it has been continuously tested for decades. As a result, the limits of oxidation states of the elements were thought to be well-established across the periodic table.

However, in the past few years the special environment provided by three cyclopentadienyl ligands substituted with silyl groups has led to the discovery of molecular complexes containing the first examples of the formal +2 oxidation states for the rare-earth metals Y,[5] Ho,[6] Er,[6] Pr,[7] Gd,[7] Tb,[7] and Lu[7] and for the actinides U[8] and Th.[9] This tutorial describes the chronological sequence of events that led to these unexpected results and the integral role that the cyclopentadienyl ligand has played in expanding the oxidation states of these nine elements. Hopefully, this tutorial will inspire deeper thinking on the use of traditional ligands and principles to make chemical advances in the future.

BACKGROUND

Traditional Ln^{2+} Chemistry. To put these discoveries in perspective, some background is needed. For the first 90 years of reported rare-earth chemistry, the oxidation states commonly available in molecular species in solution were those shown in Figure 1.[10,11] The +3 oxidation state was the most stable for all the lanthanides regardless of the number of 4f valence electrons in the metal ion.[12]

The invariance of oxidation state with $4f^n$ configuration is consistent with calculations which indicate that the 4f orbitals have a limited radial extension beyond the inert gas core electron cloud[13] and therefore do not have a strong effect on the chemistry. Spectroscopic and magnetic studies support this view such that the Ln^{3+} ions are considered good examples of unligated "free ions" in which the electronic

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	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Valence Electrons	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Oxidation States	3	4 3	3	3	3	3 2	3 2	3	3	3	3	3	3	3 2	3

Figure 1. Early table of oxidation states of the lanthanide metals commonly available in molecular complexes.

structure of the $4f^n$ manifold is not significantly perturbed by the ligand field at room temperature.[13−15] For example, complexes of Ln^{3+} ions are typically pale in color since their 4f−4f absorptions are Laporte forbidden. The 4f orbitals do not have the radial extension[13] to overlap with ligand orbitals to relax the Laporte rule through vibronic coupling, as is possible with transition-metal d−d transitions.

Synthetic, structural, and reactivity studies also support the idea that the 4f orbitals have limited interaction with ligands. As a result, the chemistry of the lanthanides is much more ionic than that of the d^n transition metals.[16−18] Wilkinson and Birmingham demonstrated these features in the 1950s when they reported the first well-characterized organometallic lanthanide complexes which were obtained using the cyclopentadienyl ligand.[19,20] These tris(cyclopentadienyl) complexes, $(C_5H_5)_3Ln$ (Scheme 1), were chemically similar for all the lanthanide elements in the series regardless of the number of electrons in their $4f^n$ electron configurations. Their ionic character was demonstrated by the fact that they released the cyclopentadienyl ligands to $FeCl_2$ to make ferrocene (Scheme 1), much like an alkali-metal cyclopentadienyl complex.[20]

Scheme 1. Synthesis of Cp_3Ln and Reaction with $FeCl_2$ To Form Ferrocene

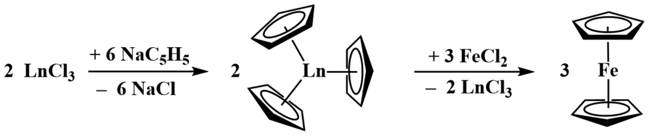


Figure 1 shows that initially only three Ln^{2+} ions were known in the lanthanide series in molecular complexes in solution, the half-filled shell $4f^7$ Eu^{2+}, the filled shell $4f^{14}$ Yb^{2+}, and the approaching half-filled shell $4f^6$ Sm^{2+}.[10,11] The existence of these ions was explained by the quantum mechanical stabilization associated with half-filled and filled shells. Since a half-filled shell is more stable than a filled shell, the electron configuration could also explain the relative order of $4f^n$ Ln^{3+} + e^- → $4f^{n+1}$ Ln^{2+} standard aqueous reduction potentials for Eu and Yb: − 0.35 and −1.15 V vs SHE, respectively (Table 1).[10] Since $4f^6$ Sm^{2+} was only approaching a half-filled shell, it was the most reactive (−1.55 V vs SHE). The $4f^{13}$ Tm^{2+} ion that was "approaching" a less-stable filled shell had a much more negative estimated standard reduction potential of −2.3 V vs SHE.[10] For many years, it was thought that this ion was inaccessible in solution, since it was expected to decompose any solvent that could dissolve it.

It should be noted that the conditions of these standard reduction potentials rarely match those of actual reactions such that redox potentials in specific reactions can vary significantly from these values. It also should be realized that experimental redox potentials were known only for Eu^{2+}, Yb^{2+}, and Sm^{2+}. The other values given in Table 1 were estimated from these three experimental values through a relationship that involved effective nuclear charge, Racah crystal field parameters, spin−orbit coupling parameters, and f−d absorption energies for the Ln^{3+} ions.[10b] The estimated error of these calculated values was ±0.2 V. Other estimates of lanthanide redox potentials were made on the basis of thermodynamic cycles[10a] which had a slightly different ordering for the elements beyond Nd, but, in general, followed the order of the first six metals in the table. One further point on the values in Table 1 is that they were calculated for $4f^n + e^- \rightarrow 4f^{n+1}$ processes.

Table 1. Estimated Ln^{3+}/Ln^{2+} Standard Reduction Potentials (±0.2 V) of Yttrium and the Lanthanides Based on Experimental, Spectroscopic, and Thermodynamic Data[10]

Ln	potential (V vs SHE)	Ln	potential (V vs SHE)
Eu	−0.35	Pr	−2.7
Yb	−1.15	Y	−2.8
Sm	−1.55	Ho	−2.9
Tm	−2.3	Er	−3.1
Dy	−2.5	La	−3.1
Nd	−2.6	Ce	−3.2
Pm	−2.6	Tb	−3.7
Lu	−2.7	Gd	−3.9

A structural characteristic of the three known Ln^{2+} ions was that bond distances in their complexes could be estimated from analogous complexes of Ln^{3+} ions by adding the differences in ionic radii between Ln^{2+} and Ln^{3+}.[21−23] For Eu^{2+}, Yb^{2+}, and Sm^{2+}, the Ln^{2+} ions were larger than the Ln^{3+} ions by about 0.16−0.19 Å. For example, the metal−(C_5Me_5 ring centroid) distances of $4f^6$ Sm^{2+} $(C_5Me_5)_2Sm(THF)_2$[24] and its +3 analogue, $4f^5$ Sm^{3+} $[(C_5Me_5)_2Sm(THF)_2]^+$,[25] are 2.42 and 2.60 Å, respectively, an increase of 0.18 Å for the Ln^{2+} complex. Extensive data showed a regular relationship between ionic radius and bond distance from lanthanide to lanthanide and between oxidation states. This was consistent with the ionic nature of these complexes arising from the limited radial extension of the 4f orbitals.

Another characteristic of Ln^{2+} ions is that they typically have intense colors that can be attributed to Laporte-allowed 4f−5d transitions.[14] In Ln^{3+} complexes, the 5d levels are too high in energy (generally 40000−50000 cm^{-1})[26−28] for such transitions to be observable in the visible region except for Ce^{3+}. However, atomic spectra show the 5d orbitals of Ln^{2+} ions to be 20000−30000 cm^{-1} above the 4f levels,[26−28] and hence the 4f−5d transitions can generate highly colored complexes.

In the solid state, three more lanthanide elements were known to have accessible +2 oxidation states. As early as the 1960s, it was known that $4f^{13}$ Tm^{2+}, $4f^{10}$ Dy^{2+}, and $4f^4$ Nd^{2+} ions were accessible in compounds such as LnX_2, where X was a halide.[29−33] These $(Ln^{2+})(X^-)_2$ salts could be made in sealed tantalum crucibles at high temperatures by reduction of LnX_3 with Ln metal. Compounds with formulas of LnX_2 could also be made for Ln = La, Ce, Pr, Gd, Y, but these were not saltlike

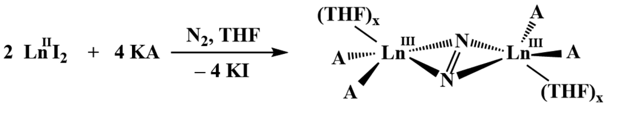
$(Ln^{2+})(X^-)_2$ species. Instead, these compounds were black insoluble materials characterized as $(Ln^{3+})(X^-)_2(e^-)$ containing Ln^{3+}, not Ln^{2+}, with an electron delocalized in a 5d band in the lattice that made them either semiconducting or metallic.[31−33] This was further evidence that only Eu, Yb, Sm, Tm, Dy, and Nd would form isolable compounds of +2 ions.

Hence, it was expected that +2 ions of the other metals, La, Ce, Pr, Gd, Tb, Ho, Er, and Lu, would only be accessible transiently under special conditions. Such species had been reported in gas-phase atomic spectra,[27,34] in ion cyclotron resonance studies,[35−37] in spectroscopic studies of Ln^{3+} ions doped into CaF_2 and treated with γ radiation,[38] and in electrochemical experiments in molten salts[10,39,40] and THF.[41] All of these studies suggested that these ions would be too reactive to isolate in molecular species.

Attempts to make Tm^{2+}, Dy^{2+}, and Nd^{2+} in solution had been reported in the literature, but typically these studies only reported the observation of transient colors that could be attributed to 4f−5d absorptions from the highly reactive Ln^{2+} ions.[42−47] However, between 1997 and 2001, Bochkarev and co-workers developed syntheses of the solvated lanthanide diiodides of Tm, Dy, and Nd that were crystallographically characterizable.[47−51] We were fortunate to be able to collaborate with the Bochkarev group in obtaining X-ray crystallographic data on $TmI_2(DME)_3$[48] and $DyI_2(DME)_3$.[49] The structure of $NdI_2(THF)_5$ was obtained in a separate collaboration between Bochkarev and Schumann.[50] These syntheses and structures demonstrated that Tm^{2+}, Dy^{2+}, and Nd^{2+} could also be accessed in molecular species. This result eliminated the belief that molecular complexes of these ions would decompose any solvent.

Dinitrogen Reduction via Tm^{2+}, Dy^{2+}, and Nd^{2+}. Our attempts to make derivatives of the new Tm^{2+}, Dy^{2+}, and Nd^{2+} complexes by substitution of the iodide ligands with amides, aryloxides, or cyclopentadienides revealed another reason why stable complexes of these ions had not been discovered earlier: reactions of the Tm^{2+}, Dy^{2+}, and Nd^{2+} diiodides with other ligands can lead to reduction of dinitrogen.[52−55] Hence, addition of KC_5Me_5,[52] $KC_5H_4SiMe_3$,[52] $KC_5H_3(SiMe_3)_2$,[52] $NaN(SiMe_3)_2$,[53] and $KOC_6H_3{}^tBu_2$[53,54] to LnI_2 did not lead to substitution of the iodides and new Ln^{2+} complexes, but instead generated complexes of $(N{=}N)^{2-}$ (Scheme 2)[52−54] and $(N_2)^{3-}$.[54]

Scheme 2. Generation of $(N{=}N)^{2-}$ Complexes from LnI_2 (Ln = Tm, Dy, Nd)



Ln = Tm, Dy, Nd

A = C_5Me_5, $C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2$, $N(SiMe_3)_2$, $OC_6H_3{}^tBu_2$-2,6; x = 0-1

Since $(C_5Me_5)_2Sm$ can reduce N_2[55] and the Tm^{2+}, Dy^{2+}, and Nd^{2+} ions are more reducing than Sm^{2+},[10] this may not seem surprising in retrospect. However, the dinitrogen reductive capacity of complexes of Tm^{2+}, Dy^{2+}, and Nd^{2+} had gone undetected for many years. It is likely that, in some of the early attempts to make these ions decades before Scheme 2 was discovered, the fleeting colors described in the literature arose because the Ln^{2+} ions were reducing N_2 to make pale-colored Ln^{3+} complexes of $(N{=}N)^{2-}$!

Dinitrogen Reduction via LnA_3/M. Since we were interested in studying the $(N_2)^{2-}$ complexes in Scheme 2, we wondered if it was possible to access the putative Ln^{2+} intermediate in an easier way: e.g., by direct reduction of a Ln^{3+} complex with an alkali metal. This was a classic method to make Ln^{2+} complexes, as exemplified by the early synthesis of insoluble $[(C_5H_5)_2Sm(THF)_x]_n$ from $(C_5H_5)_3Sm$ and K in 1969.[56] Attempting the synthesis of $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ complexes in this way (Scheme 2, A = $N(SiMe_3)_2$) was attractive, since the $Ln[N(SiMe_3)_2]_3$ complexes had been prepared by Bradley and co-workers in 1973 from $LnCl_3$ and $LiN(SiMe_3)_2$.[57] These complexes were much easier to prepare than the DyI_2 and NdI_2 in Scheme 2 that required temperatures of 500 °C and a quartz furnace (Figure 2) to prepare the compounds from the elements in a melt of LnI_2.[58]

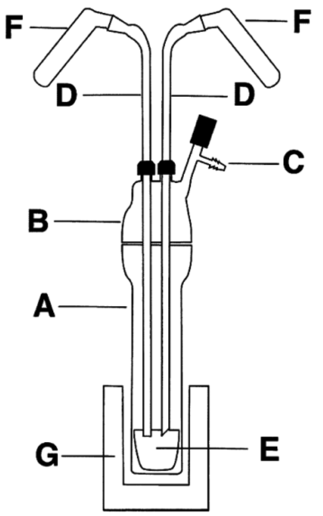
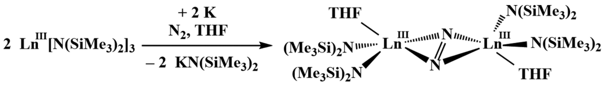


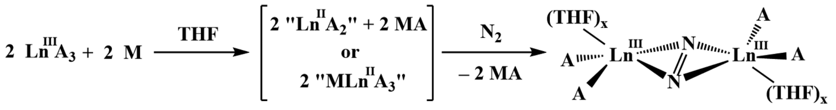
Figure 2. Apparatus used to generate LnI_2 from Ln and I_2:[58] (A) quartz tube; (B) top O-ring joint; (C) valve to vacuum line; (D) quartz addition tubes; (E) quartz crucible; (F) Schlenk solid addition funnel; (G) furnace.

Much to our delight, the $(N{=}N)^{2-}$ complexes could be prepared by reduction of $Ln[N(SiMe_3)_2]_3$ with K (eq 1; Ln = Tm, Dy, Nd).[59] It is interesting to note that all of this chemistry could have been discovered as early as 1973 when the $Ln[N(SiMe_3)_2]_3$ complexes were first made.[57] If someone had tried to synthesize the Tm^{2+}, Dy^{2+}, and Nd^{2+} ions known in the solid state[29−33] and had examined the pale-colored "decomposition" products, they might have discovered the $(N{=}N)^{2-}$ complexes long before the first example was reported![55]

 (1)

During the course of the $Ln[N(SiMe_3)_2]_3$/M reactions of eq 1 (Ln = Tm, Dy, Nd), not even a fleeting color change indicative of a possible Ln^{2+} "$Ln[N(SiMe_3)_2]_2$"[60] or "$KLn[N(SiMe_3)_2]_3$"[61,62] intermediate was observed.[59] We wondered if the reaction really proceeded through a Ln^{2+} intermediate and decided to test this with a metal for which a Ln^{2+} ion was not known. Holmium was chosen since it is similar in size to Dy and Tm. Surprisingly, the reaction of $Ho[N(SiMe_3)_2]_3$ with K under N_2 also made a reduced dinitrogen complex,

Scheme 3. Generation of $(N{=}N)^{2-}$ Complexes through the LnA_3/M Reaction



$Ln = Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu$
$A = N(SiMe_3)_2, OC_6H_3{}^tBu_2\text{-}2,6, C_5Me_5, C_5Me_4H, C_5H_4SiMe_3, C_5H_2{}^tBu_3$
$M = K, KC_8, Na; x = 0\text{-}2$

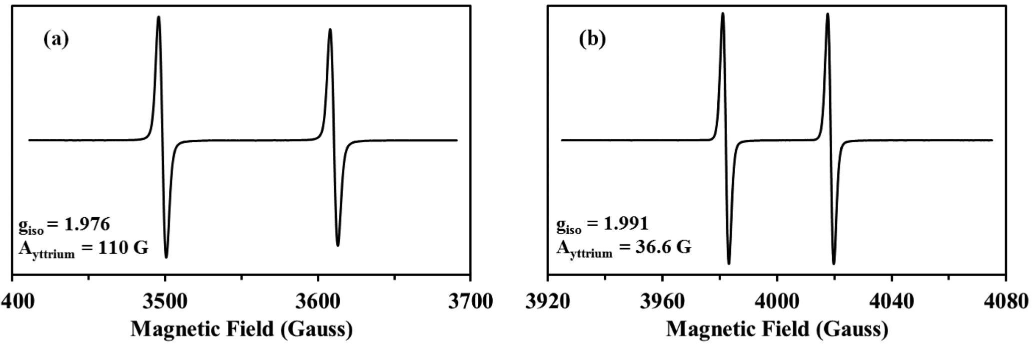
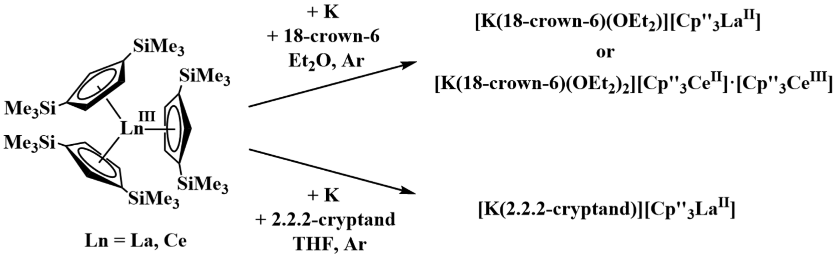


Figure 3. EPR spectra of Y^{2+} in THF from the reduction of (a) $Y[N(SiMe_3)_2]_3$ and (b) $(C_5H_4SiMe_3)_3Y$.

Scheme 4. Syntheses of La^{2+} and Ce^{2+} Complexes Reported by Lappert and Co-workers[81]



$\{[(Me_3Si)_2N]_2(THF)Ho\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (eq 1; Ln = Ho).[59] Other metals were examined, and crystallographically characterizable reduced dinitrogen complexes were obtained in the $Ln[N(SiMe_3)_2]_3$/M reaction according to eq 1 for Ln = Er, Tb, Gd, Y, and Lu as well.[63] Similar dinitrogen reduction could also be accomplished with La, Ce, and Pr, but with these larger metals, larger ligands were necessary to get crystallographically characterizable $(N{=}N)^{2-}$ complexes. For example, $[(C_5Me_4H)_2(THF)Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ complexes could be made from $(C_5Me_4H)_3Ln$ precursors.[63,64] On the basis of the −3.1 to −3.9 V vs SHE calculated Ln^{3+}/Ln^{2+} reduction potentials for Er, La, Ce, Tb and Gd (Table 1),[10] these reactions should not be possible with potassium, which has a standard K^+/K reduction potential of −2.9 V vs SHE.

The $Ln[N(SiMe_3)_2]_3$/K reaction in eq 1 turned out to be general and was labeled simply the LnA_3/M reduction reaction, since the mechanism was unknown and the reaction applied to a variety of anions (A), in addition to the bis(trimethylsilyl)amide ligand, and could be done with M = Na as well as M = K (Scheme 3).[59,63−73] In all cases, these reactions generate MA as a byproduct. Heteroleptic LnA_2A'/M reactions with A′ = BPh_4, I, and H were also observed in which MA′ was the byproduct.[64,65,70−73]

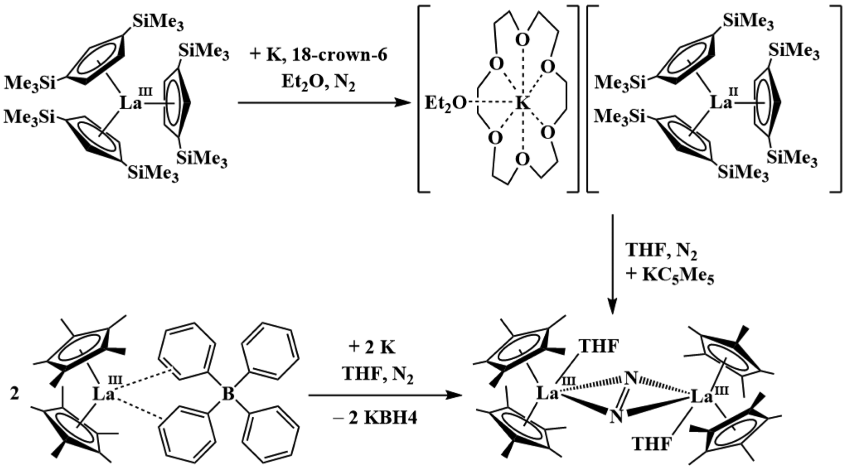
Although the LnA_3/M reaction generated the reactivity expected from a Ln^{2+} complex such as "LnA_2" or "$KLnA_3$", it proved difficult to isolate any Ln^{2+} intermediates by conducting the reactions under argon. However, by careful choice of conditions, an EPR spectrum consistent with a complex of Y^{2+} was obtained from a $Y[N(SiMe_3)_2]_3$/K reaction at −35 °C (Figure 3a).[67] A two-line pattern characteristic of the ^{89}Y nucleus which has a spin of 1/2 and is 100% naturally abundant was observed.

■ CYCLOPENTADIENYL CHEMISTRY

Lappert's Cyclopentadienyl Studies. LnA_3/M reactions were also being investigated by Lappert and co-workers with Cp''_3Ln ($Cp'' = C_5Me_3(SiMe_3)_2$-1,3) in efforts, not to reduce dinitrogen, but rather to make complexes in the +2 oxidation state.[74−82] EPR evidence obtained in 1997[76] was pursued for over 10 years, and finally in 2008, an unequivocal crystal structure was obtained that showed the existence of La^{2+} ions in the molecular complexes, $[K(18\text{-crown-}6)(OEt_2)][Cp''_3La]$ and $[K(2.2.2\text{-cryptand})][Cp''_3La]$ (Scheme 4).[81]

The structure of the $(Cp''_3La)^-$ anion was unusual in that the La−ring centroid distance (2.632 Å) was only slightly longer than that in the analogous Ln^{3+} complex Cp''_3La (2.600 Å).[81] This was significantly different from the 0.16−0.19 Å differences that had previously been observed between $4f^n$ Ln^{3+} and $4f^{n+1}$ Ln^{2+} complexes.[21−23] This small difference in bond distances was rationalized by suggesting that La^{2+} was a $5d^1$ ion and not a $4f^1$ ion.[81] It was argued that this was possible because La was the first element in the lanthanide series where the 4f and 5d orbital energies are similar.[26−28,34,83] Since transition-metal complexes do not show such a large change in radius with oxidation state as the lanthanides,[81,84] this small

Scheme 5. Syntheses of $[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$



difference in distances was reasonable for a 5d^1 ion. This assignment was also consistent with the EPR spectrum and magnetic susceptibility of the La complexes and density functional theory (DFT) studies that indicated the unpaired electron was in a d_{z^2} orbital.[81]

Importance of the Specific Cyclopentadienyl Ligand to Dinitrogen Reduction vs Ln^{2+} Formation. Surprisingly, no N_2 reduction was reported with the La^{2+} $(Cp''_3La)^-$ complexes.[74−82] After Professor Lappert retired, we decided to prepare this anion independently to determine if it would reduce dinitrogen. Not only did the complex not reduce dinitrogen but also, as shown in Scheme 5, it could be prepared under N_2![5] This seemed strange, since reduction of $(C_5Me_5)_2La(\mu\text{-}Ph)_2BPh_2$ with potassium graphite (KC_8) in a LnA_2A'/M reaction yielded the reduced dinitrogen complex $[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$[68] (Scheme 5) and $[(C_5Me_4H)_2(THF)La]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$ could be prepared by potassium reduction of $(C_5Me_4H)_3La$ under N_2.[68] Clearly, the substituents of the cyclopentadienyl rings made a big difference in reactivity. To probe this further, KC_5Me_5 was added to $[K(18\text{-crown-}6)(OEt_2)][Cp''_3La]$[81] and it was found that the $(N{=}N)^{2-}$ complex, $[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$, was formed (Scheme 5).[5] In this reaction, La^{2+} ions are reducing N_2, but only in the presence of $(C_5Me_5)^-$. These results indicated that some ligands. e.g., $[N(SiMe_3)_2]^-$ and $(C_5Me_5)^-$, were good for N_2 reduction and others, e.g. $[C_5H_3(SiMe_3)_2]^-$, were better for isolating Ln^{2+} complexes.

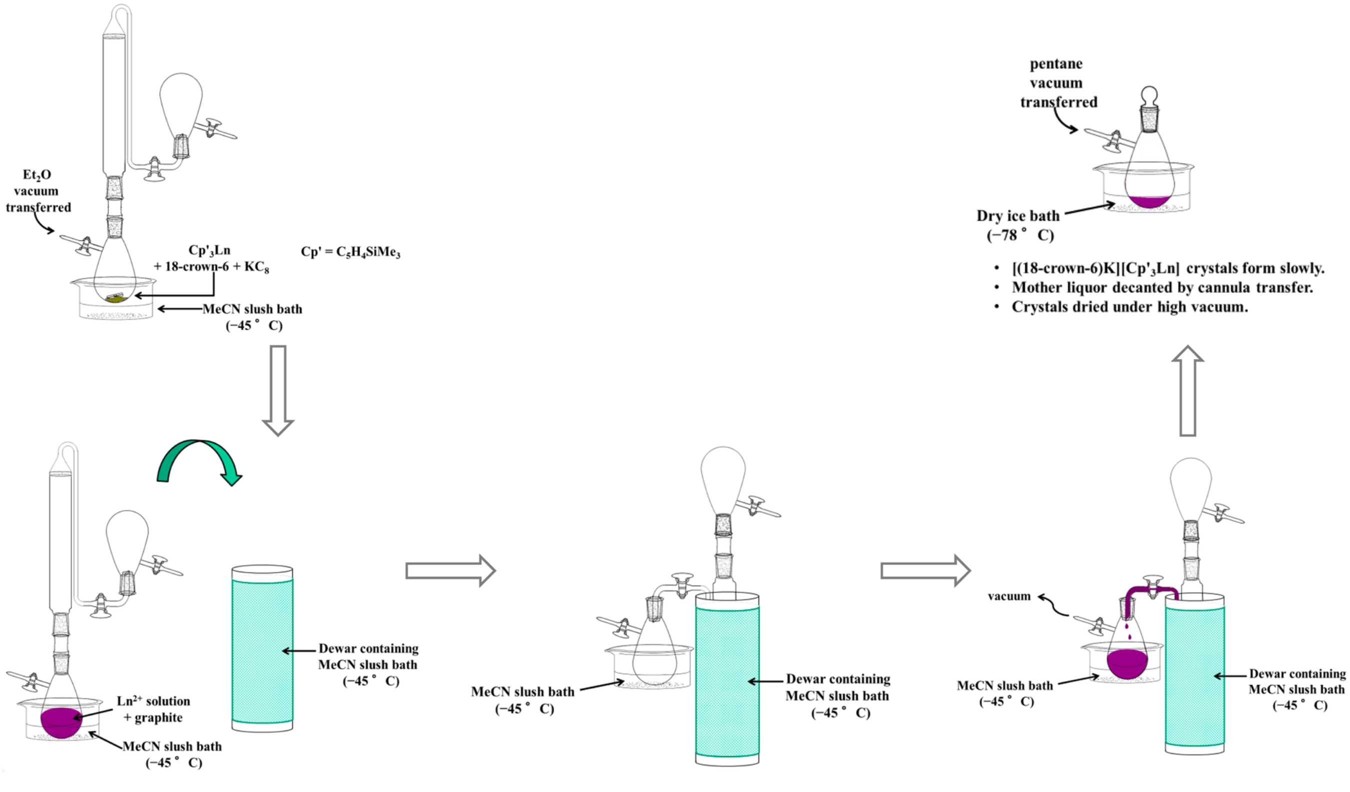
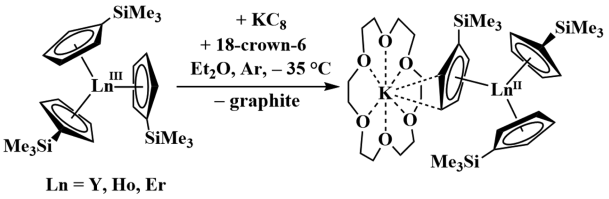


Figure 4. Procedure to make $(Cp'_3Ln)^-$ at −45 °C by Schlenk techniques.

Accordingly, we decided to revisit the Ln[N(SiMe$_3$)$_2$]$_3$/K reduction system that gave the EPR spectrum for Y^{2+} (Figure 3a),[67] but with the Lappert ligand [C$_5$H$_3$(SiMe$_3$)$_2$]$^-$ (=(Cp″)$^-$).[74−82,85] Since (C$_5$H$_4$SiMe$_3$)$^-$ (=(Cp′)$^-$) is a precursor to (Cp″)$^-$, the reaction was initially tried with Cp′$_3$Y rather than Cp″$_3$Y. This "short cut" proved to be an excellent decision, as Cp″$_3$Ln complexes of the smaller lanthanides later in the series are more difficult to synthesize and subsequent attempts to make (Cp″$_3$Ln)$^-$ complexes of the smaller lanthanides gave much less stable complexes.[86]

■ NEW OXIDATION STATES VIA CYCLOPENTADIENYL LIGANDS

Examination of a LnA$_3$/M reaction with A = Cp′ allowed the isolation of the first crystallographically characterizable complex of Y^{2+}, namely [K(18-crown-6)][Cp′$_3$Y] (eq 2; Ln = Y).[5]



(2)

The complex had an EPR spectrum (Figure 3b) similar to that in Figure 3a with A = N(SiMe$_3$)$_2$[67] and an intense dark color. The difference between Y−(ring centroid) distances for the Y^{2+} and Y^{3+} complexes (0.031 Å) was small, like that in Lappert's La^{2+} case.[81] However, since Y^{2+} is a 4d^1 ion and not a 4f^n system, this was consistent with the small changes in distances observed between ions in different oxidation states with d electron configurations.[81,84]

Following the yttrium result, it was of interest to examine the similarly sized holmium (nine-coordinate ionic radii:[21] Y^{3+}, 1.075 Å; Ho^{3+}, 1.072 Å). An analogous result was obtained (eq 2; Ln = Ho), and the first molecular complex of Ho^{2+} was characterized by X-ray diffraction.[6] The holmium complex was isomorphous with the yttrium compound,[5] and again a small difference (0.032 Å) in the Ln−(ring centroid) distances was observed between the Ho^{2+} and Ho^{3+} complexes, [K(18-crown-6)][Cp′$_3$Ho], and Cp′$_3$Ho. This was surprising, since reduction of 4f^{10} Ho^{3+} would be expected to form 4f^{11} Ho^{2+} and this ion would be expected to be 0.16−0.19 Å larger than 4f^{10} Ho^{3+}. Subsequently, it was found that an analogous result could be obtained with Ln = Er[6] via eq 2, even though the calculated Er^{3+}/Er^{2+} reduction potential of −3.1 V vs SHE[10] (Table 1) was more negative than the −2.9 V value for K$^+$/K.

The formation of the three new oxidation states for Y, Ho, and Er in eq 2 may look simple in retrospect, but it should be realized that all chemical manipulations were done at −40 °C or below.[5,6] In each case, the Cp′$_3$Ln starting material, potassium graphite, and 18-crown-6 were placed in a Schlenk flask fitted with an inverted low-temperature Schlenk filtration funnel and a receiving flask (Figure 4). The flask was cooled in an acetonitrile slush bath (−40 to −45 °C), and Et$_2$O was vacuum-transferred onto the reagents. After the reaction was over, the apparatus was inverted into a Dewar containing an acetonitrile slush bath so the mixture could be filtered at low temperature to remove graphite. The cold filtrate was pulled into the receiver flask chilled in an acetonitrile slush bath and the filter detached. The product was crystallized by concentrating the solution by removal of Et$_2$O, adding pentane, and cooling to −78 °C.

The UV−visible spectra of the Ho^{2+} and Er^{2+} complexes were unusual in that they were very similar to the spectrum of 4d^1 Y^{2+} (see below).[5,6] A further surprise was observed when DFT studies in collaboration with the group of Furche revealed that the LUMO of the Cp′$_3$Ln precursors and the HOMO of the (Cp′$_3$Ln)$^-$ products were d$_{z^2}$ orbitals (Figure 5).[6] Although this was normal for 4d^1 Y^{2+}, it was surprising for Ho^{2+} and Er^{2+}, which were expected to be 4f^{10} and 4f^{11} ions, respectively, if a traditional 4f^n to 4f^{n+1} reduction had occurred. These results suggested that the reduction of the 4f^n Ln^{3+} cyclopentadienyl complexes of Ho and Er made 4f^{n}5d^1 Ln^{2+} products and not the expected traditional 4f^{n+1} Ln^{2+} ions.

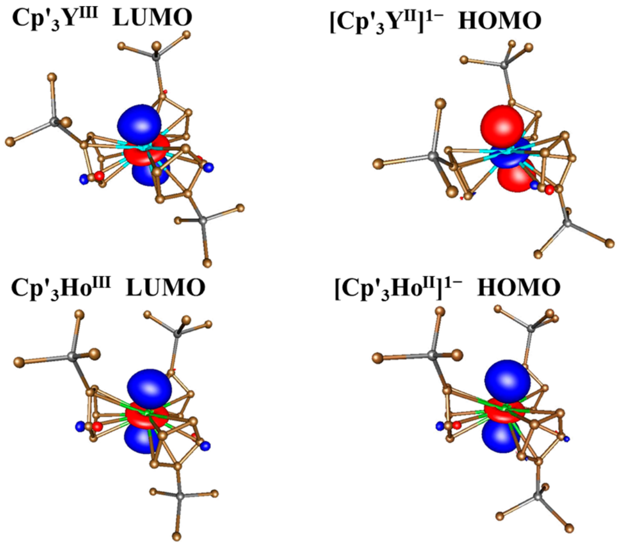


Figure 5. LUMOs of the neutral Ln^{3+} complexes Cp′$_3$Ln and HOMOs of the anionic Ln^{2+} complexes (Cp′$_3$Ln)$^-$.

A rationale for populating the 5d orbitals in these tris(cyclopentadienyl) complexes could be found in numerous theoretical studies[87−91] of Cp$_3$M complexes dating back to the classic 1976 paper by Lauher and Hoffmann on bent metallocenes.[87] The ligand field created by three cyclopentadienyl ligands gives the splitting diagram in Figure 6. Presumably the 2 over 2 over 1 pattern puts the d$_{z^2}$ orbital low

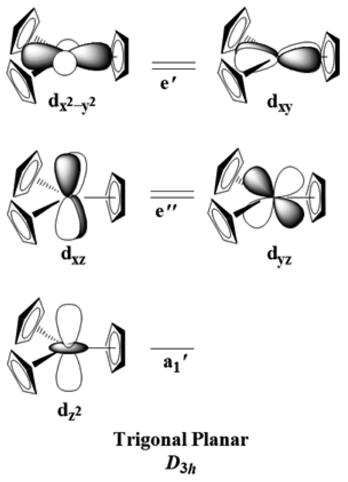


Figure 6. Splitting diagram caused by the ligand field of three cyclopentadienyl ligands.[87−91]

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enough in energy that it can be populated competitively with the 4f orbitals in the $(Cp'_3Ln)^-$ complexes.

To simplify the synthesis of the $(Cp'_3Ln)^-$ complexes from the all-day −45 °C Schlenk procedure (Figure 4), a new method was developed that involved a flash reduction column (Figure 7) so that the reaction could be done completely in a glovebox.[6] In this case, a concentrated solution of Cp'_3Ln and 18-crown-6 in Et_2O was chilled to −35 °C in the glovebox freezer. A 1 × 10 cm chromatography column with a filter frit at the bottom was packed with potassium graphite and chilled to −35 °C in the glovebox freezer. Passing the Et_2O solution through the column at the proper rate produced a concentrated solution of product below the filter frit, which was collected in a chilled flask in a bath of cold hexane chilled to −35 °C in the glovebox freezer. This allowed the complexes to be prepared in a much shorter time and immediately put into the glovebox freezer for crystallization.

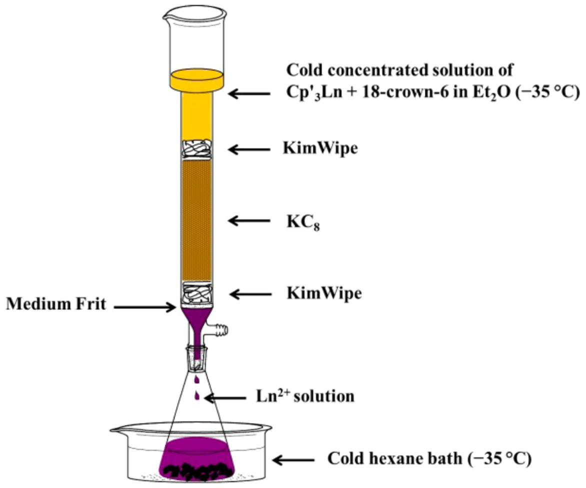
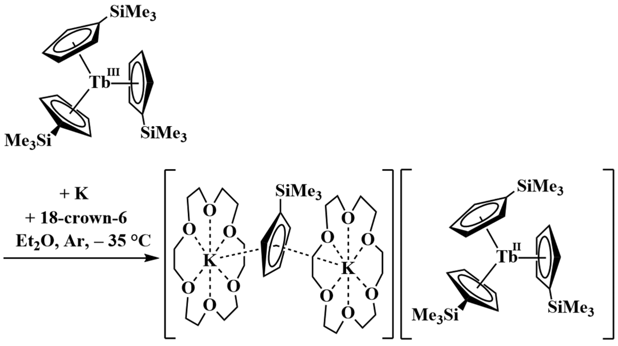


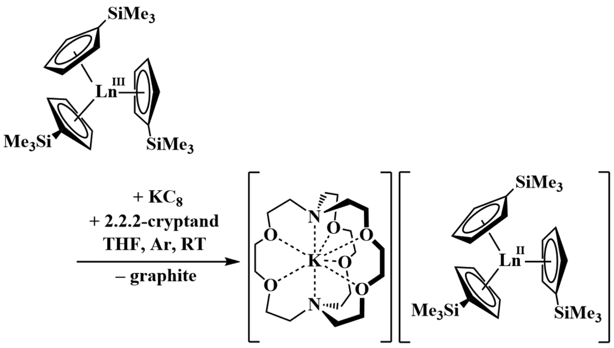
Figure 7. Apparatus to make $(Cp'_3Ln)^-$ in the glovebox by flash reduction (YouTube: New Reaction Overturns Periodic Table Assumptions; https://youtu.be/CoGFF4YReFo?list=PLEQ2r9YGFNevddQRI17uMMc8Q5HDbuhGh).

This new flash reduction technique facilitated the examination of other lanthanides. The Cp'_3Tb/K reaction was special in that the first known Tb^{2+} complex crystallized with a countercation different from the $[K(18\text{-crown-6})]^+$ cations found in eq 2. In the terbium case, the $(Cp'_3Tb)^-$ anion in the product had an inverse cyclopentadienyl sandwich countercation, $\{[K(18\text{-crown-6})]_2(\mu\text{-}Cp')\}^+$, that was well-separated from the $(Cp'_3Tb)^-$ anion (eq 3).[7]



(3)

This result demonstrated that $[K(18\text{-crown-6})]^+$ was not essential for isolating these complexes. Consequently, an alternative potassium chelator was examined, the 2.2.2-cryptand encapsulating molecule employed earlier by Lappert (Scheme 4).[81] With the cryptand sequestering the potassium ion, $[K(2.2.2\text{-cryptand})][Cp'_3Ln]$ complexes of Y^{2+}, Ho^{2+}, Er^{2+}, and Tb^{2+} could be made (eq 4) that were not as temperature sensitive as the $[K(18\text{-crown-6})][Cp'_3Ln]$ complexes in eq 2.[7] In addition, with the cryptand present, it was found that syntheses could be run at room temperature if the flash reductions were carried out very quickly. Using 2.2.2-cryptand, complexes of Pr^{2+}, Gd^{2+}, and Lu^{2+} were also isolated[7] such that Ln^{2+} ions are now known for all the lanthanides except Pm, which was not investigated because of its radioactivity (Figure 8). *This tris(trimethylsilylcyclopentadienyl) ligand environment showed for the first time that molecular complexes of +2 ions were available for the entire lanthanide series.*



(4)

As shown in Figure 9, the UV−visible spectra for the $[K(2.2.2\text{-cryptand})][Cp'_3Ln]$ complexes for all the new ions[7] match those of $4d^1$ Y^{2+} and the Lu^{2+} complex, which also is a d^1 ion since Lu^{3+} is $4f^{14}$ and Lu^{2+} must be $4f^{14}5d^1$. The similarity of the spectra is consistent with $4f^n5d^1$ configurations for all the new ions and not the traditional $4f^{n+1}$ configurations. *Hence, the tris(cyclopentadienyl) ligand environment also showed that new oxidation states could be accessed using higher lying orbitals in the proper ligand field.*

■ A SURPRISE WITH TRADITIONAL OXIDATION STATES FROM CYCLOPENTADIENYL LIGANDS

At this point, the view of +2 oxidation states in the lanthanide series appeared to be as follows: the traditional six +2 ions, Eu^{2+}, Yb^{2+}, Sm^{2+}, Tm^{2+} Dy^{2+}, and Nd^{2+}, were obtained by reduction of $4f^n$ Ln^{3+} ions to make $4f^{n+1}$ Ln^{2+} ions, whereas with the rest of the metals in the series reduction of $4f^n$ Ln^{3+} ions generated $4f^n5d^1$ ions. This dichotomy matched that which was previously observed in the solid state: Eu, Yb, Sm, Tm, Dy, and Nd form saltlike $Ln^{2+}(X^-)_2$ compounds (X = halide), whereas reduction of La, Ce, Pr, Gd, and Y in the solid state gave $4f^n$ Ln^{3+} ions with the extra electron delocalized in the lattice in a level comprised of 5d orbitals: i.e., $Ln^{3+}(X^-)_2(e^-)$.[12,31,32,93] In this sense, the new $(Cp_3Ln)^-$ complexes are molecular examples of the LnX_2 solid-state systems except that the added electron resides in a 5d orbital in the molecule. In addition, these molecular $4f^n5d^1$ $(Cp'_3Ln)^-$ analogues of the $Ln^{3+}(X^-)_2(e^-)$ solids were obtainable not only for the La, Ce, Pr, Gd, and Y metals in the solid-state LnX_2 series, but also with Tb, Ho, Er, and Lu.

The structural and spectroscopic data collected on the new Pr^{2+}, Gd^{2+}, Ho^{2+}, Y^{2+}, Er^{2+}, Tb^{2+}, and Lu^{2+} ions shown in eq 4

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Valence Electrons	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Oxidation States		4													
	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	2	2	2	2		2	2	2	2	2	2	2	2	2	2

Figure 8. Updated version of the Figure 1 table of oxidation states of the lanthanide metals commonly available in molecular species.[92]

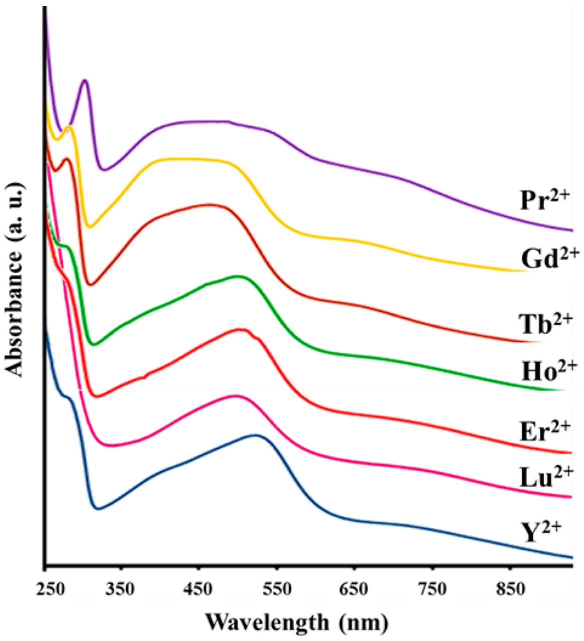


Figure 9. UV−visible spectra for the [K(2.2.2-cryptand)][Cp'_3Ln] complexes.[7]

Table 2. Comparison of Ln−(Ring Centroid) Distances for Ln^{3+} Cp'_3Ln Complexes and for Ln^{2+} $(Cp'_3Ln)^-$ Complexes and the Difference between Them

	metal−(ring centroid) distance (Å)		difference in metal−(ring centroid) distance (Å)	
Ln	Cp'_3Ln (Ln^{3+})	$(Cp'_3Ln)^-$ (Ln^{2+})	new Ln^{2+} ions	traditional Ln^{2+} ions
La	2.559	2.586	0.027	
Ce	2.529	2.558	0.029	
Pr	2.508	2.535	0.027	
Nd	2.489	2.519		0.030
Sm	2.459	2.608		0.149
Eu	2.451	2.607		0.156
Gd	2.437	2.468	0.031	
Tb	2.423	2.454	0.031	
Dy	2.407	2.443		0.036
Y	2.405	2.436	0.031	
Ho	2.394	2.426	0.032	
Er	2.386	2.416	0.030	
Tm	2.379	2.502		0.123
Yb	2.365	2.508		0.143
Lu	2.361	2.392	0.031	

involved $(Cp'_3Ln)^-$ complexes. These data could not be compared directly to data on complexes of the traditional six Eu^{2+}, Yb^{2+}, Sm^{2+}, Tm^{2+}, Dy^{2+}, and Nd^{2+} ions, since previous data on these ions had been obtained on complexes with different ligand sets. As a result, it was deemed necessary to prepare the Cp'_3Ln complexes with the traditional six metals and reduce them to $(Cp'_3Ln)^-$ for a direct comparison in the same ligand environment. Cp'_3Ln and $(Cp'_3Ln)^-$ complexes of La and Ce were also prepared, since La^{2+} and Ce^{2+} were only in the literature with $(Cp'')^-$ (Scheme 4).[81]

Initially this seemed like a significant amount of synthetic work to do a necessary blank, but the result turned out to be much more interesting. Table 2 shows the first comparison of metrical data for all the lanthanides in both +3 and +2 oxidation states in the same coordination environment (except radioactive Pm).[94] The data on Cp'_3Ln and $(Cp'_3Ln)^-$ for the new $4f^n5d^1$ Ln^{2+} ions discussed above, namely Pr^{2+}, Gd^{2+}, Ho^{2+}, Y^{2+}, Er^{2+}, Tb^{2+}, and Lu^{2+}, all showed small differences in the metal−(ring centroid) distances between complexes of the +2 and +3 ions consistent with addition of an electron to a 5d orbital. The results with La and Ce also showed small differences like the other new ions and similar to Lappert's data on the La complexes of Cp'' (eq 4).[81] This is consistent with $5d^1$ and $4f^15d^1$ configurations for the $(Cp'_3Ln)^-$ complexes of La^{2+} and Ce^{2+}, respectively.

It was expected that the pairs of distances for the Ln^{2+} and Ln^{3+} complexes of the other six elements, Eu, Yb, Sm, Tm, Dy, and Nd, would show large differences as had been observed in the past in other complexes of these metals. The $(Cp'_3Ln)^-$ complexes of Eu^{2+}, Yb^{2+}, Sm^{2+}, and Tm^{2+} showed these much larger differences, 0.123−0.156 Å, in comparison to their Cp'_3Ln Ln^{3+} analogues. However, this was not observed for Dy^{2+} and Nd^{2+}! The data on $(Cp'_3Dy)^-$ and $(Cp'_3Nd)^-$ show that the distances in these complexes are only slightly larger than those in the Ln^{3+} Cp'_3Ln complexes.[94] This suggested that Dy^{2+} and Nd^{2+} were $4f^n5d^1$ ions in the $[Cp'_3]^{3-}$ coordination environment rather than $4f^{n+1}$ ions. The UV−visible spectra of the Dy^{2+} and Nd^{2+} complexes were consistent with this assignment in that the spectra were more like those in Figure 9 than like

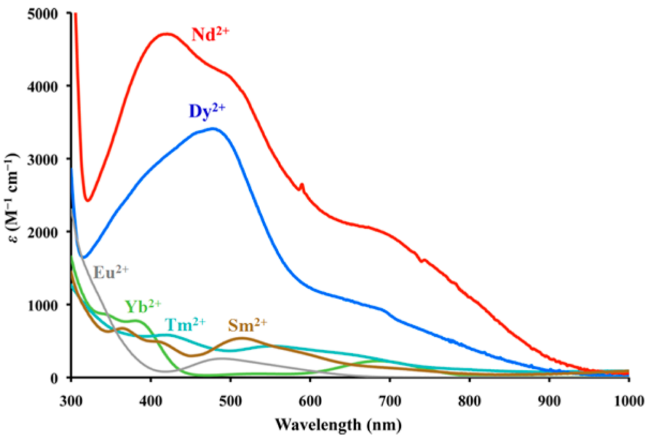


Figure 10. UV−visible spectra for the [K(2.2.2-cryptand)][Cp'_3Ln] complexes of Nd^{2+} (top), Dy^{2+} (second), Sm^{2+} (third at 500 nm), Tm^{2+} (fourth at 500 nm), Eu^{2+} (fifth at 500 nm), and Yb^{2+} (bottom at 500 nm).

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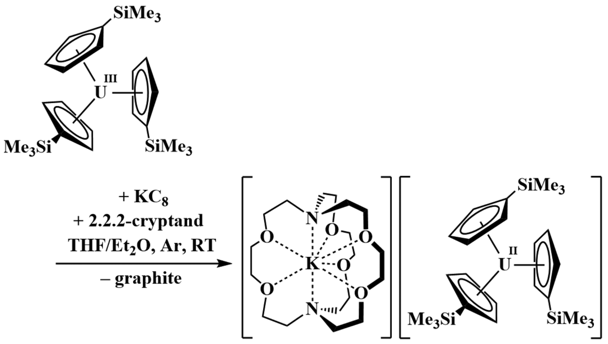
those of the Eu^{2+}, Yb^{2+}, Sm^{2+}, and Tm^{2+} complexes (Figure 10).[94] Hence, it appears that the electronic ground state of complexes of Dy^{2+} and Nd^{2+} depends on the ligand environment. In $(Cp'_3Ln)^-$, these ions are $4f^95d^1$ and $4f^35d^1$, respectively; in previously examined examples they are reported as $4f^{10}$ and $4f^4$, respectively. *The tris(cyclopentadienyl) ligand environment revealed for the first time in lanthanide chemistry that the electronic ground state of a complex could be varied by the ligand environment.*

■ A NEW URANIUM OXIDATION STATE VIA CYCLOPENTADIENYL LIGANDS

The discovery of new Ln^{2+} ions for the rare earths raised the possibility that U^{2+} could be synthesized similarly. The analogous precursor, Cp'_3U, had been known since 1985.[95] However, since the redox chemistry of uranium is quite different from that of the rare-earth metals, with +3, + 4, + 5, and +6 oxidation states accessible,[96,97] it was also possible that uranium would differ with respect to +2 ions. Attempts to synthesize complexes of U^{2+} were published as early as 1980[98] and numerous papers had discussed the possibility of U^{2+} intermediates and components in complexes of redox-active ligands.[98−109] Although U^{2+} had been reported in the gas phase,[110] as a transient radiolytically formed species,[111] and as OUCO in a neon matrix,[112] no molecular species containing an unequivocal example of U^{2+} had been isolable in solution. For this reason, the synthesis of a U^{2+} complex seemed like a project with a low probability of success.

Nevertheless, the reduction of Cp'_3U was attempted in analogy to the rare-earth metal reactions described above, and the first molecular complex of U^{2+}, namely [K(2.2.2-cryptand)][Cp'_3U], was synthesized and crystallographically characterized (eq 5).[8] The complex was found to be isomorphous with the rare-earth metal complexes.



(5)

Since it was anticipated that the reviewers could propose that the product in eq 5 was a U^{3+} hydride, containing a $(UH)^{2+}$ moiety indistinguishable by X-ray crystallography from U^{2+}, we felt that the analogous hydride complex had to be synthesized. The $(Cp'_3UH)^-$ anion was known,[113] but not with the $[K(2.2.2\text{-cryptand})]^+$ countercation. The direct analogue was synthesized, as shown in Scheme 6, and [K(2.2.2-cryptand)][Cp'_3UH] was found to be a distinct complex from [K(2.2.2-cryptand)][Cp'_3U]:[8] i.e., it was a bona fide U^{2+} complex.

The UV−visible spectrum of [K(2.2.2-cryptand)][Cp'_3U], like those of the $(Cp'_3Ln)^-$ complexes, was much more intense than those of U^{3+} complexes with the same ligand set (Figure 11).

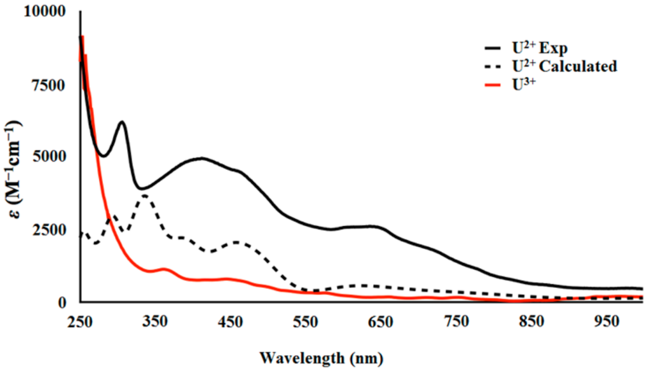
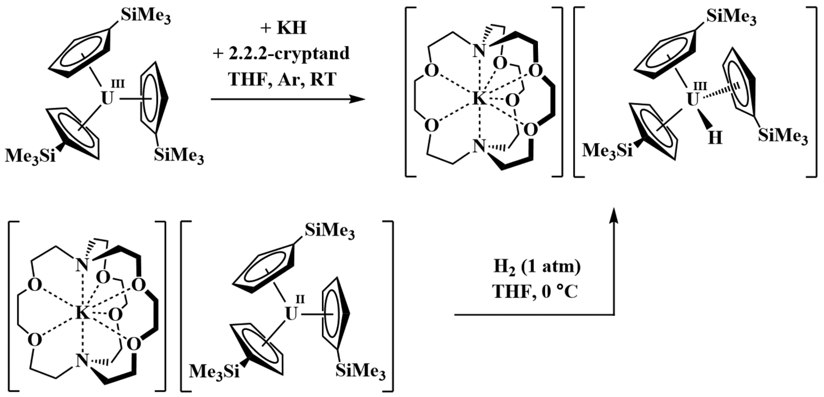


Figure 11. Experimental (top) and calculated (dotted) UV−visible spectra of the [K(2.2.2-cryptand)][Cp'_3U] as well as the experimental UV−visible spectrum of Cp'_3U (bottom).

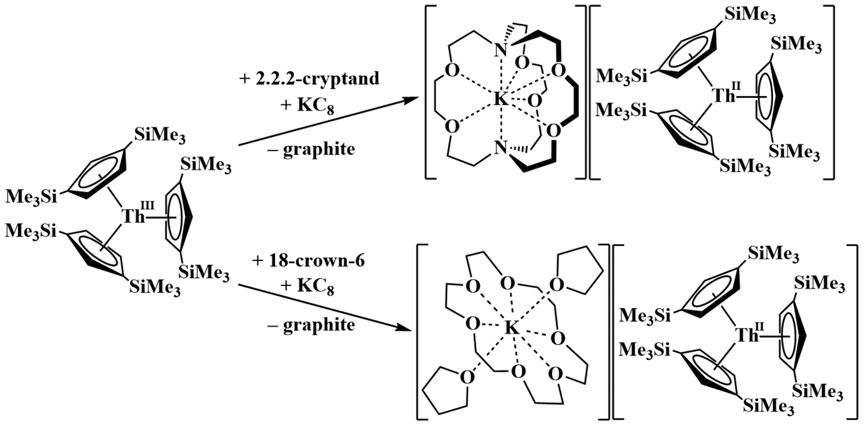
Consistent with this, DFT analysis suggested that the U^{2+} ion in [K(2.2.2-cryptand)][Cp'_3U] had a $5f^36d^1$ electron configuration.[8]

Shortly after this first molecular complex of U^{2+} was reported, Meyer and co-workers effected a similar potassium-based reduction of a U^{3+} complex of an arene-anchored tris(aryloxide) ligand to produce a second example of a U^{2+} complex, [K(2.2.2-cryptand)][$(^{Ad,Me}ArO)_3mes$]U].[114] Interestingly, in this noncyclopentadienyl coordination environment, the data suggest that the U^{2+} ion has the traditionally expected f^{n+1} electron configuration: i.e., it is $5f^4$. Hence, the ground state of U^{2+} complexes also appears to be dependent on the ligand field. *Once again the tris(cyclopentadienyl) ligand environment*

Scheme 6. Syntheses of [K(2.2.2-cryptand)][Cp'_3UH]



Scheme 7. Syntheses of the Th^{2+} Species $[K(2.2.2\text{-cryptand})][Cp''_3Th]$ and $[K(18\text{-crown-6})(THF)_2][Cp''_3Th]$



delivered new results: the first molecular complex of U^{2+} and the demonstration that ground states of actinides could be modified by the ligand field.

A NEW THORIUM OXIDATION STATE VIA CYCLOPENTADIENYL LIGANDS

Synthesis of a Th^{2+} complex analogous to the $(Cp'_3Ln)^-$ and $(Cp'_3U)^-$ complexes in eqs 4 and 5, respectively, seemed unlikely for several reasons. Complexes of Th^{3+} are already difficult to obtain; the Th^{4+}/Th^{3+} redox potential is estimated to be between −3.0 and −3.8 V vs SHE.[115−117] The Th^{3+}/Th^{2+} redox potential in the literature, −4.9 V vs SHE, is even more negative.[118] Reduction to metallic thorium would be predicted to be favored over formation of a Th^{2+} species. In addition, many attempts had been made to synthesize complexes with thorium in oxidation states lower than the predominant +4 oxidation state,[119−133] but only five Th^{3+} complexes had ever been structurally characterized: $[C_5H_3(SiMe_3)_2]_3Th$,[129] $[C_5H_3(SiMe_2{}^tBu)_2]_3Th$,[131] $(C_5Me_4H)_3Th$,[133] $[K(DME)_2]\{[C_8H_6(SiMe_2{}^tBu)_2]_2Th\}$,[130] and $(C_5Me_5)_2[{}^iPrNC(Me)N{}^iPr]Th$.[132] Th^{2+} ions had been observed only in the gas phase[134,135] and in atomic spectra.[136] A reaction directly analogous to eqs 4 and 5 was not possible, since the necessary Th^{3+} precursor, Cp'_3Th, was unknown.

Despite these issues, thorium reduction chemistry was examined using as a precursor, Cp''_3Th, a complex prepared by Lappert et al. in 1986.[129] This produced the first examples of molecular complexes of Th^{2+} (Scheme 7).[9] DFT analysis of the intensely colored $(Cp''_3Th)^-$ anion indicated that this was a $6d^2$ ion.[9] This is the first example of this fourth-row transition-metal electron configuration. This configuration is that expected for the ground state of superheavy ions such as Rf^{2+} and Db^{3+}. *For thorium, the tris(cyclopentadienyl) ligand environment allowed isolation of a new oxidation state and, in this case, a new electron configuration in the periodic table: one expected for superheavy elements.*

THE CYCLOPENTADIENYL CONTRIBUTION

All of the new oxidation states reported here in eqs 4 and 5 arose from tris(cyclopentadienyl) complexes of the type first prepared as shown in Scheme 1 by Wilkinson and Birmingham in 1954![19,20] In the coordination environment of three cyclopentadienyl rings, one d orbital, the d_{z^2} orbital, evidently is comparable in energy to the 4f valence orbitals so that it is possible for potassium to reduce an f^n M^{3+} ion to an f^nd^1 M^{2+} product. Since the Ln^{3+}/Ln^{2+} redox potentials in Table 1[10] were calculated for $4f^n + e^- \rightarrow 4f^{n+1}$ processes, they do not apply to this $4f^n + e^- \rightarrow 4f^n5d^1$ reduction.

For yttrium, reduction of Cp'_3Y generates the first molecular complex of $4d^1$ Y^{2+}. For La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu, reduction of Cp'_3Ln complexes gives Ln^{2+} ions with electronic configurations described by the mixed principal quantum number configuration $4f^n5d^1$. The tris(cyclopentadienyl) coordination environment provided the first U^{2+} complex also with a mixed configuration, $5f^36d^1$, and the first example of a $6d^2$ ion of any metal via reduction of $6d^1$ Th^{3+}. Since these electronic descriptions are at the single electron approximation level, they constitute rather primitive models for the electronic structures of these ions. However, these configurations serve to make the point that certain coordination environments can allow new oxidation states to be accessed by changing the relative energies of the ground state orbitals with respect to higher energy orbitals. In addition, this is the first demonstration that the electronic structure of Ln^{2+} and An^{2+} ions in molecular complexes can be varied by the ligand set.

Although these advances should not be limited only to organometallic environments, it is the cyclopentadienyl ligand that made these discoveries possible for the first time. BRAVO, Cp! It is a ligand that should not be overlooked just because it is very old.

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Notes

The author declares no competing financial interest.

Biography

William Evans was born in Madison, Wisconsin, and raised in Menomonee Falls, Wisconsin. He received a B.S. degree from the University of Wisconsin, where he did undergraduate research on pentaboranes with Professor Donald F. Gaines. He obtained a Ph.D. from UCLA under the direction of Professor M. Frederick Hawthorne studying metallocarboranes. He did postdoctoral research on transition-metal phosphite complexes with the late Professor Earl L. Muetterties at Cornell University. When he began his independent career in 1975 at the University of Chicago, he chose an area of research completely different from his training and experience, namely the chemistry of the rare-earth metals and actinides, with the central thesis that the special properties of these metals should lead to unique chemistry. After receiving tenure at Chicago in 1982, he was recruited to the University of California, Irvine, where he has been a Professor since 1983. He has

received the American Chemical Society Award in Inorganic Chemistry, the American Chemical Society Award in Organometallic Chemistry, the Sir Edward Franklin Award of the Royal Society of Chemistry, the Frank Spedding Award for Excellence in the Science and Technology of Rare Earths, the Terrae Rarae Award of the Tage der Seltenen Erden Society in Germany, the Richard C. Tolman Award of the Southern California Section of the American Chemical Society, a Special Creativity Extension Award from the National Science Foundation, the UCI Distinguished Faculty Award for Research, and the UCI Physical Sciences Outstanding Contributions to Undergraduate Education Award. He was recently named Distinguished Professor by the University of California.

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