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Review

# The expansion of divalent organolanthanide reduction chemistry via new molecular divalent complexes and sterically induced reduction reactivity of trivalent complexes

William J. Evans

*Department of Chemistry, University of California, Irvine, CA 92697-2025, USA*

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**Abstract**

For over 20 years, the reductive chemistry of organometallic Sm(II) complexes has provided an efficient approach to new types of organolanthanide chemistry. Although many advances have been made via Sm(II), it has never been possible to optimize the chemistry on the basis of metal size as is commonly done with trivalent lanthanides. However, recent results have presented opportunities to expand reductive Sm(II)-type reactivity to all of the lanthanides. This review summarizes recent progress from our laboratory on this topic. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Lanthanide; Actinide; Organometallic; Sterically induced reduction; Dinitrogen complexes

## 1. Introduction

The discovery of a convenient preparation of $SmI_2$ in 1977 [1] and the isolation of the first soluble organometallic complex of Sm(II), $(C_5Me_5)_2Sm(THF)_2$ in 1981 [2], initiated a series of advances in organometallic lanthanide chemistry based on the special reductive chemistry of the Sm(II) ion [3–5]. This chemistry is driven by the one electron Sm(III)–Sm(II) redox couple, which is reported as $-1.55$ V versus NHE in the literature [6], but which varies considerably as a function of ligand attached to samarium [7].

Reductive Sm(II) chemistry has made contributions to lanthanide chemistry in several different areas. In the past 20 years, the use of $SmI_2$ as a one electron reductant in organic synthesis has grown extensively such that it is now a standard reagent in synthetic organic laboratories [8]. $SmI_2$ is also important as a conveniently obtained precursor for organometallic Sm(II) complexes [9,10]. The solvated Sm(II) metallocene, $(C_5Me_5)_2Sm(THF)_2$ [2,9] reacts with a wide range of organic and inorganic substrates accomplishing unusual small molecule transformations [3,11,12] as well as polymerizations [2,13]. The unsolvated metallocene, $(C_5Me_5)_2Sm$ [10], obtained from $(C_5Me_5)_2Sm(THF)_2$ is more reactive [14] and even reacts with dinitrogen [15]. In addition, it has an unexpected bent structure that has generated numerous theoretical studies [16].

Although organometallic Sm(II) complexes have provided many successes with a variety of substrates, there have also been many systems for which clean reaction chemistry and isolation of fully characterizable products has not been possible. In these cases, adjusting the size of the metal to optimize the chemistry, as is commonly done with trivalent lanthanide complexes, would have been desirable.

Indeed, metal size optimization is one of the special aspects available to the lanthanide elements for controlling reactivity [4,17]. Due to the limited radial extension of the 4f-orbitals [18], the 4f-electron configuration often does not have a major effect on the chemistry. Hence, it is possible to optimize the size of the ligand set, as is done with all metals, *and* also to vary the size of the lanthanide metal within a given ligand set. Choices of metal size for trivalent metals range from 1.16 Å La(III) (eight-coordinate radius) to 0.977 Å for Lu(III) with variations of 0.01–0.02 Å from metal to metal [19]. Unfortunately, this size optimization was not possible for $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$, since analogs were known for only two other metals,

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*E-mail address:* wevans@uci.edu (W.J. Evans).

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Eu [10,20] and Yb [20,21], and their reduction potentials are significantly less (literature Ln(III)–Ln(II) vs. NHE for Eu, − 0.35; Yb, − 1.15 V [6]).

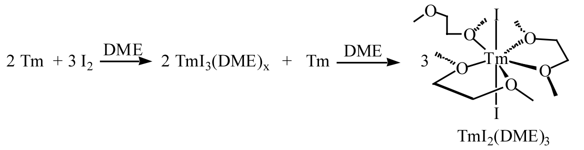
However, major advances have recently occurred in lanthanide reduction chemistry which suggest that (a) divalent lanthanide chemistry is available to more elements than just Eu(II), Yb(II), and Sm(II) and (b) the special chemistry of Sm(II) can be extended to the entire series. The next two sections summarize the results in these areas from our laboratory. The first section describes the isolation of new divalent lanthanide precursors analogous to $SmI_2$. The second section describes a ligand-based reduction scheme that can bring reduction chemistry to all of the lanthanides. It is exciting to note that these are only part of the advances in reduction chemistry currently occurring [3,22–25] as described in some of the other contributions in this issue.

## 2. New molecular divalent lanthanide reagents

For decades, the only divalent molecular lanthanides available were $EuI_2$, $YbI_2$, and $SmI_2$ [26]. Accordingly, divalent lanthanide chemistry focused on these metals. A few reports of molecular divalent lanthanide complexes involving metals other than Eu, Yb, and Sm were in the literature [3,27], but none were confirmed by X-ray crystallography. More importantly, none were synthetically accessible and useful as precursors to a wider divalent chemistry.

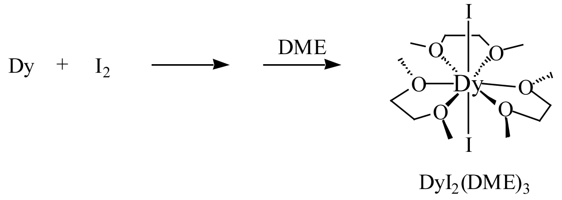
In contrast to this limited molecular divalent solution chemistry, divalent lanthanide systems are widely available in the solid state. Solid state materials containing formally divalent lanthanides can be made by high temperature ( > 600 °C) reductions of $LnX_3$ ($X =$ halide) by lanthanide metals in tantalum crucibles [28], by solid state alkali metal reduction [29], and by radiolytic reduction of trivalent ions doped into divalent metal host matrices [30]. However, these solid state results were not used extensively to develop molecular divalent chemistry in solution. Transient observations of Tm(II), Dy(II) and Nd(II), ions in solution were reported as early as the 1960s [31], but these also did not lead to new divalent chemistry. These three metals, Tm(II), Dy(II) and Nd(II), were chosen for those studies because they are the next most likely divalent lanthanides to be isolable after Eu(II), Yb(II), and Sm(II) on the basis of reduction potentials (Ln(III)–Ln(II) vs. NHE for Tm, − 2.3; Dy, − 2.5. Nd, − 2.6 V [6]). However, it was generally believed that these systems were too unstable in solution to be useful.

The situation for divalent iodides changed in 1997 [32], when the synthesis and structure of the first molecular divalent Tm(II) complex was reported, equation (1).



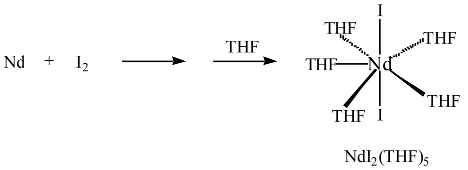
(1)

Once $TmI_2(DME)_3$ was fully characterized, crystallographic data on a molecular Dy(II) analog followed soon after, equation (2) [33]. And more recently, the



(2)

first molecular Nd(II) complex has been crystallographically identified by Bochkarev and co-workers, equation (3) [34].

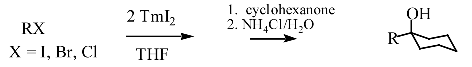


(3)

The fact that the number of soluble molecular $LnI_2(solvent)_x$ complexes available in the lanthanide series has doubled in the past 4 years is remarkable considering that for decades the molecular divalent chemistry of the lanthanides was thought to be limited to Eu(II), Yb(II), and Sm(II). The advances required the development of convenient syntheses and crystallographic data to confirm the molecular nature of the compounds.

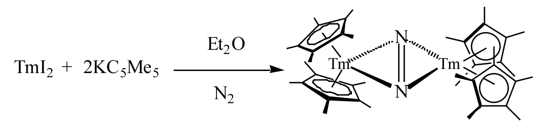
Although the number of molecular divalent lanthanide diiodides had expanded, it was not immediately clear how much this would advance reductive lanthanide chemistry. In fact, following the isolation of $TmI_2(DME)_3$, initial studies suggested that this would be so reactive that it would be of limited value [23,35]. Attempts to make even simple derivatives of $TmI_2$ often gave immediate oxidation to Tm(III). Hence, it seemed possible that Tm(II) might not have an extensive chemistry like that of Sm(II).

However, efforts to use Tm(II) in situ revealed how the chemistry of this new divalent system could be utilized [36,37]. Initially, $TmI_2$ was used in situ as a replacement for $SmI_2$–HMPA (HMPA = hexamethylphosphoramide) [38]. In the latter system, HMPA is used to enhance the reduction potential of Sm(II). Although this is quite successful, HMPA is carcinogenic and alternatives are preferred. $TmI_2$ in situ could accomplish the same reductive coupling of alkyl halides with ketones as was done with $SmI_2$–HMPA. In fact, it was found that Tm could do chloride couplings, a reaction not possible with $SmI_2$–HMPA, equation (4) [36].



(4)

Following the in situ organic reaction chemistry, in situ organometallic chemistry was attempted with $TmI_2$ [37]. These studies revealed in part why this highly reactive ion was so difficult to handle: nitrogen is not an inert atmosphere for organometallic Tm(II) complexes. Addition of cyclopentadienide ions to $TmI_2$ in ethers under nitrogen produced dinitrogen complexes, e.g. equation (5). Tm(II) is sufficiently reducing that it does not require the common $C_5Me_5$ ligand for these dinitrogen reductions and the reaction can be accomplished even with mono-substituted cyclopentadienyl ligands in the presence of THF, equation (6).



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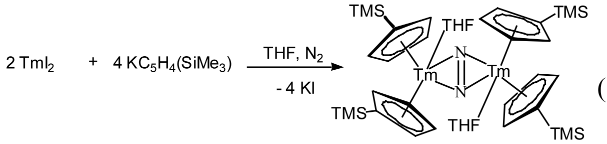
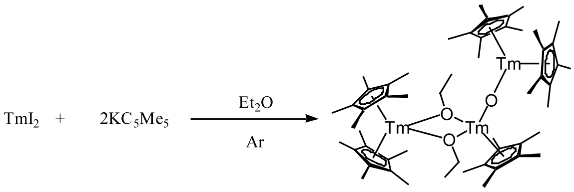


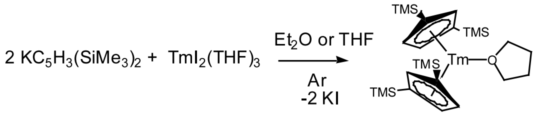
(6)

In light of the dinitrogen results, in situ reactions were conducted under argon. However, in $Et_2O$, organometallic Tm(II) complexes can decompose the solvent to make oxide and alkoxide components, equation (7) [37].



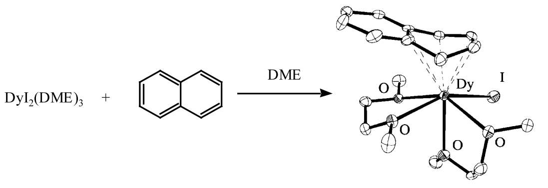
(7)

Despite these difficulties, it has been possible to make an isolable Tm(II) organometallic complex by proper choice of solvent, ligand, and reaction conditions, equation (8) [39].



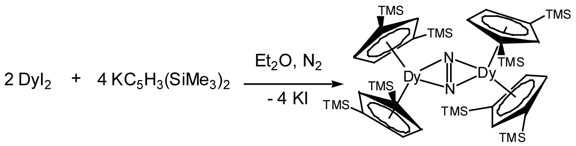
(8)

Examination of the chemistry of $DyI_2$ has shown that it can be similarly useful for in situ organic syntheses [33]. In fact it is so powerful that it can reduce naphthalene directly, equation (9). Accordingly, $DyI_2$ may have applications where a strong reduction potential is needed in an ether soluble complex, e.g. as an alternative to liquid ammonia based Birch reductions. In situ organometallic reactions involving $DyI_2$ also generate dinitrogen complexes, equation (10) [39].



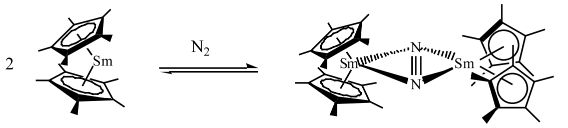
(9)

$(C_{10}H_8)DyI(DME)_2$



(10)

These dinitrogen systems exemplify the value of extending divalent lanthanide reduction chemistry beyond samarium. The reduction of nitrogen by $(C_5Me_5)_2Sm$ to $[(C_5Me_5)_2Sm]_2N_2$, equation (11) [15], provided the first example of an $M_2N_2$ complex in which the two metals were coplanar with the side bound dinitrogen. However, the NN bond in the dinitrogen complex of samarium was not significantly elongated compared with free dinitrogen and the nitrogen was easily displaced by THF to form $(C_5Me_5)_2Sm(THF)_2$. This meant the nitrogen was not strongly activated for further reaction chemistry. However, the more strongly reducing Tm(II) and Dy(II) systems give complexes with longer NN bonds and further lanthanide dinitrogen chemistry is now possible.



(11)

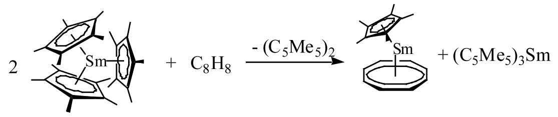
As yet, $NdI_2$ chemistry has not been developed as extensively as the $TmI_2$ and $DyI_2$ systems [34]. However, preliminary results indicate that it will have its own special utility in organic reaction chemistry [40].

Although the development of this new $Ln^*I_2$ chemistry ($Ln^* = Tm$, Dy, Nd) will expand reductive lanthanide chemistry considerably, it still does not allow metal size optimization of the Sm(II) chemistry as discussed above. The new Ln*(II) states offer three new metal size options compared with Sm(II), but they have much different reduction potentials and a correspondingly different chemistry. However, as described below, another recent development in reductive lanthanide chemistry may make it possible to size optimize Sm(II)-type chemistry.

## 3. Sterically induced reduction

Investigation of the chemistry of the sterically crowded trivalent samarium complex, $(C_5Me_5)_3Sm$

[41,42], revealed that it had reductive reactivity [43] similar to that of the divalent samarium complex $(C_5Me_5)_2Sm$ [4,10]. The parallel reductive reactivity of $(C_5Me_5)_3Sm$ and $(C_5Me_5)_2Sm$ is illustrated with three different types of substrates in equations (12–17). In each pair of equations, identical organosamarium products were obtained from both the trivalent and divalent organosamarium complexes [43]. Since the samarium products of reaction (12), reaction (14), and reaction (16) are in the same trivalent oxidation state as the starting material, it appeared that the reduction must involve the ligand rather than the metal. Consistent with this, $(C_5Me_5)_2$ was isolated as a byproduct in each of the $(C_5Me_5)_3Sm$ reactions. This suggested that reduction was being achieved via a $(C_5Me_5)/(C_5Me_5)^-$ redox couple, equation (18). The reason that both $(C_5Me_5)_3Sm$ and $(C_5Me_5)_2Sm$ give the same reduction products can be seen from the two half reactions, equations (19) and (20). In each case the same organosamarium cation, $[(C_5Me_5)_2Sm]^+$, is formed. This common product binds the reduced substrate to give the same end result.



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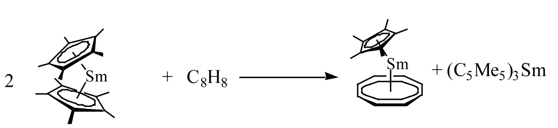

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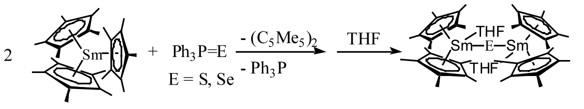

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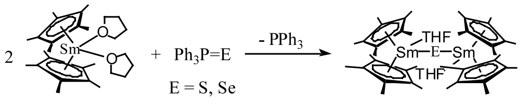


(15)

$$3(C_5Me_5)_3Sm + 6Me_3CNC \xrightarrow{-3/2(C_5Me_5)_2} [(C_5Me_5)_2Sm(\mu\text{-CN})(CNCMe_3)]_3 \quad (16)$$

$$3(C_5Me_5)_2Sm + 6Me_3CNC \rightarrow [(C_5Me_5)_2Sm(\mu\text{-CN})(CNCMe_3)]_3 \quad (17)$$

$$C_5Me_5^- \rightarrow e^- + 1/2(C_5Me_5)_2 \quad (18)$$

$$(C_5Me_5)_2Sm \rightarrow e^- + [(C_5Me_5)_2Sm]^+ \quad (19)$$

$$(C_5Me_5)_2Sm \rightarrow e^- + [(C_5Me_5)_2Sm]^+ + 1/2(C_5Me_5)_2 \quad (20)$$

Ligand based reductions are not unknown in lanthanide chemistry, e.g. equation (21) shows a reduction driven by a $(PhS)^-$–PhSSPh redox couple [44].

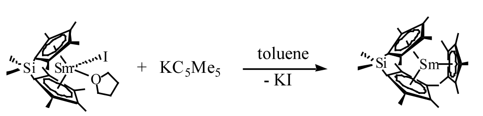
$$8Ln(SPh)_3 + 6S \rightarrow Ln_8S_6(SPh)_{12}(THF)_8 + 6PhSSPh \quad (21)$$

Moreover, it is known that $NaC_5Me_5$ can act as a reductant as shown in the Eu(III) to Eu(II) conversion in equation (22) [20]. However, what is unique about the $(C_5Me_5)^-$ based reductions of $(C_5Me_5)_3$ Sm is that they are only observed in sterically crowded complexes. None of the scores of $(C_5Me_5)$–Ln complexes isolated previously showed any of this reductive chemistry [45].

$$EuCl_3 + 3NaC_5Me_5 \xrightarrow{THF} (C_5Me_5)_2Eu(THF) \quad (22)$$

Hence, one possible explanation for the origin of the surprising reductive reactivity of trivalent $(C_5Me_5)_3Sm$ involves the steric crowding in this molecule. For many years, it was thought that three $(C_5Me_5)^-$ ligands were too large to fit around any metal ion since the cone angle of this ligand was thought to be significantly greater than 120°. The formation of $(C_5Me_5)_3Sm$ using the special Sm(II) chemistry of $(C_5Me_5)_2Sm$ showed that this was synthetically possible [41]. The X-ray crystal structure of this complex revealed how the existence of this complex was sterically possible. $(C_5Me_5)_3Sm$ displayed Sm(III)–C($C_5Me_5$) distances ca. 0.1 Å larger than conventional Sm(III)–C($C_5Me_5$) distances in the literature [46]. By placing each of the $C_5Me_5$ rings further away from the metal, three rings could be sterically accommodated. Since the $(C_5Me_5)^-$ ligands are farther from the metal than their usual optimal distance, they are not electrostatically stabilized as well as in conventional $(C_5Me_5)^-$ complexes. This could explain why the $(C_5Me_5)^-$ reductive chemistry is observed. Due to this possible rationale and to provide a distinguishing label to this type of reduction, these reactions have been called sterically induced reduction [3].

To evaluate the idea that this reductive chemistry was coupled to steric crowding, an ansa ligand complex, $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$, very similar to but somewhat less sterically crowded than $(C_5Me_5)_3Sm$, was synthesized as shown in equation (23) [47]. Since the $Me_2Si$ bridge in $Me_2Si(C_5Me_4)_2Ln$ complexes typically decreases the (ring centroid)–metal–(ring centroid) angle [48], this provides more room for the other ligands. Indeed, the Sm–C($C_5Me_5$) distances are in the normal range for trivalent samarium $C_5Me_5$ complexes, i.e. they are shorter than those in $(C_5Me_5)_3Sm$. Correspondingly, $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ does not display the reductive chemistry of $(C_5Me_5)_3Sm$ [47].



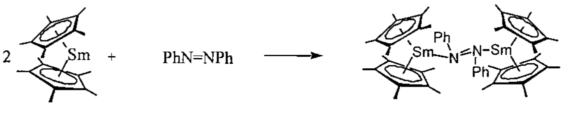
(23)

The chemistry of $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$ supported the idea that the reductive chemistry of $(C_5Me_5)_3Sm$ was sterically induced, but it could not eliminate the possibility that $(C_5Me_5)_3Sm$ was somehow achieving reduction by conversion through an intermediate Sm(II) species. Evidence that the $(C_5Me_5)_3Sm$

reduction was not occurring via a $(C_5Me_5)_2Sm$ intermediate was obtained by comparing reductions of PhN=NPh. Equations (24–26) show that $(C_5Me_5)_3Sm$ is not quite as strong a reductant as $(C_5Me_5)_2Sm$.

$$2(C_5Me_5)_3Sm + PhN{=}NPh \xrightarrow{-(C_5Me_5)_2} (C_5Me_5)_2Sm(Ph_2N_2) \quad (24)$$

$$(C_5Me_5)_2Sm + PhN{=}NPh \rightarrow (C_5Me_5)_2Sm(Ph_2N_2) \quad (25)$$



(26)

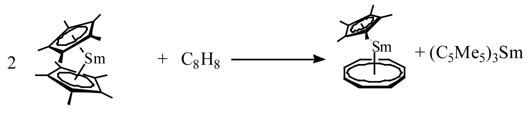
$(C_5Me_5)_3Sm$ reduces azobenzene by one electron, equation (24) [43], whereas $(C_5Me_5)_2Sm$ can effect both a one electron reduction [49] and a two electron reduction [50] depending on the reaction stoichiometry, equations (25) and (26).

Although all of the above data supported the idea that $(C_5Me_5)_3Sm$ was achieving one electron reduction chemistry through steric crowding of the $C_5Me_5$ ligands, the most conclusive evidence would come by doing a reduction with the complex of a metal that did not have a divalent state as accessible as Sm(II). Indeed, extending sterically induced reduction to lanthanides for which traditional divalent reduction was not possible was the most important aspect of this chemistry.

If trivalent $(C_5Me_5)_3Ln$ complexes in which Ln is not Sm could accomplish one electron reduction chemistry analogous to that of $(C_5Me_5)_3Sm$, it would extend $(C_5Me_5)_2Sm$-like chemistry to all of the lanthanides. This would allow metal size optimization of the $(C_5Me_5)_2Sm$ chemistry and it would give all the other lanthanides access to the fruitful reduction chemistry which has made samarium rather unique in the lanthanide series. Many types of lanthanide complexes are available only with samarium because they can be made by reductive syntheses using the special properties of Sm(II). For this reason, samarium is often the preferred lanthanide for a variety of chemical studies. However, as discussed above, the size of samarium is not likely to be optimum for all substrates. Hence, extension of sterically induced reduction chemistry to $(C_5Me_5)_3Ln$ complexes of all the lanthanides would allow the choice of the optimum radial size.

Samarium is also not always the optimum lanthanide in terms of physical properties for all systems. Samarium is better than many of the other paramagnetic lanthanides in terms of NMR characterization, since NMR spectra can be observed for both Sm(II) and Sm(III) despite their $\mu = 3.6$ and $1.7\mu_B$ magnetic moments, respectively [51]. However, NMR analysis on diamagnetic La(III), Y(III), and Lu(III) would be easier and more informative. In addition, if complexes with high paramagnetism or fluorescence were desired, complexes of Gd or Tb would be preferred to Sm. If $(C_5Me_5)_3Ln$ complexes of these other non-samarium elements could accomplish Sm(II) reduction chemistry, a much wider range of complexes would be synthetically accessible to these metals.

To examine sterically induced reduction chemistry with $(C_5Me_5)_3Ln$ complexes other than $(C_5Me_5)_3Sm$, new syntheses had to be developed, since initially, the only routes to $(C_5Me_5)_3Ln$ involved Sm(II) precursors, equation (27) [41] and equation (28) [42]. Fortunately, the necessary synthetic breakthroughs, were achieved: two additional syntheses of $(C_5Me_5)_3Sm$ were developed which started with trivalent precursors, equation (29) [52] and equation (30) [53].



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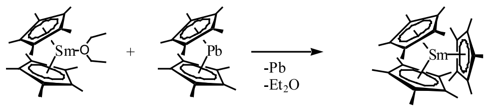

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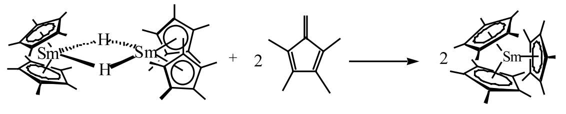

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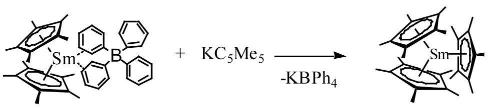
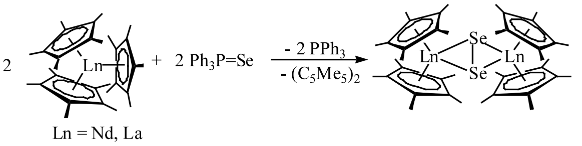


(30)

Initially, extension of these syntheses to other lanthanides was examined with the larger metals, La–Nd, since $(C_5Me_5)_3Ln$ complexes of these metals should be less crowded than $(C_5Me_5)_3Sm$ and should be sterically accessible. Equation (30) was used to make crystallographically characterizable $(C_5Me_5)_3Nd$ [53] and diamagnetic $(C_5Me_5)_3La$ in good yield [54]. Surprisingly, the La synthesis, which formed the least sterically crowded of the series, was the more difficult and required silylated glassware not necessary for the analogous Nd and Sm syntheses.

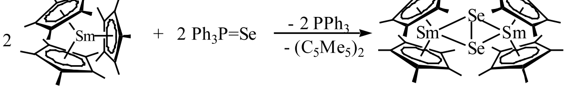
Examination of the reduction chemistry of $(C_5Me_5)_3La$ [55] and $(C_5Me_5)_3Nd$ [56] not only supported the sterically induced reduction scenario described above, but it also revealed an additional feature. Both complexes reduce $Se{=}PPh_3$ to form $PPh_3$ and $(C_5Me_5)_2$, the expected byproduct of sterically induced reduction according to equation (18). However, the selenium products isolated from these reactions, equation (31), were different from that isolated from the samarium reaction, equation (14)! In equation (31), the $Se{=}PPh_3$ reduction product was $(Se_2)^{2-}$ rather than the $(Se)^{2-}$ product obtained from $(C_5Me_5)_3Sm$ in equation (14). The more reduced $(Se_2)^{2-}$ product could not be obtained by use of excess $(C_5Me_5)_3La$ or $(C_5Me_5)_3Nd$.



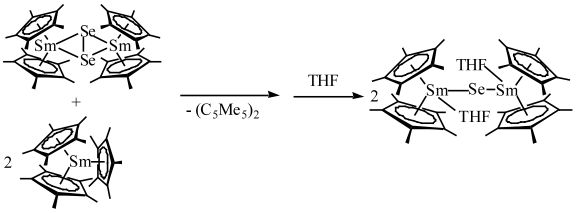
(31)

Apparently, neither $(C_5Me_5)_3La$ nor $(C_5Me_5)_3Nd$ are as reducing as $(C_5Me_5)_3Sm$. Since the La and Nd complexes are not as sterically crowded as the Sm complex, this suggests that the reduction potentials arising from sterically induced reduction can be varied by changing the degree of steric crowding. Hence, an additional level of control appears to be available.

Since $(C_5Me_5)_3Sm$ was a stronger reductant, it was conceivable that by controlling stoichiometry, the $(C_5Me_5)_3Sm$ reduction could go stepwise via the $(Se_2)^{2-}$ analogs of the La and Nd products. Equation (32) shows that this idea was correct [56]. Moreover, the isolated $[(C_5Me_5)_2Sm]_2Se_2$ product could be subsequently reduced with additional $(C_5Me_5)_3Sm$, equation (33), such that equation (14) could be done stepwise by $(C_5Me_5)_3Sm$ [56]. Hence, $(C_5Me_5)_3Sm$ can effect both one and two electron reductions when used in 1:1 and 1:2 ratios, respectively. This is another similarity between $(C_5Me_5)_3Sm$ and divalent $(C_5Me_5)_2Sm(THF)_y$: as shown in equations (25) and (26), $(C_5Me_5)_2Sm(THF)_2$ can also reduce some substrates by one or two electrons depending on the stoichiometry.



(32)

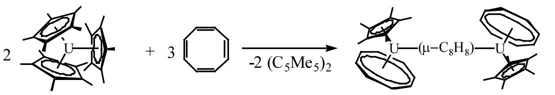


(33)

These results indicate that sterically induced reduction can bring the one electron reduction chemistry of Sm(II) to all of the lanthanides if synthetic routes to the appropriately crowded complexes are found. Although to date this sterically induced reduction has been demonstrated only with homoleptic $(C_5R_5)_3Ln$ compounds, this type of reduction should also be accessible to mixed ligand $(C_5R_5)_2Ln(C_5R'_5)$ and (large ligand)$_2$Ln$(C_5Me_5)$ complexes. Complexes such as (large ligand)$_3$Ln could also display this chemistry if the large ligand will do reduction. In fact this type of sterically induced reduction may have happened before in other systems, but was not identified. Reactions designed to make sterically crowded complexes which 'failed' may actually have generated the desired sterically crowded complex, but it went on to react via sterically induced reduction pathways to give unexpected products.

To obtain more information about sterically induced reduction, the chemistry of the trivalent uranium complex, $(C_5Me_5)_3U$ [52], was explored. This compound was of interest since not only is it sufficiently sterically crowded to do sterically induced reduction, but it also has a redox active metal center due to the U(IV)–U(III) redox couple [57]. Hence, $(C_5Me_5)_3U$ had the potential to be a net two electron reductant, a type of reactant which is rare for monometallic f element compounds. This complex would also allow a direct comparison of the two types of reductions in a single molecule.

The reduction chemistry of $(C_5Me_5)_3U$ was initially examined with 1,3,5,7-cyclooctatetraene, $C_8H_8$, since it could be reduced by two electrons to the common f element ligand, $(C_8H_8)^{2-}$ [58]. $(C_5Me_5)_3U$ reduces $C_8H_8$, but not with the expected 1:1 stoichiometry. Instead a 2:3 ratio is found to give a clean reaction. $(C_5Me_5)_2$, the product expected from the sterically induced reduction reaction, equation (18), was obtained along with a U(IV) product, $[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$, equation (34) [59].



(34)

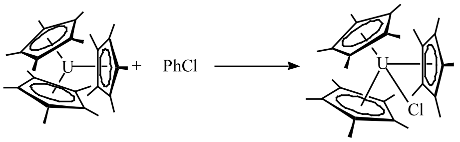
Since this product contained U(IV) and had lost $C_5Me_5$ ligands, this reaction apparently involved both U(III) reduction and sterically induced reduction. However, not one but two $C_5Me_5$ ligands were lost from the $(C_5Me_5)_3U$ starting material and the net final stoichiometry in equation (34) showed that $(C_5Me_5)_3U$ was functioning as a three electron reductant rather than a two electron reducing agent as originally expected! Two equivalents of $(C_5Me_5)_3U$ formed three $(C_8H_8)^{2-}$ dianions. The reduction half reaction is shown in equation (35). This reaction demonstrated that multi-electron reductions previously not possible with the f elements can be achieved by combining sterically induced reduction chemistry with traditional metal based redox chemistry. It also showed that a series of reductions can occur which includes two $(C_5Me_5)^-$ reduction processes and a traditional redox electron transfer. Presumably, one of the intermediates in this system was sufficiently sterically crowded to undergo further sterically induced reduction after initial reduction by $(C_5Me_5)^-$ or U(III).

$$(C_5Me_5)_3U \rightarrow 3e^- + [(C_5Me_5)U]^{3+} + (C_5Me_5)_2 \qquad (35)$$

Determining the sequence of the fast reductions observed in the $C_8H_8$ reaction seemed difficult. However, examination of the reduction of PhCl by $(C_5Me_5)_3U$ revealed that reduction occurred in two steps with an isolable intermediate [60]. The main overall reaction is shown in equation (36), in which $(C_5Me_5)_3U$ acts as a two electron reductant. The reaction can be conducted stepwise with one equivalent of PhCl at a time. If the first step involves sterically induced reduction, the product would be the U(III) complex $[(C_5Me_5)_2UCl]_3$ as shown in equation (37). This compound has been known since 1982 [61]. If, on the other hand, the first step involved U(III) reduction, the product would be the extremely crowded $(C_5Me_5)_3UCl$ complex shown in equation (38). Since this compound has one more ligand than $(C_5Me_5)_3U$ and a smaller metal center (U(IV) is smaller than U(III) [19]), it would have been expected that its formation would be sterically prohibited. However, an X-ray crystal structure of the intermediate showed it to be $(C_5Me_5)_3UCl$, i.e. equation (38) is correct [60].

$$(C_5Me_5)_3U + 2PhCl \xrightarrow[-1/2(C_5Me_5)_2\ -Ph\text{–}Ph]{} (C_5Me_5)_2UCl_2 \quad (36)$$

$$(C_5Me_5)_3U + PhCl \rightarrow 1/3[(C_5Me_5)_2UCl]_3 \quad (37)$$



(38)

Hence, in this system U(III) reduction precedes sterically induced reduction. If the same sequence occurs in the $C_8H_8$ reaction, equation (34), it means that two sterically induced reductions occur with the U(IV) intermediates. As is necessary from the overall reaction of $(C_5Me_5)_3U$ and PhCl, equation (36), the U(IV) intermediate is found to reduce a second equivalent of PhCl to form the final U(IV) product, equation (39) [60].

$$(C_5Me_5)_3UCl + PhCl \xrightarrow[-(C_5Me_5)_2]{} (C_5Me_5)_2UCl_2 + 1/2Ph\text{–}Ph \quad (39)$$

The formation of $(C_5Me_5)_3UCl$ is not only important in defining the reduction sequence in this mixed mechanism reduction system, but it also defines a new level of steric crowding in $(C_5Me_5)_3M$ complexes. It indicates that not only can a metal accommodate three $C_5Me_5$ rings, but it can also fit in another ligand as well. Once the existence of $(C_5Me_5)_3UCl$, was known, a fluoride analog was also synthesized, $(C_5Me_5)_3UF$, equation (40) [60]. Moreover, several additional syntheses of $(C_5Me_5)_3UCl$ were discovered, equations (41–43).

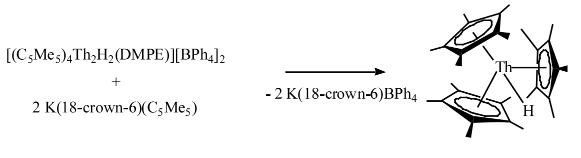
$$2(C_5Me_5)_3U + HgF_2 \xrightarrow[-\,Hg^\circ]{} 2(C_5Me_5)_3UF \quad (40)$$

$$(C_5Me_5)_3U + (C_5Me_5)_2UCl_2 \rightarrow (C_5Me_5)_3UCl + 1/3[(C_5Me_5)_2UCl]_3 \quad (41)$$

$$2[(C_5Me_5)_2UCl]_3 + 3(C_5Me_5)_2Pb \xrightarrow[-Pb^\circ]{} 6(C_5Me_5)_3UCl \quad (42)$$

$$(C_5Me_5)_3U + PbCl_2 \xrightarrow[-Pb^\circ]{} 2(C_5Me_5)_3UCl \quad (43)$$

The $(C_5Me_5)_3UCl$ result also encouraged attempts to make a $(C_5Me_5)_3ThZ$ complex (Z = monoanion). Application of sterically induced reduction to expand the reduction chemistry of thorium would be useful since access to Th(III) complexes is difficult. Indeed, a thorium species can be made and this synthesis provided the first $(C_5Me_5)_3MH$ complex, equation (44) [62].

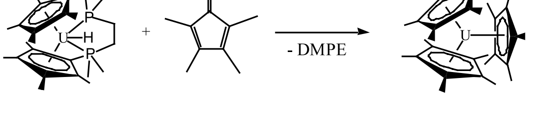


(44)

## 4. The synthetic and crystallographic bases for these advances

It should be noted that the advances described here involving divalent lanthanide diiodide precursors and sterically induced reduction first required major advances in synthesis and then structural confirmation of existence by X-ray crystallography. Hence, the discovery of a convenient solution route to $TmI_2$ led to its crystallization [32]. This allowed its identity to be confirmed crystallographically. Elemental analysis and a magnetic moment were supportive, but not definitive. Once the structure of $TmI_2(DME)_3$ was confirmed, the isolation of the Dy [33] and Nd [34] analogs followed in a relatively short time.

The development of $(C_5Me_5)_3M$ chemistry required the initial synthesis of $(C_5Me_5)_3Sm$ and its structural confirmation [41]. The existence of this complex was not believable only on the basis of elemental analysis and a single $C_5Me_5$ NMR resonance. Unfortunately, because the initial synthesis of $(C_5Me_5)_3Sm$ was not a convenient route to quantities large enough for extensive chemical study, this chemistry developed slower. Discovery of the second synthesis of $(C_5Me_5)_3Sm$, equation (28) [42], opened this complex to exploration. Once the importance of its chemistry was demonstrated, other synthetic routes soon followed [52,53]. As mentioned above, there are now four different routes to $(C_5Me_5)_3Sm$, equations (27–30). Likewise, there are some four routes to $(C_5Me_5)_3U$ [52,63], equations (45–48), four routes to $(C_5Me_5)_3UCl$, equation (38) and



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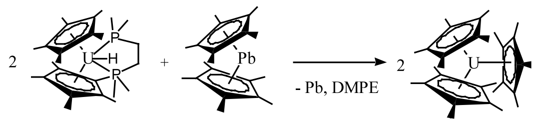

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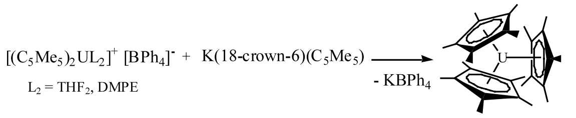

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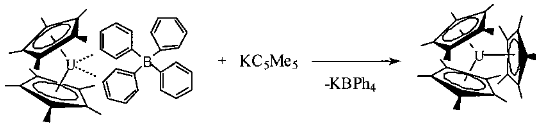

(48)

equations (41)–(43) [60], a synthesis of $(C_5Me_5)_3UF$, equation (40) [60], and even a route to the thorium hydride, $(C_5Me_5)_3ThH$, equation (44) [62]. Hence, there are now some 14 reactions to crystallographically characterized molecules containing the $(C_5Me_5)_3M$ unit which throughout decades of $C_5Me_5$ research was thought to be too sterically crowded to exist. This augurs well for future syntheses needed to fully expand lanthanide reduction chemistry.

## 5. Conclusion

Although reductive divalent organometallic lanthanide chemistry has been a major source of advancement in the f element area for many years, it has been previously limited to only three metals, Eu(II), Yb(II), and Sm(II). This limitation seemed insurmountable since it was based on electrochemical data and decades of results that indicated that these were the only divalent ions accessible for solution molecular chemistry. This limitation has been completely eliminated in the past few years. Via sterically induced reduction, Sm(II)-type reactivity should be available to all of the lanthanides regardless of the accessibility of a divalent state. In addition, the new lanthanide divalent diiodides, $Ln^*I_2$ ($Ln^* = Tm$, Dy, Nd) open up the exploration of the reductive chemistry of these elements via conventional metal-based redox couples. These results, plus the other new reduction chemistry described elsewhere in this issue, indicate that a new era of reductive chemistry is beginning which is likely to supercede the spectacular results already achieved with the conventional Ln(II) systems. Each type of new reductive chemistry will have its challenges. Sterically induced reduction is predicated on clever syntheses of molecules too sterically crowded to have normal bond distances. The reduction chemistry of Ln*(II) requires careful choice of solvent and inert atmosphere. However, the recent results as detailed here indicate that these problems can be overcome and there are many opportunities for the future.

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