ELSEVIER

Journal of Organometallic Chemistry 652 (2002) 61–68

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

# Recent advances in f element reduction chemistry

William J. Evans [*]

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

Received 27 November 2001

**Abstract**

One of the most rapidly changing frontiers in organometallic chemistry involves the reductive chemistry of organolanthanide and organoactinide complexes. This contribution summarizes recent advances in this area arising from newly available divalent lanthanide systems and the sterically crowded $(C_5Me_5)_3M$ complexes as presented at the ‘Frontiers in Organometallic Chemistry Symposium’ at the National Meeting of the American Chemical Society in Chicago in August 2001. © 2002 Published by Elsevier Science B.V.

*Keywords:* Lanthanide; Actinide; Organometallic; Reduction; Steric crowding

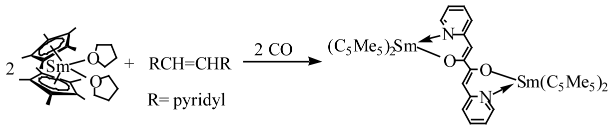
## 1. Introduction

For decades, molecular divalent lanthanide chemistry has involved just three ions, $Eu^{2+}$, $Yb^{2+}$ and $Sm^{2+}$ [1]. Despite the fact that only three of the 14 lanthanide elements had readily accessible divalent chemistry in solution, an extensive reduction chemistry has been developed [2–5]. Recently, however, the opportunities in reductive lanthanide chemistry have expanded dramatically. This is surprising since the available redox chemistry of the lanthanide ions was previously thought to be well established. A further surprise is that part of this expansion has been based on $(C_5Me_5)_3M$ complexes, compounds thought to be too sterically crowded to exist. The recent expansion in reductive f element chemistry is detailed in Sections 3 and 4, which are preceded by a background section that puts the results in perspective.

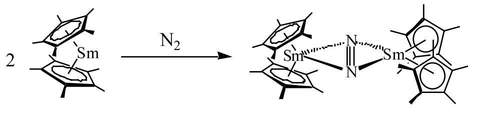
## 2. Background

The three lanthanide elements with the most readily accessible divalent oxidation states are the half-filled shell $4f^7$ $Eu^{2+}$, the filled shell $4f^{14}$ $Yb^{2+}$, and $Sm^{2+}$, which has a $4f^6$ electron configuration which approaches a half filled shell. Their one electron Ln(III)/Ln(II) reduction potentials versus NHE are −0.35, −1.15 and −1.55 V, respectively [6].

The chemistry of the most reactive of these, $Sm^{2+}$, has contributed broadly to the advancement of organometallic lanthanide chemistry [2–5]. For example, $SmI_2(THF)_x$ has become a widely used reducing agent in synthetic organic laboratories with applications in many types of transformations [5,7]. $(C_5Me_5)_2Sm(THF)_2$ [8], which is made from $SmI_2(THF)_x$, and its unsolvated analog, the surprisingly bent $(C_5Me_5)_2Sm$ [9], have advanced lanthanide chemistry not only along organic and organometallic lines, but also in the inorganic and polymerization areas. These molecules accomplish unusual small molecule transformations [10], dinitrogen activation [11], and olefin [12] and polar monomer [13,14] polymerizations, among others. Some representative examples are shown in Eqs. (1)–(3).



(1)

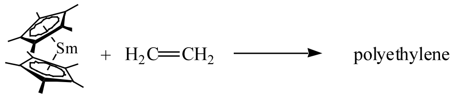


(2)

---

[*] Fax: +1-949-824-2210.
*E-mail address:* wevans@uci.edu (W.J. Evans).

0022-328X/02/$ - see front matter
PII: S0022-328X(02)01308-6



(3)

The impact of $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ on f element chemistry can be seen from the fact that samarium is often the metal of choice among the 14 lanthanides for new types of investigations using these metals. Examples of the preference for samarium can be found in areas as diverse as polymerization [12,14,15], thermochemistry [16], C–H and Si–H activation [17], and organometallic applications to organic synthesis [18]. Samarium is the choice for two reasons: the strongly reducing nature of $Sm^{2+}$ provides convenient synthetic access to trivalent complexes and $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ have provided a wide range of trivalent compounds with which to make comparisons.

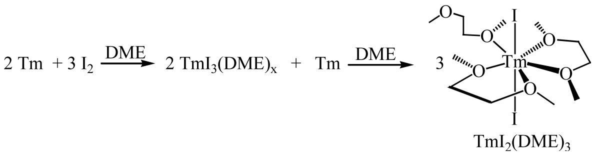
Although the $Sm^{3+}/Sm^{2+}$ redox couple has led to many advances in lanthanide chemistry, one limitation of $Sm^{2+}$ reduction chemistry is that metal size optimization has not been possible. This is unfortunate since metal-based size optimization is one of the most powerful features of lanthanide reactivity [19]. Since the 4f valence orbitals of the lanthanides have a limited radial extension compared to the size of their core orbitals [20], it is possible to choose the lanthanide with the optimal radial size to accomplish a specific reaction without concern for the specific $4f^n$ electron configuration. Hence, reactions involving trivalent lanthanides can be optimized sterically not only with the ligand set, as is traditionally done with all metals, but also by choosing the best metal size from 15 choices, La–Lu plus chemically similar Y excluding radioactive Pm. The size of these metals varies gradually from 1.03 Å $La^{3+}$ (six coordinate radius [21]) to 0.86 Å $Lu^{3+}$ with a 0.01–0.02 Å change from element to element. No other series of metals in the periodic table has so many chemically similar metals with such a selection of gradually changing radial sizes. Changing the size of the metal can have major effects on the reactivity of trivalent lanthanides. Small changes in metal radius can sometimes convert unfavorable reactions into successful ones [19]. However, metal size optimization of $Sm^{2+}$ reduction chemistry has not been possible, since $Sm^{2+}$ was the only divalent ion in the lanthanide series sufficiently reducing to accomplish the unusual transformations of the type described above.

However, recent synthetic advances now make size optimization of $Sm^{2+}$ reduction chemistry possible. Given the importance of $Sm^{2+}$ reductive reactivity to lanthanide chemistry, this is an exciting prospect for the field. Two aspects of these breakthroughs are discussed in the next two sections.

## 3. Newly accessible divalent oxidation states

Prior to 1997, the only molecular divalent lanthanide complexes confirmed in the literature by X-ray crystallography involved $Eu^{2+}$, $Yb^{2+}$ and $Sm^{2+}$[1–4]. Although a few other divalent lanthanides had been reported in solution [22], no X-ray data were available to confirm their existence. A variety of divalent lanthanide ions were known in the solid state [23], but no molecular chemistry was reported for these species. These solid state compounds were typically made via metallothermic reductions, e.g. by lanthanide metal/lanthanide trihalide reactions in tantalum crucibles at 600–1000 °C.

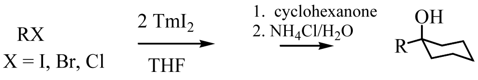
In 1997, the first molecular complex of $Tm^{2+}$, $TmI_2(DME)_3$, was identified by X-ray crystallography [24], Eq. (4). Since the range of oxidation states of all of the elements in the periodic table has been thoroughly studied, it is rare to find the first example of a new oxidation state. The literature estimate of the reduction potential of the $4f^{13}$ $Tm^{2+}$ ion was −2.3 V versus NHE [6]. This strong reduction potential had suggested that $Tm^{2+}$ complexes would not be isolable as molecular species in solution.



(4)

Preliminary reactivity studies with $TmI_2(DME)_x$ showed it to be so reactive that it was unlikely to have a useful chemistry [25,26]. Indeed, for several years no new $Tm^{2+}$ derivatives were isolated and the chemistry appeared to be too difficult to control. These initial results supported the earlier ideas that the only divalent lanthanides useful for molecular solution chemistry were $Eu^{2+}$, $Yb^{2+}$ and $Sm^{2+}$.

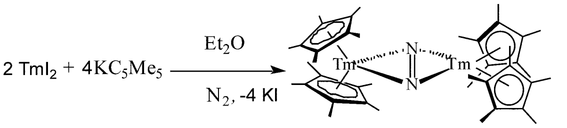
However, recent efforts to use the highly reactive $Tm^{2+}$ in situ showed how it can be used and why the isolation of new complexes was so difficult. One major advance [27] involved using $TmI_2$ in situ as a replacement for $SmI_2$/HMPA (HMPA = hexamethylphosphoramide) [28] in organic synthetic reactions. As shown in Eq. (5), $TmI_2$ can be used to couple alkyl halides with



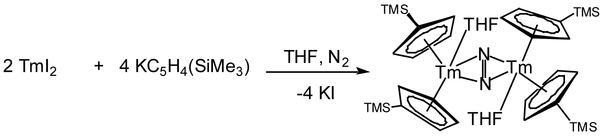
(5)

ketones. This can be accomplished with $SmI_2$/HMPA for iodides and bromides, but not for chlorides. $TmI_2$ can accomplish the reductions even with chlorides at low temperature and without the carcinogenic HMPA additive [27].

Once the in situ organic chemistry of $TmI_2$ was established, in situ organometallic chemistry was examined [29]. This revealed why $Tm^{2+}$ chemistry was so difficult to control: $Tm^{2+}$ reacts with the 'inert' nitrogen atmosphere, Eq. (6). Hence, addition of cyclopentadienyl reagents to $TmI_2$ in solution under nitrogen forms dinitrogen complexes as shown. The $Tm^{2+}$ ion is so reactive that this can be accomplished without using the ubiquitous $C_5Me_5$ ligand and even in the presence of THF, Eq. (7). The structures of these thulium dinitrogen complexes have the unusual coplanar $M_2N_2$ arrangement found in $[(C_5Me_5)_2Sm]_2N_2$ [11]. However, crystallographic evidence shows that the NN bond in the thulium dinitrogen complexes is significantly longer than that in the Sm system, Eq. (2). Hence, by expanding divalent lanthanide chemistry to $Tm^{2+}$, there are significantly more opportunities to study dinitrogen reduction than were available with $Sm^{2+}$.

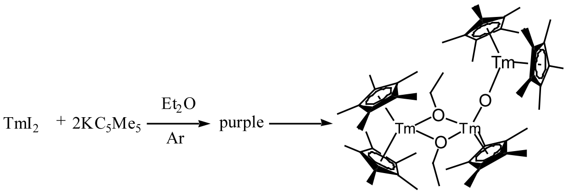


(6)



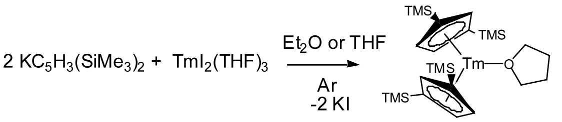
(7)

Since organometallic $Tm^{2+}$ complexes reduce nitrogen, reactions under argon were examined. In this case, the $Et_2O$ solvent was attacked by $Tm^{2+}$ [29], Eq. (8).



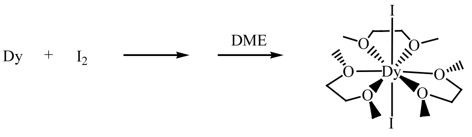
(8)

Eqs. (6)–(8) suggested that $Tm^{2+}$ would not lead to a stable organometallic complex. However, using the proper combination of ligands and reaction conditions, the first molecular organometallic complex of $Tm^{2+}$ was isolated and structurally characterized [30], Eq. (9).



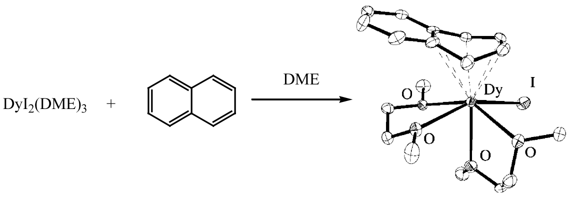
(9)

The success obtained with $Tm^{2+}$ initiated efforts to tame the next most accessible divalent lanthanide ion, $Dy^{2+}$, which has an estimated $Dy^{3+}/Dy^{2+}$ reduction potential of −2.5 V versus NHE [6]. Indeed, the first molecular complex of Dy(II) could also be isolated as a diiodide with dimethoxyethane supporting ligands [31], Eq. (10). $DyI_2$ is sufficiently reducing that it can reduce naphthalene directly [31], Eq. ( 11). As might be expected, in situ organometallic chemistry of $Dy^{2+}$ also leads to reduction of dinitrogen [30], Eq. (12).



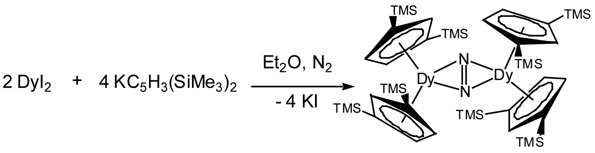
(10)

$DyI_2(DME)_3$



(11)

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



(12)

Recently, this list of new molecular divalent lanthanide diiodides has been extended to $Nd^{2+}$ by the Bochkarev group [32] and preliminary data indicate it will also be useful in organic synthesis [33]. Hence, in the past four years the number of crystallographically identified molecular divalent lanthanide halide starting materials, $LnI_2$, has been doubled. This is exceptional and unexpected progress considering that the molecular divalent redox chemistry of the lanthanides had been believed to be limited to $Eu^{2+}$, $Yb^{2+}$, and $Sm^{2+}$ for several decades. Recent results in alkali metal reduction chemistry of the lanthanides suggest that even more diversity is accessible [34].

Despite the dramatic increase in the number of molecular divalent lanthanide halides, this still has not allowed metal size optimization of $Sm^{2+}$ chemistry, since these new divalent species have different reduction potentials and gradual changes in metal size are still not present. The opportunity to do metal size optimization of $Sm^{2+}$ reduction required a breakthrough of another type as discussed in the next section.

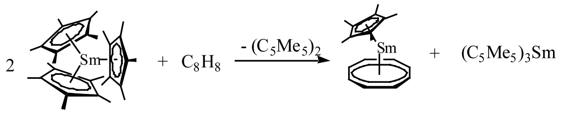
## 4. Sterically induced reduction

An alternative approach to $Sm^{2+}$ reductive chemistry was discovered in the course of investigating the chemistry of the sterically crowded complex,

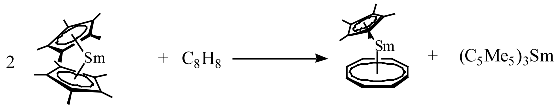
$(C_5Me_5)_3Sm$ [35–37]. For many years it was believed that it was impossible to make a metal complex of this type containing three pentahapto $C_5Me_5$ ligands, since the cone angle of a $C_5Me_5$ ligand was estimated to be much greater than the 120° required for a tris ligand structure. However, isolation of $(C_5Me_5)_3Sm$ showed that this was possible [35]. The $C_5Me_5$ ligands have a 120° cone angle in $(C_5Me_5)_3Sm$ because they are further away from the metal than in conventional $C_5Me_5$ compounds: the Sm–C(ring carbon) distances are 0.1 Å longer than normal [38].

Since the $(C_5Me_5)^-$ ligands are farther from the metal than their optimal distance, their electrostatic stabilization is not likely to be as strong as in conventional $C_5Me_5$ complexes. This may explain the high reactivity observed for $(C_5Me_5)_3Sm$. One pattern of reactivity is for the complex to act as a bulky alkyl bis(cyclopentadienyl) complex, $(C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)$ [37,39]. In attempts to get structural information on this monohapto complex by addition of Lewis bases, a second pattern of reactivity was observed.

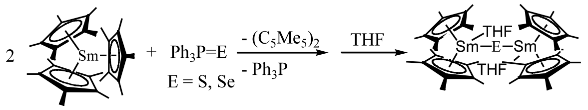
It was discovered that $(C_5Me_5)_3Sm$ was capable of one electron reductive reactivity even though the complex contained trivalent samarium [37]. Moreover the complex has reductive reactivity similar to that of the divalent complex $(C_5Me_5)_2Sm$ [4,9,10]. This unusual reactivity was observed in several sets of parallel reactions, Eqs. (13)–(14), (15)–(16) and (17)–(18), in which the identical organosamarium products were obtained from both trivalent $(C_5Me_5)_3Sm$ and divalent $(C_5Me_5)_2Sm$. A diverse group of substrates can be reduced as shown here for the reduction of cyclooctatetraene, triphenylphosphine sulfide and selenide (E = S, Se) and *tert*-butyl nitrile [37].



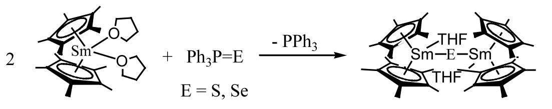
(13)



(14)



(15)



(16)

$$3(C_5Me_5)_3Sm + 6Me_3CNC \xrightarrow{-3/2(C_5Me_5)_2} [(C_5Me_5)_2Sm(\mu\text{-CN})(CNCMe_3)]_3 \qquad (17)$$

$$3(C_5Me_5)_2Sm + 6Me_3CNC \rightarrow [(C_5Me_5)_2Sm(\mu\text{-CN})(CNCMe_3)]_3 \qquad (18)$$

The fact that there is no net change in oxidation state of the metal in reactions (13), (15) and (17) and the isolation of $(C_5Me_5)_2$ as the byproduct in each case suggested that $(C_5Me_5)_3Sm$ reduces through a $(C_5Me_5)/(C_5Me_5)^-$ redox couple, Eq. (19). Comparison of the

$$C_5Me_5^- \rightarrow e^- + 1/2(C_5Me_5)_2 \qquad (19)$$

half reactions for $(C_5Me_5)_2Sm$ and $(C_5Me_5)_3Sm$, Eqs. (20) and (21) respectively, shows why they give the same

$$(C_5Me_5)_2Sm \rightarrow e^- + [(C_5Me_5)_2Sm]^+ \qquad (20)$$

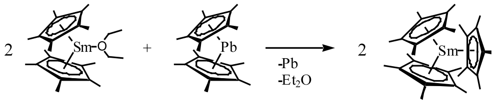
$$(C_5Me_5)_3Sm \rightarrow e^- + [(C_5Me_5)_2Sm]^+ + 1/2(C_5Me_5)_2 \qquad (21)$$

product. In both cases, a one electron reduction occurs with the formation of the same organosamarium cation, $[(C_5Me_5)_2Sm]^+$, to which the reduced substrate is bound.

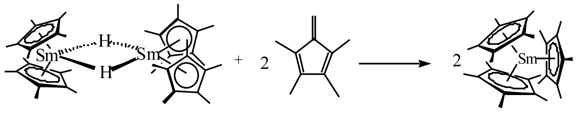
This type of reactivity has been labelled sterically induced reduction [3] because its origin can be rationalized by the steric crowding of the molecule. Indeed, comparable reductive reactivity has not been observed with any of the many previously reported classes of tris(cyclopentadienyl)lanthanide complexes, $(C_5R_5)_3Ln$, in which there is no significant steric crowding [2,40]. Similarly, none of the $C_5Me_5$ ligands in the scores of trivalent $(C_5Me_5)_2LnZ$ (Z = monoanionic ligand) complexes in the literature act as reducing agents. These complexes have conventional bond distances [38] and apparently adequate electrostatic stabilization of the cyclopentadienide ligands. Simple ionic $(C_5Me_5)^-$ salts also fail to have this reductive reactivity presumably because they also are much better electrostatically stabilized in their sterically uncrowded environments. For example, the $Se{=}PPh_3$ reduction of Eq. (15) is not found with $KC_5Me_5$, $(C_5Me_5)MgCl$ or $(C_5Me_5)_2Pb$.

The fact that trivalent $(C_5Me_5)_3Sm$ can accomplish one electron reductions like $(C_5Me_5)_2Sm$ was highly significant for the expansion of lanthanide reductive chemistry. The importance was not for samarium, since good reducing agents such as $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ were already available for this metal, but for the other elements. If the $(C_5Me_5)_3Sm$ reductive reactivity were due to steric crowding and if similar sterically crowded $(C_5Me_5)_3Ln$ complexes could be synthesized, this would allow an extension of the one electron reduction chemistry of divalent $(C_5Me_5)_2Sm$ to other lanthanides. This would allow metal-based size optimization in $Sm^{2+}$ reductive chemistry, a situation that had never been possible before. This would also allow the synthesis via reductive methods of many types of trivalent lanthanide complexes previously accessible only to samarium via its reductive chemistry. By this route magnetic, electronic or optical properties could be optimized for specific applications. In addition, if extension could be made to $La^{3+}$, $Y^{3+}$, or $Lu^{3+}$, it would be possible to do reductive lanthanide chemistry with diamagnetic products for the first time. NMR characterization of organosamarium chemistry has always been more difficult since both $Sm^{2+}$ and $Sm^{3+}$ are paramagnetic [41].

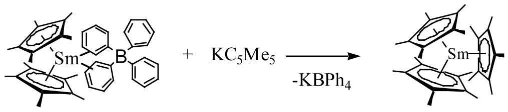
To test the viability of extending sterically induced reduction to other metals, new synthetic routes were necessary since initially the only two synthetic routes to $(C_5Me_5)_3Sm$ involved the special chemistry of divalent $(C_5Me_5)_2Sm$, Eq. (14) [35] and Eq. (22) [36]. Extending this chemistry to other metals was also crucial to exclude the possibility that the reduction was occurring via a pathway that required $Sm^{2+}$. Fortunately two syntheses of $(C_5Me_5)_3Sm$ from trivalent precursors were discovered involving hydrides [42] and unsolvated cation complexes [43], Eqs. (23) and (24), respectively. This allowed other $(C_5Me_5)_3Ln$ complexes to be made and the concept of sterically induced reduction to be tested with other metals.



(22)

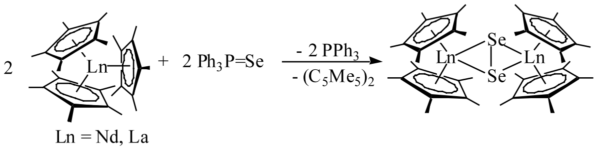


(23)



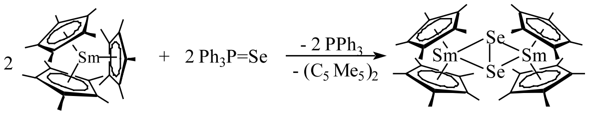
(24)

Initial studies of $(C_5Me_5)_3Nd$ and $(C_5Me_5)_3La$ showed that they do function as one electron reductants with $Se=PPh_3$ [44–46]. The expected byproduct from the sterically induced reduction half reaction, Eq. (19), namely $(C_5Me_5)_2$, was observed in both cases. However, the selenium product isolated from the Nd and La reactions, Eq. (25), was different from that isolated from the $(C_5Me_5)_3Sm$ reduction [37], Eq. (15). Reduction of $Se=PPh_3$ to a $(Se_2)^{2-}$ product, Eq. (25), was observed instead of reduction to $(Se)^{2-}$ as was found in Eq. (15). Excess $(C_5Me_5)_3Ln$ (Ln = La, Nd) would not reduce the $(Se_2)^{2-}$ product further. This result not only validated the concept that sterically crowded $(C_5Me_5)_3Ln$ complexes could act as reductants without a Ln=Sm requirement, but it also suggested that the reduction potentials of $(C_5Me_5)_3Ln$ would vary depending upon the metal. $(C_5Me_5)_3La$ and $(C_5Me_5)_3Nd$ were evidently not as reducing as $(C_5Me_5)_3Sm$, since selenium was reduced to a formal −1 oxidation state with La and Nd instead of the −2 oxidation state with Sm.



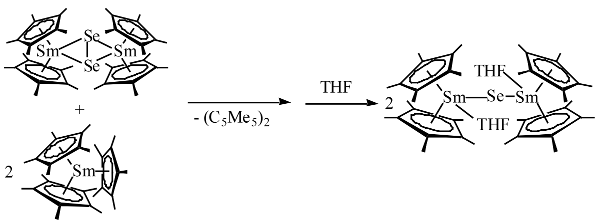
(25)

The weaker reductive capacity of the Nd and La complexes could be rationalized by the fact that Nd and La are larger than Sm and hence their $(C_5Me_5)_3Ln$ complexes are less crowded than $(C_5Me_5)_3Sm$. If this idea was correct, it seemed possible that $(C_5Me_5)_3Sm$ should be able to make the $(Se_2)^{2-}$ product as well as the $(Se)^{2-}$ product. This was examined by conducting a reaction using a 1:1 ratio of $(C_5Me_5)_3Sm:Se=PPh_3$, Eq. (26), instead of the 2:1 stoichiometry used in Eq. (15).



(26)

As shown in Eq. (26), $(C_5Me_5)_3Sm$ does form the $(Se_2)^{2-}$ product analogous to the Nd complex under these conditions. Moreover, it was subsequently shown that $(C_5Me_5)_3Sm$ would reduce the $(Se_2)^{2-}$ product to the $Se^{2-}$ product, Eq. (27), i.e. Eq. (15) could be done stepwise by $(C_5Me_5)_3Sm$ [44]. Hence, $(C_5Me_5)_3Sm$ can effect both one and two electron reductions when used in 1:1 and 1:2 ratios, respectively.



(27)

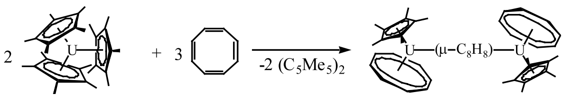
These results indicate that sterically induced reduction can be used to bring the special chemistry of $Sm^{2+}$ to complexes of the other metals in the lanthanide series. The $Sm^{2+}$ reductive approach, which has formed so many types of trivalent $[(C_5Me_5)_2Sm]_2$(substrate) and

$(C_5Me_5)_2Sm(substrate–substrate)Sm(C_5Me_5)_2$ complexes for samarium [2,4], can now be extended to the other elements. These classes of samarium complexes can be opened up to metals with other physical properties including diamagnetic $La^{3+}$, $Y^{3+}$ and $Lu^{3+}$, luminescent $Tb^{3+}$, and highly paramagnetic $Gd^{3+}$. This should also allow the special chemistry of $Sm^{2+}$ to be size optimized. In addition, since $(C_5Me_5)_3Sm$ appears to be more reducing than $(C_5Me_5)_3Nd$ and $(C_5Me_5)_3La$, it appears that the reduction reactivity can be varied within a series as a function of the degree of steric crowding.

Extension of this one electron reduction chemistry to the other lanthanides requires the synthesis of suitably crowded molecules. Although this will be challenging, it is encouraging to think that there are now some fourteen separate syntheses of $(C_5Me_5)_3M$ complexes [35–37,42,43,47–49], a class that for decades was thought to be too crowded to exist. In addition, it does not seem necessary to do such reduction chemistry only with homoleptic $(C_5R_5)_3Ln$ compounds. Similar reductive chemistry could be accomplished by complexes of general formula (large ligand)$_2$Ln$(C_5Me_5)$ or even (large ligand)$_3$Ln if that ligand will do reduction as is found with $(C_5Me_5)^-$. In fact it is possible that this type of reduction has happened before in other systems, but has gone undetected. Reactions designed to make sterically crowded complexes which have 'failed' because a complex mixture of unisolable products is obtained, may actually have involved formation of the desired sterically crowded complex. However, the complex may have been so reactive via sterically induced reduction pathways that only a mixture of products was obtained. It may be worth re-examining some of these reactions designed to make crowded molecules in the presence of reducible substrates to see if conventional reduction chemistry can be mimicked.

Further advances in sterically induced reduction chemistry have resulted by examining the $U^{3+}$ analog of $(C_5Me_5)_3Sm$, namely $(C_5Me_5)_3U$ [48]. This molecule provides the opportunity to combine one electron sterically induced reduction chemistry with a conventional metal redox $U^{4+}/U^{3+}$ couple [50]. As a result, $(C_5Me_5)_3U$ could be a monometallic two-electron reductant, something rare in f element chemistry.

Examination of the two electron reduction chemistry of $(C_5Me_5)_3U$ was initially tested with 1,3,5,7-cyclooctatetraene, $C_8H_8$, since it could be reduced to a dianion. Interestingly, $(C_5Me_5)_3U$ does not react cleanly with $C_8H_8$ in a 1:1 stoichiometry, but rather a 2:3 ratio is found to be optimum [51]. The product expected from the sterically induced reduction reaction, $(C_5Me_5)_2$, was identified along with a $U^{4+}$ product identified as $[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$, by X-ray crystallography, Eq. (28). Hence, both sterically induced reduction chemistry and a $U^{3+}$ to $U^{4+}$ conversion occurred. Examination of the final stoichiometry in Eq. (28) shows that $(C_5Me_5)_3U$ is not a two electron reductant as originally hypothesized, but rather a three electron reductant. Two equivalents of $(C_5Me_5)_3U$ form three $(C_8H_8)^{2-}$ dianions. The net reaction is accomplished via two $(C_5Me_5)/(C_5Me_5)^-$ couples as well as the $U^{3+}$ reduction. The net half reaction is shown in Eq. (29).



(28)

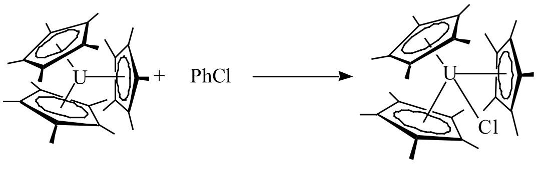
$$(C_5Me_5)_3U \rightarrow 3e^- + [(C_5Me_5)U]^{3+} + (C_5Me_5)_2 \qquad (29)$$

This result shows that sterically induced reduction chemistry can be coupled to traditional metal based redox chemistry to accomplish multi-electron reductions previously not possible with the f elements. Hence, coupling of low oxidation states of the f elements with steric crowding should open even more opportunities for new f element based reductive chemistry.

Eq. (28) above raised the question about which reduction occurred first, sterically induced reduction or reduction by $U^{3+}$. Although this seemed like a difficult question to answer, some information in this regard was obtained using PhCl as a substrate. $(C_5Me_5)_3U$ reacts with two equivalents of PhCl as a two electron reductant to form primarily $(C_5Me_5)_2UCl_2$, as shown in Eq. (30).

$$(C_5Me_5)_3U + 2PhCl \xrightarrow[\substack{-1/2(C_5Me_5)_2 \\ -Ph–Ph}]{} (C_5Me_5)_2UCl_2 \qquad (30)$$

This reaction occurs stepwise and the intermediate from the one equivalent reaction could be isolated. If the first equivalent of PhCl was reduced by sterically induced reduction the product would be the known compound, $[(C_5Me_5)_2UCl]_3$ [52]. On the other hand, if the first electron transfer was a result of a $U^{3+}/U^{4+}$ redox process, the composition of the product would be $(C_5Me_5)_3UCl$. Such a product would be most surprising, since it would be much more crowded than $(C_5Me_5)_3U$, due to the extra ligand, and since $U^{4+}$ is 0.135 Å smaller than $U^{3+}$ [21]. An X-ray diffraction study of the intermediate showed that it was in fact the second option, $(C_5Me_5)_3UCl$ [47], Eq. (31). This is the most crowded $(C_5Me_5)_3M$ complex isolated to date. Since $U^{4+}$ is similar in size to $Tb^{3+}$ [21], this suggests that isolation of the $(C_5Me_5)_3Ln$ complexes of the smaller lanthanides should be sterically possible. This result also shows that reduction by $U^{3+}$ occurs first in this case.



(31)

## 5. Conclusion

Reductive f element chemistry is a rapidly expanding frontier of organometallic chemistry. The number of accessible divalent lanthanide diiodide starting materials has been doubled from the traditional $EuI_2$, $YbI_2$, and $SmI_2$ systems to $TmI_2$, $DyI_2$, and $NdI_2$. The discovery that tris(pentamethylcyclopentadienyl) metal complexes could exist, a result which again overturned a long standing assumption, revealed another method for achieving divalent type reductive reactivity. Both results are quite unexpected. One would have assumed that the limitations on accessible divalent states, which were adhered to for years, would have been correct. One would also not expect a sterically crowded molecule to lead to new reduction chemistry, since steric factors and redox are not normally connected. These results suggest that organometallic reductive lanthanide chemistry is likely to expand more in the future. This will require clever synthetic approaches, but recent discoveries indicate that new and more reactive targets should be accessible.

## Acknowledgements

I am grateful to the National Science Foundation for support of this project and Nathan T. Allen for the graphics.

## References

[1] (a) T. Moeller, in: J.C. Bailer, Jr (Ed.), Comprehensive Inorganic Chemistry 4, Ch. 44, Pergamon Press, Oxford, UK 1973;
(b) F.A. Hart, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Ch. 39, Pergamon Press, Oxford 1987.

[2] (a) M.N. Bochkarev, L.N. Zakharov, G.S. Kalinina, Organoderivatives of the Rare Earth Elements, Kluwer Academic, Dordrecht 1996;
(b) R. Anwander, W.A. Herrmann, Top. Curr. Chem. 179 (1996) 1;
(c) F.T. Edelmann, in: M.F. Lappert (Ed.), Comprehensive Organometallic Chemistry II, Ch. 2, vol. 4, Pergamon, Oxford 1995;
(d) C.J. Schavarien, Adv. Organomet. Chem. 36 (1994) 283;
(e) H. Schumann, W. Genthe, in: K.A. Gschneidner, L. Eyring (Eds.), Handbook on the Physics, Chemistry of Rare Earths, Ch. 53, vol. 7, Elsevier, Amsterdam 1985;
(f) T.J. Marks, R.D. Ernst, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Ch. 21, Pergamon, Oxford 1982.

[3] W.J. Evans, Coord. Chem. Rev. 206–207 (2000) 263.

[4] W.J. Evans, Polyhedron 6 (1987) 803.

[5] H.B. Kagan, New J. Chem. 14 (1990) 453.

[6] L.R. Morss, Chem. Rev. 76 (1976) 827 (and references therein).

[7] (a) P. Girard, J.L. Namy, H.B. Kagan, J. Am. Chem. Soc. 102 (1980) 2693;
(b) G.A. Molander, Chem. Rev. 92 (1992) 29;
(c) L.A. Paquette, Encyclopedia of Reagents for Organic Synthesis, Wiley, New York 1995, p. 4428.

[8] W.J. Evans, I. Bloom, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 103 (1981) 6507.

[9] (a) W.J. Evans, L.A. Hughes, T. Hanusa, J. Am. Chem. Soc. 106 (1984) 4270;
(b) W.J. Evans, L.A. Hughes, T. Hanusa, Organometallics 5 (1986) 1285.

[10] (a) W.J. Evans, J.W. Grate, L.A. Hughes, H. Zhang, J.L. Atwood, J. Am. Chem. Soc. 107 (1985) 3728;
(b) W.J. Evans, R.A. Keyer, H. Zhang, J.L. Atwood, J. Chem. Soc. Chem. Commun. (1987) 837;
(c) W.J. Evans, D.K. Drummond, J. Am. Chem. Soc. 110 (1988) 2772;
(d) W.J. Evans, D.K. Drummond, Organometallics 7 (1988) 797;
(e) W.J. Evans, D.K. Drummond, J. Am. Chem. Soc. 111 (1989) 3329;
(f) W.J. Evans, T.A. Ulibarri, J.W. Ziller, J. Am. Chem. Soc. 112 (1990) 219;
(g) W.J. Evans, T.A. Ulibarri, J.W. Ziller, J. Am. Chem. Soc. 112 (1990) 2314;
(h) W.J. Evans, S.L. Gonzales, J.W. Ziller, J. Am. Chem. Soc. 113 (1991) 9880;
(i) W.J. Evans, S.L. Gonzales, J.W. Ziller, J. Am. Chem. Soc. 116 (1994) 2600.

[11] W.J. Evans, T.A. Ulibarri, J.W. Ziller, J. Am. Chem. Soc. 110 (1988) 6877.

[12] (a) W.J. Evans, L.R. Chamberlain, T.A. Ulibarri, J.W. Ziller, J. Am. Chem. Soc. 110 (1988) 6423;
(b) W.J. Evans, D.M. DeCoster, J. Greaves, Macromolecules 28 (1995) 7929;
(c) W.J. Evans, D.M. DeCoster, J. Greaves, Organometallics 15 (1996) 3210.

[13] W.J. Evans, H. Katsumata, Macromolecules 27 (1994) 2330, 4011.

[14] (a) H. Yasuda, M. Furo, H. Yamamoto, A. Nakamura, S. Miyake, N. Kibino, Macromolecules 25 (1992) 5115;
(b) E. Ihara, M. Taguchi, H. Yasuda, Appl. Organomet. Chem. 9 (1995) 427;
(c) M. Yamashita, Y. Takemoto, E. Ihara, H. Yasuda, Macromolecules 29 (1996) 1798;
(d) H. Yasuda, H. Tamamoto, K. Yokota, S. Miyake, A. Nakamura, J. Am. Chem. Soc. 114 (1992) 4908.

[15] (a) L.S. Boffa, B.M. Novak, Macromolecules 30 (1997) 3494;
(b) Y.G. Zhang, Z. Hou, Y. Wakatsuki, Macromolecules 32 (1999) 939;
(c) Z. Hou, H. Tezuka, Y. Zhang, H. Yamazaki, Y. Wakatsuki, Macromolecules 32 (1998) 8650;
(d) D. Barbier-Baudry, S. Heiner, M.M. Kubicki, E. Vigier, M. Visseaux, A. Hafid, Organometallics 20 (2001) 4207.

[16] S.P. Nolan, D. Stern, T.J. Marks, J. Am. Chem. Soc. 111 (1989) 7844.

[17] (a) I. Castillo, T.D. Tilley, J. Am. Chem. Soc. 123 (2001) 10526;
(b) N.S. Radu, S.L. Buchwald, B. Scott, C.J. Burns, Organometallics 15 (1996) 3913.

[18] (a) M.R. Douglass, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 123 (2001) 10221;
(b) M.R. Gagné, S.P. Nolan, T.J. Marks, Organometallics 9 (1990) 1716;
(c) Y. Li, P.F. Fu, T.J. Marks, Organometallics 13 (1994) 439;
(d) K.N. Harrison, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 9220;
(e) P.F. Fu, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 10747.

[19] (a) W.J. Evans, in: F.R Hartley, S. Patai (Eds.), The Chemistry of the Metal–Carbon Bond, Ch. 12, Wiley, New York 1982;
(b) W.J. Evans, Adv. Organomet. Chem. 24 (1985) 131;
(c) W.J. Evans, R. Dominguez, T.P. Hanusa, Organometallics 5

(1986) 263;
(d) D. Alvarez, Jr, K.G. Caulton, W.J. Evans, J.W. Ziller, J. Am. Chem. Soc. 112 (1990) 5674.
[20] A.J. Freeman, R.E. Watson, Phys. Rev. 127 (1962) 2058.
[21] R.D. Shannon, Acta Crystallogr. Sect. A 32 (1976) 751.
[22] (a) M. Wedler, A. Recknagel, F.T. Edelmann, J. Organomet. Chem. 395 (1990) C26;
(b) A. Greco, S. Cesca, G. Bertolini, J. Organomet. Chem. 113 (1976) 321.
[23] (a) J.D. Corbett, in: G. Meyer, L.R. Morss (Eds.), Synthesis of Lanthanide, Actinide Compounds, Kluwer Academic, Dordrecht 1991, p. 159;
(b) G. Meyer, H.-J. Meyer, Chem. Mater 4 (1992) 1157;
(c) G. Meyer, Chem. Rev. 88 (1988) 93;
(d) H.A. Eick, in: K.A. Gschneidner, Jr, L. Eyring, G.R. Choppin, G.H. Lander (Eds.), Handbook on the Physics, Chemistry of Rare Earths, vol. 18, Elsevier, Amsterdam 1994, p. 365;
(e) R.E. Araujo, J.D. Corbett, Inorg. Chem. 20 (1981) 3082;
(f) U. Lochner, J.D. Corbett, Inorg. Chem. 14 (1975) 426;
(g) L.F. Druding, J.D. Corbett, J. Am. Chem. Soc. 83 (1961) 2462.
[24] M.N. Bochkarev, I.L. Fedushkin, A.A. Fagin, T.W. Petrovskaya, J.W. Ziller, R.N.R. Broomhall-Dillard, W.J. Evans, Angew. Chem. Int. Ed. Engl. 36 (1997) 133.
[25] W.J. Evans, R.N.R. Broomhall-Dillard, J.W. Ziller, Polyhedron 17 (1998) 3361.
[26] (a) M.N. Bochkarev, I.L. Fedushkin, A.A. Fagin, H. Schumann, J. Demtschuk, Chem. Commun. (1997) 1783.;
(b) I.L. Fedushkin, M. Weydert, A.A. Fagin, S.E. Nefedov, I.L. Eremenko, M.N. Bochkarev, H. Schumann, Z. Naturforsch. Teil B 54 (1999) 466;
(c) I.L Fedushkin, F. Girgsdies, H. Schumann, M.N. Bochkarev, Eur. J. Inorg. Chem. (2001) 2405.
[27] W.J. Evans, N.T. Allen, J. Am. Chem. Soc. 122 (2000) 2118.
[28] (a) K. Otsubo, J. Inanaga, M. Yamaguchi, Tetrahedron Lett. 57 (1986) 2237;
(b) R.A. Flowers, M. Shabangi, Tetrahedron Lett. 38 (1997) 1137;
(c) R.J. Enemaerke, T. Hertz, T. Skrydstrup, K. Daasbjerg, Chem. Eur. J. 6 (2000) 3747.
[29] W.J. Evans, N.T. Allen, J.W. Ziller, J. Am. Chem. Soc. 123 (2001) 7927.
[30] W.J. Evans, N.T. Allen, J.W. Ziller, Angew. Chem. Int. 41 (2002) 359.
[31] (a) W.J. Evans, N.T. Allen, J.W. Ziller, J. Am. Chem. Soc. 122 (2000) 11749;
(b) M.N. Bochkarev, A.A. Fagin, Chem. Eur. J. 5 (1999) 2990.
[32] M.N. Bochkarev, I.L. Fedushkin, S. Dechert, A.A. Fagin, H. Schumann, Angew. Chem. Int. Ed. Engl. 40 (2001) 3176.
[33] W.J. Evans, P.S. Workman, N.T. Allen, in preparation.
[34] (a) Yu.K. Gun'ko, B. Hitchcock, M.F. Lappert, J. Organomet. Chem. 499 (1995) 213;
(b) M.C. Cassani, M.F. Lappert, F. Laschi, Chem. Commun. (1997) 1563.;
(c) M.C. Cassani, D.J. Duncalf, M.F. Lappert, J. Am. Chem. Soc. 120 (1998) 12958;
(d) M.C. Cassani, Y.K. Gun'ko, P.B. Hitchcock, M.F. Lappert, F. Laschi, Organometallics 18 (1999) 5539;
(e) Y.K. Gun'ko, P.B. Hitchcock, M.F. Lappert, Organometallics 19 (2000) 2832.
[35] W.J. Evans, S.L. Gonzales, J.W. Ziller, J. Am. Chem. Soc. 113 (1991) 7423.
[36] W.J. Evans, K.J. Forrestal, J.T. Leman, J.W. Ziller, Organometallics 15 (1996) 527.
[37] W.J. Evans, K.J. Forrestal, J.W. Ziller, J. Am. Chem. Soc. 120 (1998) 9273.
[38] W.J. Evans, S.E. Foster, J. Organomet. Chem. 433 (1992) 79.
[39] (a) W.J. Evans, K.J. Forrestal, J.W. Ziller, J. Am. Chem. Soc. 117 (1995) 12635;
(b) W.J. Evans, K.J. Forrestal, M.A. Ansari, J.W. Ziller, J. Am. Chem. Soc. 120 (1998) 2180.
[40] H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865.
[41] W.J. Evans, M.A. Hozbor, J. Organomet. Chem. 326 (1987) 299.
[42] W.J. Evans, K.J. Forrestal, J.W. Ziller, Angew. Chem. Int. Ed. Engl. 36 (1997) 774.
[43] W.J. Evans, C.A. Seibel, J.W. Ziller, J. Am. Chem. Soc. 120 (1998) 6745.
[44] W.J. Evans, G.W. Nyce, R.D. Clark, R.J. Doedens, J.W. Ziller, Angew. Chem. Int. Ed. Engl. 38 (1999) 1801.
[45] W.J. Evans, B.L. Davis, J.W. Ziller, Inorg. Chem. 40 (2001) 6341.
[46] W.J. Evans, B.L. Davis, J.W. Ziller, in preparation.
[47] W.J. Evans, G.W. Nyce, J.W. Ziller, J. Am. Chem. Soc. 122 (2000) 12019.
[48] W.J. Evans, K.J. Forrestal, J.W. Ziller, Angew. Chem. Int. Ed. Engl. 36 (1997) 774.
[49] (a) W.J. Evans, G.W. Nyce, J.W. Ziller, Organometallics 20 (2001) 5489;
(b) W.J. Evans, G.W. Nyce, K.J. Forrestal, J.W. Ziller, Organometallics 21 (2002) 1050.
[50] (a) R.G. Finke, Y. Hirose, G. Gaughan, J. Chem. Soc. Chem. Commun. (1981) 232.;
(b) J.G. Brennan, R.A. Andersen, J. Am. Chem. Soc. 107 (1985) 514;
(c) J.G. Brennan, R.A. Andersen, A. Zalkin, Inorg. Chem. 25 (1986) 1756, 1761;
(d) L.R. Avens, D.M. Barnhart, C.J. Burns, S.D. McKee, W.H. Smith, Inorg. Chem. 33 (1994) 4245.
[51] W.J. Evans, G.W. Nyce, J.W. Ziller, Angew. Chem. Int. Ed. Engl. 39 (2000) 240.
[52] P.J. Fagan, J.M. Manriquez, T.J. Marks, C.S. Day, S.H. Vollmer, V.W. Day, Organometallics 1 (1982) 170.