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Perspectives in reductive lanthanide chemistry

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Contents

Abstract

For several decades the reductive chemistry of the lanthanide metals in soluble, fully characterized molecular species has focused primarily on just three elements: europium,

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ytterbium, and samarium. Recent developments suggest that the reductive chemistry of the lanthanides is likely to expand greatly beyond these three elements in the new millennium and will be a major area of advancement in lanthanide inorganic, organometallic, and coordination chemistry. This paper previews some possibilities in this field.

Keywords: Lanthanide; Reduction; Steric; Cyclopentadienyl; Low valent; Organometallic

1. Introduction

1.1. Traditional divalent lanthanide solution chemistry

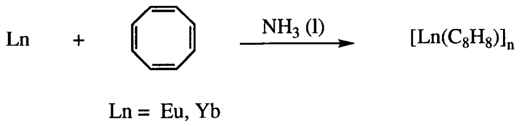
The three lanthanide elements with the most readily accessible divalent oxidation states, europium, ytterbium, and samarium, have provided a wealth of unusual molecular reductive chemistry to this series of metals [1–4]. The three divalent ions, in order of increasing reactivity, are the half-filled shell $4f^7$ Eu(II), the filled shell $4f^{14}$ Yb(II), and Sm(II), which has a $4f^6$ electron configuration which approaches a half filled shell. The general Ln(III)/Ln(II) reduction potentials for these ions are compared with those for the rest of the lanthanides in Table 1 [5].

The molecular divalent chemistry of Eu, Yb, and Sm has been successfully pursued in a variety of applications. Perhaps the oldest use has been in the area of aqueous redox chemistry, in which Eu(II) has been used as a simple one-electron reductant for many years [6]. In the organometallic area, Eu and Yb were used as early as the 1964 to make the first divalent organolanthanide complexes since these metals dissolve in liquid ammonia [7]. This provides a convenient synthetic entry to divalent chemistry and was used to make cyclopentadienyl [8] and cyclooctatetraenyl [9] complexes of these elements starting from cyclopentadiene and 1,3,5,7-cyclooctatetraene (Eqs. (1)–(2)).

$$\mathrm{Eu} + \mathrm{C_5H_6} \xrightarrow{\mathrm{NH_3\ (l)}} (\mathrm{C_5H_5})_2\mathrm{Eu}(\mathrm{NH_3}) + \mathrm{C_5H_8} \qquad (1)$$

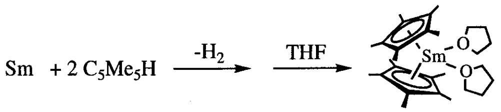
Table 1
Ln(III)/Ln(II) reduction potentials (versus NHE) in order of increasing reducing power [5] and the electron configurations of the Ln(II) reductant

Eu	−0.35 V	$[Xe]4f^7$	Ho	−2.9 V	$[Xe]4f^{11}$
Yb	−1.15 V	$[Xe]4f^{14}$	La	−3.1 V	$[Xe]4f^1$
Sm	−1.55 V	$[Xe]4f^6$	Er	−3.1 V	$[Xe]4f^{12}$
Tm	−2.3 V	$[Xe]4f^{13}$	Ce	−3.2 V	$[Xe]4f^2$
Nd	−2.6 V	$[Xe]4f^4$	Tb	−3.7 V	$[Xe]4f^9$
Dy	−2.6 V	$[Xe]4f^{10}$	Gd	−3.9 V	$[Xe]4f^8$
Pr	−2.7 V	$[Xe]4f^3$			



(2)

The chemistry of divalent samarium developed later. This occurred for several reasons. It was assumed that this metal would be much more difficult to handle experimentally because it was a much stronger reductant and because it was so large. Early organometallic lanthanide chemistry focused on the smaller metals later in the series since they were easier to stabilize by steric saturation of the coordination sphere of the metal [10]. Development of samarium was also impeded by lack of convenient starting materials and the fact that it did not dissolve in liquid ammonia. Hence, the first crystallographically characterized Sm(II) organometallic compound required synthesis by metal vapor methods (Eq. (3)) [11].

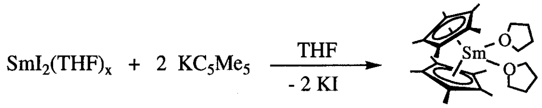


(3)

It was also necessary to utilize a larger ligand than simple cyclopentadienide to stabilize and solubilize this larger metal. Consequently, the $(C_5Me_5)^-$ ligand [12,13] played an important role in developing Sm(II) chemistry.

Introduction of the conveniently prepared THF-soluble $SmI_2(THF)_x$ by Kagan [14] in 1980 (Eq. (4)) provided an excellent starting material for divalent samarium complexes (Eq. (5)) [15].

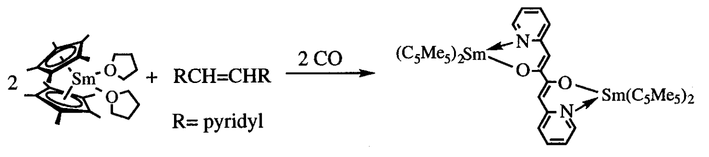
$$\mathrm{Sm} + \mathrm{ICH_2CH_2I} \xrightarrow{\mathrm{THF}} \mathrm{SmI_2(THF)}_x \xleftarrow{\mathrm{THF}} \mathrm{I_2} + \mathrm{Sm} \tag{4}$$



(5)

Like $SmI_2(THF)_x$, the analogous diiodides of Eu and Yb are also available and soluble. These have also become standard precursors and have helped advance the divalent chemistry of these metals [14,16].

$SmI_2(THF)_x$ subsequently became a broadly useful reducing agent in synthetic organic laboratories with applications in many types of transformations [17]. $(C_5Me_5)_2Sm(THF)_2$ [15] and its unsolvated, surprisingly bent analog, $(C_5Me_5)_2Sm$ [18], have also been found to have an extensive chemistry. A diverse range of reactivity has been observed for these complexes including unusual small molecule transformations [19,20], dinitrogen activation [21], and olefin polymerization [22] among others, e.g. Eqs. (6)–(8).



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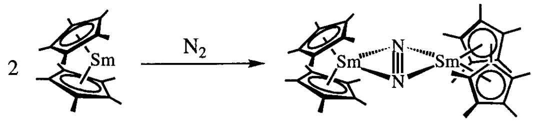

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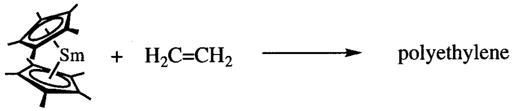


(8)

The broad utilization of the reductive chemistry of Eu, Yb, and Sm occurred because of two main factors: first, these elements have redox potentials which are readily accessible under normal solution conditions and second, they have convenient synthetic precursors which allow their chemistry to be explored. This combination has expanded molecular lanthanide chemistry enormously.

Only a few reports of molecular divalent lanthanide complexes involving metals other than Eu, Yb, and Sm have appeared in the literature over the years, but these have not been confirmed by X-ray crystallography. As early as 1960, there were descriptions of transient aqueous solutions of Tm(II) [23]. In the late 1970s, Kamenskaya spectroscopically examined solutions obtained from Ln/LnX$_3$ reaction products (see Section 1.2) and reported transient observations of Tm(II), Nd(II), and Dy(II) [24]. As seen in Table 1, these three ions are the next most likely to be isolable after Eu, Yb, and Sm on the basis of reduction potentials. In 1979, Rossmanith reported a Nd(II) product from the reduction of NdCl$_3$ with Li/naphthalene [25], a product which was subsequently used in 1990 with $(C_5Me_5)^-$ ligands to make 'non-classical organolanthanide(II) complexes' of Nd [26]. In 1976, the reduction of a trivalent cerium complex, [K(glyme)][Ce(C$_8$H$_8$)$_2$], with K was reported to make the divalent complex [K(glyme)]$_2$[Ce(C$_8$H$_8$)$_2$] [27]. Although these reports suggested the presence of new reductive chemistry for the lanthanides, they provided neither the crystallographic proof nor the convenient precursors which had helped Eu, Yb, and Sm develop.

Although the divalent chemistry of Eu, Yb, and Sm has led to advances in a variety of different areas of chemistry, this solution molecular reductive chemistry has been limited to just these three elements. This is unfortunate, since one of the powerful features of the lanthanide series metals is that one can use the gradually changing radial size of the elements to optimize the chemistry in ways not possible for other series of metals in the periodic table [10]. Since the 4f valence orbitals of the lanthanides have a limited radial extension compared to the size of their core orbitals [28], one can choose the lanthanide with the optimal radial size to accomplish a specific reaction without concern for the specific 4f^n electron configuration. Hence, for reactions involving trivalent lanthanides, one can optimize steric factors not only with the ligand set, as is traditionally done with all metals, but also by choosing the best metal size from 15 non-radioactive choices. These vary gradually from 1.03 Å La^{3+} (six-coordinate radius [29]) 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. However, optimization of radial factors has not been possible in reductive lanthanide chemistry because only three of the fifteen elements have easily accessible divalent states.

1.2. Divalent solid state chemistry

In contrast to the solution molecular chemistry discussed above, solid state chemistry provides divalent lanthanide ions for all of the metals. As early as 1963, divalent ions were studied spectroscopically in CaF_2 matrices by radiolytic reduction of trivalent ions doped into the matrix [30]. Solid state materials containing divalent and even monovalent lanthanide ions can also be made by reductions of lanthanide trihalides with the lanthanide metal in tantalum crucibles at temperatures in the 600–1000°C range [31], e.g. Eq. (9). These metallothermic reductions also can be accomplished with alkali metals, e.g. Eq. (10) [32]. Hence, in the solid state, divalent lanthanides are much more widely available.

$$2LnX_3 + Ln \xrightarrow{700-1000°C,\ weeks} 3LnX_2 \tag{9}$$

$$2DyCl_3 + 2Li \xrightarrow[-LiCl]{700°C,\ 1\ week} LiDy_2Cl_5 \tag{10}$$

1.3. Future opportunities

Although for decades, Eu(II), Yb(II), and Sm(II) have dominated solution molecular lanthanide reduction chemistry, in recent years several new opportunities for reduction with other lanthanide elements have been reported. This appears to be a fertile area for future development and may be one of the most rapidly growing areas of lanthanide chemistry and coordination chemistry in the new millennium. An expanded reductive chemistry would be expected to have a great influence on future lanthanide chemistry, since it has previously been shown that even the development of one new divalent state, e.g. Sm(II), has had a tremendous impact [1–3]. Since just a few complexes of Sm(II) were needed to have this effect, e.g. $SmI_2(THF)_2$ [14], $(C_5Me_5)_2Sm(THF)_2$ [15], and $(C_5Me_5)_2Sm$ [18], it is possible that a few key developments with the other lanthanides could open up many new options in reductive chemistry.

Some of the future opportunities in molecular reductive lanthanide chemistry involve access to oxidation states heretofore available only in the solid state. Recent results in this area will only be summarized here in Section 2.1 since the direction for their development is clear. A more detailed analysis will be made in Section 2.2 of a different approach to reductive lanthanide chemistry in which reduction chemistry is developed via ligands and steric effects. This ‘sterically induced reduction chemistry’ is just beginning to be realized as an approach to redox chemistry. As described below, it has the potential to extend redox chemistry to all of the lanthanide elements which could prove to be quite powerful in advancing this field.

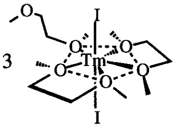
2. Discussion

2.1. Molecular low valent lanthanide complexes beyond the traditional Eu(II), Yb(II), and Sm(II) compounds

2.1.1. Divalent thulium

As shown in Table 1, the divalent lanthanide ion which is expected to be the next most accessible after Eu(II), Yb(II), and Sm(II) is Tm(II). Although Tm(II) solutions were described in the literature in the past [23,24], only recently has crystallographic evidence on the first molecular Tm(II) complex been reported in a collaborative study by the Bochkarev group and our laboratory [33]. $TmI_2(DME)_3$ can be made from TmI_3 and Tm in dimethoxyethane (DME) (Eq. (11)) and material formed in this way provided single crystals suitable for X-ray crystallography.

$$2\,Tm + 3\,I_2 \xrightarrow{DME} 2\,TmI_3(DME)_x + Tm \xrightarrow{DME} 3$$



$TmI_2(DME)_3$ (11)

The pentagonal bipyramidal coordination environment around Tm(II) with axial iodide ligands is very similiar to that of solvated SmI_2 analogs [34,35] and the bond distances are just as expected for Tm(II). The Tm(II) reagent is also similar to $SmI_2(THF)_x$ ($x = 2$ as a powder [16] and $x = 5$ as single crystals [34]) in that it exists in a less solvated form as a powder, $TmI_2(DME)_2$ [35].

Preliminary reactivity studies show that $TmI_2(DME)_x$ is highly reactive [35,36]. DME appears to be crucial to its isolation and formation of even simply related Tm(II) derivatives has proven challenging. However, as control is gained over this compound, it has the potential for exceptional chemistry. There is precedent for this situation in the history of Sm(II) chemistry. The organometallic chemistry of this oxidation state initially seemed to be experimentally difficult, but the problems were subsequently overcome.

2.1.2. Alkali metal reduced $[C_5H_3R_2]_3Ln$ complexes

A recent series of papers by Lappert and coworkers have reported on the reductive chemistry arising from potassium and lithium reduction of two types of substituted tris(cyclopentadienyl) lanthanide complexes, $[C_5H_3(SiMe_3)_2]_3Ln$ and $[C_5H_3(CMe_3)_2]_3Ln$ [37–39]. Initial studies with Ce and Nd complexes led to some unusual chemistry, most notably C–O cleavage in dimethoxyethane. In both cases, the formation of transient divalent '$[C_5H_3R_2]_2Ln$' complexes was proposed (Eqs. (12)–(14)) [37].

$$
\begin{aligned}
&2(C_5H_3R_2)_3Ce + 2Li \xrightarrow{\text{DME}} 2[Li(DME)_x][(C_5H_3R_2)_3Ce]\\
&\rightarrow 2Li(C_5H_3R_2) + 2\text{'}(C_5H_3R_2)_2Ce\text{'} \xrightarrow{\text{DME}} [(C_5H_3R_2)_2Ce(OMe)]_2\\
&\qquad R = CMe_3,\ SiMe_3 \qquad (12)
\end{aligned}
$$

$$
\begin{aligned}
&2[C_5H_3(SiMe_3)_2]_3Nd + 2K \xrightarrow{\text{DME}} 2[K(DME)_x]\{[C_5H_3(SiMe_3)_2]_3Nd\}\\
&\rightarrow 2K[C_5H_3(SiMe_3)_2] + 2\text{'}[C_5H_3(SiMe_3)_2]_2Nd\text{'} \xrightarrow{\text{DME}} \{[C_5H_3(SiMe_3)_2]_2Nd(OMe)\}_2 \qquad (13)
\end{aligned}
$$

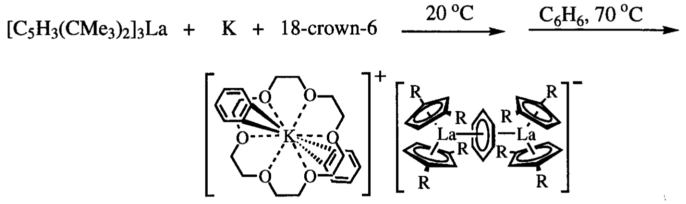
$$
\begin{aligned}
&[C_5H_3(SiMe_3)_2]_3Nd + Li \rightarrow [Li(DME)_x]\{[C_5H_3(SiMe_3)_2]_3Nd\}\\
&\qquad \rightarrow Li[C_5H_3(SiMe_3)_2] + \text{'}[C_5H_3(SiMe_3)_2]_2Nd\text{'}\\
&\qquad \rightarrow \{[C_5H_3(SiMe_3)_2]_2Nd(OMe)_2Li(DME) \qquad (14)
\end{aligned}
$$

It is interesting to note that the first organometallic Sm(II) complex, $[(C_5H_5)_2Sm(THF)]_n$, was made similarly by potassium reduction of a tris(cyclopentadienyl) complex (Eq. (15)) [40].

$$(C_5H_5)_3Sm + K/\text{naphthalene} \rightarrow [(C_5H_5)_2Sm(THF)]_n \qquad (15)$$

Although the divalent product could be isolated in this Sm(II) case, its insolubility detracted from its development until many years later [41]. Just as the introduction of substituents on the cyclopentadienyl ring opened up Sm(II) organometallic chemistry [3,11], the reduction of more soluble $[C_5H_3R_2]_3Ln$ complexes in Eqs. (12)–(14) has led to new chemistry.

Subsequent studies by the Lappert group focused on the $4f^0$ La(III) starting material since the spectroscopic and magnetic interpretations should be less complicated. In addition to C–O cleavage in dimethoxyethane, EPR and electrochemical evidence for La(II) were presented [38] as well as a crystal structure of a 'subvalent organolanthanum compound' obtained from benzene at 70°C (Eq. (16)) [39].



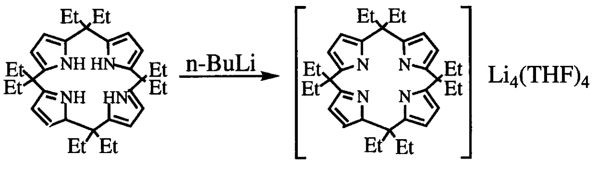
(16)

This complex was described as 'a salt containing as anion two $[C_5H_3(CMe_3)_2]_2La(II)$ moieties bridged by an η^6-benzenide monoanionic ligand'. This formulation was considered more plausible than 'two $[C_5H_3(CMe_3)_2]_2La(III)$ moieties bridged by an $[\eta^6\text{-}C_6H_6]^{3-}$'. The fact that a complex containing such highly reactive components has this thermal stability is encouraging in terms of making other compounds of this type.

Comparison of the Ln(III)/Ln(II) reduction potentials for La, Ce, and Nd with the others in Table 1 shows that if one can make isolable soluble molecular divalent complexes of lanthanum, it should be possible in terms of reduction potentials to make divalent complexes of many of the other lanthanides. The chemistry of the $(C_5R_5)_3Ln/K$ reaction system is just being developed and should strongly influence new reductive reactivity with the lanthanides in the near future.

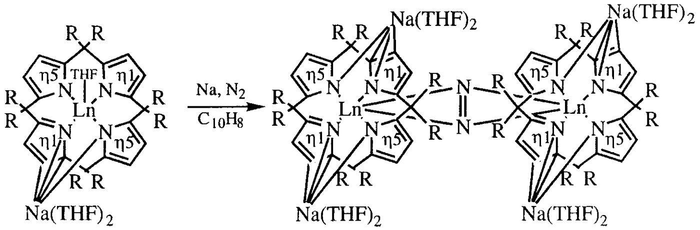
2.1.3. Alkali metal reduced lanthanide porphyrinogen complexes

Alkali metal reduction of trivalent lanthanide complexes of a much different ligand system, the tetraanions derived from octaalkylporphyrinogens (also called R_8-calix-pyrroles) (Scheme 1) [42], by the groups of Floriani and Gambarotta also suggests new avenues for reductive lanthanide chemistry. Floriani has reported that reduction of Pr(III) and Nd(III) porphyrinogen complexes by sodium in the presence of naphthalene under nitrogen led to the formation of new complexes of reduced dinitrogen (Eq. (17)) (Ln = Pr, Nd; R = Et) [43].



"$LLi_4(THF)_4$"

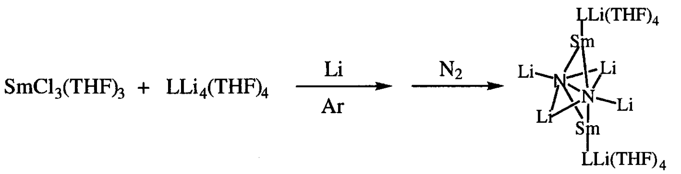
Scheme 1.



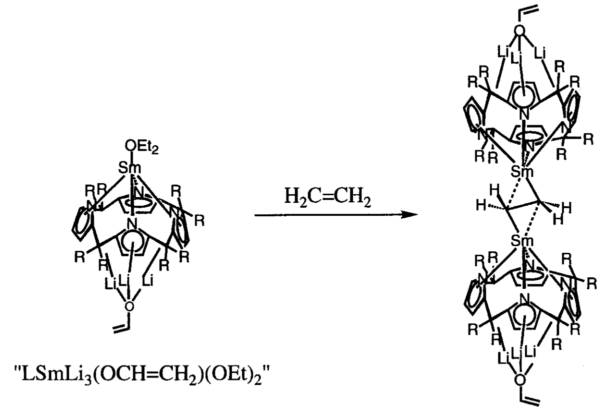
"$LLnNa(THF)_3$" (17)

Although no low valent complexes were specifically cited in this study, the results raise interesting questions about the order and pathway of the movement of the electrons from the alkali metal to dinitrogen. The degree of metal and ligand involvement and the intermediacy of possible divalent states in these heteropolymetallic systems remain to be revealed.

Gambarotta has examined lithium reduction of Sm(III) complexes of these ligands. Although these reactions apparently involve Sm(II) at some stage, the sequence of reduction and the role of the alkali metal again is intriguing. Unusual mixed metal Sm/Li complexes of dinitrogen [44] and ethylene [45] are isolated as shown in Eqs. (18)–(19).



(18)

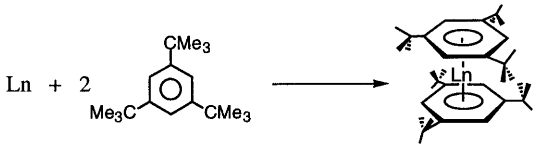


(19)

The fact that these reactions are apparently very sensitive to distant substitution on the tetrapyrrole periphery (the R groups and $(OCH=CH_2)^-$ versus halide) suggests that there may be many options to vary this chemistry via the ligand system.

2.1.4. *Bis(tri-tert-butylbenzene) lanthanide complexes*

It is also appropriate to include in this discussion the formally zero valent bis(arene) lanthanide complexes discovered by Cloke and coworkers in 1987 [46–48], since this is another area which has considerable potential for future development in reductive lanthanide chemistry. Metal atom reactions between 1,3,5-tris(*tert*-butyl)benzene and Nd, Gd, Tb, Dy, Ho, Y, Er, and Lu were found to give isolable, crystallographically characterizable (Gd, Ho, Y) bis(arene) complexes as shown in Eq. (20).



(20)

Earlier metal vapor work with the lanthanides and organic substrates had demonstrated that unusual materials could be generated by metal vapor reactions [10,49], but crystallographic evidence on the identity of these compounds was lacking. The tris(*tert*-butyl)benzene ligand allowed structural data to be obtained. The structures of the $Ln[\eta^6\text{-}C_6H_3(CMe_3)_3]_2$ complexes (Eq. (20)), showed that the two rings are arranged in a staggered arrangement with two of the three methyl groups on each *tert*-butyl group oriented between the rings. This provides a structure in which the metal was protected on the top and bottom by arene rings and on the sides by twelve methyl groups arranged to maximize the steric encapsulation of the metal [46].

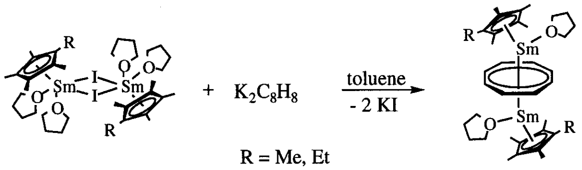
Interestingly, the metals for which room temperature stable bis(arene) complexes could be obtained are complementary to the metals which form the most stable divalent states. Hence, Eu, Yb, and Tm bis(arene) complexes were not isolable and the Sm complex decomposed above −30°C. Also difficult to form in this series were the larger metals La (decomposes above 0°C), Ce (unisolable), and Pr (decomposes above 40°C). Hence, development of new reductive lanthanide chemistry via the known bis(arene) complexes would focus on the metals which have not been developed by the other means described in the sections above.

To date the chemistry of the bis(arene) lanthanide complexes has primarily involved direct conversion to known types of trivalent complexes and a future challenge is to use these unusual compounds to do heretofore unknown types of lanthanide reduction chemistry. It is encouraging along these lines to note that these bis(arene) complexes can initiate ethylene polymerization [47].

2.1.5. Multi-electron reductions from bridged divalent complexes

One of the limitations attributed to the lanthanide metals is that their redox chemistry involves only one-electron processes. Hence, it has been suggested that the two-electron oxidative addition and reductive elimination reactions common for transition metals are unavailable for the f elements [50]. In fact, the $(C_5Me_5)_2Sm(THF)_y$ complexes ($y = 0, 1, 2$) are often involved in two-electron reductions by virtue of the fact that two equivalents of the one-electron reductants are involved in the reaction (e.g. Eqs. (6)–(7)) [3,19,21,22]. However, recently some strongly reducing bimetallic Sm(II) complexes have been isolated which demonstrate the potential to do two-electron reductions with a single molecular species [51]. This provides another new avenue for reductive lanthanide chemistry and synthetic access to new types of highly reactive intermediates.

The bimetallic cyclooctatetraenyl-bridged complexes $[(C_5Me_4R)Sm(THF)]_2(\mu\text{-}C_8H_8)$ (R = Me, Et), are readily prepared from $[(C_5Me_4R)Sm(\mu\text{-}I)(THF)_2]_2$ [15] and $K_2C_8H_8$ (Eq. (21)). These complexes can be easily desolvated to make a new series of bimetallic bent metallocenes (Eq. (22) [51]).



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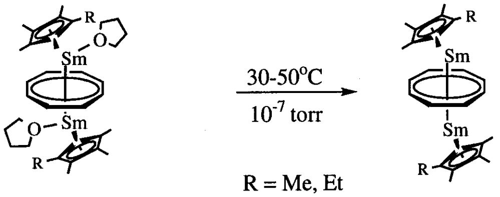
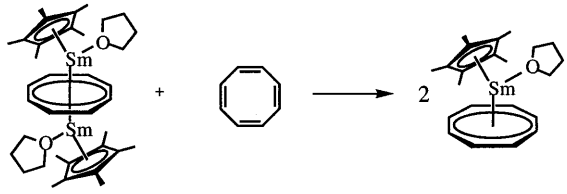
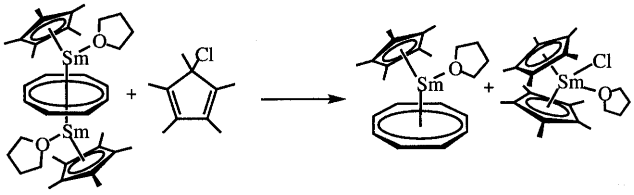


(22)

These compounds provide two electrons to substrates and in reactions studied to date with $[(C_5Me_5)Sm(THF)_z]_2(\mu\text{-}C_8H_8)$ ($z = 0, 1$), generate $(C_5Me_5)Sm(C_8H_8)(THF)_z$ complexes as by-products (e.g. Eqs. (23)–(24)).



(23)



(24)

The formation of the $(C_5Me_5)Sm(C_8H_8)(THF)_z$ by-products in the $[(C_5Me_5)Sm(THF)_z]_2(\mu\text{-}C_8H_8)$ reactions leaves as the remainder the $[(C_5Me_5)Sm(THF)]^{2+}$ or $[(C_5Me_5)Sm]^{2+}$ ions. These are the species which bind the substrate which has been reduced by two electrons. Monocyclopentadienyl moieties of this type are rare in lanthanide chemistry [1–3] and these bimetallic complexes provide a route to access them. Interestingly, since the reaction puts a $[(C_5Me_5)Sm(THF)_z]^{2+}$ unit and two electrons together with the substrate, the net reaction is formally equivalent to a two-electron oxidation addition of the substrate to a $(C_5Me_5)Sm(THF)_z$ moiety. The analogous M(I)/M(III) redox reaction is shown in Eq. (25).

$$M^I + C_5Me_5Cl \rightarrow (C_5Me_5)M^{III}Cl \qquad (25)$$

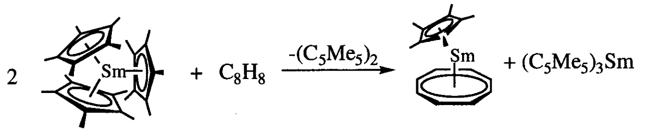
The formation of the $(C_5Me_5)_2SmCl(THF)$ product in Eq. (24) is formally similar, but that reaction proceeds through two one-electron redox couples and Sm(II) ions not via Sm(I). The mechanism and sequence of electron transfer from the two separated Sm(II) ions in the $[(C_5Me_5)Sm(THF)_z]_2(\mu\text{-}C_8H_8)$ complexes to the substrate and the role of the bridging $(C_8H_8)^{2-}$ ligand in the reduction remain to be defined.

However, it is clear that the $(C_8H_8)^{2-}$ ion can bridge two Sm(II) ions and form a bimetallic two-electron reductant equivalent to two $(C_5Me_5)_2Sm(THF)_y$ complexes. More generally, this points the way to multi-electron reductions with polymetallic divalent compounds as they become synthetically available [52,53].

2.2. Sterically induced reduction

2.2.1. Reduction chemistry of trivalent $(C_5Me_5)_3Sm$

Recently, a new approach to reductive lanthanide chemistry was discovered when it was found that the trivalent lanthanide complex $(C_5Me_5)_3Sm$ [54,55] had reductive reactivity [56] similar to that of the divalent complex $(C_5Me_5)_2Sm$ [3,18]. This unusual reactivity was observed in several sets of parallel reactions (Eqs. (26)–(27) [54]; Eqs. (28)–(29) [57]; Eqs. (30)–(31) [58]) 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*-butylisocyanide [56].



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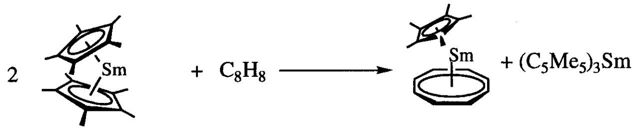

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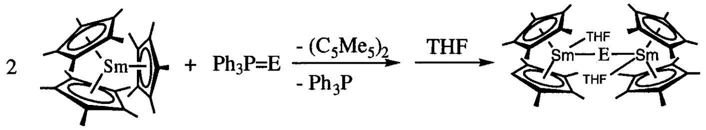

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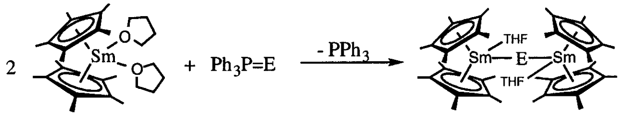


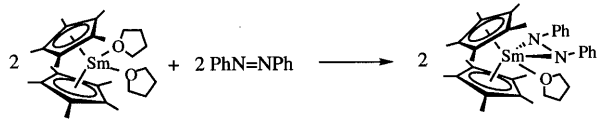
(29)

$$3(C_5Me_5)_3Sm + 6Me_3CNC \xrightarrow{-3/2\ (C_5Me_5)_2} [(C_5Me_5)_2Sm(\mu\text{-}CN)(CNCMe_3)]_3 \tag{30}$$

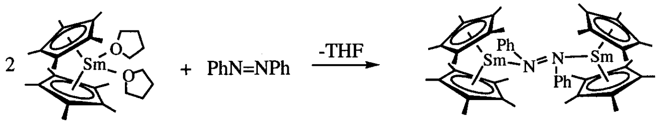
$$3(C_5Me_5)_2Sm + 6Me_3CNC \rightarrow [(C_5Me_5)_2Sm(\mu\text{-}CN)(CNCMe_3)]_3 \tag{31}$$

The reductions of PhN=NPh (Eq. (32)–(34)) showed that $(C_5Me_5)_3Sm$ was not quite as strong a reductant as $(C_5Me_5)_2Sm(THF)_2$. $(C_5Me_5)_3Sm$ reduces azobenzene by one electron (Eq. (32)) [56] whereas the divalent reagent can effect both a one-electron reduction [59] and a two-electron reduction [60] depending on the reaction stoichiometry (Eqs. (33)–(34)).

$$(C_5Me_5)_3Sm + PhN{=}NPh \xrightarrow{-1/2\ (C_5Me_5)_2} (C_5Me_5)_2Sm(Ph_2N_2) \tag{32}$$



(33)



(34)

How does trivalent $(C_5Me_5)_3Sm$ accomplish reduction chemistry? The $(C_5Me_5)_2$ by-product is consistent with a pathway involving a $(C_5Me_5)/(C_5Me_5)^-$ redox couple. The half reaction for reduction by trivalent $(C_5Me_5)_3Sm$ is given in Eq. (35). In comparison, the conventional Sm(II) half reaction for $(C_5Me_5)_2Sm$ is given in Eq. (36).

$$(C_5Me_5)_2Sm \rightarrow e^- + [(C_5Me_5)_2Sm]^+ \tag{35}$$

$$(C_5Me_5)_3Sm \rightarrow e^- + [(C_5Me_5)_2Sm]^+ + 1/2(C_5Me_5)_2 \tag{36}$$

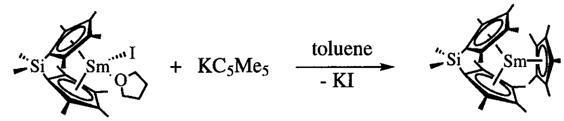
The $(C_5Me_5)_3Sm$ and $(C_5Me_5)_2Sm$ reductions give the same organosamarium products because in both cases the organosamarium cation in each of the half reactions is the same, $[(C_5Me_5)_2Sm]^+$.

The origin of the surprising reductive chemistry of trivalent $(C_5Me_5)_3Sm$ can be rationalized by considering 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. Hence, the isolation of $(C_5Me_5)_3Sm$ was surprising [54]. The crystal structure of $(C_5Me_5)_3Sm$ revealed the largest $Sm{-}C(C_5Me_5)$ distances observed to date in an organosamarium complex. 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. As a result, it is apparently favorable for one of the $(C_5Me_5)^-$ rings to do reductive chemistry.

Comparable reductive reactivity has not been observed with any of the other many classes of tris(cyclopentadienyl)lanthanide complexes, $(C_5R_5)_3Ln$, reported in the past in which there is no significant steric crowding [1]. These complexes have conventional bond distances 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. (28) is not found with KC_5Me_5, $(C_5Me_5)MgCl$, or $(C_5Me_5)_2Pb$. However, it is known that NaC_5Me_5 can reduce Eu(III) to Eu(II) as shown in Eq. (37) [61]. This is in part related to the facile formation of Eu(II) (see Table 1).

$$EuCl_3 + 3NaC_5Me_5 \xrightarrow{THF} (C_5Me_5)_2Eu(THF) \tag{37}$$

One way to evaluate the idea that this reductive chemistry was coupled to steric crowding was to synthesize a complex very similar to $(C_5Me_5)_3Sm$ which had somewhat less steric crowding. This was accomplished by assembling the ansa complex, $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$, shown in Eq. (38) [62].



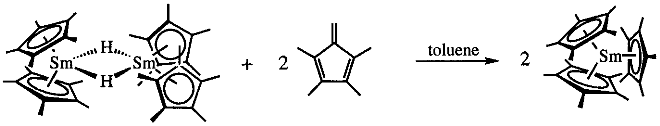
(38)

Since the Me_2Si bridge in *ansa* complexes reduces the (ring centroid)–metal–(ring centroid) angle in metallocenes compared to a $(C_5Me_5)_2$ ligand set, the *ansa* complex was slightly less crowded than $(C_5Me_5)_3Sm$. The Sm–C(C_5Me_5) distances in this complex were consistent with less steric crowding in that they were in the normal range. As expected, the *ansa* complex showed none of the reductive chemistry of $(C_5Me_5)_3Sm$, a result which supported the concept of sterically induced reductive chemistry.

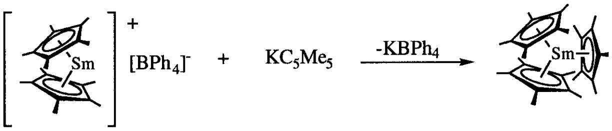
2.2.2. Reduction chemistry of trivalent $(C_5Me_5)_3Nd$

Although the reductive reactivity of $(C_5Me_5)_3Sm$ seemed to arise from a sterically crowded $(C_5Me_5)^-$ ligand, there was always a possibility that an undetected Sm(II) intermediate was causing the reduction. For example, homolytic cleavage of a Sm–(C_5Me_5) bond to form $(C_5Me_5)^\cdot$ and $(C_5Me_5)_2Sm$ would lead to reductive chemistry from Sm(II) and the observed $(C_5Me_5)_2$ by-product from radical coupling. This seemed unlikely since $(C_5Me_5)_3Sm$ was less strongly reducing than $(C_5Me_5)_2Sm$ with Ph=NNPh as shown above in Eq. (32)–(34). However, it was desirable to demonstrate that this sterically induced reduction reactivity could occur with a $(C_5Me_5)_3Ln$ complex which did not have a divalent state as accessible as Sm(II).

Since the first two syntheses of $(C_5Me_5)_3Sm$ relied on Sm(II) precursors [54,55], it was necessary to develop some new syntheses to obtain a $(C_5Me_5)_3Ln$ complex in which Ln was not Sm. Two new syntheses of $(C_5Me_5)_3Sm$ were developed which started with trivalent precursors (Eqs. (39)–(40)) [63,64] and the latter was used to obtain crystallographically characterizable $(C_5Me_5)_3Nd$ in good yield [64].



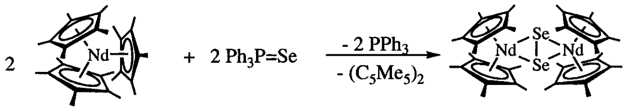
(39)



(40)

Once $(C_5Me_5)_3Nd$ was obtained, the necessary comparative chemistry with a lanthanide other than samarium could be done. As discussed below, this has broadened the scope of this sterically induced reductive chemistry even further.

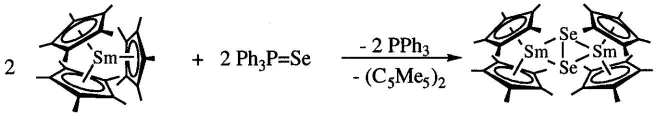
It was found that $(C_5Me_5)_3Nd$ does react as a reductant with Se=PPh_3 and forms the expected by-products, PPh_3 and $(C_5Me_5)_2$ [65]. Hence, the concept that sterically crowded $(C_5Me_5)_3Ln$ complexes can be reductants and do not require Ln=Sm was validated. However, the selenium product isolated from the neodymium reaction (Eq. (41)) was different from that isolated from the samarium reaction (Eq. (28))!



(41)

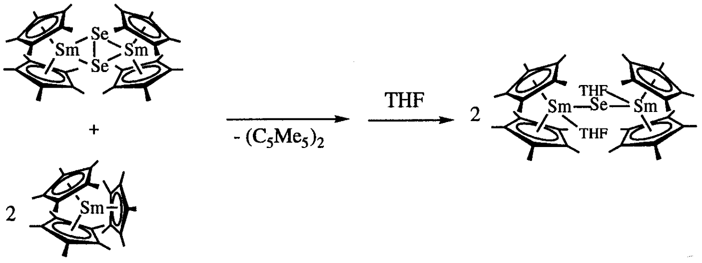
Instead of reduction of Se=PPh_3 to $(Se)^{2-}$ as found in Eq. (28), a $(Se_2)^{2-}$ product was formed in Eq. (41). Excess $(C_5Me_5)_3Nd$ would not reduce the $(Se_2)^{2-}$ product further. This suggested that $(C_5Me_5)_3Nd$ was not as strong a reductant as $(C_5Me_5)_3Sm$ since selenium was reduced to a formal -1 oxidation state with Nd instead of a -2 oxidation state with Sm.

The weaker reduction capacity of the Nd complex could be rationalized by the fact that Nd is larger than Sm and hence $(C_5Me_5)_3Nd$ is 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. (42)), instead of the 2:1 stoichiometry used in Eq. (28). As shown in Eq. (42), $(C_5Me_5)_3Sm$ does form the $(Se_2)^{2-}$ product analogous to the Nd complex under these conditions.



(42)

Moreover, it was subsequently shown that $(C_5Me_5)_3Sm$ would reduce the $(Se_2)^{2-}$ product to the Se^{2-} product (Eq. (43)), i.e. Eq. (28) could be done stepwise by $(C_5Me_5)_3Sm$.



(43)

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 to the divalent $(C_5Me_5)_2Sm(THF)_y$ complexes: as shown in Eqs. (33)–(34), $(C_5Me_5)_2Sm(THF)_2$ can reduce some substrates by one or two electrons depending on the stoichiometry.

2.2.3. Implications of $(C_5Me_5)_3Ln$ reduction chemistry

The fact that trivalent $(C_5Me_5)_3Sm$ and $(C_5Me_5)_3Nd$ can do one-electron reduction chemistry analogous to that of the divalent $(C_5Me_5)_2Sm$ suggests that the special one-electron reduction chemistry of Sm(II) can be extended to lanthanides beyond those with accessible divalent states if suitably crowded complexes can be synthesized. Hence, *it should be possible to transform all of the lanthanides into one-electron reductants if the appropriate degree of steric crowding is achieved.*

Extension of samarium-like reduction chemistry to the other lanthanides would be quite valuable for several reasons. First, it would allow size optimization in reductive chemistry. As described in the introduction, this has not been possible with just Eu, Yb, and Sm. By picking the lanthanide of just the proper size to optimize a specific reduction, selectivity can be enhanced beyond what is possible with samarium. In addition, since $(C_5Me_5)_3Sm$ appears to be a stronger reductant than $(C_5Me_5)_3Nd$, it appears that the reduction potential can be optimized within a sterically crowded series as a function of the degree of steric crowding and the metal size. Second, this allows optimization of physical properties in classes of complexes previously only available for samarium. Various lanthanides have unique magnetic, electronic, and optical properties, but syntheses of complexes of most of these ions depended previously only on non-redox reactions of trivalent precursors. The reductive approach which has formed so many types of $[(C_5Me_5)_2Sm]_2$(substrate) and $(C_5Me_5)_2$Sm(substrate-substrate)$Sm(C_5Me_5)_2$ complexes for samarium can now be extended to the other elements. Third, we anticipate that investigation of the reductive chemistry of other $(C_5Me_5)_3Ln$ complexes of metals will lead to new classes of lanthanide metallocene complexes as demonstrated by the syntheses of $[(C_5Me_5)_2Nd]_2Se_2$ and $[(C_5Me_5)_2Sm]_2Se_2$, complexes which were previously unknown and inaccessible via traditional divalent reductive chemistry.

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 four separate syntheses of $(C_5Me_5)_3Sm$ [54,55,63,64], the molecule that was thought to be too crowded to exist. Synthesis of the sterically crowded molecules will require careful manipulation of the ligand size. For metals larger than Nd, ligands slightly larger than C_5Me_5 may be needed, e.g. C_5Me_4Et. For the smaller metals in the lanthanide series, smaller ligands or a combination of smaller ligands may be necessary to isolate $(C_5R_5)_3Ln$ or the equivalent molecules.

Homoleptic $(C_5R_5)_3Ln$ compounds are not the only complexes that could have this sterically induced reduction chemistry. Complexes of general formula (large ligand)$_2$Ln(C_5Me_5) could have the same chemistry or even complexes such as (large ligand)$_3$Ln if that ligand will do reduction as is found with $(C_5Me_5)^-$. Examination of the reductive chemistry of a range of sterically crowded molecules is clearly warranted to determine the importance of the $(C_5Me_5)^-$ ligand to this chemistry.

Ligands such as naphthalenide [66], anthracenide [67], $(Ph_4C_2)^{2-}$ [68], $(C_8H_8)^{2-}$ [69], and $(C_6H_6)^{n-}$ [39], all have the potential to act as reductants and could convey reductive chemistry on trivalent complexes without accessing a divalent state. The complexes most useful for such purposes may be those of general formula $(C_5Me_5)_2$Ln(reducing ligand)Ln$(C_5Me_5)_2$, since these will give rise to $[(C_5Me_5)_2Ln]^+$ cations. These cations will mimic $[(C_5Me_5)_2Sm]^+$, which is obtained from $(C_5Me_5)_2Sm$ reductions and which is known to stabilize a variety of complexes. The half reaction for these systems would then be that shown in Eq. (44).

$$[(C_5Me_5)_2Ln]_2(\text{dianionic ligand}) \rightarrow 2e^- + 2[(C_5Me_5)_2Ln]^+ + \text{neutral ligand} \tag{44}$$

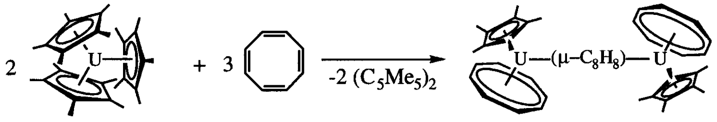
The alternative reducing ligands listed above are already known on lanthanide complexes and it remains then to put these on sterically crowded molecules to test this idea.

The results of the sterically induced reduction reactions of the $(C_5Me_5)_3Ln$ complexes raise the question of whether this type 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, this complex may have been so reactive via sterically induced reduction pathways that only a mixture of products was obtained. For example, attempted formation of $(C_5Me_5)_3Y$ via Eq. (40) gives a myriad of products (W.J. Evans, M.A. Johnston, unpublished results). Although the desired yttrium complex was not formed, this is not a ‘no reaction’ or ‘failed reaction’ system. 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 divalent reduction chemistry can be mimicked.

2.2.4. Three-electron reduction from a monometallic complex

If the sterically induced one-electron reduction chemistry of the $(C_5Me_5)_3Ln$ complexes could be coupled to a redox active metal reduction reaction, it seemed conceivable that two-electron reductions would be possible using a single monometallic compound. Synthesis of the uranium complex $(C_5Me_5)_3U$ [63] offered this opportunity, since it is sterically crowded enough to provide a one-electron reduction via a $(C_5Me_5)/(C_5Me_5)^-$ half reaction and also has a U^{IV}/U^{III} redox couple available. This complex is not a lanthanide complex, but it will be described here since it too points to a new way of doing f element reductive chemistry in the future.

The concept that $(C_5Me_5)_3U$ could be a two-electron reductant was tested with 1,3,5,7-cyclooctatetraene, C_8H_8. 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. The product expected from the sterically induced reduction reaction, $(C_5Me_5)_2$, was identified along with a U(IV) product identified as $[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$, by X-ray crystallography (Eq. (45)) [70].



(45)

Hence, both sterically induced reduction chemistry and a U(III) to U(IV) conversion occurred. However, examination of the final stoichiometry in Eq. (45) 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^{III} reduction. The net half reaction is shown in Eq. (46).

$$(C_5Me_5)_3U \rightarrow 3e^- + [(C_5Me_5)U]^{3+} + (C_5Me_5)_2 \qquad (46)$$

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.

3. Conclusion

The future of reductive lanthanide chemistry looks quite promising. Just as the more reactive Sm(II) chemistry initially developed slower than Eu(II) and Yb(II) chemistry, the even more reactive divalent lanthanides have required more time. However, progress is being made. A molecular Tm(II) precursor has been crystallographically confirmed and evidence for divalent complexes of the early metals La, Ce, Pr, and Nd has accumulated rapidly in the past few years. For many of these ions, the reductive divalent chemistry is intimately involved with alkali metal reductants, Li, Na, and K, sometimes in conjunction with additives such as naphthalene and 18-crown-6. In this respect, there are similarities to sterically induced reduction in which $(C_5Me_5)^-$ is the active reductant. In the alkali metal cases, the presence of the alkali metal complicates the analysis of the systems, but this does not detract from the fact that this approach provides opportunities for new lanthanide reductive reactivity.

Complementary to this list of early metal ions (La–Nd) and the ions with the smallest Ln(III)/Ln(II) reduction potentials (Eu, Yb, Sm, and Tm) is the list of ions which form formally zero valent bis(arene) complexes: Nd, Gd, Tb, Dy, Ho, Y, Er, and Lu. Since the bis(arene) complexes offer another route to reductive lanthanide chemistry and since these lists taken together cover all of the metals in the series (except radioactive promethium), there are low valent options for new reductive chemistry for all the of the metals beyond the traditional three Eu, Yb, and Sm reductants.

Beyond these low valent options, sterically induced reduction chemistry offers the possibility of doing reductive chemistry with all of the trivalent metals regardless of the stability of their lower oxidation states. This approach avoids the thermal instability which will be inherent with the more strongly reducing divalent ions which will not even tolerate common solvents. Since this approach should be readily applicable to all of the metals once the appropriate degree of steric crowding is established for each metal, the metal can be chosen not on the basis of the Table 1 reduction potential, but on the basis of need: the metal can be selected for its size/reactivity optimum, or its magnetic, electronic, or optical properties. In addition, a promising feature of the sterically induced reduction chemistry is that it appears to be tunable depending on the degree of steric crowding.

Although reductive lanthanide chemistry is poised for some great advances in the new millennium, it should be noted that these will not come without considerable synthetic effort. Taming the highly reducing oxidation states and controlling the alkali metal chemistry will not be easy, nor has it been easy to make complexes sterically crowded enough to do sterically induced reduction chemistry. Clever approaches will be needed to fully utilize these new aspects of reductive chemistry, but the results described here tell us that the chemistry is there to be developed.

Acknowledgements

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