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Mini review

Lanthanide(II) complexes bearing mixed linked and unlinked cyclopentadienyl–monodentate-anionic ligands

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Abstract

This paper is intended to provide an overview on recent progress in the chemistry of divalent lanthanide complexes bearing mixed (linked and unlinked) cyclopentadienyl–monodentate-anionic ligands. The synthesis, structures, and one-electron-transfer and polymerization reactions of these complexes are described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Divalent lanthanides; Metallocene complex; Mixed ligands; Monodentate-anion ligand; Polymerization; Reduction

1. Introduction

The organometallic chemistry of the lanthanides in low oxidation states has long been dominated by the metallocene complexes that bear two pentamethylcyclopentadienyl (C_5Me_5) ligands [1]. Attempts to extend the lanthanide organometallic chemistry beyond the traditional realm of the metallocene complexes have led to the synthesis and structural characterization of a number of lanthanide(II) complexes bearing various ligand systems, most of which are analogous to the metallocenes in that they all bear two identical ancillary ligands [2]. Reactivity comparison studies on these complexes have shown that the reactivity of a lanthanide(II) complex is strongly influenced by both the steric and the electronic properties of the ancillary ligands. The sterically demanding and electronically donating bis(pentamethylcyclopentadienyl) ligand set $(C_5Me_5)_2$ can offer excellent solubility, reducing power, and protection for the metal center, which, for example, has enabled the samarocene(II) complex $(C_5Me_5)_2Sm(thf)_x$ ($x = 0$ or 2) to activate small molecules such as N_2 [3], CO [4], or CO_2 [5]. However, the steric bulkiness of the $(C_5Me_5)_2$ ligand set could, on the other hand, become a drawback particularly in catalytic reactions involving sterically demanding substrates. Thus $(C_5Me_5)_2Sm(thf)_x$ ($x = 0$ or 2) can polymerize ethylene, but cannot polymerize styrene or dienes owing to steric hindrance [6]. In contrast, heteroatom-containing monodentate-anionic ligands such as aryloxide, silylamide, and thiolate are less sterically demanding and more flexible than C_5Me_5, but the electron-donating power of these ligands is not strong enough to enable the Ln(II) center to transfer an electron to an unactivated olefin monomer.

In principle, the mixed C_5Me_5–monodentate-anionic ligand systems should offer a sterically and electronically unique environment for the lanthanide(II) center. The combination of the strong electron-donating ability of C_5Me_5 (which is important for a Ln(II) complex to initiate a reaction) and the good flexibility of a monodentate-anionic ligand (which is important for a catalytic process) would create a new (catalytic) system that is different from the homoleptic analogs. Toward this end, several types of such mixed-ligand-supported lanthanide(II) complexes have been recently synthesized and have had their reactivity studied. Here we wish to make an overview on the progress in this field.

2. Synthesis and structures of lanthanide(II) complexes with mixed C_5Me_5–monodentate-anionic ligands

The mono(pentamethylcyclopentadienyl)lanthanide(II) iodide complexes $[(C_5Me_5)Ln(\mu\text{-}I)(thf)_2]_2$ (Ln = Sm

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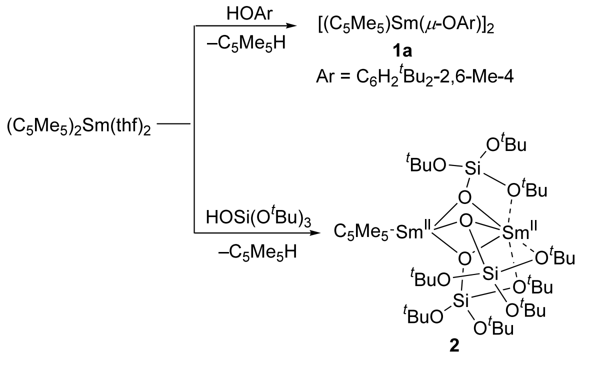
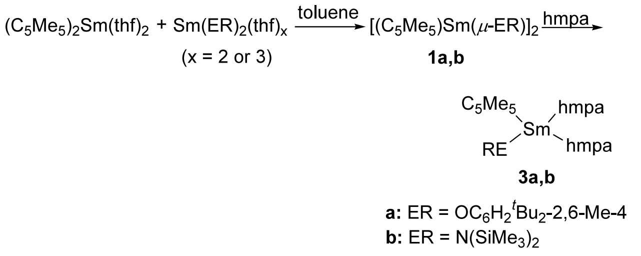
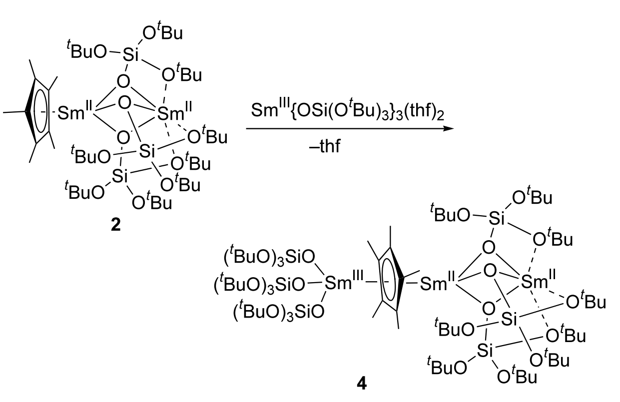
[7a] or Yb [7b]) could be obtained by reaction of LnI_2 with one equivalent of MC_5Me_5 (M = Na or K) or $(C_5Me_5)_2Ln(thf)_2$. These complexes usually adopt a dimeric structure when in solid state, but exist in equilibrium with other species in THF solution [7]. In contrast, the reaction of the more sterically demanding $LiC_5Me_4SiMe_2^tBu$ with one equivalent of YbI_2 afforded the hexanuclear Yb(II) species $\{Yb_6(C_5Me_4SiMe_2^tBu)_6I_8\}\{Li(thf)_4\}_2$ [7b]. Derivation of other mono(cyclopentadienyl)lanthanide(II) complexes from these iodide complexes has not been reported. Formation of the (pentamethylcyclopentadienyl)ytterbium(II) stannyl complex $(C_5Me_5)Yb\{Sn(CH_2^tBu)_3\}(thf)_2$ was observed in an NMR tube reaction between $Yb\{Sn(CH_2^tBu)_3\}_2(thf)_2$ and one equivalent of C_5Me_5H, but it was not clear whether this complex was isolable [8].



Scheme 1.



Scheme 2.



Scheme 3.

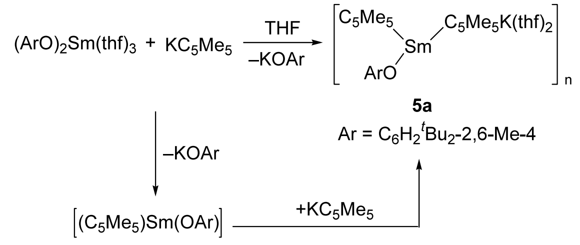
The C_5Me_5–OAr-ligated samarium(II) complex **1a** was first obtained by partial protonation of $(C_5Me_5)_2Sm(thf)_2$ with one equivalent of HOAr (Ar = $C_6H_2^tBu_2$-2,6-Me-4) in toluene (Scheme 1) [9]. This complex adopts a dimeric structure via μ-OAr bridges as shown by X-ray analysis. Analogous protonation of $(C_5Me_5)_2Sm(thf)_2$ with $HOSi(O^tBu)_3$ yielded the unsymmetrical binuclear Sm(II) complex **2**, which contains one terminal C_5Me_5 and three bridging $OSi(O^tBu)_3$ ligands (Scheme 1) [10]. Complex **2** could formally be viewed as a combination of the mixed ligand complex '$(C_5Me_5)Sm\{OSi(O^tBu)_3\}$' and the bis(siloxide) complex '$Sm\{OSi(O^tBu)_3\}_2$'.

Complex **1a** could also be synthesized by reaction of $(C_5Me_5)_2Sm(thf)_2$ with one equivalent of $Sm(OAr)_2(thf)_3$ in toluene (Scheme 2) [9]. Similar reaction of $(C_5Me_5)_2Sm(thf)_2$ with $Sm\{N(SiMe_3)_2\}_2(thf)_2$ afforded the $N(SiMe_3)_2$ analog **1b** [11]. These heteroleptic, dimeric complexes **1a**,**b** were stable in toluene, but existed in an equilibrium with $(C_5Me_5)_2Sm(thf)_2$ and $Sm(ER)_2(thf)_x$ (ER = OAr or $N(SiMe_3)_2$) in THF. Addition of two equivalents of hexamethylphosphoric triamide (hmpa) to **1a**,**b** in THF, however, afforded in high yield the hmpa-coordinated, monomeric complexes **3a**,**b**, respectively (Scheme 2) [9,12].

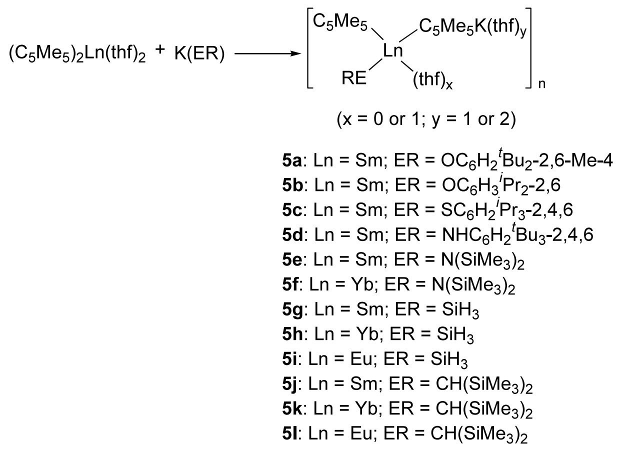
The siloxide complex **2** was stable both in toluene and in THF, but reacted with hmpa in THF to give the monomeric complex $(C_5Me_5)Sm\{OSi(O^tBu)_3\}(hmpa)_2$ as the only isolable product [10]. It is also noteworthy that **2** could act as a neutral coordination ligand through the C_5Me_5 unit. The reaction of **2** with $Sm\{OSi(O^tBu)_3\}_3(thf)_2$ yielded the inverse sandwich Sm(III)–Sm(II) trinuclear complex **4**, showing that the coordination of **2** to the Sm(III) center is stronger than that of THF (Scheme 3).

An attempt to synthesize **1a** by the metathetical reaction of $Sm(OAr)_2(thf)_3$ with one equivalent of KC_5Me_5 yielded the unexpected product **5a**, which could be viewed as a C_5Me_5–OAr-ligated Sm(II) complex coordinated by the neutral '$(C_5Me_5)K(thf)_2$' ligand (Scheme 4) [9]. In fact, addition of two equivalents of KC_5Me_5 to a THF solution of **1a** did give **5a** in almost quantitative yield.

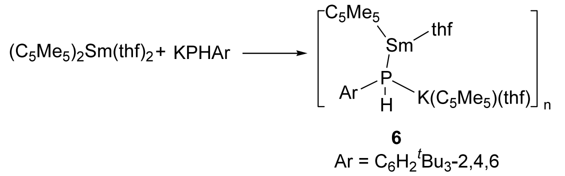
The most efficient route to **5a** is the reaction of $(C_5Me_5)_2Sm(thf)_2$ with one equivalent of KOAr. This route could be successfully extended to the synthesis of the analogous thiolate (**5c**) [12], amide (**5e**–**f**) [12], silyl (**5g**–**i**) [13], and alkyl (**5j**–**l**) [14] lanthanide(II) complexes as shown in Scheme 5. Complexes **5a**–**l** all adopt a similar polymeric structure via 'intermolecular' interactions between the K atom and a C_5Me_5 ligand. Reaction of **5a**,**e** with two equivalents of hmpa (per Sm) in THF afforded the corresponding hmpa-coordinated, monomeric complexes **3a**,**b**, respectively, showing that the 'C_5Me_5K' ligand in this type of complexes could be replaced by an appropriate coordinative ligand.



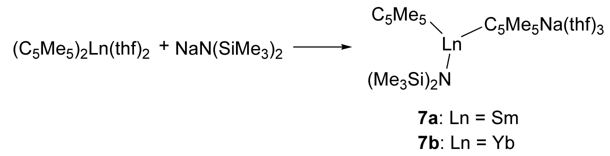
Scheme 4.



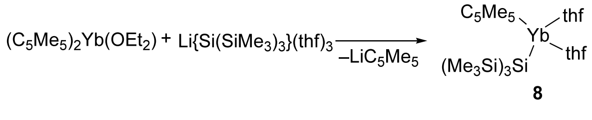
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

The analogous reaction of $(C_5Me_5)_2Sm(thf)_2$ with one equivalent of KPHAr (Ar = $C_6H_2^tBu_3$-2,4,6) afforded the phosphide complex **6** (Scheme 6) [12]. In contrast with **5a**–**l**, in which the 'C_5Me_5K' unit is bonded to the Ln(II) center with the C_5Me_5 part, the 'C_5Me_5K' unit in **6** is bonded to the phosphide site with its K atom, probably owing to the stronger electron-donating ability of the phosphide ligand.

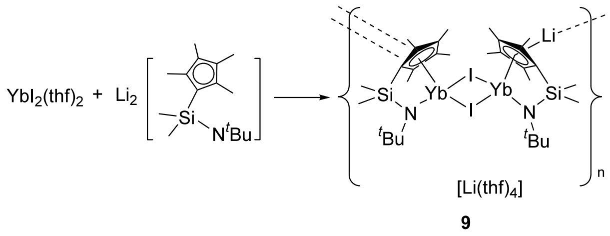
'C_5Me_5Na' could also act as a stabilizing ligand for the C_5Me_5–$N(SiMe_3)_2$-ligated lanthanide(II) complexes. The use of $NaN(SiMe_3)_2$ in place of $KN(SiMe_3)_2$ in the reactions with $(C_5Me_5)_2Ln(thf)_2$ afforded the '$C_5Me_5Na(thf)_3$'-coordinated Ln(II) complexes **7a** (Ln = Sm) and **7b** (Ln = Yb), respectively (Scheme 7) [12]. In contrast with the 'C_5Me_5K'-coordinated complexes **5a**–**l**, which adopt a polymeric structure through 'intermolecular' K···C_5Me_5 interactions, the 'C_5Me_5-Na'-coordinated complexes **7a**,**b** adopt a 'monomeric' form owing to coordination of more (three) THF ligands to the Na atom.

The reaction of $(C_5Me_5)_2Yb(OEt_2)$ with one equivalent of $Li\{Si(SiMe_3)_3\}(thf)_3$ in toluene gave the monomeric, mixed ligand complex **8**, with release of LiC_5Me_5 (Scheme 8) [15]. This reaction contrasts with those described above for the formation of the 'C_5Me_5M'-coordinated complexes **5**–**7** (M = K or Na).

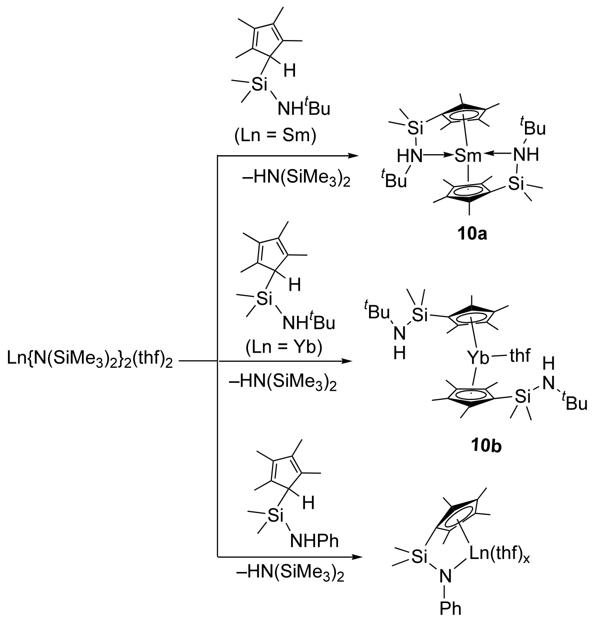
3. Synthesis and structures of lanthanide(II) complexes with silylene-linked C_5Me_4-amido or -siloxo ligands

As described above, lanthanide(II) complexes bearing mixed cyclopentadienyl–monodentae-anionic ligands often suffer from ligand redistribution problem. One way to solve this problem could be linking of the two ligands. It is well known that the silylene-linked cyclopentadienyl-amido unit $[Me_2Si(C_5Me_4)N^tBu]^{2-}$ acts as a useful ancillary ligand for Group 4 metals and the lanthanides in +3 oxidation state [16]. Attempts to apply this ligand to the synthesis of analogous lanthanide(II) complexes were, however, unsuccessful. The reaction between $SmI_2(thf)_2$ and $Li_2[Me_2Si(C_5Me_4)$-$N^tBu]$ yielded an unidentified yellow, possibly Sm(III) compound, while the similar reaction with $YbI_2(thf)_2$ led to incorporation of LiI into the Yb(II) product (**9**) (Scheme 9) [17,18]. The acid–base reactions between $Ln\{N(SiMe_3)_2\}_2(thf)_2$ (Ln = Sm, Yb) and (C_5Me_4H)-$SiMe_2NH^tBu$ resulted in metallation only at the cyclopentadienyl unit, affording the metallocene complexes **10a** and **10b**, respectively (Scheme 10) [17,18].

The use of the more protonic aniline derivatives such as $(C_5Me_4H)SiMe_2NHPh$ to react with $Ln\{N(SiMe_3)_2\}_2$-

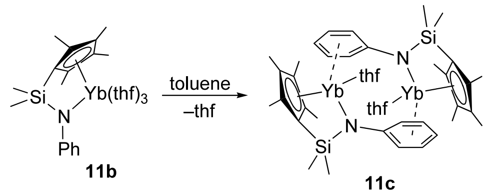


Scheme 9.

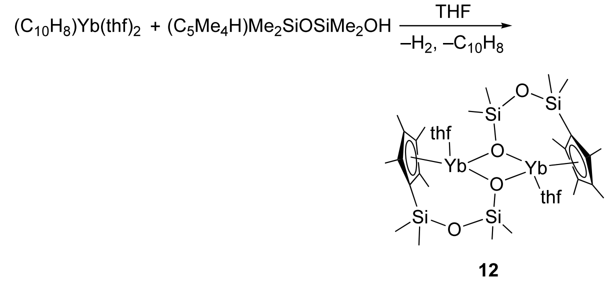


11a: Ln = Sm, x = 0–1
11b: Ln = Yb, x = 3

Scheme 10.



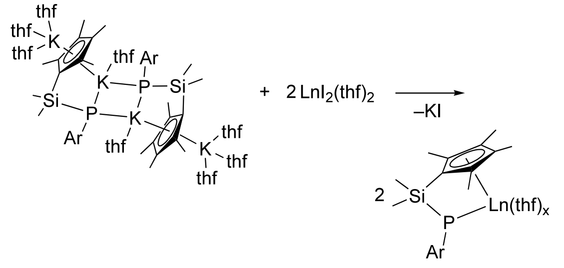
Scheme 11.



Scheme 12.

$(thf)_2$ successfully afforded the corresponding cyclopentadienyl–anilido lanthanide(II) complexes **11a**,**b** (Scheme 10) [18]. Recrystallization of **11b** from toluene–hexane removed two of its three THF ligands to give **11c** (Scheme 11). Complex **11c** adopts a dimeric structure via 'intermolecular' interaction between the Yb atom and the Ph group.

The linked cyclopentadienyl–siloxo ytterbium(II) complex **12**, which forms a dimeric structure via the siloxo-bridges, was obtained by reaction of the ytterbium(II) naphthalenide $(C_{10}H_8)Yb(thf)_2$ with (C_5Me_4H)-$SiMe_2OSiMe_2OH$ as shown in Scheme 12 [19].



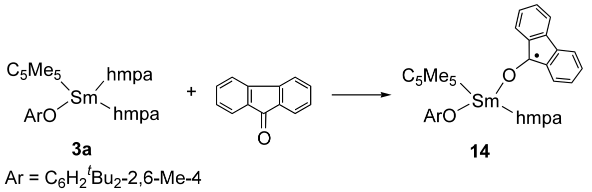
Ar = $C_6H_2{}^tBu_3$-2,4,6
13a: Ln = Sm, x = 3
13b: Ln = Sm, x = 1
13c: Ln = Yb, x = 3
13d: Ln = Yb, x = 0

Scheme 13.

4. Synthesis and structures of lanthanide(II) complexes with silylene-linked C_5Me_4-phosphido ligands

In sharp contrast with the plenty of linked cyclopentadienyl–amido complexes of various metals [16], the analogous phosphido compounds remain very rare. Previous attempts to obtain silylene-linked cyclopentadienyl–phosphido zirconium complexes by reactions of $Li_2[Me_2Si(C_5Me_4)(PR)]$ (R = cyclohexyl or $C_6H_2Me_3$-2,4,6) with $ZrCl_4$ did not give the expected cyclopentadienyl–phosphido complexes, but instead led to P–Si bond cleavage of the ligands [20].

Lanthanide complexes bearing silylene-linked cyclopentadienyl–phosphido ligands seemed to be more stable than the Group 4 metal analogs. The metathetical reaction between $[K_2\{Me_2Si(C_5Me_4)(PAr)\}(thf)_4]_2$ and two equivalents of $SmI_2(thf)_2$ in THF easily afforded the corresponding cyclopentadienyl–phosphido samarium(II) complex **13a** (Scheme 13) [21]. Analogous reaction with $YbI_2(thf)_2$ gave the Yb(II) analog **13c**. Two of the three THF ligands in **13a** could be removed under vacuum to give the corresponding mono-solvated Sm(II) complex **13b**, while dissolving of **13c** in toluene followed by evaporation of the solvent under vacuum yielded the unsolvated Yb(II) complex **13d**. Treatment of **13a** with hmpa or dimethoxyethane (dme) afforded the corresponding hmpa- or dme-coordinated Sm(II) complex $Me_2Si(C_5Me_4)(PAr)Sm(L)_2$ (L = hmpa (**13e**) or dme (**13f**)), respectively [21]. Complexes **13a**–**f**, together with the potassium complex $[K_2\{Me_2Si(C_5Me_4)$-$(PAr)\}(thf)_4]_2$, represent the first examples of structurally characterized, silylene-linked cyclopentadienyl–phosphido complexes. These complexes were stable in solid state at room temperature under an inert atmosphere, but the lanthanide(II) complexes **13a**–**f** gradually decomposed into yet unidentified products



Scheme 14.

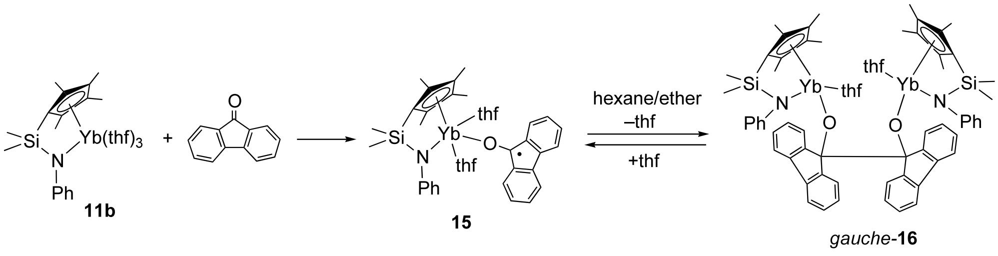
in THF solution. Nevertheless, their reduction chemistry could be examined in THF or toluene.

5. One-electron transfer reactions

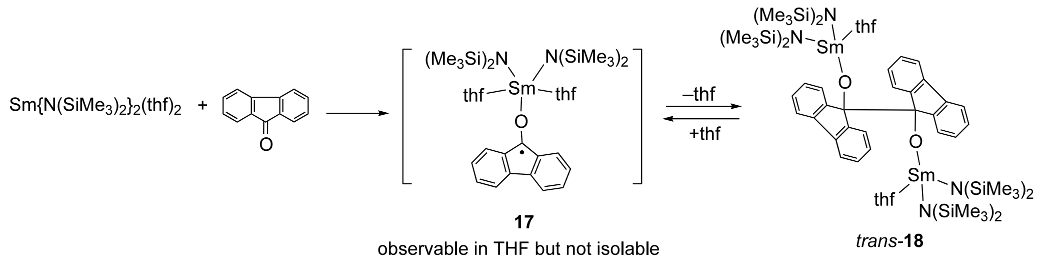
The reaction of the C_5Me_5–OAr-ligated Sm(II) complex **3a** with one equivalent of fluorenone yielded the corresponding structurally characterizable Sm(III) ketyl complex **14** (Scheme 14) [22a], showing that the mixed C_5Me_5–OAr ligand system is able to support both Sm(II) and Sm(III) species. Complex **14** represents a rare example of a lanthanide complex bearing all different ligands.

Analogous reaction of the silylene-linked cyclopentadienyl–anilido ytterbium(II) complex **11b** with one equivalent of fluorenone afforded the Yb(III) ketyl complex **15** (Scheme 15) [18]. Treatment of **15** with hexane–ether removed one of its two THF ligands, and led to dimerization of the radical unit to give the pinacolate complex **16**. Dissolving **16** in THF cleaved the central C–C bond of the pinacolate unit and regenerated the ketyl species **15** quantitatively. These reactions are analogous to those reported for the bis(aryloxide)- or bis(silylamido)-supported lanthanide(III) ketyl–pinacolate complexes (cf. Schemes 16 and 17), but are in contrast with those reported for the lanthanidocene(III) ketyl complexes **21a**,**b**, which remained unchanged under the similar conditions (Scheme 18) [22]. It is also noteworthy that the pinacolate unit in **16** is arranged in a *gauche* conformation, which is in sharp contrast with the *trans* form found in the bis(aryloxide)- and bis(silylamido)-supported pinacolate complexes **18** and **20**.

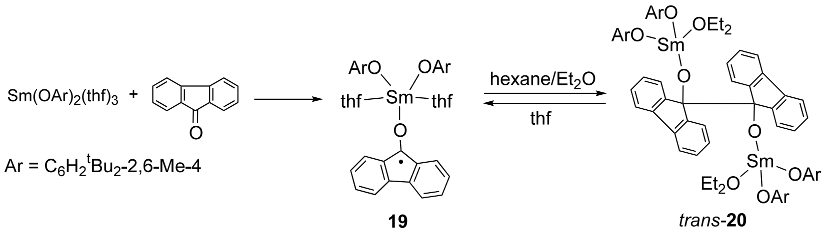
The reaction of the silylene-linked cyclopentadienyl–phosphido samarium(II) complex **13a** with benzophenone gave the corresponding disamarium(III) benzophenone–dianion complex **22** as the only isolable



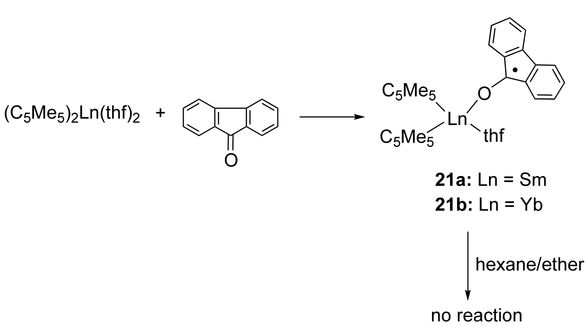
Scheme 15.



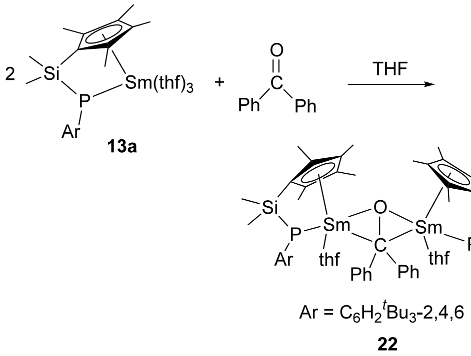
Scheme 16.



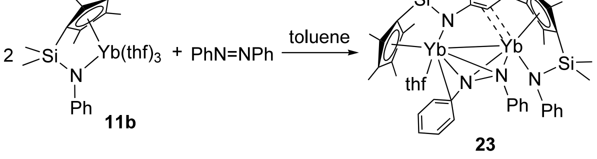
Scheme 17.



Scheme 18.



Scheme 19.



Scheme 20.

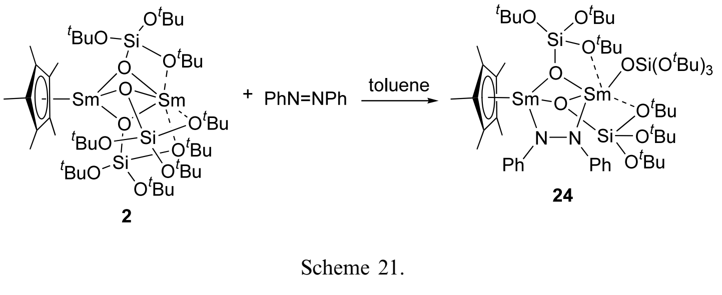
product no matter whether one or two equivalents of **13a** were employed (Scheme 19) [21]. These results suggest that the formation of a benzophenone–dianion complex is easier than that of a ketyl one in the present reaction. This is in contrast with the reactions of the homoleptic Sm(II) complexes, such as $Sm(Tp')_2$ ($Tp' = BH(3,5\text{-dimethylpyrazolyl})_3$) [2b], $Sm\{C(SiMe_3)_2(SiMe_2OMe)\}_2(thf)$ [23], $(C_5Me_5)_2Sm(thf)_2$ [22], and $Sm(OAr)_2(thf)_3$ ($Ar = C_6H_2{}^tBu_2$-2,6-Me-4) [22], with one equivalent of benzophenone or fluorenone, which selectively yielded the corresponding ketyl complexes [24]. Complex **22** represents the first example of a structurally characterized lanthanide(III) ketone–dianion complex. The only other structurally characterized lanthanide ketone–dianion complex is the Yb(II) complex $[Yb(\mu\text{-}\eta^1{:}\eta^2\text{–}OCPh_2)(hmpa)_2]_2$ [25–27].

Reduction of azobenzene with either one or two equivalent of **11b** in toluene afforded the same 1:2 product **23** (Scheme 20) [18], which is in contrast with the previously reported analogous reactions of lanthanide(II) complexes bearing other ligand systems such as $(C_5Me_5)_2Sm(thf)_2$ [28a], $(C_5H_5)_2Yb(thf)$ [28a], and $Sm(Tp')_2$ ($Tp' = BH(3,5\text{-dimethylpyrazolyl})_3$) [28b]. The two Yb atoms in **23** are unsymmetrically bridged by a *cis*-oriented azobenzene–dianion unit, which is bonded in a η^3 fashion to one Yb atom and in a η^2 fashion to the other.

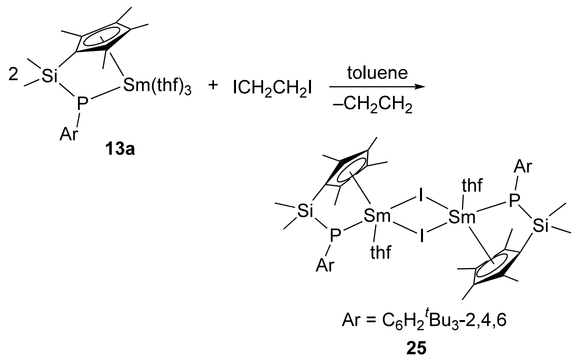
The binuclear C_5Me_5–siloxo Sm(II) complex **2** could act as a two-electron reducing agent, which upon reaction with one equivalent of azobenzene gave the corresponding binuclear Sm(III) azobenzene–dianion complex **24** (Scheme 21) [10]. The azobenzene unit bridges the two Sm atoms in a μ_2-η^1 fashion, with each N atom bonding to one Sm.

Treatment of **13a** with ICH_2CH_2I in toluene easily produced the corresponding samarium(III) iodide complex **25** (Scheme 22) [21]. The iodide complex **25** could be used as a starting material for the synthesis of other derivatives such as aryloxide and silylamide analogs [29]. The silylene-linked cyclopentadienyl–phosphido lanthanide(III) complexes seemed to be more stable than the analogous lanthanide(II) complexes in THF solution.

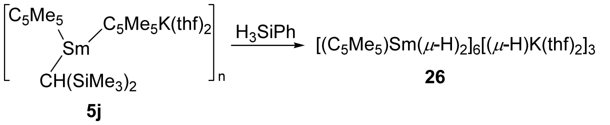
When the 'C_5Me_5K'-coordinated, (pentamethylcyclopentadienyl)samarium(II) alkyl complex **5j** was stirred with two or more equivalents of H_3SiPh in THF, the polyhydrido Sm(III)–K cluster complex **26** was obtained (Scheme 23) [14]. Complex **26** consists formally of six '$(C_5Me_5)SmH_2$' and three '$KH(thf)_2$' units (Fig. 1). The six Sm atoms form a trigonal prism whose three squares are each capped by one K atom. There are 15 hydrido ligands in this molecule, one being body-centered in μ_6-H–Sm_6 fashion and others each capping a metal triangle in either μ_3-H–Sm_3 or μ_3-H–Sm_2K form. This complex represents the first example



Scheme 21.



Scheme 22.



Scheme 23.

of a structurally characterized *dihydrido* lanthanide complex and also the first example of a structurally characterized polyhydrido lanthanide cluster with an interstitial hydrogen atom.

6. Polymerization and other catalytic reactions

The silylene-linked cyclopentadienyl–anilido samarium(II) complex **11a** showed a moderate activity (44.8 kg-polymer (mol-Sm)$^{-1}$ h^{-1}) for the polymerization of ethylene in toluene at room temperature under 1 atm, which afforded linear polyethylene with high molecular weight ($M_n = 7.26 \times 10^5$) and narrow polydispersity ($M_w/M_n = 1.58$) [18]. The mixed-ligand effect is obvious in the present reaction on comparison of these results with those reported for the samarocene(II) complex $(C_5Me_5)_2Sm(thf)$ (5.06 kg-polymer (mol-Sm)$^{-1}$ h^{-1}, $M_n < 2.5 \times 10^4$, $M_w/M_n = 2.28$) [12,30] and the bis(silylamido) samarium(II) complex $Sm\{N(SiMe_3)_2\}_2(thf)_2$, which was inert for ethylene polymerization [12]. The mono(thf)-coordinated, cyclopentadienyl–phosphido samarium(II) complex **13b** was also active for ethylene polymerization (13.6 kg-polymer (mol-Sm)$^{-1}$ h^{-1}), which yielded an extremely high molecular-weight polymer that was insoluble in *ortho*-dichlorobenzene at 135 °C ($M_n > 4 \times 10^6$) [21]. In contrast, the tris(thf)-, hmpa-, or dme-coordinated Sm(II) analogs **13a**,**e**,**f** did not show an activity for ethylene polymerization under the same conditions. It is evident from these results that creation of a sterically (or coordinatively) unsaturated metal center is essential for a polymerization reaction. On the other hand, the THF-free or mono(thf)-coordinated, less reducing Yb(II) complex **13d** or **11c** showed no activity for the polymerization of ethylene under the same conditions [18,21], suggesting that one-electron transfer from the Ln(II) center to an ethylene monomer plays a very important role in the initiation of the present polymerization reactions.

The C_5Me_5–ER-ligated Sm(II) complexes **5a**–**e**,**g**,**j**, **6**, and **7a**, which bear the neutral 'C_5Me_5M' ligand (M = K or Na), all showed high activity for the polymerization of ethylene at 25 °C under 1 atm, yielding linear polyethylene with M_n up to 3×10^6 (against polystyrene standard) [12–14,31]. These unlinked, mixed-ligand-supported complexes are generally more active than the samarocene(II) complexes $(C_5Me_5)_2Sm(thf)_n$ ($n = 0$–2) and also than the silylene-linked cyclopentadienyl–anilido and –phosphido analogs **11a** and **13b**, probably owing to easy dissociation of the 'C_5Me_5M' ligand to generate a coordinatively/sterically unsaturated, more flexible C_5Me_5–ER-ligated-Sm(II) center. The ER-ligand dependence of the reactivity in this series of complexes was also observed. The 4-Me-2,6-$^tBu_2C_6H_2O$-

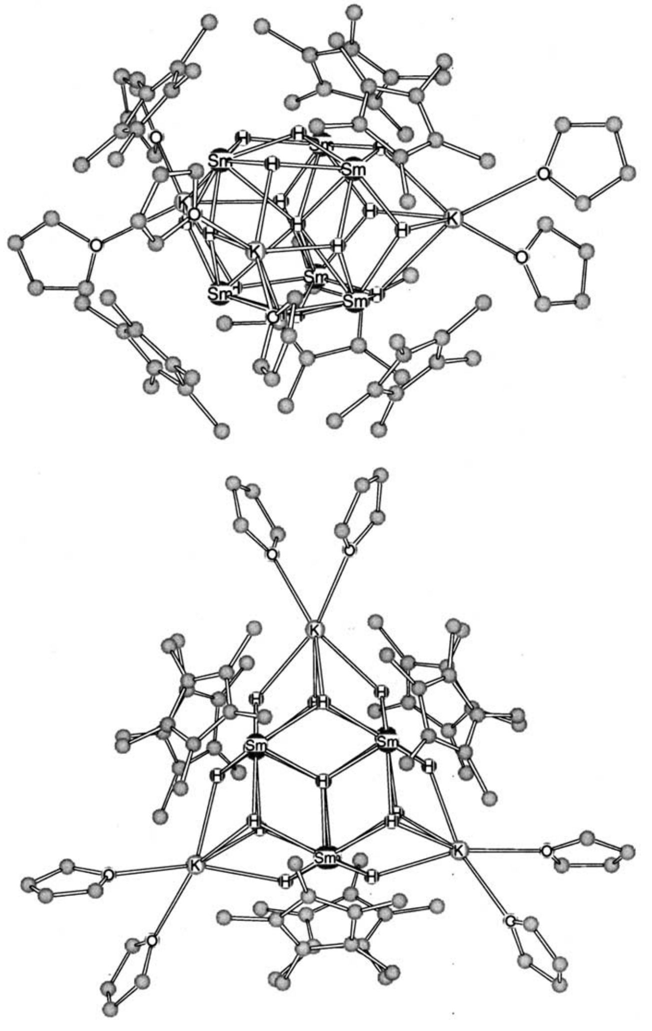
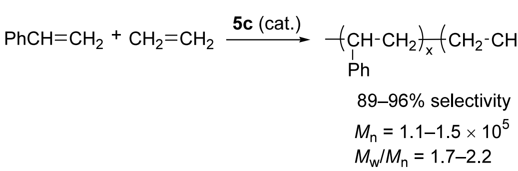


Fig. 1. X-ray structure of **26**. Top: a general view. Bottom: a view along the threefold axis. The Sm–C_5Me_5 bonds are omitted for clarity.



$$PhCH{=}CH_2 + CH_2{=}CH_2 \xrightarrow{\mathbf{5c}\text{ (cat.)}} -\!\!\left(\underset{\displaystyle Ph}{CH}\text{-}CH_2\right)_x\!\!\left(CH_2\text{-}CH_2\right)_y\!\!-$$

Scheme 24.

ligated complex **5a** showed the highest activity (194.4 kg-polymer (mol-Sm)$^{-1}$ h^{-1}), while the $(Me_3Si)_2N$-ligated complex **5e** gave the highest molecular weight of polyethylene ($M_n = 3.10 \times 10^6$).

Complexes **5a**–**e**,**g**,**j** showed high activity also for the polymerization of styrene at room temperature [12–14,31]. In most cases, a quantitative conversion was achieved in less than 1 h, affording atactic polystyrenes with M_n ranged from 8.2×10^4 to 3.5×10^5 and $M_w/M_n = 1.45–2.45$. These results are in striking contrast with what was observed in the case of the samarocene(II) complexes $(C_5Me_5)_2Sm(thf)_n$ ($n = 0$ or 2), which were inactive for styrene polymerization even under more severe conditions [6a]. More remarkably, these complexes, especially the thiolate complex **5c**, showed a unique reactivity for the copolymerization of styrene and ethylene, which yielded the corresponding block copolymers under the presence of both monomers (Scheme 24). The polystyrene content in the resulting copolymers could be adjusted simply by changing the feeding amount of styrene monomer under an atmosphere of ethylene. Although extensive studies on styrene–ethylene copolymerization reactions have been carried out by use of various catalytic systems [16b,32], this is the first example of selective block copolymerization of styrene and ethylene.

The ring-opening polymerization of ε-caprolactone (CL) occurred vary rapidly, when the C_5Me_5–OAr-ligated dimeric Sm(II) complex **1a** [33] or the silylene-linked cyclopentadienyl–phosphido Sm(II) complex **13b** [21] was used as a catalyst. These complexes, together with the samarium(II) bis(aryloxide) complex $Sm(OAr)_2(thf)_3$, are among the most active catalysts ever reported for the ring-opening polymerization of lactones [33,34]. Complex **13b** was active also for 1,4-*cis* selective polymerization of 1,3-butadiene (1,4-*cis*–1,4-*trans*–1,2- = 92.8:4.0:3.2; $M_n = 3.07 \times 10^5$, $M_w/M_n = 1.99$) in the presence of MMAO (MMAO = modified-methylaluminoxane which contains isobutylaluminoxane) as a cocatalyst, although its activity and stereoselectivity were not as high as those of the samarocene-based systems [35].

The (pentamethylcyclopentadienyl)samarium(II) alkyl complex **5j** showed good activity and selectivity for the hydrosilylation of several types of olefins [14]. Some of these reactions are in contrast with those reported for the lanthanide metallocene catalysts [36].

7. Conclusion

It is clear from the above studies that lanthanide(II) complexes bearing mixed cyclopentadienyl–monodentate-anionic ligands can serve as a new class of one-electron transfer agents and polymerization catalysts. In many cases these complexes behave differently than ordinary metallocene complexes, as a result of the interplay between the steric and electronic effects of the mixed ligands. The reactivity of such a complex can be tuned by changing the monodentate anion part, as shown in the **5a**–**l** series.

On the other hand, since the mixed ligand systems usually offer a more open ligand sphere for the metal center than the metallocenes, such mixed-ligand-supported complexes need to adopt a dimeric structure, or to bear more additional neutral, coordinative ligands to compensate the steric unsaturation. Therefore, the use of an easily dissociable, neutral stabilization ligand becomes more critical for creation of a highly reactive system in this case. In this regard, the 'C_5Me_5K' unit is more suitable than the conventional coordinative ligands such as THF or hmpa for the C_5Me_5–ER-ligated Ln(II) species (e.g. **5a**–**l**). Further search for a good neutral ligand for the complexes bearing the linked ligands will be of great importance. Compared to the homoleptic analogs, lanthanide complexes bearing mixed ligand systems still remain much less extensively explored. As the expertise in this field increases and more new ligand systems are developed, the diverse chemistry available from the lanthanide elements will be further extended.

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