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Synthesis and reactivity of cationic lanthanide metallocene complexes. Hexabromocarborane and tetraphenylborate as counter ions

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Treatment of unsolvated $Cp''_2Ln(II)$ [$Cp'' = 1,3\text{-}(Me_3Si)_2C_5H_3$] with 1 equivalent of Ag(I)Y, or reaction of $[Cp''_2LnI]_2$ with 2 molar equivalents of $Ag(CB_{11}Br_6H_6)$ in pure toluene at room temperature gave “Lewis base-free” cationic lanthanide metallocene complexes $[Cp''_2Ln]Y$ ($Y = BPh_4^-$, Ln = Sm **1**, Yb **2**; $Y = CB_{11}Br_6H_6^-$, Ln = Sm **3**, Er **4**) in good yield. They slowly undergo decomposition reaction at room temperature. The reactivity of these “Lewis base-free” cationic complexes is highly dependent upon the coordinating nature of the counter ions. Complexes **3** and **4** are much more reactive than **1** and **2**. Recrystallization of **1** and **2** from 1,2-dimethoxyethane (DME) and THF yielded $[Cp''_2Sm(DME)][BPh_4]$ **5** and $[Cp''_2Yb(THF)_2][BPh_4]$ **6**, respectively. However, recrystallization of **3** and **4** from THF resulted in the ring-opening polymerization of THF. The THF coordinated complexes $[Cp''_2Ln(THF)_2][CB_{11}Br_6H_6]$ (Ln = Sm **7**, Er **8**) were isolated *via* recrystallization of **3** and **4** from toluene containing a small amount of THF. The “Lewis base-free” cation “Cp''_2Er^+” can abstract one bromine atom from the counter ion $CB_{11}Br_6H_6^-$ or one chlorine atom from CH_2Cl_2 to form $[Cp''_2ErBr]_2$ or $[Cp''_2ErCl]_2$, respectively. Unfortunately, these cations do not exhibit reactivity towards 1-hexene at room temperature. Molecular structures of **5**, **7**, **8** and $[Cp''_2ErBr]_2$ have been confirmed by single-crystal X-ray analyses.

Introduction

Cationic Group 4 metallocene complexes have been the subject of intensive research activity over the past decade because of their extraordinary characteristics as olefin polymerization catalysts.[1] These studies have helped chemists to better understand the fundamental aspects of olefin oligomerization and polymerization reactions. In contrast to this Group 4 system, cationic lanthanide metallocene chemistry is much less developed.[2] Only a few reports on this type of complex have appeared in the literature.[3–9] All of the known cationic lanthanide metallocene complexes are those in which a lanthanide metal is strongly bound to the Lewis bases (donor solvents), $[Cp_2LnL_2][X]$ [$L = OC_4H_8$, SC_4H_8, N_2H_4, DME; Ln = La,[4] Ce,[5] Sm,[3,6] Yb;[7–9] $X = BPh_4$,[3–8] $Co(CO)_4$[9]]. The coordinated Lewis bases cannot be removed from the metal centre under very high vacuum on heating,[3] which results in very unreactive cationic species. In fact, $[Cp^*_2Sm(THF)_2]^+$ ($Cp^* = C_5Me_5$) has shown no reactivity towards CO, azobenzene, ethylene, phenylacetylene, epoxybutane or pyridine.[3] In view of recent developments in cationic Group 4 metallocene chemistry,[10] the synthesis, structure and reactivity studies of “base-free” cationic lanthanide metallocene compounds becomes a very interesting subject. The first example of such a “base-free” cationic Group 3 metallocene compound, $Cp'_2YMe\cdot B(C_6F_5)_3$ ($Cp' = C_5H_5$, $C_5H_4SiMe_3$), has been reported very recently.[11] It is much more reactive than the Lewis base coordinated cationic Group 3 species, $[Cp_2LnL_2][X]$.[3–9] We are interested in the effect of counter ions on the stability and reactivity of cationic lanthanide metallocene compounds. We report here the synthesis and reactivity of several new cationic lanthanide metallocene compounds in which the counter ions are the hexabromocarborane anion $[7,8,9,10,11,12\text{-}Br_6\text{-}1\text{-}closo\text{-}CB_{11}H_6]^-$ and tetraphenylborate BPh_4^-, respectively.

Results and discussion

Synthesis

Treatment of unsolvated $Cp''_2Ln(II)$ [$Cp'' = 1,3\text{-}(SiMe_3)_2C_5H_3$] with 1 equivalent of AgY in toluene at room temperature and removal of the Ag precipitate gave a complex which has been formulated as $[Cp''_2Ln]Y$ on the basis of elemental analyses and chemical analyses [eqn. (1), $Y = BPh_4^-$, Ln = Sm **1**, Yb **2**;

$$Cp''_2Ln + AgY \xrightarrow{\text{toluene}} [Cp''_2Ln]Y + Ag \qquad (1)$$

$Y = CB_{11}Br_6H_6^-$, Ln = Sm **3**]. Complex $[Cp''_2Yb][CB_{11}Br_6H_6]$ was not isolated in the pure form because of its decomposition at room temperature. For those metals, for which a divalent precursor is not available, an unsolvated trivalent complex $[Cp''_2LnI]_2$ can be used instead. Reaction of $[Cp''_2LnI]_2$ with two molar equivalents of $Ag(CB_{11}Br_6H_6)$ in toluene at room temperature, and removal of the AgI precipitate yielded a complex $[Cp''_2Ln][CB_{11}Br_6H_6]$ as shown in eqn. (2) (Ln = Sm **3**, Er **4**).

$$\tfrac{1}{2}[Cp''_2LnI]_2 + Ag(CB_{11}Br_6H_6) \xrightarrow{\text{toluene}} [Cp''_2Ln][CB_{11}Br_6H_6] + AgI \qquad (2)$$

These new complexes (**1**–**4**) are extremely air and moisture sensitive, and relatively thermally unstable. They do not redissolve in arene solvents once isolated, so that recrystallization from toluene, benzene or fluorobenzene is extremely difficult. Numerous attempts were made during the course of this study to grow single crystals of complexes **1**–**4** from their mother-liquor suitable for X-ray analysis. However, all efforts were hampered by the slow decomposition of these complexes at room temperature, resulting in difficulty in the characterization of these complexes. The reaction of $[Cp''_2SmI]_2$ with $AgSbF_6$ gave the fluoride abstraction product $[Cp''_2SmF]_2$.[12a] The reaction of $[Cp''_2SmCl]_2$ with $Ag(CB_{11}Br_6H_6)$ was slow and did not proceed to completion.

Reactivity

Complexes **1**–**4** are not thermally stable, and **3** and **4** are even less stable than **1** and **2**. They slowly undergo decomposition at room temperature. Not surprisingly, heat can dramatically increase the thermolysis rate. Thus complex **1** decomposed into the more stable Cp''_3Sm in 50% isolated yield at 80 °C. The decomposition of complex **2** may be complicated. Unlike complex **1**, no Cp''_3Yb was isolated presumably due to the smaller size of the ytterbium ion which makes the formation of Cp''_3Yb extremely difficult.[13] On the other hand, a small amount of benzene was detected by GC/MS from its hydrolysis products, suggesting that Cp''_2Yb^+ may abstract one phenyl group from the counter ion BPh_4^-.[14] Thermal decomposition of **3** in toluene or fluorobenzene produced Cp''_3Sm, and some unidentified species. No $[Cp''_2SmF]_2$[12] was detected by MS spectroscopy. Complex **4** in toluene or fluorobenzene decomposed to generate $[Cp''_2ErBr]_2$, and some unidentified species at room temperature. No fluoride abstraction product was observed either. Reaction of Cp''_2Yb with 1 equivalent of $Ag(CB_{11}Br_6H_6)$ in toluene at room temperature resulted in the isolation of $[Cp''_2YbBr]_2$ in 11% yield which could be increased to 41% at 40 °C. It is rational to propose that compounds $[Cp''_2LnBr]_2$ resulted from the bromide abstract reaction between "Cp''_2Ln^+" and the counter ion $CB_{11}Br_6H_6^-$. The above results indicate that "Cp''_2Ln^+" is an extremely strong electrophile and its electrophilicity is even higher than that of the silylium ion (R_3Si^+) at least with respect to the bromide abstraction reactions.[15] These cationic lanthanide metallocene species can also abstract the chloride from CH_2Cl_2. For example, treatment of **4** with CH_2Cl_2 at room temperature afforded $[Cp''_2ErCl]_2$ in 65% yield; reaction of Cp''_2Yb with $Ag(CB_{11}Br_6H_6)$ in CH_2Cl_2 gave $[Cp''_2YbCl]_2$ in 70% yield.

"Base-free" cationic lanthanide metallocene complexes are strong Lewis acids. Recrystallization of complex **1** from DME/toluene produced a DME coordinated cationic complex $[Cp''_2Sm(DME)][BPh_4]$ **5**. Complex **2** dissolved in THF to yield a THF coordinated ionic complex $[Cp''_2Yb(THF)_2][BPh_4]$ **6**. No obvious THF ring-opening polymerization products were observed. On the other hand, recrystallization of complex **3** or **4** from THF resulted in the formation of a gum identified as poly(tetrahydrofuran). The THF coordinated complex $[Cp''_2Ln(THF)_2][CB_{11}Br_6H_6]$ (Ln = Sm **7**, Er **8**) can be isolated by recrystallization of the corresponding "Lewis base-free" complex $[Cp''_2Ln][CB_{11}Br_6H_6]$ from toluene containing a small amount of THF. Like other Lewis base coordinated cationic lanthanide metallocene complexes,[3–9] **7** and **8** cannot initiate the ring-opening polymerization of THF. Attempts to prepare complexes **7** and **8** by the reaction of Cp''_2Ln with $Ag(CB_{11}Br_6H_6)$ in THF, a well-established method for the preparation of $[Cp_2Ln(THF)_2][BPh_4]$,[3–9] failed due to the formation of poly(tetrahydrofuran). These results imply that $[Cp''_2Ln][CB_{11}Br_6H_6]$ is much more electrophilic than $[Cp''_2Ln][BPh_4]$, suggesting that the less coordinating carborane anion can largely enhance the electrophilicity (Lewis acidity) of Cp''_2Ln^+ cation, which is consistent with cationic Group 4 and silylium ion chemistry.[1,10,15] However, neither **3** nor **4** exhibits any reactivity towards 1-hexene at room temperature.

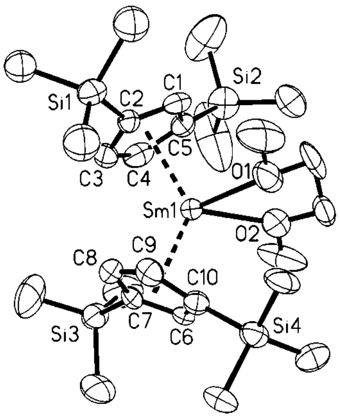

Fig. 1 Perspective ORTEP[16] drawing of the molecular structure of $[Cp''_2Sm(DME)]^+$ in **5**·$0.25C_7H_8$. All hydrogen atoms are omitted for clarity (thermal ellipsoids drawn at the 35% probability).

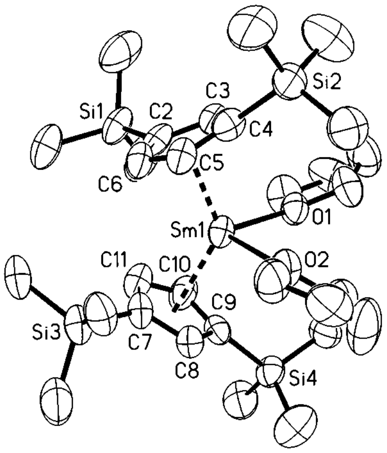

Fig. 2 Perspective ORTEP drawing of the molecular structure of $[Cp''_2Sm(THF)_2]^+$ in **7**·OC_4H_8. All hydrogen atoms are omitted for clarity (thermal ellipsoids drawn at the 35% probability).

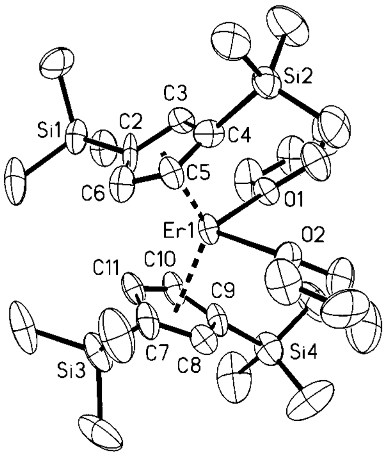

Fig. 3 Perspective ORTEP drawing of the molecular structure of $[Cp''_2Er(THF)_2]^+$ in **8**·$1.25C_7H_8$. All hydrogen atoms are omitted for clarity (thermal ellipsoids drawn at the 35% probability).

Structure

Crystal structures of cationic lanthanide metallocene complexes 5, 7 and 8. The solid state structures of **5**, **7** and **8** as derived from single-crystal X-ray diffraction studies all consist of well separated, alternating layers of $[Cp''_2LnL_2]^+$ (L_2 = DME, 2THF) cations and $CB_{11}Br_6H_6^-$ or BPh_4^- anions. The apparent voids in the structures are filled by several disordered solvent molecules. Complexes **7** and **8** are isomorphous. In each cation, the lanthanide ion is η^5 bound to each of two cyclopentadienyl rings and two oxygen atoms from the coordinated THF or DME molecules in a distorted tetrahedral geometry (Figs. 1–3), which is similar in structure to the reported lanthanide metallocene cations of the type $Cp_2LnL_2^+$.[3–9] Selected bond distances and angles for each complex are summarized in Tables 1–3, respectively. Table 4 lists some structural parameters for lanthanide metallocene cations of the type $Cp_2LnL_2^+$. Both BPh_4^- and $CB_{11}Br_6H_6^-$ anions have normal distances and angles.

The two cations, $[Cp''_2Sm(DME)]^+$ and $[Cp''_2Sm(THF)_2]^+$, have a very similar geometry in terms of average Sm–C, Sm–Cent (centroid of the cyclopentadienyl ring), Sm–O bond distances and Cent–Sm–Cent angles. These structural parameters can be compared to those found in $[(C_5Me_5)_2Sm(THF)_2]^+$ (Table 4).[3] The Er–C distances in $[Cp''_2Er(THF)_2]^+$ range from 2.563(6) to 2.694(7) Å with an average value of 2.627(6) Å. This measured value is identical to the 2.629(2) Å in $[Cp''_2ErBr]_2$. It is about 0.083 Å shorter than the average Sm–C distance of 2.71(2) Å in **7**. The average Er–O distance of 2.336(4) Å is 0.075 Å shorter than that of Sm–O in **7**. These differences can be compared to the 0.075 Å difference between Shannon's ionic radii[17] of eight-coordinate Sm^{3+} (1.079 Å) and Er^{3+} (1.004 Å). The 131.4(1)° Cent–Er–Cent angle is quite similar to the 130.2(3)° in **7** and the 129.4(4)° in **5**.

Crystal structure of $[Cp''_2ErBr]_2$. $[Cp''_2ErBr]_2$ is a centrosymmetric bromide-bridging dimer with pseudo-tetrahedral geometry around each Er atom, typical of the structures of $[Cp''_2LnX]_2$ dimeric organolanthanide fluoride[12] and chloride[18a–c] complexes (Fig. 4). Selected bond distances and angles are listed in Table 5. The average Er–C distance of 2.629(2) Å compared to the 2.640(9) Å in $Cp''_2ErI(THF)$[19] and the 2.59(1) Å in $[(C_5H_5)_2ErBr]_2$.[18d] The 2.875(1) Å average Er–Br distance is longer than the value of 2.820(1) Å in $[(C_5H_5)_2ErBr]_2$ probably due to steric reasons. The 83.2(1)° Br(1)–Er(1)–Br(1A) angle is smaller than the 84.2(1)° in $[(C_5H_5)_2ErBr]_2$.

Table 1 Selected bond distances (Å) and angles (°) for compound **5**

Sm(1)–C(1)	2.732(16)	Sm(1)–C(7)	2.710(16)
Sm(1)–C(2)	2.720(17)	Sm(1)–C(8)	2.693(17)
Sm(1)–C(3)	2.680(18)	Sm(1)–C(9)	2.695(16)
Sm(1)–C(4)	2.719(21)	Sm(1)–C(10)	2.739(18)
Sm(1)–C(5)	2.753(17)	Sm(1)–O(1)	2.432(17)
Sm(1)–C(6)	2.695(15)	Sm(1)–O(2)	2.386(14)
Sm(1)–Cent(1)	2.436	Sm(1)–Cent(2)	2.427
O(1)–Sm(1)–O(2)	65.1(5)	Cent(1)–Sm(1)–O(2)	115.0
Cent(1)–Sm(1)–Cent(2)	129.4	Cent(2)–Sm(1)–O(1)	110.4
Cent(1)–Sm(1)–O(1)	106.4	Cent(2)–Sm(1)–O(2)	111.5

Table 2 Selected bond distances (Å) and angles (°) for compound **7**

Sm(1)–C(2)	2.70(2)	Sm(1)–C(8)	2.74(2)
Sm(1)–C(3)	2.70(2)	Sm(1)–C(9)	2.74(2)
Sm(1)–C(4)	2.77(2)	Sm(1)–C(10)	2.69(2)
Sm(1)–C(5)	2.68(2)	Sm(1)–C(11)	2.69(2)
Sm(1)–C(6)	2.67(2)	Sm(1)–O(1)	2.424(12)
Sm(1)–C(7)	2.70(2)	Sm(1)–O(2)	2.401(11)
Sm(1)–Cent(1)	2.420	Sm(1)–Cent(2)	2.432
O(1)–Sm(1)–O(2)	94.1(4)	Cent(1)–Sm(1)–O(2)	108.2
Cent(1)–Sm(1)–Cent(2)	130.2	Cent(2)–Sm(1)–O(1)	109.0
Cent(1)–Sm(1)–O(1)	104.1	Cent(2)–Sm(1)–O(2)	105.4

Table 3 Selected bond distances (Å) and angles (°) for compound **8**

Er(1)–C(2)	2.590(8)	Er(1)–C(8)	2.655(8)
Er(1)–C(3)	2.666(8)	Er(1)–C(9)	2.694(7)
Er(1)–C(4)	2.641(7)	Er(1)–C(10)	2.613(6)
Er(1)–C(5)	2.608(6)	Er(1)–C(11)	2.563(6)
Er(1)–C(6)	2.608(7)	Er(1)–O(1)	2.335(4)
Er(1)–C(7)	2.630(8)	Er(1)–O(2)	2.336(4)
Er(1)–Cent(1)	2.324	Er(1)–Cent(2)	2.342
O(1)–Er(1)–O(2)	91.2(2)	Cent(1)–Er(1)–O(2)	107.7
Cent(1)–Er(1)–Cent(2)	131.4	Cent(2)–Er(1)–O(1)	108.2
Cent(1)–Er(1)–O(1)	106.4	Cent(2)–Er(1)–O(2)	104.5

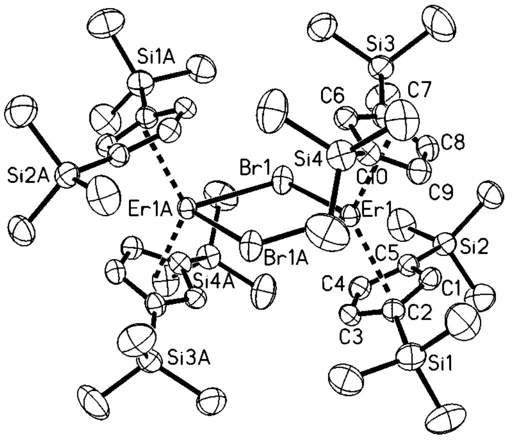

Fig. 4 Perspective ORTEP drawing of the molecular structure of $[Cp''_2ErBr]_2$. All hydrogen atoms are omitted for clarity (thermal ellipsoids drawn at the 35% probability).

Table 5 Selected bond distances (Å) and angles (°) for compound $[Cp''_2ErBr]_2$

Er(1)–C(1)	2.631(2)	Er(1)–C(9)	2.586(2)
Er(1)–C(2)	2.644(2)	Er(1)–C(10)	2.659(2)
Er(1)–C(3)	2.617(2)	Er(1)–Br(1)	2.878(1)
Er(1)–C(4)	2.616(2)	Er(1)–Br(1A)	2.872(1)
Er(1)–C(5)	2.627(2)	Br(1)–Er(1A)	2.872(1)
Er(1)–C(6)	2.659(2)	Er(1)–Cent(1)	2.334
Er(1)–C(7)	2.655(2)	Er(1)–Cent(2)	2.338
Er(1)–C(8)	2.600(2)		
Br(1)–Er(1)–Br(1A)	83.2(1)	Cent(1)–Er(1)–Br(1A)	107.0
Cent(1)–Er(1)–Cent(2)	130.3	Cent(2)–Er(1)–Br(1)	109.2
Cent(1)–Er(1)–Br(1)	107.2	Cent(2)–Er(1)–Br(1A)	109.7

Table 4 Selected structural parameters for some lanthanide metallocene cations

	ave. Ln–C/Å	ave. Ln–O/Å	Cent(1)–Ln–Cent(2)/°	O(1)–Ln–O(2)/°	Ref.
$[Cp''_2Sm(DME)]^+$	2.714(14)	2.409(17)	129.4	65.1(5)	This work
$[Cp''_2Sm(THF)_2]^+$	2.71(2)	2.413(12)	130.2	94.1(4)	This work
$[Cp''_2Er(THF)_2]^+$	2.627(7)	2.335(4)	131.4	91.2(2)	This work
$[Cp^*_2Sm(THF)_2]^+$	2.69(2)	2.46(1)	134.2	92.9(4)	3
$[Cp^*_2Sm(N_2H_4)(THF)]^+$	2.73(2)	2.470(2)	138.9		6
$[Cp''_2La(DME)(MeCN)]^+$	2.83(1)	2.627(8)		61.5(3)	4
$[Cp^*_2Ce(SC_4H_8)_2]^+$	2.74(3)		134.6(1)		5
$[(MeOCH_2CH_2C_5H_4)_2Yb(THF)]^+$	2.57(2)	2.32(1)	126.0		9
$[Cp^*_2Yb(THF)_2]^+$	2.619(4)	2.341(3)	137.2	92.2(1)	8
$[(Bu^tC_5H_4)_2Yb(THF)_2]^+$	2.586(1)	2.290(5)	126.4	86.0(3)	7

Conclusions

The preparation and reactivity of "Lewis base-free" cationic lanthanide metallocene complexes of the type $[Cp''_2Ln][CB_{11}Br_6H_6]$ and $[Cp''_2Ln][BPh_4]$ have been described for the first time. They can be synthesized by the reaction of unsolvated $Cp''_2Ln(II)$ or $[Cp''_2LnI]_2$ with silver(I) salts of the weakly coordinating anions in pure toluene. Their chemical reactivities are highly dependent upon the coordinating nature of the counter ions. The more weakly coordinating carborane anion $CB_{11}Br_6H_6^-$ can greatly enhance the reactivity (electrophilicity) of the cation Cp''_2Ln^+. For example, $[Cp''_2Ln][CB_{11}Br_6H_6]$ can initiate the ring-opening polymerization of THF, abstract one bromine atom from the counter ion $CB_{11}Br_6H_6^-$ or one chlorine atom from the solvent CH_2Cl_2.

Experimental

General procedures

All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone or CaH_2 immediately prior to use. Cp''_2Sm,[20] Cp''_2Yb,[21] $Ag(BPh_4)$,[22] and $Ag(CB_{11}Br_6H_6)$[23] were prepared according to the literature methods. $[Cp''_2LnI]_2$ (Ln = Sm, Er) can be conveniently prepared from $Cp''_2LnI(THF)$[19] by sublimation at 200–230 °C at 10^{-2} Torr. All other chemicals were purchased from Aldrich Chemical Company and used as received unless otherwise noted. Infrared spectra were obtained from a KBr pellet, prepared in the glovebox, on a Nicolet Magna 550 Fourier-transform spectrometer. MS spectra were recorded on a Bruker APEX FTMS spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Bruker ARX-500 spectrometer at 160.46 MHz. All chemical shifts are reported in δ units with reference to the residual protons of deuteriated solvent or external $SiMe_4$ (0.00 ppm) for proton and carbon chemical shifts, to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. Complexometric metal analyses were conducted by titration with EDTA.

Preparations

$[Cp''_2Sm][BPh_4]$ 1. To a mixture of Cp''_2Sm (0.207 g, 0.36 mmol) and $Ag(BPh_4)$ (0.202 g, 0.47 mmol) was added toluene (30 cm^3) with stirring at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. A black precipitate formed during this period, and then was filtered off. Removal of most of the solvent under vacuum gave a yellow solid which was washed with toluene and then hexane to afford **1** as a yellow powder (0.207 g, 64%) (Found: C, 61.81; H, 7.18; Sm, 16.86. $C_{46}H_{62}BSi_4Sm$ requires C, 62.18; H, 7.03; Sm, 16.92%); IR (KBr, ν/cm^{-1}): 3086w, 3052w, 2954s, 1252s, 833vs.

Complex **1** does not redissolve in toluene once isolated, so the NMR data are not available. Recrystallization of **1** from hot toluene (80 °C) afforded orange crystals identified as Cp''_3Sm (50% based on **1**) by MS and ^1H NMR spectroscopy as well as the unit cell measurements.[12,20]

$[Cp''_2Sm(DME)][BPh_4]$ 5. Recrystallization of **1** (0.20 g, 0.22 mmol) from DME/toluene (10 : 1, 20 cm^3) at room temperature gave complex **5** (0.18 g, 84%) as yellow crystals over a period of 2 d (Found: C, 61.12; H, 7.35. $C_{50}H_{72}BO_2Si_4Sm$ requires C, 61.36; H, 7.42%); δ_H (C_5D_5N): −0.42 (s, Me_3Si), 2.84 (br, DME), 3.06 (br, DME), 6.72 (m, C_6H_5), 6.90 (m, C_6H_5), 7.70 (br, C_5H_3), 9.61 (br, C_5H_3); δ_C (C_5D_5N): −0.87 (Me_3Si), 58.14, 71.58 (DME), 121.9, 125.8, 136.8 (C_5H_3), 164.9, 164.2, 163.6, 162.9 (BPh_4^-); δ_B (C_5D_5N): −14.6; IR (KBr, ν/cm^{-1}): 3088w, 2965s, 1437m, 1255s, 1079s, 922m, 833vs.

$[Cp''_2Yb][BPh_4]$ 2. To a mixture of Cp''_2Yb (0.157 g, 0.26 mmol) and $Ag(BPh_4)$ (0.131 g, 0.30 mmol) was added toluene (30 cm^3) at 0 °C under stirring. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. A black precipitate formed during this period, and then was filtered off. Removal of most of the solvent under vacuum gave a red solid which was washed with toluene and then hexane to afford **2** as a red solid (0.18 g, 74%) (Found: C, 60.12; H, 6.75; Yb, 19.25. $C_{46}H_{62}BSi_4Yb$ requires C, 60.60; H, 6.86; Yb, 18.99%); IR (KBr, ν/cm^{-1}): 3089w, 2954s, 2899m, 1579m, 1479m, 1251s, 912s, 831vs.

$[Cp''_2Yb(THF)_2][BPh_4]{\cdot}2THF$ 6·2THF. Recrystallization of **2** (0.15 g, 0.16 mmol) from THF/toluene (10 : 1, 20 cm^3) at room temperature gave complex **6**·2THF (0.16 g, 83%) as red crystals over a period of 2 d (Found: C, 62.33; H, 7.76. $C_{62}H_{94}BO_4Si_4Yb$ requires C, 62.08; H, 7.90%); δ_H (C_5D_5N): 0.45 (s, Me_3Si), 1.27 (m, THF), 3.34 (m, THF), 6.96 (m, C_6H_5), 7.23 (m, C_6H_5), 8.44 (br, C_5H_3), 8.64 (br, C_5H_3); δ_C (C_5D_5N): 2.49 (Me_3Si), 27.25, 69.30 (THF); 124.6, 128.4, 139.5 (C_5H_3), 165.5, 165.0, 164.2, 163.9 (BPh_4^-); δ_B (C_5D_5N): −6.90; IR (KBr, ν/cm^{-1}): 3050m, 3032m, 2955s, 2898m, 1578m, 1478m, 1448m, 1250s, 1080s, 921s, 831vs, 731s.

$[Cp''_2Sm][CB_{11}Br_6H_6]$ 3. To a suspension of $Ag(CB_{11}Br_6H_6)$ (0.193 g, 0.27 mmol) in 15 cm^3 of toluene was added a toluene solution (15 cm^3) of Cp''_2Sm (0.146 g, 0.26 mmol) with stirring at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 2 d, followed by the procedure similar to that used in the synthesis of **1**, yielding **3** as a yellow solid (0.155 g, 51%) (Found: C, 22.87; H, 3.95; Sm, 12.55. $C_{23}H_{48}B_{11}Br_6Si_4Sm$ requires C, 23.30; H, 4.08; Sm, 12.68%); IR (KBr, ν/cm^{-1}): 3057w, 2957m, 2603s (br), 1251m, 835s.

Compound **3** can also be prepared by the reaction of $[Cp''_2SmI]_2$ with 2 equivalents of $Ag(CB_{11}Br_6H_6)$ in toluene in 40% yield.

Compound **3** does not redissolve in pure toluene or fluorobenzene once isolated, so that NMR data are not available. If this suspension is heated for 2 h at 45 °C, a small amount of orange crystals can be isolated and identified as Cp''_3Sm by MS and ^1H NMR spectroscopy.[12,20]

Complex **3** (23 mg) was dissolved in 5 cm^3 of THF with stirring at room temperature. The clear yellow solution slowly became sticky and finally became a gum after 12 h. An additional 5 cm^3 of THF was added to the gum giving a very viscous solution which became a gum again after 10 h. This gum was identified as poly(tetrahydrofuran) by ^1H and ^{13}C NMR spectroscopy.[24]

$[Cp''_2Sm(THF)_2][CB_{11}Br_6H_6]$ 7. Recrystallization of **3** (0.15 g) from toluene containing 5% THF (35 cm^3) at room temperature gave complex **7** as yellow crystals (0.10 g, 60%) (Found: C, 28.61; H, 4.67. $C_{31}H_{64}B_{11}Br_6O_2Si_4Sm$ requires C, 28.00; H, 4.85%); δ_H (C_5D_5N): −0.08 (s, Me_3Si), 1.52 (m, THF), 3.56 (m, THF), 3.40 (s, CH of carborane), 8.20 (br, C_5H_3), 10.12 (br, C_5H_3); δ_C (C_5D_5N): −1.24 (Me_3Si), 25.29, 67.31 (THF), 118.6, 128.1, 135.9 (C_5H_3); δ_B (C_5D_5N): 4.8 (s, 1 B), −3.6 (s, 5 B), −15.2 (d, 5 B); IR (KBr, ν/cm^{-1}): 3057w, 2958m, 2896m, 2603s (br), 1450m, 1385vs, 1250m, 1077s, 953m, 834s.

Reaction of Cp''_2Yb with $Ag(CB_{11}Br_6H_6)$. A suspension of Cp''_2Yb (0.320 g, 0.54 mmol) and $Ag(CB_{11}Br_6H_6)$ (0.392 g, 0.54 mmol) was mixed in toluene (40 cm^3) under stirring at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 2 d. The black precipitate was filtered off. Slow evaporation of the solvent gave red crystals (0.04 g, 11% based on Cp''_2Yb) identified as $[Cp''_2YbBr]_2$. No pure $[Cp''_2Yb][CB_{11}Br_6H_6]$ was isolated. Repeating the above experiment at 40 °C resulted in the isolation of red crystals identified as $[Cp''_2YbBr]_2$ (0.15 g, 41% based on Cp''_2Yb) (Found: C, 39.33; H, 6.76. $C_{44}H_{84}Br_2Si_8Yb_2$ requires C, 39.33; H, 6.30%); IR (KBr, *ν*/cm^{-1}): 3067w, 2954s, 2898m, 1438w, 1249s, 1085s, 835vs, 753s; MS (EI, *m*/*z*): 672 ($\frac{1}{2}M^+$, 4%), 592 ($[Cp''_2Yb]^+$, 30%), 383 ($[Cp''Yb]^+$, 5%).

If the above reaction was conducted in CH_2Cl_2, $[Cp''_2YbCl]_2$ was isolated as red crystals in 70% yield (Found: C, 41.95; H, 6.65%. Calc. for $C_{44}H_{84}Cl_2Si_8Yb_2$: C, 42.11; H, 6.75%) which was also identified by MS.[13] If the reaction was carried out in THF, poly(tetrahydrofuran) was obtained.

$[Cp''_2Er][CB_{11}Br_6H_6]$ 4. $Ag(CB_{11}Br_6H_6)$ (0.147 g, 0.20 mmol) and $[Cp''_2ErI]_2$ (0.148 g, 0.10 mmol) were mixed in toluene (30 cm^3) under stirring at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 2 d, the yellow precipitate was filtered off. Concentration of the clear filtrate gave a pink solid which was washed with toluene and then hexane to yield **4** as a pink solid (0.145 g, 60%) (Found: C, 22.65; H, 4.00; Er, 13.78. $C_{23}H_{48}B_{11}Br_6ErSi_4$ requires C, 22.97; H, 4.02; Er, 13.91%); IR (KBr, *ν*/cm^{-1}): 2955s, 2900m, 2603s (br), 1251s, 835vs.

Complex **4** does not redissolve in toluene. Recrystallization of **4** (0.10 g) from hot toluene (50 cm^3, 60 °C) gave pink crystals identified as $[Cp''_2ErBr]_2$ (Found: C, 40.01; H, 6.65. $C_{44}H_{84}Br_2Er_2Si_8$ requires C, 39.67; H, 6.36%); IR (KBr, *ν*/cm^{-1}): 3054w, 2955s, 2897m, 1439w, 1249s, 1078s, 834vs, 753s.

Recrystallization of **4** from CH_2Cl_2 at room temperature resulted in the isolation of $[Cp''_2ErCl]_2$[13,18a,b] in 65% yield (Found: C, 42.08; H, 6.75. Calc. for $C_{44}H_{84}Cl_2Er_2Si_8$: C, 42.50; H, 6.82%).

$[Cp''_2Er(THF)_2][CB_{11}Br_6H_6]$ 8. Recrystallization of **4** (0.13 g) from toluene containing 5% THF (35 cm^3) at room temperature gave compound **8** as pink crystals (0.06 g) (Found: C, 27.35; H, 4.80. $C_{31}H_{64}B_{11}Br_6ErO_2Si_4$ requires C, 27.65; H, 4.79%); δ_B (C_5D_5N): 10.6 (s, 1 B), 2.85 (s, 5 B), −8.23 (d, 5 B); IR (KBr, *ν*/cm^{-1}): 3066w, 2955s, 2900m, 2603s (br), 1436m, 1251s, 1078s, 1001s, 835vs, 799s. The ^1H and ^{13}C NMR spectra consisted of many broad, unresolved resonances.

Crystallography

A summary of crystal data and details of data collection and structure refinement for compounds **5**·$0.25C_7H_8$, **7**·OC_4H_8, **8**·$1.25C_7H_8$ and $[Cp''_2ErBr]_2$ is given in Table 6. Due to the facile loss of the solvent molecules in the crystal lattices of compounds **5**·$0.25C_7H_8$, **7**·OC_4H_8 and **8**·$1.25C_7H_8$, these crystals were sealed with a drop of mother-liquor under N_2 in a thin-walled glass capillary. Data were collected at 294 K on a MSC/Rigaku RAXIS-IIC imaging plate using Mo-Kα radiation (0.71073 Å) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program.[25] All structures were solved by direct methods and subsequent Fourier-difference techniques, and refined anisotropically for all non-hydrogen atoms by full-matrix least squares, on F^2 for **7**·OC_4H_8 and **8**·$1.25C_7H_8$ using the Siemens SHELXTL V 5.03 program package (PC version),[26a] and on *F* for **5**·$0.25C_7H_8$ and $[Cp''_2ErBr]_2$ using the Siemens SHELXTL V 4.1 program package (PC version).[26b] The hydrogen atoms were geometrically fixed using the riding model. One of the Me_3Si groups (Si1) in **5**·$0.25C_7H_8$ is disordered over two sets of positions with 0.60 : 0.40 occupancies. The toluene molecule in the lattice of **5**·$0.25C_7H_8$ is also disordered over two sets of positions with 0.50 : 0.50 occupancies. One toluene molecule in the lattice of **8**·$1.25C_7H_8$ is disordered over two sets of positions with 0.50 : 0.50 occupancies. The other toluene molecule in the lattice of **8**·$1.25C_7H_8$ is highly disordered, so that only the hexagonal ring could be found.

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Table 6 Crystal data and summary of data collection and refinement for **5**·$0.25C_7H_8$, **7**·OC_4H_8, **8**·$1.25C_7H_8$ and $[Cp''_2ErBr]_2$

	5·$0.25C_7H_8$	**7**·OC_4H_8	**8**·$1.25C_7H_8$	$[Cp''_2ErBr]_2$
Formula	$C_{51.75}H_{74}BO_2Si_4Sm$	$C_{35}H_{72}B_{11}Br_6O_3Si_4Sm$	$C_{39.5}H_{69.5}B_{11}Br_6O_2Si_4Er$	$C_{44}H_{84}Br_2Si_8Er_2$
Crystal size/mm	0.12 × 0.15 × 0.40	0.30 × 0.10 × 0.30	0.14 × 0.12 × 0.14	0.12 × 0.25 × 0.40
M	1001.63	1402.01	1454.44	1332.20
Crystal class	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	13.281(1)	13.487(3)	13.444(3)	10.686(2)
b/Å	22.413(1)	33.769(7)	33.625(7)	11.663(2)
c/Å	19.449(1)	14.365(3)	14.327(3)	13.233(2)
α/°	90.00	90.00	90.00	73.24(2)
β/°	95.14(1)	99.34(3)	99.17(3)	83.89(2)
γ/°	90.00	90.00	90.00	76.62(2)
U/Å^3	5766(3)	6456(2)	6394(2)	1534.9(8)
Z	4	4	4	1
D_c/Mg m^{-3}	1.154	1.443	1.511	1.411
Radiation (*λ*/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
2*θ* Range/°	3.0–55.0	3.0–55.0	3.0–55.0	3.0–55.0
μ/mm^{-1}	1.134	4.725	5.166	4.198
F(000)	2094	2756	2864	666
T/K	294	294	294	294
No. observed reflections [$I > X\sigma(I)$]	3540 ($X = 3$)	8494 ($X = 2$)	5665 ($X = 2$)	5509 ($X = 3$)
No. parameters refined	537	573	564	256
Goodness of fit	1.53	0.89	0.98	2.65
*R*1	0.067	0.061	0.069	0.037
*wR*2	0.190	0.168	0.171	0.152

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