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Displacement, reduction, and ligand redistribution reactivity of the cationic mono-C_5Me_5 Ln^{2+} complexes $(C_5Me_5)Ln(BPh_4)$ (Ln = Sm, Yb)

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Dedicated to Chris Elschenbroich for his outstanding contributions to organometallic chemistry.

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ABSTRACT

The reactivity of the mono(pentamethylcyclopentadienyl) divalent lanthanide tetraphenylborate complexes, $(C_5Me_5)Ln(BPh_4)$ (Ln = Sm, **1**; Yb, **2**), was investigated to determine how Ln^{2+} and $(BPh_4)^{1-}$ reactivity would combine in these species. The $(BPh_4)^{1-}$ ligand in $(C_5Me_5)Yb(BPh_4)$ can be displaced with $KN(SiMe_3)_2$ to form the heteroleptic divalent dimer, $\{(C_5Me_5)Yb[\mu\text{-}N(SiMe_3)_2]\}_2$ (**3**). Both **1** and **2** reduce phenazine to give the bis(pentamethylcyclopentadienyl) ligand redistribution products, $[(C_5Me_5)_2Ln]_2(\mu\text{-}C_{12}H_8N_2)$. 2,2-Bipyridine is reduced by **1** to yield the ligand redistribution product, $(C_5Me_5)_2Sm(C_{10}H_8N_2)$ (**4**), while **2** does not react with bipyridine. *Tert*-butyl chloride is reduced by **1** to form the trimetallic pentachloride complex $[\{(C_5Me_5)(THF)Sm\}_3(\mu\text{-}Cl)_5][BPh_4]$ (**6**), in a reaction that appears to use the reductive capacity of both Sm^{2+} and $(BPh_4)^{1-}$.

1. Introduction

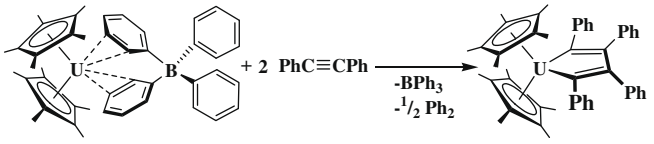
The reactivity of mono(pentamethylcyclopentadienyl) f-element complexes has been studied to a lesser extent than that of the bis(ring) metallocene counterparts in part because lanthanide and actinide complexes containing a single $(C_5Me_{5-x}H_x)^{1-}$ ring are rare [1]. Although this mono-ring chemistry is not common, some spectacular trivalent lanthanide reactivity has resulted from mono-ring complexes [2].

Recently, the synthesis of the unsolvated *divalent* mono-ring complexes $(C_5Me_5)Ln(BPh_4)$ (Ln = Sm, **1**; Yb, **2**) was reported [3]. Complexes **1** and **2** provide an opportunity to expand mono-ring f-element reaction chemistry since several reaction pathways could be accessible to provide new mono(pentamethylcyclopentadienyl) products. It has previously been shown that the $(BPh_4)^{1-}$ ligand can be easily substituted in the bis(ring) complexes, $(C_5Me_5)_2M(\mu\text{-}Ph_2BPh_2)$, and effectively provides access to highly reactive, unsolvated, sterically unsaturated complexes, $(C_5Me_5)_2LnX$ [4]. Analogous, ionic metathesis with **1** and **2** would result in the formation of new divalent mono-ring products. Since **1** and **2** are divalent lanthanide complexes, this displacement could also be accompanied by the reduction chemistry of Sm^{2+} and Yb^{2+} [5].

The $(BPh_4)^{1-}$ ligand also offers another option in reactivity for **1** and **2**, namely reduction. Reactions of $(C_5Me_5)_2U(\mu\text{-}Ph_2BPh_2)$ [6] have shown that the $(BPh_4)^{1-}$ ligand can provide an electron *via* Eq. (1) in combination with the reductive reactivity of U^{3+} to provide multi-electron reduction reactivity [7]. The two electron reductive coupling of diphenylacetylene in Eq. (2) is an example.

$$(BPh_4)^{1-} \rightarrow BPh_3 + 1/2Ph_2 + e^{1-} \quad (1)$$

Although the redox reactivity of $(BPh_4)^{1-}$ has been known for decades [8],



(2)

the only time it has been combined with metal based reduction, to our knowledge, is with $(C_5Me_5)_2U(\mu\text{-}Ph_2BPh_2)$. It was of interest to

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see if $(BPh_4)^{1-}$ would also act as a reductant in divalent $(C_5Me_5)Ln(BPh_4)$ complexes such that **1** and **2** could effect two electron reductions from the monometallic starting materials. Accordingly, the reaction chemistry of **1** and **2** was surveyed.

2. Experimental

The manipulations described below were performed under argon or nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were sparged with UHP argon and dried over columns containing Q-5 and molecular sieves. NMR solvents were dried over NaK alloy and vacuum transferred prior to use. ^1H and ^{13}C NMR spectra were recorded with a Bruker GN 500 MHz spectrometer. $(C_5Me_5)Sm(BPh_4)$ (**1**), and $(C_5Me_5)Yb(BPh_4)$ (**2**), were prepared according to literature procedures [3]. Phenazine, 2,2-bipyridine, and bathocuproine were purchased from Aldrich and sublimed prior to use. $KN(SiMe_3)_2$ was purchased from Aldrich and used as received. *Tert*-butyl chloride was dried over CaH_2 for two days and distilled onto molecular sieves.

2.1. $\{(C_5Me_5)Yb[\mu\text{-}N(SiMe_3)_2]\}_2$ (**3**)

In an argon glovebox free of coordinating solvents, $KN(SiMe_3)_2$ (11 mg, 0.055 mmol) was added slowly to a stirred solution of $(C_5Me_5)Yb(BPh_4)$ (**2**), (35 mg, 0.056 mmol) in 10 mL of benzene. The green solution immediately changed color to red-brown. After 15 min, the mixture was filtered and solvent was removed from the solution under vacuum leaving **3** as a red-brown solid (19 mg, 72%). Single crystals of **3** suitable for X-ray diffraction were grown by slow evaporation of C_6D_6 at 25 °C. ^1H NMR (C_6D_6, 298 K): δ 0.25 (s, 18H, Si*Me*$_3$), 2.11 (s, 15H, C_5*Me*$_5$). ^{13}C NMR (C_6D_6, 298 K): δ 5.51 (s, Si*Me*$_3$), 14.67 (s, C_5*Me*$_5$), 116.13 (s, *C*$_5$Me$_5$). Anal. Calc. for $C_{32}H_{66}N_2Si_4Yb_2$: C, 41.00; H, 7.11; N, 2.99; Si, 11.99; Yb, 36.92. Found: C, 41.69; H, 7.14; N, 2.92; Si, 11.76; Yb, 36.13%.

2.2. $[(Me_3Si)_2N]_2Sm(THF)_2$

In an argon atmosphere glovebox free of coordinating solvents, $KN(SiMe_3)_2$ (87 mg, 0.44 mmol) was added to a stirred solution of **1** (265 mg, 0.438 mmol) in toluene (10 mL). The green solution immediately changed to purple. Upon centrifugation, a purple precipitate was obtained. The purple, toluene insoluble product, was transferred to a glovebox containing coordinating solvents and dissolved in THF and identified by ^1H NMR spectroscopy as the previously characterized, $[(Me_3Si)_2N]_2Sm(THF)_2$ [9].

2.3. $[(C_5Me_5)_2Sm]_2(C_{12}H_8N_2)$

In a nitrogen atmosphere glovebox containing coordinating solvents, phenazine, $C_{12}H_8N_2$, (16 mg, 0.89 mmol) was added to a stirred solution of **1** (73 mg, 0.090 mmol) in 8 mL of THF. The green-brown solution immediately turned brown. After 30 min, dark brown material was separated by filtration and the solvent was removed from the solution under vacuum to form the previously characterized $[(C_5Me_5)_2Sm]_2(C_{12}H_8N_2)$ [10] as a brown powder (32 mg, 49%).

2.4. $(C_5Me_5)_2Sm(C_{10}H_8N_2)$ (**4**)

In a nitrogen glovebox containing coordinating solvents, **1** (42 mg, 0.069 mmol) was treated with 2,2-bipyridine (11 mg, 0.070 mmol) in 5 mL benzene. The solution immediately turned color from dark green to dark brown. After 10 min, dark brown material was removed by centrifugation and the solvent was removed from the solution under vacuum. The previously characterized $(C_5Me_5)_2Sm(bipy)$ [11], **4**, was isolated as a brown powder (11 mg, 53%) and identified by ^1H NMR spectroscopy.

2.5. $(C_5Me_5)_2Sm(C_{26}H_{20}N_2)$ (**5**)

In an argon glovebox free of coordinating solvents, **1** (104 mg, 0.172 mmol) was dissolved in 12 mL of benzene and bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) (62 mg, 0.172 mmol) was added to the stirred solution. The dark green solution immediately became green-blue. After 10 min, dark green material was removed by filtration and the solvent was removed from the solution under vacuum to yield **5** as a dark green-blue powder (83 mg, 62%). ^1H NMR (C_6D_6, 298 K): δ 2.79 (s, 30H, C_5*Me*$_5$) ppm. ^{13}C NMR (C_6D_6, 298 K) δ 130.39 (*C*$_5$Me$_5$), 32.93 (C_5*Me*$_5$) ppm. APCI mass spectrometry: $[(C_5Me_5)_2Sm(C_{26}H_{20}N_2)]^+$ was observed at m/z = 782.1. Anal. Calc. for $C_{46}H_{50}N_2Sm$: C, 70.72; H, 6.45; N, 3.59; Sm, 19.25. Found: C, 70.48; H, 5.75; N, 3.32; Sm, 18.60%.

2.6. $[\{(C_5Me_5)(THF)Sm\}_3(\mu\text{-}Cl)_5][BPh_4]$ (**6**)

In a nitrogen atmosphere glovebox containing coordinating solvents, *tert*-butyl chloride (6 μL, 0.06 mmol) was added to **1** (29 mg, 0.048 mmol) in benzene (10 mL). The dark green solution immediately became light purple. The solution was filtered and the solvent removed from the solution under vacuum to obtain **6** as a red solid. Upon vapor diffusion of THF into an NMR tube at 25 °C, a few red crystals of **6** suitable for X-ray analysis were obtained. ^1H NMR (C_6D_6, 298 K): δ 7.71 (d, 8H, Ph), 7.42 (t, 4H, Ph), 7.25 (t, 8H, Ph), 3.52 (br s, THF), 2.08 (br s, THF), 1.26 (s, 45H, C_5*Me*$_5$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ 136.47 (*C*$_5$Me$_5$), 31.80 (C_5*Me*$_5$) ppm. In addition, resonances at δ 7.67, 7.30, and 7.24 ppm were observed in the ^1H NMR spectrum consistent with the presence of BPh_3.

2.7. X-ray data collection, structure determination, and refinement. $\{(C_5Me_5)Yb[\mu\text{-}N(SiMe_3)_2]\}_2$ (**3**)

A red crystal of approximate dimensions 0.20 × 0.24 × 0.31 mm was mounted on a glass fiber and transferred to a Bruker CCD plat-

Table 1
X-ray data collection parameters for $\{(C_5Me_5)Yb[\mu\text{-}N(SiMe_3)_2]\}_2$ (**3**), and $[\{(C_5Me_5)(THF)Sm\}_3(\mu\text{-}Cl)_5][BPh_4]$ (**6**).

Empirical formula	$C_{32}H_{66}N_2Si_4Yb_2$ **3**	$C_{80}H_{83}BCl_5O_3Sm_3$ **6**
Formula weight	937.31	1731.57
Temperature (K)	163(2)	100(2)
Crystal system	Orthorhombic	Hexagonal
Space group	*Pbca*	*P*6(3)
a (Å)	15.9601(13)	21.8760(12)
b (Å)	14.0790(12)	21.8760(12)
c (Å)	17.0231(14)	28.729(3)
α (°)	90	90
β (°)	90	90
γ (°)	90	120
Volume (Å^3)	3825.1(5)	11906.7(15)
Z	4	6
$\rho_{calcd.}$ (mg/m^3)	1.628	1.449
μ (mm^{-1})	5.008	None
R_1[a] ($I > 2.0\sigma(I)$)	0.0156	0.0374
wR_2[b] (all data)	00377	0.0902

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

form diffractometer. Details of data collection are given in Table 1. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *Pbca* which was later determined to be correct. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}). The molecule was located about an inversion center. At convergence, $wR_2 = 0.0377$ and GOF = 1.071 for 314 variables refined against 4747 data. As a comparison for refinement on F, $R_1 = 0.0156$ for those 4062 data with $I > 2.0\sigma(I)$. The SMART [12] program package was used to determine the unit-cell parameters and for data collection (40 s/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT [13] and SADABS [14] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL [15] program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors [16] for neutral atoms were used throughout the analysis.

2.8. [{(C_5Me_5)(THF)Sm}$_3$(μ-Cl)$_5$][BPh_4] (**6**)

A red crystal 0.40 × 0.10 × 0.10 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 20 s per frame using a scan width of 0.3°. Data collection was 99.8% complete to 25.00° in θ. A total of 59963 reflections were collected covering the indices, $-29 \le h \le 25$, $-28 \le k \le 28$, $-37 \le l \le 33$. 17991 reflections were found to be symmetry independent, with an R_{int} of 0.0429. Indexing and unit-cell refinement indicated a primitive, triclinic lattice. The space group was found to be $P\bar{6}(3)$. The data were integrated using the Bruker SAINT software program and scaled using the TWINABS software program. Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

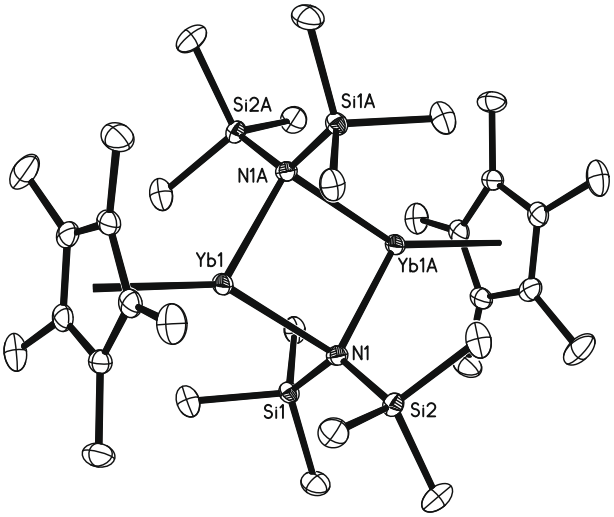


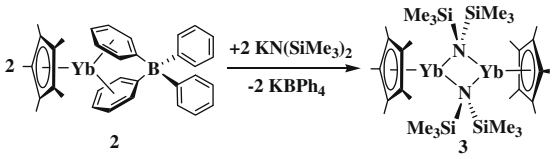
Fig. 1. Thermal ellipsoid plot of {(C_5Me_5)Yb[μ-N($SiMe_3$)$_2$]}$_2$ (**3**), with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

Table 2
Selected bond distances (Å) and bond angles (°) in {(C_5Me_5)Yb[μ-N($SiMe_3$)$_2$]}$_2$ (**3**).

Bond distances/angles	**3**
Yb(1)–(C_5Me_5 ring centroid)	2.471
Yb(1)–C(C_5Me_5) avg	2.75(2)
Yb(1)–N(1)	2.6224(15)
Yb(1)–N(1A)	2.4532(15)
N(1)–Si(1)	1.7109(16)
N(1)–Si(2)	1.7161(16)
(C_5Me_5 ring centroid)–Yb(1)–N(1)	149.7
(C_5Me_5 ring centroid)–Yb(1)–N(1A)	127.3
N(1)–Yb(1)–N(1A)	83.02(5)
Yb(1)–N(1)–Yb(1A)	96.98(5)

3. Results and discussion

The reaction of $KN(SiMe_3)_2$ with **1** and **2** was examined to determine if the $(BPh_4)^{1-}$ ion could be displaced to form unsolvated (C_5Me_5)Ln[$N(SiMe_3)_2$] complexes. (C_5Me_5)Yb[$N(SiMe_3)_2$](THF)$_2$ [17] had previously been reported from the reaction of [(C_5Me_5)-YbI(THF)$_2$]$_2$ with $KN(SiMe_3)_2$ in THF. Addition of $KN(SiMe_3)_2$ to a green solution of (C_5Me_5)Yb(BPh_4) immediately caused a color change to red-brown. The unsolvated ligand displacement product, {(C_5Me_5)Yb[$N(SiMe_3)_2$]}$_2$, **3**, was isolated in 70% yield according to Eq. (3). The ^{1}H NMR spectrum of diamagnetic **3** contained $(C_5Me_5)^{1-}$



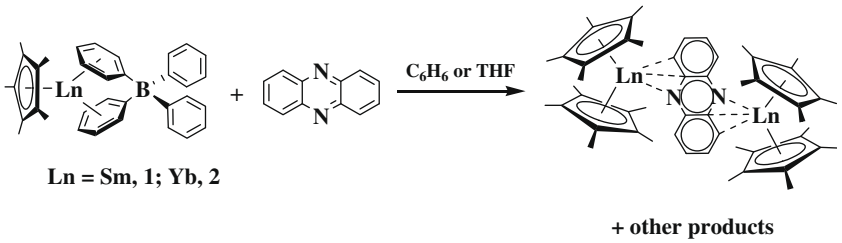
(3)

and $[N(SiMe_3)_2]^{1-}$ resonances in a 15:18 ratio and a dimeric structure was identified by X-ray crystallography, Fig. 1. Selected bond distances and angles are given in Table 2.

Dimeric **3** has an inversion center in the $\overline{\text{Yb-N-Yb-N}}$ ring and an asymmetric bridging structure with 2.6224(15) Å Yb(1)–N(1) and 2.4532(15) Å Yb(1)–N(1A) distances. These are longer than the 2.346(2) Yb–N distance in the terminal $[N(SiMe_3)_2]^{1-}$ ligand of (C_5Me_5)Yb[$N(SiMe_3)_2$](THF)$_2$ [17], as is typical for bridging ligands. The Yb(1)–N(1) distance is also longer than the Yb–N[(μ-$N(SiMe_3)_2$] bridging distances of 2.45(2)–2.47(2) Å in $NaYb[N(SiMe_3)_3]_3$ [18] and 2.510(2)–2.573(2) Å in $Yb[N(SiMe_3)_2]_2[AlMe_3]_2$ [19], which involve Yb–N–Na and Yb–N–Al linkages, respectively. The 2.727(2)–2.777(2) Å Yb–C(C_5Me_5) distances in **3** can be compared to the 2.653(4)–2.682(4) Å, 2.675(4)–2.727(4) Å, 2.643(7)–2.694(8) Å, 2.692(7)–2.770(8) Å, and 2.70(4)–2.83(3) Å ranges found in **2**, (C_5Me_5)Yb[$N(SiMe_3)_2$](THF)$_2$ [17], (C_5Me_5)$_2$Yb(THF) [20], (C_5Me_5)$_2$Yb(pyridine)$_2$ [21], and (C_5Me_5)$_2$Yb(NH_3)(THF) [22], respectively. The methyl displacements for each $(C_5Me_5)^{1-}$ ring range from 0.14 to 0.25 Å [23]. The four atom $\overline{\text{Yb-N-Yb-N}}$ ring is planar and the $(C_5Me_5)^{1-}$ rings on Yb(1) and Yb(1A) are eclipsed as shown in Fig. 2.

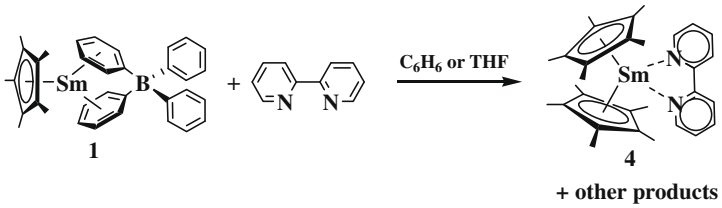
In contrast to Eq. (3), the analogous reaction of **1** with $KN(SiMe_3)_2$ afforded a product insoluble in toluene. Addition of THF, generated the ligand redistribution product [(Me_3Si)$_2$N]$_2$Sm(THF)$_2$ [9], which was identified by ^{1}H NMR spectroscopy.

Ligand redistribution had previously been observed in the reduction of phenazine by **1** and **2** in benzene [3], Eq. (4). This reaction was also examined in a coordinating solvent, THF, and ligand redistribution was again observed. A similar reaction



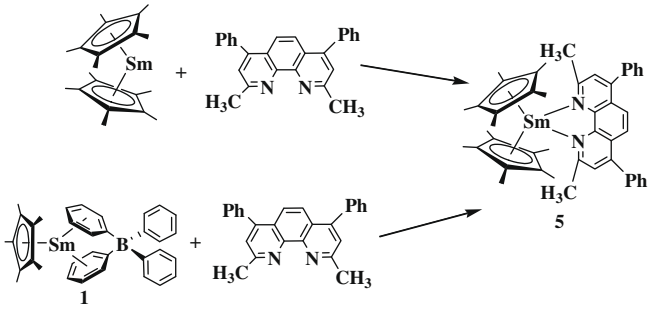
(4)

occurs between **1** and 2,2-bipyridine, Eq. (5). The ligand redistribution reduction product $(C_5Me_5)_2Sm(bipy)$ [11], **4**, was identified by ^1H NMR spectroscopy.



(5)

Bathocuproine reacts with **1** to produce a blue-green, alkane soluble product that has an identical $(C_5Me_5)^{1-}$ resonance in the ^1H NMR spectrum to that obtained from the reaction of $(C_5Me_5)_2Sm$ with bathocuproine, Eq. (6). The formula of **5** is consistent with

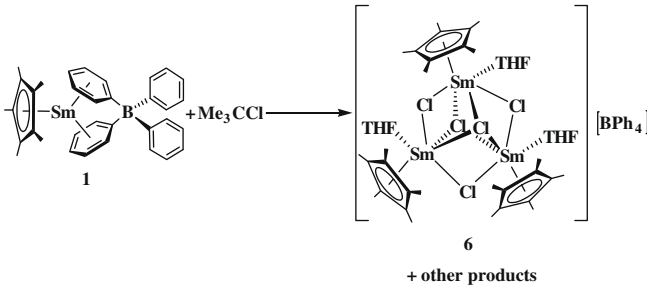


(6)

$(C_5Me_5)_2Sm(C_{26}H_{20}N_2)$ based on elemental analysis and atmospheric pressure chemical ionization (APCI) mass spectrometry which showed a molecular ion peak at $m/z = 782.1$ corresponding to $[(C_5Me_5)_2Sm(C_{26}H_{20}N_2)]^+$. The ^{13}C NMR spectrum of **5** is consistent with Sm^{3+} [24], suggesting that the bathocuproine has been reduced to a radical anion. Consistent with this, a signal was observed by EPR spectroscopy with a *g*-value of 1.96.

In each of the reactions involving $(C_5Me_5)Ln(BPh_4)$ (Ln = Sm, Yb) with 2,2-bipyridine, bathocuproine, and phenazine, bis(pentamethylcyclopentadienyl) products were isolated instead of mono-ring complexes. The ligand redistribution that makes the bis-ring products necessarily produces some other cyclopentadienyl-free product. In each of the above reactions, dark insoluble material was separated by filtration upon completion of the reaction. Elemental analysis of this insoluble material was consistent with $Ln(BPh_4)_3$.

The reaction of **1** with *tert*-butyl chloride in benzene differed significantly from those described above. After crystallization with vapor diffusion of THF, the one isolable product was the trimetallic complex $[\{(C_5Me_5)(THF)Sm\}_3(\mu\text{-}Cl)_5][BPh_4]$ (**6**), which was obtained in low yield and identified by X-ray diffraction, Fig. 3, Eq. (7). Neither of the common ligand redistribution products, $[(C_5Me_5)_2SmCl]_3$ [25] nor $(C_5Me_5)_2SmCl(THF)$ [26], were observed in the ^1H NMR spectrum.



(7)

The structure of **6** indicates that ligand redistribution to form a bis(pentamethylcyclopentadienyl) product did not occur in this case: each samarium retains a single $(C_5Me_5)^{1-}$ ligand. However, only one $(BPh_4)^{1-}$ ligand remains in the structure and it is now an outer sphere anion. Five chloride ligands are present with the three trivalent samarium atoms, a result that requires at least five equivalents of a reductant. Three reducing equivalents are available from the Sm^{2+} ions that become Sm^{3+} in the product. The other two may arise from two $(BPh_4)^{1-}$ ligands via Eq. (1).

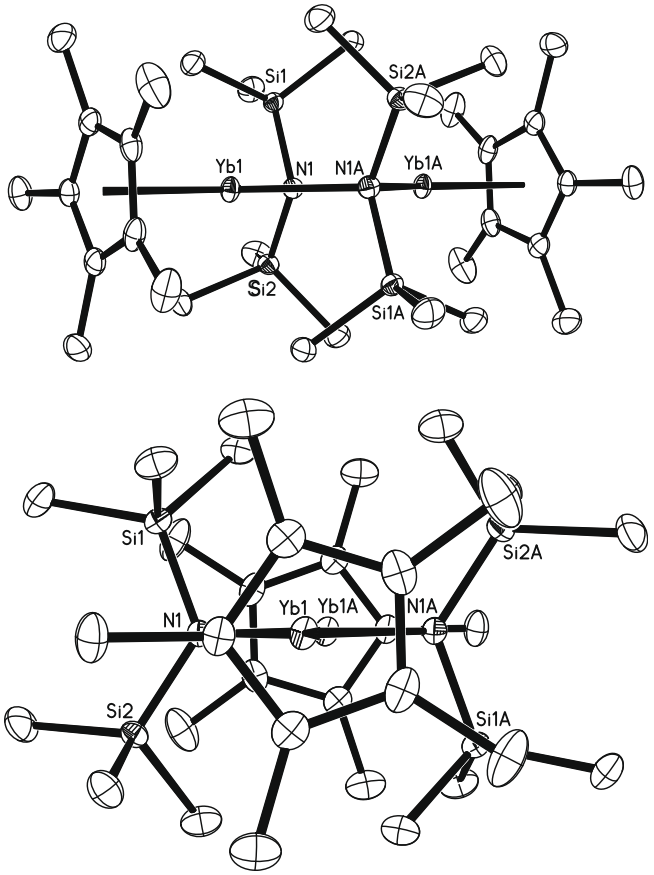


Fig. 2. Thermal ellipsoid side-on and end-on views of $\{(C_5Me_5)Yb[\mu\text{-}N(SiMe_3)_2]\}_2$ (**3**).

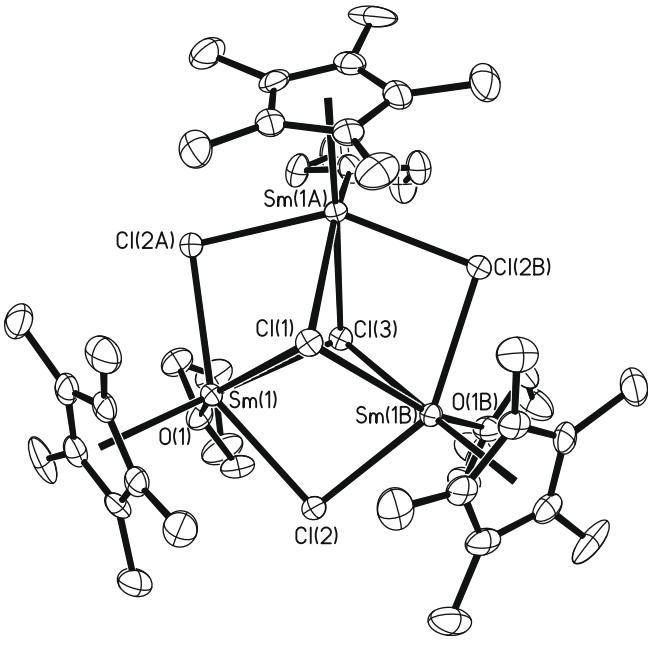


Fig. 3. Thermal ellipsoid plot of $[\{(C_5Me_5)(THF)Sm\}_3(\mu\text{-}Cl)_5]^{1+}$ (**6**), with the probability ellipsoids drawn at the 50% level. Hydrogen atoms and $(BPh_4)^{1-}$ have been excluded for clarity.

Consistent with this, BPh_3 was identified in both the ^1H and ^{13}C NMR spectra. However, the other expected byproduct of $(BPh_4)^{1-}$ oxidation, Ph_2, could not be located in either spectrum.

Table 3
Selected bond distances (Å) and bond angles (°) for $[\{(C_5Me_5)(THF)Sm\}_3(\mu\text{-}Cl)_5][BPh_4]$ (**6**).

Bond distance/angles	**6**
Sm(1)–Cl(1)	2.8748(13)
Sm(1)–Cl(2)	2.7752(13)
Sm(1)–Cl(3)	2.9017(13)
Sm(1)–Cl(2A)	2.7645(13)
Sm(1)–(C_5Me_5 ring centroid)	2.379
Sm(1)–O(1)	2.402(4)
(C_5Me_5 ring centroid)–Sm(1)–Cl(1)	107.4
(C_5Me_5 ring centroid)–Sm(1)–Cl(2)	104.2
(C_5Me_5 ring centroid)–Sm(1)–Cl(3)	178.6
Cl(1)–Sm(1)–Cl(2)	78.30(3)
Cl(1)–Sm(1)–Cl(3)	72.38(5)

The structure of **6** has a triangle of samarium ions bridged by three co-planar chlorides. Above and below the plane are triply bridging chloride ligands. Each samarium is also ligated with a terminal $(C_5Me_5)^{1-}$ and a THF. The core structure, $Ln_3(\mu_3\text{-}X)_2(\mu\text{-}X)_3$, is very common in lanthanide chemistry with X = halides [27,28], alkoxides [29], and hydrides [30]. The structural parameters and selected bond distances and angles are given in Table 3. The symmetry equivalent, doubly-bridging chloride ligands, Cl(2), Cl(2A), and Cl(2B), have Sm–Cl bond distances of 2.764(1) and 2.775(1) Å which are very close to the 2.745(2) and 2.764(2) Å analogues in $[(C_5Me_5)_2Sm](\mu\text{-}Cl)_6(\mu_3\text{-}Cl)_2(\mu_4\text{-}Cl)[(C_5Me_5)Sm]_4$ [1c]. The triply bridging chlorides, Cl(1) and Cl(3), have longer Sm–Cl bond distances, 2.875(1) and 2.902(1) Å, consistent with the 2.995(2) analogue in $[(C_5Me_5)_2Sm](\mu\text{-}Cl)_6(\mu_3\text{-}Cl)_2(\mu_4\text{-}Cl)[(C_5Me_5)Sm]_4$ as well as the 2.67–3.09(1) Å Sm-(μ_3-Cl) distances in $(C_5H_5)_{12}Sm_{12}(\mu_3\text{-}Cl)_{24}$ [31]. The Sm(1)–(C_5Me_5 ring centroid) distance of 2.379 Å is shorter than the 2.43–2.47 Å seen in $(C_5Me_5)_2SmCl(THF)$ [25], but similar to the 2.376 Å observed for the samarium with one $(C_5Me_5)^{1-}$ ligand in $[(C_5Me_5)_2Sm](\mu\text{-}Cl)_6(\mu_3\text{-}Cl)_2(\mu_4\text{-}Cl)[(C_5Me_5)Sm]_4$ [1c]. The Sm(1)–O(THF) bond distance of 2.402(4) Å is similar to the 2.48(2) Å analog in $(C_5Me_5)_2SmCl(THF)$ [29].

4. Discussion

The reaction chemistry of $(C_5Me_5)Yb(BPh_4)$ (**2**), with $KN(SiMe_3)_2$ to form $\{[(C_5Me_5)Yb[N(SiMe_3)_2]\}_2$, Eq. (3), shows that this mono-cyclopentadienyl complex can be a good precursor to other mono-ring complexes by ligand displacement of $(BPh_4)^{1-}$. Hence, in this case the mono-cyclopentadienyl chemistry mimics that of $(C_5Me_5)_2Ln(BPh_4)$ complexes [32]. However, the reaction of the analogue with the larger metal, namely $(C_5Me_5)Sm(BPh_4)$ (**1**), gives the ligand redistribution product, $[(Me_3Si)_2N]_2Sm(THF)_2$ [9].

Complex **1** also is highly prone to ligand redistribution reactivity when it participates in reduction reactions with phenazine, bipyridine, and bathocuproine. Hence, as shown in Eqs. (4)–(6), reduction of these substrates with this mono-ring complex does not provide mono-ring trivalent products, but rather the more common bis(cyclopentadienyl) trivalent compounds already accessible from $(C_5Me_5)_2Sm(THF)_x$ reagents. Only in the case of the reduction of Me_3CCl by **1** was a mono-ring product isolable, Eq. (7). In this case, an unusual trimetallic complex was generated and evidence for a combination of Sm^{2+} and $(BPh_4)^{1-}$ reduction was observed.

These reactions highlight the importance of having the appropriate metal size to observe mono-cyclopentadienyl chemistry without the complication of ligand redistribution. This appears to be easier to achieve with the smaller metals in the lanthanide series than with a metal as large as samarium. This makes the expansion of mono-ring lanthanide chemistry with mono-ring divalent

reagents challenging since the smaller metal, ytterbium, is also less reducing. It is likely that other lanthanide reductive methods involving combinations of trivalent precursors with alkali metals, the so-called LnZ_3/M and LnZ_2Z'/M methods [33], would be better routes to access mono-ring products via reduction using $[(C_5Me_5)LnX_2]_n$ [1a] starting materials.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.038.

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