Synthesis and Reactivity of Mono(pentamethylcyclopentadienyl) Tetraphenylborate Lanthanide Complexes of Ytterbium and Samarium: Tris(ring) Precursors to (C_5Me_5)Ln Moieties

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The synthesis of unsolvated $(C_5Me_5)Ln(BPh_4)$ complexes (Ln = Sm, Yb) has been investigated to determine if the productive chemistry of the metallocene tetraphenylborate complexes, $(C_5Me_5)_2Ln(\mu\text{-}Ph)_2BPh_2$, can be expanded to mono(pentamethylcyclopentadienyl) systems. Precursors $(C_5Me_5)_2Yb$, **1**, and $(C_5Me_5)_2Sm$, **2**, were both prepared by desolvation of $(C_5Me_5)_2Ln(THF)_2$ under high vacuum in near quantitative yields. Compounds **1** and **2** react with $[Et_3NH][BPh_4]$ to form divalent $(C_5Me_5)Ln(\mu\text{-}\eta^6{:}\eta^1\text{-}Ph)_2BPh_2$ (**3**, Yb; **4**, Sm) complexes in which two of the phenyl rings of the tetraphenylborate counteranion coordinate η^6 to the lanthanide to generate a three-ring coordination geometry involving cyclopentadienyl and arene coordination. In contrast to the expected trigonal plane defined by the three-ring centroids in **3**, the structure of **4** is pyramidal with Sm 0.41 Å out of the plane of the three-ring centroids. Complex **3** reacts with THF to make the polysolvated complex, $[(C_5Me_5)Yb(THF)_4][BPh_4]$, **5**, which can also be obtained from $(C_5Me_5)_2Yb(THF)_2$ and $[Et_3NH][BPh_4]$. With **4**, a monosolvated complex, $(C_5Me_5)Sm[(\mu\text{-}\eta^6{:}\eta^1\text{-}Ph)(\mu\text{-}\eta^2{:}\eta^1\text{-}Ph)BPh_2](THF)$, **6**, can be isolated that retains η^6 coordination by one aryl ring and displays η^2 coordination with the other aryl ring. Reaction of phenazine with **3** and **4** is accompanied by ligand redistribution to form the trivalent bis(pentamethylcyclopentadienyl) products, $[(C_5Me_5)_2Ln]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}C_{12}H_8N_2]$, (Yb, **7**; Sm, **8**). Reduction of azobenzene by **4** generates a mono(pentamethylcyclopentadienyl)tetraphenylborate complex, $(C_5Me_5)Sm[(\mu\text{-}\eta^6{:}\eta^1\text{-}Ph)BPh_3](N_2Ph_2)$, **9**, that contains an η^6 coordinated phenyl ring and an azobenzene radical anion.

Introduction

The tetraphenylborate anion, $(BPh_4)^{1-}$, has been a useful counteranion in f element chemistry for many years. As a large non-coordinating anion, it often balances the size of the f element cation and provides fully characterizable crystalline materials.[1−11] However, the phenyl rings of the $(BPh_4)^{1-}$ anion can also interact with f elements and stabilize unsolvated cations that would ordinarily not be isolable. In this capacity, $(BPh_4)^{1-}$ has been found to have a broad range of coordination modes.[12−25] The phenyl groups in $(BPh_4)^{1-}$ ions can adopt η^1 to η^6 interactions with lanthanides. As demonstrated by Deacon et al.,[12,13] when two of the phenyl groups in the a $(BPh_4)^{1-}$ ligand coordinate as η^6 ligands, they generate a new class of lanthanide ansa-metallocenes, as exemplified by $Ph_2B(\mu\text{-}\eta^1{:}\eta^6\text{-}Ph)_2YbXL$ where X = $N(SiMe_3)_2$ and 3,5-di-*tert*-butylpyrazolyl and L = THF.

In metallocene chemistry, the tetraphenylborate complexes, $(C_5Me_5)_2Ln(\mu\text{-}Ph)_2BPh_2$ (Ln = lanthanide), have provided a convenient route to unsolvated, sterically unsaturated $[(C_5Me_5)_2LnR]_x$ complexes highly reactive for C−H activation.[24,25] With the actinide analogue, $(C_5Me_5)_2U(\mu\text{-}Ph)_2BPh_2$,[26] a complex that

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contains redox active trivalent uranium, unusual reactions involving $(BPh_4)^{1-}$ reductive chemistry,[16] and the conversion of azide to nitride[27] to make polymetallic actinide complexes of unprecedented size have been observed.

Mono(pentamethylcyclopentadienyl) analogs of the highly reactive $(C_5Me_5)_2Ln(\mu\text{-}Ph)_2BPh_2$ complexes, namely, species such as $(C_5Me_5)Ln(BPh_4)$, could also have an extensive chemistry. Mono(pentamethylcyclopentadienyl) chemistry has been much less developed than the chemistry of the bis(ring) metallocenes,[28] but recent results (e.g., with $(C_5Me_4SiMe_3)^{1-}$ complexes)[29−31] show that this area has considerable potential.

The synthesis of $(C_5Me_5)Ln(BPh_4)$ seemed reasonable since Deacon et al. had shown that the divalent $Yb[N(SiMe_3)_2]_2(THF)_2$ precursors would react cleanly with alkylammonium tetraphenylborate salts to make complexes such as $[(Me_3Si)_2N]Yb(THF)(BPh_4)$,[12] $[(Me_3Si)_2N]Yb(BPh_4)$,[13] and (3,5-di-*tert*-butylpyrazolyl)-$Yb(THF)(BPh_4)$.[13] The high reactivity of Sm^{2+} makes this more challenging,[32−35] but the product would concomitantly have a more extensive reaction chemistry. We report here the synthesis and structure of samarium and ytterbium $(C_5Me_5)Ln(BPh_4)$ complexes as well as some preliminary reactivity studies. In addition, we report a more facile route to the unsolvated ytterbium precursor, $(C_5Me_5)_2Yb$.[36,37]

Experimental Procedures

The chemistry described below was performed under argon with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. $(C_5Me_5)_2Sm$,[32] $(C_5Me_5)_2Yb(THF)_2$,[38] $AgBPh_4$,[39] and $[Et_3NH][BPh_4]$[8] were prepared as previously reported. Phenazine (Aldrich) was sublimed before use. Azobenzene (Aldrich) was recrystallized and degassed before use. C_8H_8 (Aldrich) was distilled onto activated 4 Å molecular sieves and degassed. Solvents were sparged with UHP argon (Airgas) and dried over columns containing Q-5 and sieves. NMR solvents (Cambridge Isotopes) were dried over benzophenone-ketyl, degassed, and vacuum transferred before use. ^1H and ^{13}C NMR spectra were recorded with Bruker 500 and 600 MHz spectrometers. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 2000 FT-IR or as thin films on an ASI ReactIR 1000 spectrometer.[15] Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany). Complexometric analyses were performed as previously described.[40] Details of the crystallographic studies are given in Table 1 and in the Supporting Information.

Table 1. X-ray Data Collection Parameters for $(C_5Me_5)Yb(\mu\text{-}\eta^6\text{:}\eta^1\text{-}Ph)_2BPh_2$, 3, $(C_5Me_5)Sm(\mu\text{-}\eta^6\text{:}\eta^1\text{-}Ph)_2BPh_2$, 4, $(C_5Me_5)Sm[(\mu\text{-}\eta^6\text{:}\eta^1\text{-}Ph)(\mu\text{-}\eta^2\text{:}\eta^1\text{-}Ph)BPh_2](THF)$, 6, and $(C_5Me_5)Sm[(\mu\text{-}\eta^6\text{:}\eta^1\text{-}Ph)BPh_3](N_2Ph_2)$, 9

empirical formula	$C_{34}H_{35}BYb{\bullet}1.5C_6H_6$	$C_{34}H_{35}BSm{\bullet}C_6H_6$
Compound	**3**	**4**
Fw	744.63	682.89
temp (K)	163(2)	163(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	9.4236(11)	17.081(3)
b (Å)	46.204(5)	9.9752(17)
c (Å)	15.8959(18)	18.816(3)
α (deg)	90	90
β (deg)	91.749(2)	95.676(3)
γ (deg)	90	90
vol (Å^3)	6917.9(14)	3190.2(9)
Z	8	4
ρ_{calcd} (mg/m^3)	1.430	1.422
μ (mm^{-1})	2.732	1.867
R1[a] ($I > 2.0\sigma(I)$)	0.0415	0.0326
wR2[b] (all data)	0.0841	0.0891

empirical formula	$C_{38}H_{43}BOSm$	$C_{46}H_{45}BN_2Sm{\bullet}0.5C_6H_6$
Compound	**6**	**9**
Fw	676.88	826.05
temp (K)	163(2)	158(2)
cryst syst	monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	13.4854(15)	10.7083(11)
b (Å)	16.1230(18)	12.1261(12)
c (Å)	14.6003(16)	29.779(3)
α (deg)	90	90
β (deg)	101.970(2)	97.299(2)
γ (deg)	90	90
vol (Å^3)	3105.4(6)	3835.5(7)
Z	4	4
ρ_{calcd} (mg/m^3)	1.448	1.431
μ (mm^{-1})	1.920	1.568
R1[c] ($I > 2.0\sigma(I)$)	0.0401	0.0432
wR2[d] (all data)	0.0841	0.1052

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_0^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = [\Sigma[w(F_0^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$.

$(C_5Me_5)_2Yb$, 1.[36,37] In a glovebox, a 20 mm × 320 mm tube attached to a high vacuum greaseless stopcock was charged with magenta $(C_5Me_5)_2Yb(THF)_2$ (505 mg, 0.860 mmol). The apparatus was attached to a high vacuum line that can achieve pressures of 1×10^{-6} Torr (tungsten coil gauge calibration) using a Varian VHS-4 diffusion pump. After the sample had been exposed to vacuum for approximately 36 h and the pressure had dropped to 1×10^{-6} Torr, the solid had changed color from magenta to bright orange. The tube was heated to 50 °C for at least 3 days or until all the orange solid had changed to a brown solid. Note: conditions should be avoided in which the solid sublimes. Sublimation yields only the orange solid that has a ^1H NMR spectrum identical to that of $(C_5Me_5)Yb(THF)$.[41] Addition of 15 mL of toluene to the brown solid left at the bottom of the tube followed by filtration left a red solution. Removal of solvent left **1** as a green solid (366 mg, 96%). ^1H and ^{13}C NMR spectra were consistent with the previously characterized unsolvated $(C_5Me_5)_2Yb$.[36,37]

$(C_5Me_5)_2Sm$, 2.[32] In a similar fashion as described for **1**, dark purple $(C_5Me_5)_2Sm(THF)_2$ (276 mg, 0.488 mmol) was desolvated without sublimation by heating to 45 °C for at least 3 days. Addition of 15 mL of toluene to the green solid left at the bottom of the tube followed by filtration left a green solution. Removal of solvent left **2** as a green solid (193 mg, 94%). ^1H and ^{13}C NMR spectra were consistent with the previously characterized unsolvated $(C_5Me_5)_2Sm$.[32]

$(C_5Me_5)Yb(\mu\text{-}\eta^6\text{:}\eta^1\text{-}Ph)_2BPh_2$, 3. $[Et_3NH][BPh_4]$ (100 mg, 0.234 mmol) was added slowly to a stirred solution of **1** (104 mg, 0.233 mol) in 20 mL of C_6H_6. The reaction mixture immediately changed

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color from red to dark green. After 15 min, removal of a small amount of yellow insoluble material by centrifugation and filtration left a clear green solution. Removal of volatiles and solvent under vacuum yielded **3** as a green solid (125 mg, 86%). Anal. Calcd for $\mathrm{C_{34}H_{35}BYb}$: C, 65.07; H, 5.63; B, 1.72; Yb, 27.57. Found: C, 64.94; H, 5.48; B, 1.73; Yb, 27.90. ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C) δ 1.67 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$), 7.04 (m, 12H, $\mathrm{B}\mathit{Ph}_4$), 7.66 (m, 8H, $\mathrm{B}\mathit{Ph}_4$). ^{13}C NMR δ 12.02 ($\mathrm{C_5}\mathit{Me}_5$), 116.36 ($\mathit{C}_5\mathrm{Me_5}$), 125.16 ($\mathit{C}_6\mathrm{H_5}$), 128.11 ($\mathit{C}_6\mathrm{H_5}$), 128.69 ($\mathit{C}_6\mathrm{H_5}$), 134.72 ($\mathit{C}_6\mathrm{H_5}$). Single crystals of **3** suitable for X-ray diffraction were grown by slow evaporation of $\mathrm{C_6D_6}$ at 25 °C in an NMR tube. IR (thin film) 3092s, 3073m, 3038s, 1961w, 1814w, 1575w, 1529m, 1478s, 1428w, 1393w, 1351w, 1177m, 1154w, 1034s, 849m, 776m, 749m, 710s, 676s cm^{-1}. The ^{1}H NMR spectrum of the yellow insoluble material in THF-d_8 was consistent with previously characterized $\mathrm{[Yb(THF)_6][BPh_4]_2}$.[8]

3 from $\mathbf{(C_5Me_5)_2Yb}$ and $\mathbf{AgBPh_4}$. $\mathrm{AgBPh_4}$ (51 mg, 0.120 mmol) was added slowly to a stirred solution of **1** (53 mg, 0.120 mol) in 15 mL of $\mathrm{C_6H_6}$. The reaction mixture slowly changed color from red to yellow−green. After 6 h, removal of black insoluble material by centrifugation and filtration left a clear yellow−green solution. Removal of volatiles and solvent under vacuum yielded a tacky yellow−green solid. The solid was washed with 3 × 10 mL of hexane and then dried under vacuum leaving **3** as a green solid (125 mg, 86%). ^{1}H NMR analysis confirmed the formation of $\mathrm{(C_5Me_5)_2}$.[42]

$\mathbf{(C_5Me_5)Sm(\mu\text{-}\eta^6{:}\eta^1\text{-}Ph)_2BPh_2}$, 4. $\mathrm{[Et_3NH][BPh_4]}$ (89 mg, 0.208 mmol) was added slowly to a stirred solution of **2** (87 mg, 0.206 mol) in 20 mL of $\mathrm{C_6H_6}$. The reaction mixture immediately changed color from forest green to dark blue−green. After 15 min, removal of a small amount of purple insoluble material by centrifugation and filtration left a dark blue−green solution. Removal of volatiles and solvent under vacuum yielded a dark blue−green solid (99 mg, 80%). Anal. Calcd for $\mathrm{C_{34}H_{35}BSm}$: C, 67.51; H, 5.84; B, 1.79; Sm, 24.86. Found: C, 65.67; H, 5.82; B, 1.73; Sm, 24.50. ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C) δ −2.78 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$). ^{13}C NMR δ 107.20 ($\mathrm{C_5}\mathit{Me}_5$). The $\mathrm{(BPh_4)^-}$ resonances could not be located in this paramagnetic system. Single crystals of **4** suitable for X-ray diffraction were grown by slow evaporation of $\mathrm{C_6D_6}$ at 25 °C in an NMR tube. IR (thin film) 3092s, 3073m, 3038s, 1961w, 1814w, 1575w, 1529m, 1478s, 1428w, 1393w, 1177m, 1100w, 1034s, 849m, 776m, 749m, 710s, 676s cm^{-1}. The ^{1}H NMR spectrum of the purple insoluble material in THF-d_8 was consistent with previously characterized $\mathrm{[Sm(THF)_7][BPh_4]_2}$.[8]

$\mathbf{[(C_5Me_5)Yb(THF)_4][BPh_4]}$, **5**. Addition of 1 mL of THF to solid **3** (7 mg, 0.01 mmol) immediately formed a yellow solution. Solvent was removed leaving **5** as a yellow tacky solid in quantitative yield. Anal. Calcd for $\mathrm{C_{50}H_{67}O_4BYb}$: C, 65.56; H, 7.39; Yb, 18.89. Found: C, 65.30; H, 7.21; Yb, 19.08. ^{1}H NMR (THF-d_8, 25 °C) δ 1.93 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$), 7.25 (d, 8H, *o*-$\mathrm{B}\mathit{Ph}_4$), 6.85 (t, 8H, *m*-$\mathrm{B}\mathit{Ph}_4$), 6.71 (t, 4H, *p*-$\mathrm{B}\mathit{Ph}_4$), 3.56 (s, *THF*), 1.71 (s, *THF*). ^{13}C NMR δ 113.36 ($\mathit{C}_5\mathrm{Me_5}$), 11.39 ($\mathrm{C_5}\mathit{Me}_5$), 122.00 (*p*-$\mathrm{B}\mathit{Ph}_4$), 125.87 (*m*-$\mathrm{B}\mathit{Ph}_4$), 137.29 (*o*-$\mathrm{B}\mathit{Ph}_4$), 164.75, 165.14, 165.53, 165.93 (*ipso*-$\mathrm{B}\mathit{Ph}_4$), 68.39 (*THF*), 26.54 (*THF*). Single crystals of **5** suitable for X-ray diffraction were grown at 25 °C in an NMR tube. IR (KBr) 3056s, 3025s, 2992s, 2974s, 1942w, 1578w, 1479m, 1427m, 1188w, 1039m, 870s, 737m, 706w, 535w cm^{-1}.

$\mathbf{(C_5Me_5)Sm[(\mu\text{-}\eta^6{:}\eta^1\text{-}Ph)(\mu\text{-}\eta^2{:}\eta^1\text{-}Ph)BPh_2](THF)}$, 6. Addition of THF (0.008 mL, 0.10 mmol) to solid **4** (60 mg, 0.10 mmol) in 10 mL of $\mathrm{C_6H_6}$ immediately formed a dark green solution. After 15 min, the solvent was removed under vacuum leaving a dark green solid (65 mg, 97%). Single crystals of **6** suitable for X-ray diffraction were grown from a $\mathrm{C_6H_6}$ solution of this solid at −35 °C. Anal. Calcd for $\mathrm{C_{34}H_{35}BSm}$: C, 67.41; H, 6.42; B, 1.60; Sm, 22.21. Found: C, 67.20; H, 6.31; B, 1.69; Sm, 22.21. ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C) δ −3.37 (br s, 15H, $\mathrm{C_5}\mathit{Me}_5$). Resonances attributable to THF or $\mathrm{BPh_4}$ were not observed in this paramagnetic system. No resonances were observed in the ^{13}C NMR spectra due to the limited solubility of **6** in benzene or toluene. ^{1}H NMR (THF-d_8, 25 °C) δ 0.58 (br s, 15H, $\mathrm{C_5}\mathit{Me}_5$), 6.74 (br, 4H, *p*-$\mathrm{B}\mathit{Ph}_4$), 6.84 (br, 8H, *m*-$\mathrm{B}\mathit{Ph}_4$), 7.09 (br, 8H, *o*-$\mathrm{B}\mathit{Ph}_4$). ^{13}C NMR δ 95.10 (s, $\mathrm{C_5}\mathit{Me}_5$), 121.77 (*p*-$\mathrm{B}\mathit{Ph}_4$), 125.32 (*m*-$\mathrm{B}\mathit{Ph}_4$), 136.62 (*o*-$\mathrm{B}\mathit{Ph}_4$). 164.59, 164.70, 165.38, 165.78 (*ipso*-$\mathrm{B}\mathit{Ph}_4$). IR (KBr) 3049s, 2859s, 1580w, 1480m, 1429m, 1261w, 1152w, 1029m, 868m, 737m, 708s, 495w cm^{-1}.

$\mathbf{[(C_5Me_5)_2Yb]_2[(\mu\text{-}\eta^3{:}\eta^3\text{-}C_{12}H_8N_2)]}$, 7. Phenazine (3 mg, 0.018 mmol) was added slowly to a solution of **3** (18 mg, 0.029 mol) in 2 mL of $\mathrm{C_6D_6}$. The reaction mixture immediately changed color from green to deep red−brown. After 30 min, the reaction mixture was filtered leaving a deep red solution and brown insoluble material. Anal. Calcd for $\mathrm{C_{52}H_{68}N_2Yb_2}$: Yb, 32.4. Found: Yb, 31.5. Single crystals of **7** suitable for X-ray diffraction were grown from this solution at 25 °C (6 mg, 32%). Only broad peaks were observed in the ^{1}H NMR spectrum. The brown insoluble material did not dissolve in toluene, benzene, THF, or ether. IR (KBr) 2930s, 2861s, 1595m, 1490s, 1464s, 1331s, 1283s, 849w, 717w, 477s, 466m cm^{-1}.

$\mathbf{[(C_5Me_5)_2Sm]_2[(\mu\text{-}\eta^3{:}\eta^3\text{-}C_{12}H_8N_2)]}$, 8. Following the procedure stated previously, phenazine (6 mg, 0.036 mmol) was added slowly to a solution of **4** (21 mg, 0.035 mol) in 2 mL of $\mathrm{C_6D_6}$. The reaction mixture immediately changed color from green to deep red, and insoluble material formed. After 30 min, the reaction mixture was filtered leaving a deep red solution and brown insoluble material. Solvent was removed under vacuum leaving a dark brown solid (7 mg, 23%). The insoluble material did not dissolve in toluene, benzene, THF, or ether. Both the unit cell of single crystals of $\mathrm{[(C_5Me_5)_2Sm]_2[(\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{12}H_8N_2)]}$ and the ^{1}H NMR data matched the previously characterized complex.[43]

$\mathbf{(C_5Me_5)Sm(C_8H_8)}$. $\mathrm{C_8H_8}$ (2.0 μL, 0.018 mmol) was added via syringe to a stirred solution of **4** (22 mg, 0.036) in 10 mL of $\mathrm{C_6H_6}$. After 2 h, the reaction mixture changed color from green to orange, and insoluble material formed. The orange mixture was filtered leaving an orange solution and dark insoluble material. Solvent was removed from the orange solution leaving an orange−red solid. NMR analyses of the solid confirmed the formation of $\mathrm{(C_5Me_5)Sm(C_8H_8)}$[44] and $\mathrm{(C_5Me_5)_2Sm(\mu\text{-}Ph)_2BPh_2}$[14] in a 2:1 ratio (6.5 mg, 54% yield). The insoluble material was washed with hexane and $\mathrm{C_6H_6}$ to leave a gray solid (4.7 mg, 52%). Anal. Calcd for $\mathrm{C_{34}H_{35}BSm}$: C, 79.59; H, 5.58; Sm, 13.84. Found: C, 79.36; H, 5.40; Sm, 13.98. **3** and $\mathrm{C_8H_8}$ did not react.

$\mathbf{[(C_5Me_5)_2Sm][BPh_4]}$ from 4 and $\mathbf{AgBPh_4}$. $\mathrm{AgBPh_4}$ (12 mg, 0.028 mmol) was added slowly to a stirred solution of **4** (16 mg, 0.026 mol) in 10 mL of toluene. The reaction mixture eventually changed color from green to red. After 24 h, removal of insoluble material by centrifugation and filtration left a clear red solution. Removal of solvent under vacuum yielded a rose red solid (7.5 mg, 39%). ^{1}H NMR analysis was consistent with previously characterized $\mathrm{[(C_5Me_5)_2Sm][BPh_4]}$ as the only soluble product.[14] **3** and $\mathrm{AgBPh_4}$ did not react.

$\mathbf{(C_5Me_5)[Ph_3B(\mu\text{-}\eta^1{:}\eta^6\text{-}Ph)]Sm(\eta^2\text{-}N_2Ph_2)}$, 9. Azobenzene (18 mg, 0.101 mmol) was added slowly to a stirred solution of **4** (61 mg, 0.101 mmol) in 5 mL of $\mathrm{C_6H_6}$. The green solution immediately changed color to form a deep blue color. After 1 h, solvent was removed under vacuum leaving **9** as a glassy dark blue solid (71 mg, 90%). Anal. Calcd for $\mathrm{C_{34}H_{35}BSm}$: C, 70.19; H, 5.77; N, 3.56; B, 1.37; Sm, 19.10. Found: C, 69.89; H, 6.01; N, 3.77; B, 1.27; Sm, 19.40. ^{1}H NMR ($\mathrm{C_6D_6}$, 23 °C) δ 3.53 (br s, 15H, $\mathrm{C_5}\mathit{Me}_5$), 4.5 (br s, 3H, $\mathrm{N_2C_6}\mathit{H}_5$), 5.96 (br s, 7H, $\mathrm{B(C_6}\mathit{H}_5)_4$), 8.19 (br s, 8H, $\mathrm{B(C_6}\mathit{H}_5)_4$). No resonances were observed in the ^{13}C NMR spectra of this highly paramagnetic system. Single crystals of **9** suitable for X-ray diffraction were grown by slow evaporation of $\mathrm{C_6D_6}$ at

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(42) Jutzi, P.; Kohl, F. *J. Organomet. Chem.* **1979**, *164*, 141.

(43) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2600.

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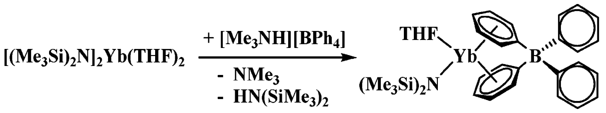
23 °C. IR (KBr) 3059s, 3046s, 3029s, 2969m, 2920s, 1597m, 1479m, 1427w, 1152w, 737m, 708m, 690m, 612w, 538w, 466w cm^{-1}.

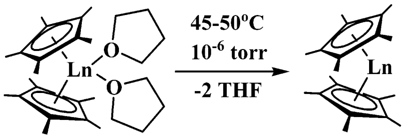
Results

Modified Syntheses of the (C_5Me_5)$_2$Ln Precursors. One direct route to the mono(ring) (C_5Me_5)Ln(BPh_4) targets was the reaction of the unsolvated metallocene precursors, (C_5Me_5)$_2$Ln (Ln = Sm, Yb), with alkylammonium tetraphenylborate salts. This method of making divalent tetraphenylborate complexes by selective protolytic cleavage of amide ligands had previously been shown to be successful by Deacon et al. with Yb[N($SiMe_3$)$_2$]$_2$(THF)$_2$ complexes (eq 1).[12,13]



(1)

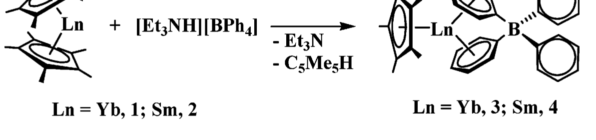
Before a reaction of this type was examined, more facile routes to the unsolvated precursors were sought. (C_5Me_5)$_2$Yb, **1**, can be isolated in 40% yield by heating (C_5Me_5)$_2$Yb(OEt$_2$)$_2$ in toluene at reflux under dynamic vacuum for 4 h.[36,37] (C_5Me_5)$_2$Sm, **2**, is typically obtained in 70% yield by desolvation of the THF solvate, (C_5Me_5)$_2$Sm(THF)$_2$, under high vacuum followed by sublimation.[32] Previously, it had been reported that (C_5Me_5)$_2$Yb(THF) could not be desolvated by the toluene reflux method or by sublimation. We have found that with a sufficiently low pressure (10^{-6} Torr) and the proper temperature, desolvation of both (C_5Me_5)$_2$Yb(THF)$_2$ and (C_5Me_5)$_2$Sm(THF)$_2$ can be effected via eq 2. A key component of this procedure is that the desolvation must be done under conditions in which formation of sublimate is avoided. For Yb, sublimation gives (C_5Me_5)$_2$Yb(THF). However, heating at 50 °C at low pressure for several days produces (C_5Me_5)$_2$Yb in >90% yield.



(2)

Ln = Yb, **1**; Sm, **2**

Synthesis of (C_5Me_5)Yb(μ-η^6:η^1-Ph)$_2$BPh$_2$, 3, and (C_5Me_5)Sm(μ-η^6:η^1-Ph)$_2$BPh$_2$, 4. The synthesis of **3** and **4** proceeded via eq 3 with yields over 80%.



(3)

Ln = Yb, **1**; Sm, **2** Ln = Yb, **3**; Sm, **4**

Evidently, [Et$_3$NH][BPh$_4$] reacts faster with the (C_5Me_5)$^{1-}$ rings in (C_5Me_5)$_2$Ln than with the remaining (C_5Me_5)$^{1-}$ rings in **3** and **4** or with the Sm^{2+} center to form Sm^{3+} and H_2. Surprisingly, these yields are even higher than the 26−67% yields observed with analogous [(Me$_3$Si)$_2$N]$_2$Yb(THF)$_2$ reactions.[12,13]

Complex **3** can also be synthesized in high yield from (C_5Me_5)$_2$Yb and AgBPh$_4$ (eq 4). Removal of (C_5Me_5)$^{1-}$ ligands by this method has previously been reported with sterically crowded (C_5Me_5)$_3$Ln complexes.[45] Since the product of eq 4 is still Yb^{2+}, this indicates that under these conditions, **1** is not sufficiently reactive to reduce Ag^{1+}. The reaction may proceed by ionic metathesis to make **3** and AgC$_5$Me$_5$ in which case the latter decomposes to the observed Ag and (C_5Me_5)$_2$ as described in the literature.[46] The reaction analogous to eq 4 with more strongly reducing (C_5Me_5)$_2$Sm produces the trivalent complex, (C_5Me_5)$_2$Sm(μ-Ph)$_2$BPh$_2$ and Ag metal.[14]

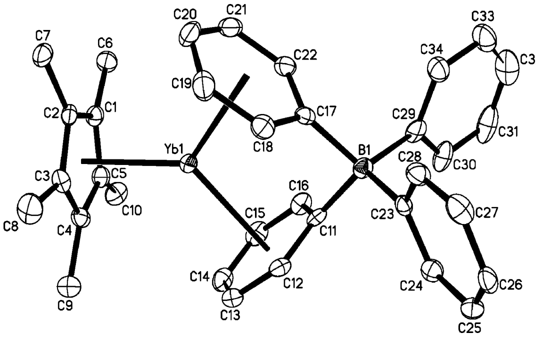
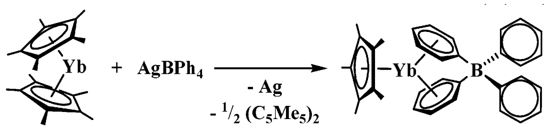


Figure 1. Thermal ellipsoid plot of (C_5Me_5)Yb(μ-η^6:η^1-Ph)$_2$BPh$_2$, **3**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity. (C_5Me_5)Sm(μ-η^6:η^1-Ph)$_2$BPh$_2$, **4**, is numbered similarly.



(4)

1 **3**

Structures of 3 and 4. Both **3** and **4** readily form crystals suitable for X-ray crystallography, and the structure of **3** is shown in Figure 1. Complexes **3** and **4** are not isomorphous, but they are similar in many respects. In the solid state, each metal in **3** and **4** is ligated by one η^5-(C_5Me_5) ring and two η^6-(C_6H_5) rings of the tetraphenylborate counteranion. Overall, this gives these tris(ring) complexes a formal coordination number of nine. Ligation by two η^6-(C_6H_5) rings from (BPh_4)$^{1-}$ ligands has been observed before in the lanthanide complexes, [(Me$_3$Si)$_2$N]Yb(THF)(μ-η^6:η^1-Ph)$_2$BPh$_2$,[12] [(Me$_3$Si)$_2$N]Yb(THF)(μ-η^6:η^1-Ph)(μ-η^1:η^1-Ph)BPh$_2$,[12] [(Me$_3$Si)$_2$N]Yb(μ-η^6:η^1-Ph)$_2$BPh$_2$,[13] and (3,5-di-*tert*-butylpyrazole)Yb(THF)(μ-η^6:η^1-Ph)$_2$BPh$_2$.[13]

An important difference between complexes **3** and **4** is the relative planarity of the three coordinating ring centroids. Trigonal planar is normally the most stable structure for ML$_3$ complexes. In complex **3**, the three-ring centroids adopt a trigonal planar arrangement around the metal that minimizes steric crowding. The Yb center and the three-ring centroids in **3** are coplanar to within 0.026 Å. In **4**, however, the samarium atom is 0.41 Å out of the plane of the three-ring centroids (i.e., the rings take on a pyramidal arrangment around Sm). The Sm−(C_5Me_5 ring centroid) vector makes a 56° angle with the plane defined by Sm and the two C_6H_5 ring centroids. This striking difference in structure between **3** and **4** is shown in Figure 2. Pyramidal structures have previously been observed for the formally three-coordinate Ln[N(SiMe$_3$)$_2$]$_3$ complexes,[47,48] but this trigonal nonplanar arrangement has been attributed to

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(45) Evans, W. J.; Perotti, J. M.; Kozimor, S. A.; Champagne, T. M.; Davis, B. L.; Nyce, G. W.; Fujimoto, C. H.; Clark, R. D.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 3916.

(46) Zybill, C.; Müller, G. *Organometallics* **1987**, *6*, 2489.

(47) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 2317.

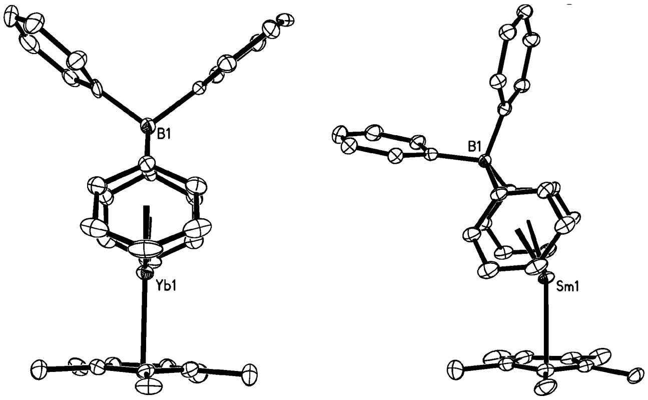


Figure 2. Side-on view of $(C_5Me_5)Yb(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})_2BPh_2$, **3**, and $(C_5Me_5)Sm(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})_2BPh_2$, **4**. Hydrogen atoms have been excluded for clarity.

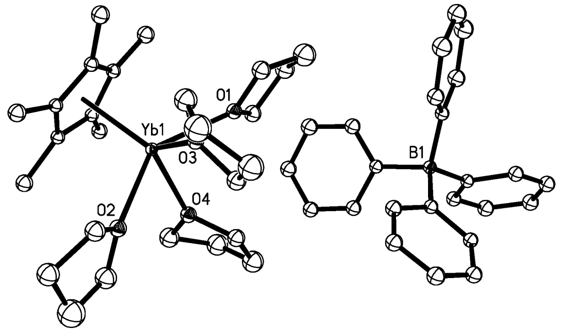


Figure 3. Thermal ellipsoid plot of $[(C_5Me_5)Yb(THF)_4][BPh_4]$, **5**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

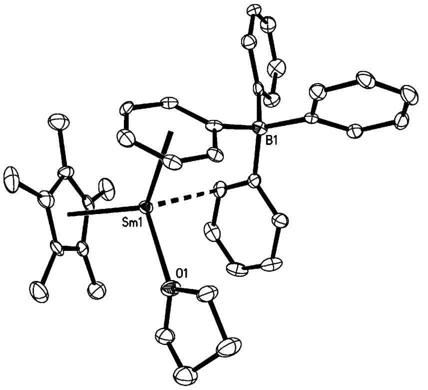


Figure 4. Thermal ellipsoid plot of $(C_5Me_5)Sm[(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph})BPh_2](THF)$, **6**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

additional bonding via agostic interations with the silyl methyls.[48] In **4**, there is no obvious additional ligation of this type.

The divalent lanthanide metallocenes, $(C_5Me_5)_2Ln$, are well-known to have coordination geometries that do not adopt the most sterically favored arrangement. Hence, $(C_5Me_5)_2Yb$,[36,37] $(C_5Me_5)_2Eu$,[32] and $(C_5Me_5)_2Sm$[32] display bent rather than linear arrangements of rings around the metal. The amount of bending in these compounds as well as alkaline earth analogues has been related to metal size.[49] Complexes of the smallest metals, which have the rings closest together, have the most linear structures. The trigonal planar versus pyramidal structures of **3** and **4** here also follow the trend that the smallest metal gives the sterically most favored structure, but with only two examples, there is no gradation of bending: the Sm example is pyramidal and the Yb analogue is not.

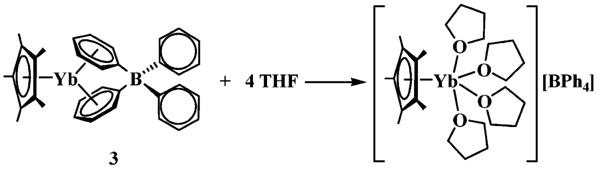
As expected for a (ring)M(ring')$_2$ system, the (ring-centroid)−Ln−(ring centroid) angles are not all equal. The 109.5 and 103.8° (C_6H_5 ring centroid)−Ln−(C_6H_5 ring centroid) angles for **3** and **4**, respectively, are reasonable since these rings are attached to tetrahedral boron. The 123.8−125.8° (C_5Me_5 ring centroid)−Ln−(C_6H_5 ring centroid) angles are small as compared to the (C_5Me_5 ring centroid)−Ln−(C_5Me_5 ring centroid) angles in the precursor metallocenes, 145−146° for $(C_5Me_5)_2$Yb, and 140.1° for $(C_5Me_5)_2Sm$, but the comparison with C_6H_5 and C_5Me_5 is not direct.

The 2.38 Å Yb−(C_5Me_5 ring centroid) distance in **3** matches that in $(C_5Me_5)_2Yb$ exactly.[37] Similarly, the 2.516 Å analogue in **4** is close to the 2.524−2.529 Å distances in $(C_5Me_5)_2Sm$.[32] The 0.136 Å difference in the distances in **3** and **4** matches the 0.13 Å difference in eight coordinate radii of Yb(II) and Sm(II) given by Shannon.[50]

In both **3** and **4**, the Ln−(C_6H_5 ring centroid) distances are about 0.2 Å longer than the Ln−(C_5Me_5 ring centroid) distances. This generates average Ln−C(C_6H_5) distances of about 0.3 Å longer than the Ln−C(C_5Me_5) distances. Although the 2.884(5)−3.128(5) Å range of Yb−C(C_6H_5) distances in **3** is quite wide, it is still within the 2.833(3)−3.297(3) Å range in $[(Me_3Si)_2N]Yb(THF)(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})_2BPh_2$.[12] The 2.784(11)−2.956(12) Å range in $[(Me_3Si)_2N]Yb(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})_2BPh_2$[13] and the 2.799(2)−3.050(2) Å range in (3,5-di-*tert*-butylpyrazole)Yb(THF)$(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})_2BPh_2$[13] have overlaps with the range in **3**, but the larger values for **3** are reasonable considering the size of $(C_5Me_5)^{1-}$ versus an $(\eta^2\text{-pyrazole})^{1-}$ or $[N(SiMe_3)_2]^{1-}$ ligand. Complex **4** has a narrower range of distances than those in **3**, 2.996(3)−3.191(4) Å.

It should be noted that in both **3** and **4**, nine to ten of the twelve Ln−C(C_6H_5) distances are within a much narrower range than two or three other values. Hence, **3** has 3.055(5) and 3.128(5) Å distances for C(19) and C(20) that are much longer than all the others that are below 3.02 Å. Likewise, in **4**, the distances to C(20), C(21), and C(22), namely, 3.168(4), 3.141(3), and 3.191(4) Å, are larger than all the rest that are 3.08 Å or less. Hence, the η^6 designator does not imply completely symmetrical bonding. A similar situation is found in $[(Me_3Si)_2N]Yb(THF)(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})_2BPh_2$[12] and (3,5-di-*tert*-butylpyrazole)Yb(THF)$(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})_2BPh_2$.[13]

Reactivity of 3 and 4. Solvation. The unsolvated tris(ring) complexes **3** and **4** readily add donor solvents such as THF to form solvated analogues. With **3**, the fully solvated $[(C_5Me_5)Yb(THF)_4][BPh_4]$, **5**, was isolated (eq 5 and Figure 3). Complex **5** is the first example of a mono(pentamethylcyclopentadienyl) lanthanide cation containing only THF as other ligands. Although the overall structure of **5** could be determined by X-ray crystallography (Figure 3), the quality of the crystals precluded detailed discussion of metrical parameters. This could be due to loss of the THF during the crystal mounting.



(5)

3

5

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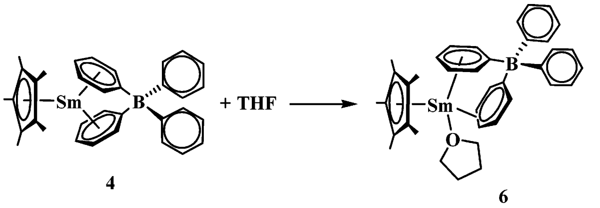
Table 2. Bond Distances (Å) and Angles (deg) in (C_5Me_5)Yb(μ-η^6:η^1-Ph)$_2$BPh$_2$, 3, (C_5Me_5)Sm(μ-η^6:η^1-Ph)$_2$BPh$_2$, 4, and (C_5Me_5)Sm[(μ-η^6:η^1-Ph)(μ-η^2:η^1-Ph)BPh$_2$](THF), 6

bond distances/angles	3	4	6
Ln(1)−Cnt(C_5Me_5)	2.381	2.516	2.512
Ln(1)−Cnt(C_6H_5)	2.605/2.639	2.700/2.776	2.652
Ln(1)−C(C_5Me_5) av	2.670(4)	2.789(4)	2.786(5)
Ln(1)−C(C_6H_5) av	2.970(4)	3.075(3)	2.999(6)
Ln(1)−C(11)	2.926(4)	3.064(3)	3.007(4)
Ln(1)−C(12)	2.932(4)	3.035(3)	3.008(4)
Ln(1)−C(13)	2.977(4)	3.020(3)	3.016(5)
Ln(1)−C(14)	3.015(5)	3.029(3)	3.001(5)
Ln(1)−C(15)	2.973(5)	3.054(3)	2.980(4)
Ln(1)−C(16)	2.911(4)	3.046(3)	2.979(4)
Ln(1)−C(17)	2.895(4)	3.080(3)	3.293
Ln(1)−C(18)	2.930(5)	2.996(3)	2.933(4)
Ln(1)−C(19)	3.055(5)	3.069(4)	3.222
Ln(1)−C(20)	3.128(5)	3.168(4)	3.807
Ln(1)−C(21)	3.010(5)	3.191(4)	4.097
Ln(1)−C(22)	2.884(5)	3.143(3)	3.849
Ln(1)···B(1)	3.712	3.874	3.883
Cnt(C_5Me_5)−Ln(1)−Cnt(C_6H_5)	124.7	125.0	124.0
Cnt(C_5Me_5)−Ln(1)−Cnt(C_6H_5)	125.8	123.8	N/A
Cnt(C_6H_5)−Ln(1)−Cnt(C_6H_5)	109.5	103.8	N/A

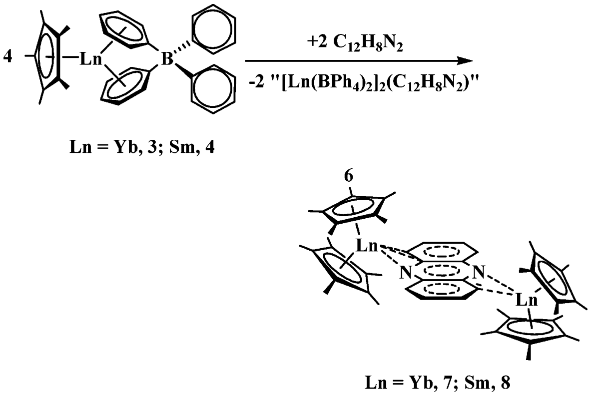
Crystallization of **4** in the presence of excess THF did not give material suitable for X-ray diffraction, but the mono-THF adduct, (C_5Me_5)Sm[(μ-η^6:η^1-Ph)(μ-η^1:η^1-Ph)BPh$_2$](THF), **6**, was obtained by the addition of 1 equiv of THF to **4** (eq 6 and Figure 4).



(6)

Complex **6** contains one hexahapto phenyl ring that displays metrical parameters similar to those in the C(11)−C(16) ring in **4**. As shown in Table 2, these have Sm−C distances in the narrow range of 2.979(4)−3.016(5) Å and a 2.652 Å Sm−(μ-η^6-C_6H_5 centroid) distance smaller than those in **4**. The other phenyl ring oriented toward samarium in **6** has one short Sm−C distance, the 2.933(4) Å Sm−C(18) length. The other Sm−C distances in this ring are all over 3.229 Å. This makes the Sm−(C_6H_5-centroid) distance much longer: 3.274 Å. As such, this ring is considered to have monohapto coordination to Sm. The 124° (C_5Me_5 centroid)−Sm−(η^6-C_6H_5 centroid) angle matches the 123 and 125° analogues found in **4**. The 111.4° (C_5Me_5−centroid)−Sm−(η^1-C_6H_5-centroid) angle is not in the metallocene range consistent with the phenyl coordination through a single carbon instead of the ring. The 2.532(3) Å Sm−O(THF) distance can be compared with the 2.62 (1) and 2.569(3) Å analogues in (C_5Me_5)$_2$Sm(THF)$_2$ and (C_5Me_5)$_2$Sm(THF),[51] respectively.

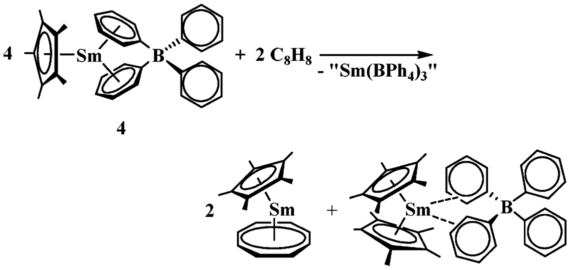
Reduction of Phenazine and C_8H_8 with Ligand Substitution. Complexes **3** and **4** react with phenazine (reduction potential −0.364 V vs SCE)[52] to form the bis(pentamethylcyclopentadienyl) products, [(C_5Me_5)$_2$Ln]$_2$[(μ-η^3:η^3-$C_{12}H_8N_2$)], (Ln = Yb, **7**; Sm, **8**) (eq 7). The connectivity of atoms in **7** was established by X-ray crystallography, but the low quality of the data precluded a detailed analysis of the structure. In the samarium case, the product of eq 7 was identified by a unit cell determination and NMR spectra comparison with the fully characterized material previously prepared from (C_5Me_5)$_2$Sm and phenazine.[43]



(7)

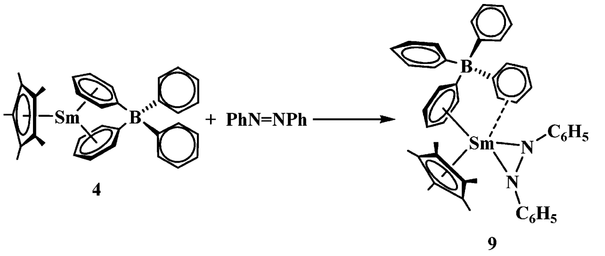
Ligand redistribution of this type to form metallocene moieties is a common reaction for mono(pentamethylcyclopentadienyl) complexes.[22] The stoichiometry requires formation of cyclopentadienyl-free byproducts. Such complexes are generally more challenging to characterize due to their lower solubility and crystallinity. To date, the byproducts of eq 7 have proven intractable.

The reduction of 1,3,5,7-C_8H_8 (reduction potentials of −1.83 and −1.99 V vs SCE)[52] by **4** does give a mono(pentamethylcyclopentadienyl) product, the known trivalent (C_5Me_5)Sm(C_8H_8),[44] but a ligand redistribution product, (C_5Me_5)$_2$Sm(μ-Ph)$_2$BPh$_2$ is also formed according to eq 8. Both products have been previously made from (C_5Me_5)$_2$Sm.[14,44] In this reaction, the stoichiometric byproduct would be Ln(BPh$_4$)$_3$. An insoluble byproduct is obtained that has the appropriate mass for this composition, but it has proven to be intractable so far.



(8)

Reduction of Azobenzene Without Ligand Substitution. In contrast to the previous reactions that all involve ligand redistribution, **4** reduces azobenzene (−1.35 to −1.41 V vs SCE)[53] to make a mono(pentamethylcyclopentadienyl) azobenzene monoanion complex, (C_5Me_5)(BPh$_4$)Sm(N$_2$Ph$_2$), **9** (eq 9 and Figure 5). In this case, as in **6** previously, the tetraphenylborate counteranion is retained in the coordination sphere of the metal. The closest analogue of **9** in the literature is the azobenzene radical anion complex, (C_5Me_5)$_2$Sm(N$_2$Ph$_2$)(THF),[54] **10**, synthesized from (C_5Me_5)$_2$Sm(THF)$_2$ and 1 equiv of azobenzene, eq 10. Both **9** and **10** are dark blue.



(9)

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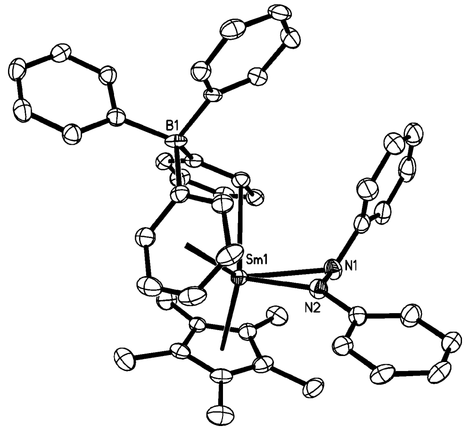
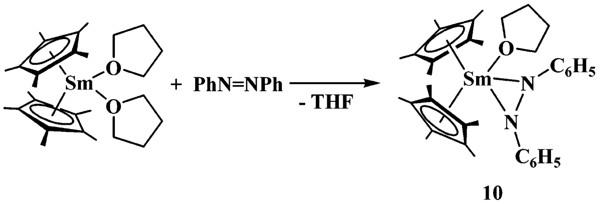


Figure 5. Thermal ellipsoid plot of $(C_5Me_5)(BPh_4)Sm(N_2Ph_2)$, **9**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

Table 3. Bond Distances (Å) and Angles (deg) in $(C_5Me_5)Sm[(\mu\text{-}\eta^6:\eta^1\text{-Ph})BPh_3](N_2Ph_2)$, 9

bond distances/angles	**11**
Sm(1)−Cnt(C_5Me_5)	2.410
Sm(1)−Cnt(C_6H_5)	2.602
Ln(1)−C(C_5Me_5) av	2.693(5)
Ln(1)−C(C_6H_5) av	2.953(11)
Sm(1)−N(1)	2.530(4)
Sm(1)−N(2)	2.249(4)
Sm(1)−C(1)	2.692(5)
Sm(1)−C(2)	2.719(4)
Sm(1)−C(3)	2.699(4)
Sm(1)−C(4)	2.673(5)
Sm(1)−C(5)	2.683(5)
Sm(1)−C(11)	2.984(4)
Sm(1)−C(12)	2.983(5)
Sm(1)−C(13)	2.968(5)
Sm(1)−C(14)	2.963(5)
Sm(1)−C(15)	2.931(5)
Sm(1)−C(16)	2.888(5)
Sm(1)−C(17)	2.871(4)
Sm(1)−C(18)	2.875(4)
N(1)−N(2)	1.435(5)
N(1)−C(35)	1.452(6)
N(2)−C(35)	1.394(6)
Cnt(C_5Me_5)−Sm(1)−Cnt(C_6H_5)	126.6
Cnt(C_5Me_5)−Sm(1)−N(1)	100.6
Cnt(C_5Me_5)−Sm(1)−N(2)	107.2
Cnt(C_6H_5)−Sm(1)−N(1)	125.7
Cnt(C_6H_5)−Sm(1)−N(2)	99.8

In both **9** and **10**, the NN distances have elongated as compared to azobenzene, and the phenyl rings are no longer coplanar. Detailed comparisons with **10** will not be made because of the large error limits in that structure. The $(PhNNPh)^{1-}$ ligand in **9** is asymmetrically bound. As shown in Table 3, Sm−N(2) is 2.239(4) Å, whereas Sm−N(1) is 2.530(4) Å. This asymmetry carries over to the N−C(Ph) distances, which are 1.394(6) Å for N(2)−C(41) and 1.452(6) Å for N(1)−C(35). The 1.435(5) Å N−N distance in **9** is closer to the 1.45 Å N−N single bond distance in hydrazine than to the 1.25 Å N═N distance typical in azobenzenes. The Ph−N−N−Ph dihedral angle is 78.4°.



(10)

10

The tetraphenylborate ligand binds to Sm in **9** as it does in **6**. Hence, one ring is hexahapto with a rather narrow range of Sm−C distances, 2.888(5)−2.984(4) Å. The other ring has one short Sm−C connection, 2.875(4) Å to C(18), and the rest of the Sm−C distances in this phenyl ring are greater than 3.3 Å. The $(PhNNPh)^{1-}$ and $(BPh_4)^{1-}$ ligands are oriented so that the short Sm−N(2) bond is closest to the $(\eta^6\text{-}C_6H_5)$ ring.

Discussion

Synthesis. Synthetic access to the $(C_5Me_5)Ln(\mu\text{-}\eta^6:\eta^1\text{-Ph})_2BPh_2$ target complexes, **3** and **4**, is readily achieved by the selective single protonation of one of the $(C_5Me_5)^{1-}$ ligands in the $(C_5Me_5)_2Yb$ and $(C_5Me_5)_2Sm$ precursors according to eq 3. The kinetics of the protonation of the $(C_5Me_5)^{1-}$ ligands of **3** and **4** are evidently slower than those of **1** and **2**. The synthesis of unsolvated $(C_5Me_5)Ln(BPh_4)$ complexes is facilitated by the fact that both $(C_5Me_5)_2Yb(THF)$ and $(C_5Me_5)_2Sm(THF)$ can be desolvated simply under vacuum. Since the solvated metallocenes are made in two steps from the metal, the synthesis of the divalent $(C_5Me_5)Ln(BPh_4)$ complexes actually takes fewer steps than the synthesis of the trivalent tetraphenylborate metallocene cations, $(C_5Me_5)_2Ln(\mu\text{-Ph})_2BPh_2$, complexes that have proven to be excellent precursors for a broad range of f element studies.[14,24,25,27,45]

Reactivity. Preliminary studies of the reactivity of the $(C_5Me_5)Ln(BPh_4)$ complexes suggest that they will be useful precursors for lanthanide chemistry like their trivalent analogues. The simple solvation reactions with THF that generate complexes **5** and **6** demonstrate that incoming substrates can readily interact with the metal centers by displacing the tetraphenylborate ions. The reaction of **3** with PhN═NPh to make $(C_5Me_5)(BPh_4)Sm(N_2Ph_2)$, **9**, shows that **3** and **4** can provide access to a new types of mono(pentamethylcyclopentadienyl) complexes. Relatively few complexes of this type are accessible as compared to $(C_5Me_5)_2Ln$ systems,[55−57] and their recently developing chemistry has been shown to be quite interesting.[29−31,49,58,59]

The reactions with phenazine and C_8H_8 show that some of the divalent reactivity of **3** and **4** will involve ligand redistribution and the formation of trivalent products containing $[(C_5Me_5)_2Ln]^+$ moieties. In the case of these two substrates, there is no advantage in using **3** and **4** over **1** and **2** for formation of the trivalent $(C_5Me_5)_2Ln$ products.

Structure. Because of the η^6 coordination mode of two of the four phenyl rings in the $(BPh_4)^{1-}$ anion in the $(C_5Me_5)Ln(\mu\text{-}\eta^6:\eta^1\text{-Ph})_2BPh_2$ complexes, the metals in **3** and **4** are surrounded by three six-electron rings. Generally, in organolanthanide chemistry, such complexes are limited to tris(cyclopentadienyl) complexes in which the rings are large enough to prevent additional coordination. Hence, the simple cyclopentadienyls, $(C_5H_5)_3Ln$, oligomerize in the solid state to

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form $[(C_5H_5)_3Ln]_x$ structures with extra intermolecular ring to metal interactions.[60,61] Monometallic complexes in which the metal is coordinated only to three six-electron rings as in **3** and **4** are found in compounds such as $[C_5H_3(SiMe_3)_2]_3Ln$,[62−64] $(C_5Me_4H)_3Ln$,[65,66] and $(C_5Me_5)_3Ln$[45,67] as well as mixed ligand complexes like $(C_5Me_5)_2Sm(C_5H_5)$.[68]

The ring centroids in these previous examples of monometallic three-ring complexes all adopt the trigonal planar arrangement that is the most efficient in terms of steric packing of three ligands. Although this expected structure is found in **3**, a pyramidal arrangement is observed in **4**. Unusual structures have previously been observed for divalent organolanthanides, but generally, the structures are unusual for both metals. The origin and consequences of the bent structure remain to be identified.

Conclusion

$(C_5Me_5)Ln(\mu\text{-}\eta^6{:}\eta^1\text{-}Ph)_2BPh_2$ complexes of ytterbium and samarium can be synthesized in good yield from $(C_5Me_5)_2Ln$ precursors obtainable by vacuum desolvation of divalent $(C_5Me_5)_2Ln(THF)_x$ complexes and constitute a new class of organometallic divalent lanthanide complexes. The unsolvated $(C_5Me_5)Ln(\mu\text{-}\eta^6{:}\eta^1\text{-}Ph)_2BPh_2$ complexes provide new opportunities to explore sterically unsaturated pentamethylcyclopentadienyl lanthanide intermediates with the added feature that a redox active divalent metal is present. Given the extensive chemistry of both sterically unsaturated complexes and divalent lanthanides, this should open many new options in the field.

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Supporting Information Available: Synthetic, spectroscopic, and X-ray diffraction details (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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