Boratabenzene Derivatives of Divalent Samarium: Syntheses, Structures and Catalytic Reactivities of $(C_5H_5BXPh_2)_2Sm(THF)_2$ (X = N, P)

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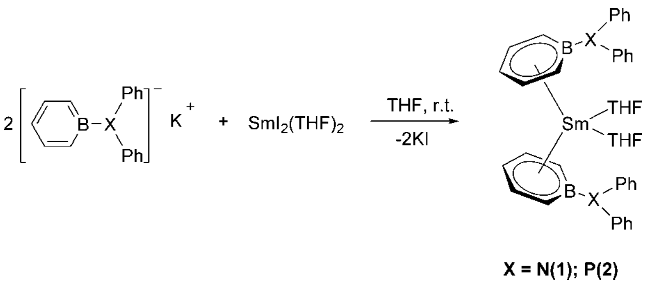
*Summary: The preparation and characterization of the complexes $(C_5H_5BXPh_2)_2Sm(THF)_2$ (X = N (**1**), P (**2**)), the first boratabenzene derivatives of a divalent lanthanide metal, are reported. Their solid-state structures display different structural features arising from the different degrees of B−X π interactions. Complexes **1** and **2** initiate the polymerization of methyl methacrylate (MMA) to a highly syndiotactic and atactic PMMA, respectively.*

Organolanthanide complexes promote a variety of useful transformations such as hydrogenation, hydroamination, hydrosilylation, hydrophosphination,[1] olefin and polar monomer polymerizations,[2] reductions, and reductive-coupling reactions.[3] The most widely investigated organolanthanides are those bearing Cp-type ligands. Our group's longstanding interest in developing organolanthanide complexes[4] has led us to prepare a new family of organolanthanides based on non-Cp ligands and to explore their reactivities. Our current efforts are concerned with the derivatives of boratabenzenes.

First reported by Herberich in 1970,[5] boratabenzenes are heterocyclic, six-π-electron, aromatic anions that have served as versatile ligands in many transition-metal complexes.[6] The coordination properties of boratabenzenes are analogous to those of cyclopentadienides in terms of their electronic contributions, which can be modulated by the choice of the exocyclic substituent on boron. On the other hand, boratabenzenes are generally weaker donors than Cp ligands and thus can generate more electrophilic metal centers. Recent reports have described an increasing number of organometallic complexes of transition metals bearing boratabenzenes,[7] in particular of derivatives of group 4, 6, and 8 metals; some of these show excellent activities in the polymerization of olefins.[7a,c,d] On the other hand, examples of boratabenzene derivatives of lanthanides are very rare, and their reactivities remain little explored.[8,9]

Scheme 1



Our choice of the specific boratabenzene ligand to use in our studies was influenced by solubility considerations, which are crucial for the purification of the envisaged complexes and reactivity studies. Thus, we selected the ligands $[C_5H_5BXPh_2]^-$ (X = N, P), which have been shown to have some advantages in the preparation of boratabenzene complexes.[7b] Reaction of $SmI_2(THF)_2$ with 2 equiv of the potassium salts of these ligands, prepared by Fu's method,[10,11] in THF at room temperature and then recrystallization of the products from THF−hexane mixtures gave the target boratabenzene complexes **1** and **2** as black crystalline blocks in 45–50% yields (Scheme 1).[12] Both complexes are soluble in toluene and benzene, and are very sensitive to air and moisture.

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(12) Preparation of **1**: $SmI_2(THF)_2$ (535 mg, 1.123 mmol) and $(K[C_5H_5BN(C_6H_5)_2])$ (639 mg, 2.247 mmol) were mixed in 15 mL of THF, and the reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum, and the solid residue was extracted with 80 mL (20 mL × 4) of toluene. Evaporation of the black extract solution in vacuo afforded a dark purple solid. The solid was washed with hexane and then dissolved in 13 mL of THF. After reduction of the solution volume to about 5 mL under vacuum, 6 mL of hexane was layered to give black crystalline blocks of **1** (433 mg, 49% yield). Mp: 243–245 °C without decomposition. Anal. Calcd for $C_{42}H_{46}B_2N_2O_2Sm$: C, 64.44; H, 5.92; N, 3.58. Found: C, 63.56; H, 5.53; N: 3.27. **1** is paramagnetic. ^1H NMR (300 MHz, $[D_8]$THF, 25 °C): δ 32.96 (s, 2H, C_5H_5B), 18.11 (s, 4H, C_5H_5B), 11.06 (s, 4H, C_5H_5B), 9.46 (d, J = 6.9 Hz, 8H, Ph), 8.12 (t, J = 6.6 Hz, 8H, Ph), 7.26 (t, J = 6.7 Hz, 4H, Ph), 3.59 (s, 8H, THF), 1.60 (s, 8H, THF). ^{13}C NMR (75 MHz, $[D_8]$THF, 25 °C): δ 151.6, 140.2, 129.0, 127.9, 127.6, 127.3, 124.5, 68.2, 25.5. ^{11}B NMR (128 MHz, $[D_8]$THF, 25 °C): δ 1.4. IR (KBr pellet, cm^{-1}): 3080, 3041, 3011, 2872, 1595, 1518, 1494, 1458, 1418, 1358, 1317, 1244, 1173, 1157, 1084, 1074, 1025, 994, 876, 748, 690.

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Single crystals suitable for X-ray analysis were obtained for **1** and **2** by diffusion of hexane in THF solutions; ORTEP figures are shown in Figures 1 and 2.[13] Both complexes exhibit a bent metallocene-type structure wherein the XPh_2 groups point away from the metallocene wedge and the Sm center adopts a pseudotetrahedral geometry. The average Sm−C bond lengths of 2.93 Å in **1** and **2** are longer than the average Sm−C distances of 2.86 Å observed in $Cp^*_2Sm(THF)_2$,[14] consistent with the weaker interaction of boratabenzene vs that of Cp. On the other hand, average Sm−O distances are shorter in **1** (2.561(3) Å) and **2** (2.50 Å) compared to the corresponding distances in $Cp^*_2Sm(THF)_2$ (average 2.63 Å)[14] and the even more unsaturated monosolvate complex $Cp^*_2Sm(THF)$ (2.569(3) Å).[15]

Many of the structural features of **1** and **2** are quite different. For example, complex **1** possesses a C_2 crystallographic symmetry such that the coordination modes of the two boratabenzene ligands are identical. Inspection of the Sm−C bond lengths in **1** shows that the Sm−C distances are significantly longer for B1 (3.051 Å), C1 (2.98 Å), and C5 (2.94 Å) vs C2 (2.92 Å), C3 (2.88 Å), and C4 (2.90 Å), indicating a slippage of Sm away from B and toward C3 to give an intermediate ($\eta^3-\eta^6$) coordination mode. In contrast, the two boratabenzene ligands in **2** coordinate differently to Sm, the ligand containing B1 showing a very long Sm−B distance of 3.00 Å and significant discrepancies in Sm−C bond distances similar to the case for **1** (2.90–2.92 Å vs 2.95–2.98 Å), while the other boratabenzene ligand is clearly η^6 coordinated (Sm−C ≈ 2.92–2.95 Å). The fairly uniform metal–carbon distances and the short Sm−B2 bond length of 2.94 Å found for the latter boratabenzene ligand are unusual, since in most boratabenzene complexes the metal slips toward the carbon opposite the boron atom. The complexes **1** and **2** are also different in the positions of the THF molecules, and the O(THF)−Sm−O(THF) angle in **1** is smaller than that in **2** (75.16(16)° vs 81.80(12)°).

Another important difference in the boratabenzene ligands of **1** and **2** relates to the B−X bonding. The nearly trigonal planar geometry around the nitrogen atom in **1** (∠B1−N1−C6 = 124.6(4)°, ∠B1−N1−C12 = 119.9(3)°, ∠C6−N1−C12 = 115.5(3)°; $\sum = 360°$) and the rather short B1−N1 bond distance of 1.477(6) Å indicate a fairly strong π interaction between boron and the NPh_2 moiety. A similar situation exists in the potassium salt of this ligand, although the B−N bond is somewhat longer in the latter (1.510(10) Å).[10] In contrast, the phosphorus atoms in **2** are pyramidal (∠B−P−C = 102–108°, $\sum = 309$ and 314°), while the B−P distances of ca. 1.94 Å fall in the range of B−P single-bond lengths (1.90–2.00 Å), indicating an absence of strong B−P π-bonding in **2**. Finally, it is worth noting that $C_5H_5BPPh_2$, an isosteric and isoelectronic variant of the widely used PPh_3, normally binds transition metals in a σ rather than π mode.[16] To our knowledge, **2** represents the first example of a transition-metal complex in which this ligand serves as a π-bound ligand.

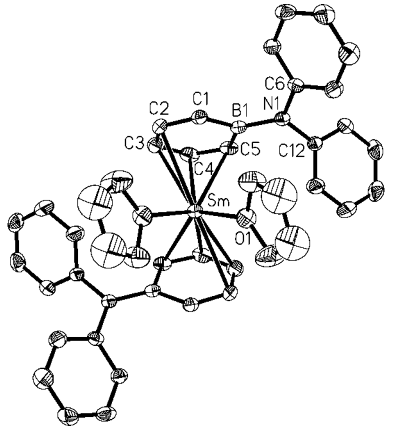

Figure 1. Molecular structure of **1** with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Sm−C1 = 2.981(4), Sm−C2 = 2.918(5), Sm−C3 = 2.881(5), Sm−C4 = 2.900(5), Sm−C5 = 2.944(5), Sm−B1 = 3.051(4), Sm−O1 = 2.561(3), B1−N1 = 1.477(6); ∠O1−Sm−O1A = 75.16(16), ∠B1−N1−C6 = 124.6(4), ∠B1−N1−C12 = 119.9(3), ∠C6−N1−C12 = 115.5(3).

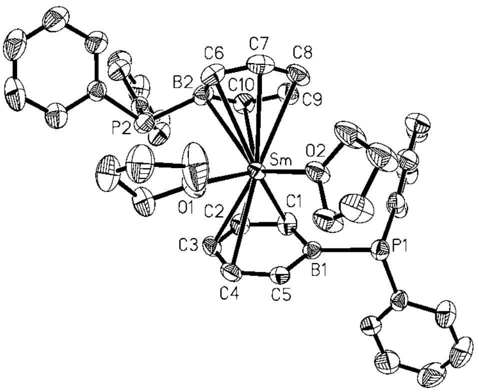

Figure 2. Molecular structure of **2** with thermal ellipsoids at the 50% probability level (THF molecule in the lattice is not included). Selected bond distances (Å) and angles (deg): Sm−C1 = 2.918(4), Sm−C2 = 2.904(4), Sm−C3 = 2.909(5), Sm−C4 = 2.952(5), Sm−C5 = 2.984(4), Sm−B1 = 3.005(5), Sm−C6 = 2.917(5), Sm−C7 = 2.948(5), Sm−C8 = 2.949(5), Sm−C9 = 2.939(5), Sm−C10 = 2.933(4), Sm−B2 = 2.938(5), Sm−O1 = 2.490(4), Sm−O2 = 2.519(3), B1−P1 = 1.943(5), B2−P2 = 1.946(6); ∠O1−Sm−O2 = 81.80(12), ∠B1−P1−C11 = 104.6(2), ∠B1−P1−C17 = 102.4(2), ∠C11−P1−C17 = 102.3(2), ∠B2−P2−C23 = 103.2(3), ∠B2−P2−C29 = 107.5(3), ∠C23−P2−C29 = 104.7(2).

Preliminary reactivity studies have shown that complexes **1** and **2** are not good catalysts for ethylene polymerization, producing only very small amounts of polyethylene at room temperature under 1 atm of ethylene. The lower catalytic activities of these complexes compared with that of $Cp^*_2Sm(THF)_2$ are probably due to the stronger Sm−THF interactions in **1** and **2** that can prevent ethylene coordination. Since polar olefins such as methyl methacrylate (MMA) tend to be stronger nucleophiles, we have examined their reactions with **1** and **2**, which showed that both of these complexes are efficient initiators for MMA polymerization and the activities are comparable to that of $Cp^*_2Sm(THF)_2$. Thus, addition of 100 equiv of MMA to a solution of **1** (32 μmol) in toluene at −50 °C resulted in 92% monomer conversion in 7 h. The M_w value of the polymer obtained was 9.52×10^4 ($M_w/M_n = 1.12$), and the microstructural analysis of the polymer shows that it is highly syndiotactic (*mm*:*mr*:*rr* = 1.0:14.2:84.8). A higher

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[13] Crystal data for **1**: $C_{42}H_{46}B_2N_2O_2Sm$, $M_r = 782.78$, $T = 293(2)$ K, monoclinic, *C*2/*c*, $a = 12.2105(11)$ Å, $b = 13.8220(13)$ Å, $c = 23.156(2)$ Å, $\beta = 104.794(2)°$, $V = 3778.5(6)$ Å^3, $Z = 4$, 10 816 reflections collected, 4100 independent reflections, R1 = 0.0461, wR2 = 0.1173 ($I > 2\sigma(I)$). Crystal data for **2**: $C_{44}H_{50}B_2O_{2.5}P_2Sm$, $M_r = 852.75$, $T = 293(2)$ K, monoclinic, $P2_1/c$, $a = 8.4309(8)$ Å, $b = 16.1377(14)$ Å, $c = 30.901(3)$ Å, $\beta = 94.062(2)°$, $V = 4193.7(7)$ Å^3, $Z = 4$, 24 474 reflections collected, 9141 independent reflections, R1 = 0.0451, wR2 = 0.0929 ($I > 2\sigma(I)$).

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syndiotactic selectivity was achieved at −70 °C (*mm*:*mr*:*rr* = 0.4:11.7:87.9) at the price of a lower monomer conversion (51%) and a somewhat smaller molecular weight ($M_w = 3.95 \times 10^4$, $M_w/M_n = 1.13$). Complex **2** gave 66% monomer conversion (−25 °C, 7 h), producing an atactic PMMA (*mm*:*mr*:*rr* = 39.9:26.9: 33.2; $M_w = 3.33 \times 10^4$; $M_w/M_n = 1.79$).

In summary, $(C_5H_5BXPh_2)_2Sm(THF)_2$ (X = N (**1**), P (**2**)) represent the first boratabenzene derivatives of a divalent lanthanide. X-ray diffraction studies have revealed a strong X−B π interaction only in **1**. These complexes are efficient initiators for MMA polymerization. Future studies will strive to prepare solvent-free analogues of these complexes in addition to amide and hydrocarbyl derivatives of trivalent lanthanides, all of which should exhibit greater reactivities.

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Supporting Information Available: Text giving synthetic details and characterization data for the complex **2** and CIF files giving X-ray crystallographic data for the complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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