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Synthesis and Structure of Bis[hydrotris(3,5-dimethylpyrazolyl)borato]samarium(II), $Sm[HB(3,5\text{-}Me_2pz)_3]_2$, and the Product of Its Reaction with Azobenzene[1]

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Summary: Treatment of $SmI_2{\cdot}2THF$ with 2 equiv of $NaHB(3,5\text{-}Me_2pz)_3$ in THF affords purple $Sm[HB(3,5\text{-}Me_2pz)_3]_2$, 1, in high yield. Despite its insoluble nature, 1 readily reacts with azobenzene to give soluble, green $Sm[HB(3,5\text{-}Me_2pz)_3]_2(N_2Ph_2)$, 2. The structures of 1 and 2 have been determined by X-ray crystallography. Complex 1 has the symmetrical metallocene structure. The η^3-bonding mode of both pyrazolylborate ligands is retained in 2, and in addition the cis-azobenzene moiety is symmetrically bonded to the samarium center via both nitrogen atoms.

The synthesis of $(C_5Me_5)_2Sm(THF)_{1-2}$[2] and its solvent free parent $(C_5Me_5)_2Sm$[3] opened a new chapter in the organometallic chemistry of samarium. The complexes exhibit remarkable and often unique reaction patterns with a variety of substrates[4] and are effective precatalysts for hydroamination/cyclization of amino olefins[5] and hydroboration of olefins.[6] The high reactivity is attributed to the strong reducing ability of Sm(II) and to the coordinative unsaturation of the metal center, especially in $(C_5Me_5)_2Sm$. The importance of steric factors controlling organolanthanide reactivity is well recognized and hence it is of obvious interest to prepare related Sm(II) complexes with ligating moieties of different sizes. The hydrotris(pyrazolyl)borate ligand ($HBpz_3^-$) and its functionalized derivatives ($HBpz'_3{}^-$, pz′ = substituted pyrazole), which can be regarded as cyclopentadienyl analogues, offer a versatile series of such ligands where the steric size can be fine tuned by judicious choice of the substituents.[7] Although Ln(III) polypyrazolylborate complexes are known,[8] the synthesis of Ln(II) derivatives has so far not been reported.[9] Here we wish to describe the synthesis and structure of $Sm[HB(3,5\text{-}Me_2pz)_3]_2$ and the product of its reaction with azobenzene.

Addition of $NaHB(3,5\text{-}Me_2pz)_3$ ($NaHBpz^*_3$) (3.20 g, 10 mmol) to a blue solution of $SmI_2{\cdot}2THF$ (2.74 g, 5 mmol) in 50 mL of THF in a glovebox gave an immediate purple precipitate of $Sm[HB(3,5\text{-}Me_2pz)_3]_2$, 1, in 90% yield.[10] Compound 1 is insoluble in common aliphatic, aromatic, and ether type solvents, and it reacts with chlorinated solvents. However, single crystals of 1, suitable for an X-ray crystallographic study,[11,12] could be grown by slow diffusion, over several weeks, of a THF solution of $NaHBpz^*_3$ into a THF solution of $SmI_2{\cdot}2THF$. The solid-state structure of 1, shown in Figure 1, corroborates the molecular formulation and establishes the monomeric, solvent-free nature of the complex.

In the solid state, 1 has crystallographically-imposed S_6-$\bar{3}$ symmetry with the Sm, both boron atoms, and their covalently-bonded hydrogens lying on the crystallographic

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[1] Presented in part at the 75th Canadian Chemical Conference and Exhibition, Edmonton, Alberta, Canada, June 1992; Abstract 352P.

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[9] The synthesis of $Sm(HBpz_3)_2(THF)_2$ and its oxidative-addition reactions with organic halides have been communicated: Marques, N. Rare Earths '92, Kyoto, Japan, June 1992; Abstract PIK-11.

[10] Data for 1: IR (KBr, cm^{-1}) 2540 (ν_{B-H}); MS (EI, 70 eV, 200 °C) *m/z* 744 (M^+). Anal. Calcd for $C_{30}H_{44}N_{12}B_2Sm$: C, 48.34; H, 5.91; N, 22.56. Found: C, 48.60; H, 5.98; N, 21.87.

[11] Single crystals of $Sm(HBpz^*_3)_2$, 1, are at 20 ± 1 °C, trigonal, space group $R\bar{3}$-C^2_{3i} (No. 148) with $a = 10.612(2)$ Å, $\alpha = 63.30(2)°$, $V = 906.8(4)$ Å^3, and $Z = 1$ formula unit ($d_{calcd} = 1.360\ g{\cdot}cm^{-3}$; $\mu(Mo\ K\bar{\alpha}) = 1.65\ mm^{-1}$). Single crystals of $Sm(HBpz^*_3)_2(N_2Ph_2)$, 2, are at 20 ± 1 °C, monoclinic, space group $P2_1/n$ (an alternate setting of $P2_1/c$-C^5_{2h} (No. 14)) with $a = 14.094(3)$ Å, $b = 17.540(3)$ Å, $c = 18.723(4)$ Å, $\beta = 103.98(3)°$, $V = 4491(2)$ Å^3, and $Z = 4$ ($d_{calcd} = 1.371\ g{\cdot}cm^{-3}$; $\mu_a(Mo\ K\bar{\alpha}) = 1.34\ mm^{-1}$). Totals of 2295 (1) and 6691 (2) independent absorption-corrected reflections having $2\theta(Mo\ K\bar{\alpha}) < 55.0°$ (1) or 45.8° (2) were collected on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated ($Mo\ K\bar{\alpha}$) radiation. Both structures were solved using the "heavy-atom" technique with the Siemens SHELXTL-PC crystallographic software package. The resulting structural parameters for both compounds have been refined to convergence [R_1 (unweighted, based on F) = 0.029 (1) and 0.040 (2) for 1274 (1) or 3196 (2) independent absorption-corrected reflections having $I > 3\sigma(I)$] using counter-weighted full-matrix least-squares techniques and structural models which utilized anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms.

[12] The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation in an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements included in the averaged value.

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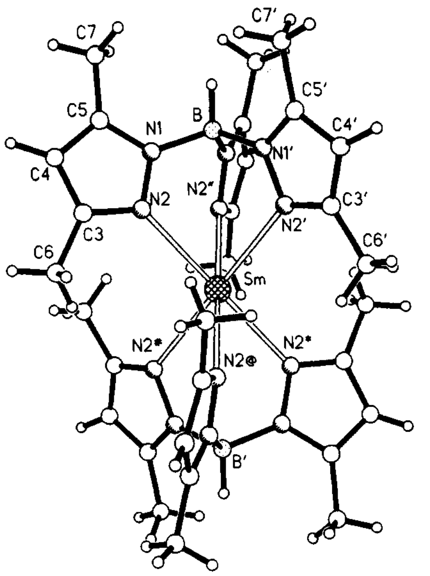

Figure 1. Perspective plot of the solid-state structure for Sm(HBpz$^*_3$)$_2$, 1, with the Sm atom represented by a large crosshatched sphere. Boron and nitrogen atoms are represented by medium-sized dotted and shaded spheres, respectively, while carbon and hydrogen atoms are represented by medium-sized and small open spheres, respectively. The molecule possesses rigorous S_6-$\bar{3}$ symmetry in the solid state with the Sm and both borons having their covalently-bonded hydrogens lying on a crystallographic C_3 axis.

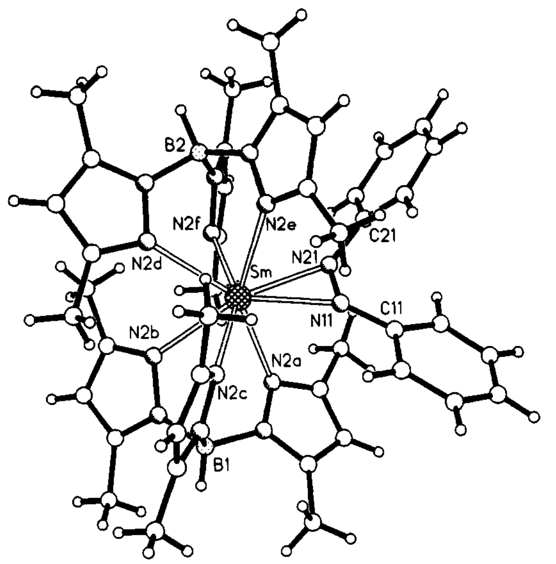

Figure 2. Perspective plot of the solid-state structure for Sm(HBpz$^*_3$)$_2$(N$_2$(C$_6$H$_5$)$_2$), 2, with atoms represented as in Figure 1.

C_3 axis at (0, 0, 0) in the unit cell. The two tridentate HBpz$^*_3$ ligands adopt a staggered conformation about this axis and produce intraligand and interligand N–Sm–N bond angles of 75.5(1) and 104.5(1)°, respectively. The Sm–N distances are all equal at 2.617(4) Å, and the pair of "octahedral" faces spanned by the two η^3-HBpz$^*_3$ ligands are required to be parallel. The "linear sandwich" structure of this complex is in contrast to the "bent metallocene" arrangement found in (C$_5$Me$_5$)$_2$Sm[3a] and the analogous Eu(II)[3a] complexes.

Despite its insoluble nature, we found that compound 1 readily reacts with azobenzene. Thus a slurry of 1 in toluene in the presence of excess azobenzene rapidly gives a green solution from which green crystals of Sm[HB-(3,5-Me$_2$pz)$_3$]$_2$(PhNNPh), 2, can be isolated in 85% yield.[13] It is interesting to note that the same complex is obtained when the reaction is carried out with 2 equiv of 1 per molecule of azobenzene, whereas with (C$_5$Me$_5$)$_2$Sm both 1:1, (C$_5$Me$_5$)$_2$Sm(η^2-N$_2$Ph$_2$)(THF), and 2:1, [(C$_5$Me$_5$)$_2$Sm]$_2$-(N$_2$Ph$_2$), complexes can be obtained.[14] The differences are clearly attributable to the sterically more demanding nature of the HBpz$^*_3$ ligand compared to the C$_5$Me$_5$ moiety. This is further reflected in the observation that the 1:1 complex with the latter ligand retains a coordinated THF whereas compound 2 is obtained as a solvent-free molecule.

The solid-state structure[11,12] of 2, shown in Figure 2, reveals that both HBpz$^*_3$ ligands retain their tridentate coordination modes and that the *cis*-azobenzene moiety is η^2-bonded to the Sm center through both nitrogen atoms. The average azobenzene Sm–N and N–N bond distances of 2.402(8,16,16,2)[8] and 1.332(12) Å are similar to the values of 2.417(11,21,33,4) and 1.356(15,33,33,2) Å, respectively, observed for similar bonds in (C$_5$Me$_5$)$_2$Sm(N$_2$Ph$_2$)(THF).[14] The coordination geometry of the Sm atom in 2 can probably best be described as (necessarily) distorted pentagonal bipyramidal, with the midpoint of the azobenzene ligand occupying one of the equatorial positions and N$_{2c}$ and N$_{2f}$ occupying the two axial positions. Although 2 is not required to possess any crystallographic symmetry in the solid state, it approximates rather closely C_2 symmetry with the 2-fold axis passing through Sm and the midpoint of the azobenzene N–N bond. ^{1}H NMR data[13] indicate that this approximate C_2 symmetry is maintained for 2 in solution; chemical shifts far away from the region of free azobenzene corroborate its coordination to samarium.

In view of the well-known variable (η^3, η^2, and even η^1) coordination modes of the HBpz'$_3$ ligand systems,[7,15] and the sterically congested nature of the parent complex, 1, the structure of 2 is remarkable. It indicates that even with the bulky HBpz$^*_3$ ligand the "bent metallocene" type structure is accessible and provides further experimental evidence for the calculated shallow potential energy surfaces for the bending motion in the series of (C$_5$H$_5$)$_2$M complexes[16] (M = Ln(II), and alkaline earth metals).[17]

In conclusion we have shown that the HBpz$^*_3$ ligand provides a convenient entry into solvent-free Sm(HBpz$^*_3$)$_2$, 1. Indeed, the synthesis can be easily extended to Yb(II) and to other substituted HBpz'$_3$ ligands.[18a] Consistent with the bulky nature of the HBpz$^*_3$ ligand the structure and reactivity of 1 are different from those of the related (C$_5$Me$_5$)$_2$Sm complex. The reactivity of 1 and related Ln-

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[13] Data for 2: IR (KBr, cm^{-1}) 2533 (ν_{B-H}); MS (EI, 70 eV, 270 °C) m/z 744 (M$^+$ − N$_2$Ph$_2$); ^{1}H NMR (toluene-d_8, 25 °C, δ (ppm)) 73.19 (s, 4H, Ph), 23.21 (s, 6H, ps*-Me), 6.35 (s, 2H, pz*-H), 5.40 (br, 2H, B–H), 5.20 (s, 2H, pz*-H), 5.00 (s, 2H, pz*-H), 4.55 (s, 6H, pz*-Me), 2.75 (s, 6H, pz*-Me), 2.40 (s, 6H, pz*-Me), 2.20 (s, 6H, pz*-Me), −4.55 (s, 6H, pz*-Me), −170.30 (s, 4H, Ph), −189.55 (s, 2H, *p*-Ph); ^{11}B NMR (toluene-d_8, 25 °C, δ (ppm)) −7.30 (s). Anal. Calcd for $C_{42}H_{54}N_{14}B_2Sm$: C, 54.41; H, 5.83; N, 21.16. Found: C, 54.43; H, 5.93; N, 21.56.

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[17] The nature of the ligand redistribution appears to be different for HBpz$_3$* and C$_5$Me$_5$ ligand systems. Slippage and twisting of the former ligands occur in the transformation of 1 into 2, whereas only simple bending of the two C$_5$Me$_5$ ligands is required to give the "bent metallocene" type structure in (C$_5$Me$_5$)$_2$M complexes.

$(HBpz'_3)_2$ complexes toward organic substrates is under active study.[18b]

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Supplementary Material Available: For **1** and **2**, a crystal structure analysis report, tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles, and an ORTEP plots (33 pages). Ordering information is given on any current masthead page.

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(18) (a) The analogous Yb[HB(3,5-Me_2pz)$_3$]$_2$ and related Ln[HB(3-Rpz)$_3$]$_2$ (Ln = Sm, Yb; R = Ph and 2′-thienyl) have been prepared: Zhang, X.-W. To be published. (b) Compound 1 also reacts with quinones and other reducible unsaturated organic substrates: Zhang, X.-W. Unpublished results.