Lewis Base Adducts of Diboron Compounds: Molecular Structures of [B_2(cat)$_2$(4-picoline)] and [B_2(cat)$_2$(4-picoline)$_2$] (cat = 1,2-$O_2C_6H_4$)

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Diboron compounds of the type $B_2(OR)_4$ are much more stable and less reactive than their B_2X_4 analogs (X = halide). While the latter add readily[1] to alkenes and alkynes, the $B_2(OR)_4$ compounds fail[2] to add to C−C multiple bonds in the absence of a transition metal catalyst. We have examined oxidative addition[3] of the B−B bond in $B_2(OR)_4$ compounds to Rh(I) phosphine complexes and have developed[4] soluble transition metal catalysts for the addition of $B_2(cat)_2$ (**1a**, cat = 1,2-$O_2C_6H_4$) to vinylarenes. Suzuki has reported[5a] that $Pt(PPh_3)_4$ catalyzes the addition of $B_2(pin)_2$ (**2**, pin = $OCMe_2CMe_2O$) to alkynes. Oxidative addition of **1a** to Pt(0) complexes[5b,c] and stoichiometric[5b] and catalytic reactions[5c] of the bis(boryl)platinum complexes have been reported. The fact that **1a**, and related Bu^t-substituted derivatives, add readily to Rh(I) centers at room temperature under stoichiometric conditions, whereas **2**, $B_2(OCH_2CMe_2CH_2O)_2$ (**3**), and $B_2(NMe_2)_4$ (**4**) fail to react under these conditions, led us to explore the molecular and electronic structures and coordination chemistry of $B_2(OR)_4$ compounds. We report herein preliminary results on the coordination of Lewis bases to $B_2(OR)_4$ compounds and the structures of the mono- and bis(4-picoline) adducts of **1a**.

Only four ligand adducts of B_2Z_4 type compounds have been characterized structurally: [$(B_2H_4)(PPh_3)_2$] (**5**),[6] [$B_2Cl_4(NMe_3)_2$] (**6**),[7] [B_2(1-pyrazolyl)$_4$(pyrazole)$_2$] (**7**),[8] and [$BCl_2BClN(Me)CH_2CH_2NMe_2$] (**8**),[9a] and the B−B distances range from 1.698(4) to 1.769(6) Å. We are not aware of any reports of ligand adducts of $B_2(OR)_4$ compounds, and examples of mono-ligand adducts of other B_2Z_4 systems are rare.[9]

We reported[3a] the molecular structures of **1a**, B_2(1,2-O_2-4-Bu^t-C_6H_3)$_2$ (**1b**), and B_2(1,2-O_2-3,5-Bu$^t_2$-C_6H_2)$_2$ (**1c**). Compound **1a** is planar with a B−B separation of 1.678(3) Å and an average B−O distance of 1.388(2) Å. Addition of 2 molar equiv of 4-picoline to **1a** in heptane gave a pale yellow-greenish precipitate (95% yield) of analytically pure[10a] [B_2(cat)$_2$(4-picoline)$_2$] (**9**). Single crystals[11a] suitable for diffraction were grown from THF (Figure 1) and contain 2 equiv of uncoordinated 4-picoline per diboron unit in addition to the two bound picolines. In **9**, the B−B distance is 1.713(4) Å, the average B−O distance is 1.494(2) Å, and the B−N distance is 1.659(2) Å. Thus, in **9**, the B−O separations are 0.106 Å longer, and the B−B distance is 0.035 Å longer than in **1a**. The lengthening of all bonds to boron may be attributed, in part, to a change in hybridization from sp^2 to sp^3 and an increase in coordination number. The disruption of B−O π-interactions as a result of the geometry change from trigonal to tetrahedral at boron will also contribute to an increase in the B−O distance. Of interest are a considerable shortening of both the O−C distances, average = 1.369(2) Å in **9** *vs* 1.387(2) Å in **1a**, and the C3−C4 distances, 1.378(3) Å in **9** *vs* 1.393(2) Å in **1a**. Thus, the changes in coordination at boron are reflected even at the most remote sites in the delocalized π-system.

Addition of 1 molar equiv of 4-picoline to **1a** in $CHCl_3$ followed by precipitation with hexane gave the mono-adduct [B_2(cat)$_2$(4-picoline)] (**10**) in 85% yield as an analytically pure[10b] pale yellow-green solid. Suitable crystals[11b] were grown from THF (Figure 1). In **10**, the B−B bond distance is 1.706(3) Å, similar to that in **9**, and at the short end of the range found in compounds **5**−**8**; *vide supra*. The B1−N1 distance of 1.644 (2) Å is only slightly (0.015 Å) shorter than that in **9**. The remainder of the structure of **10** is essentially a composite of those for **1a** and **9**.

Solid-state 160 MHz $^{11}B\{^1H\}$ MAS NMR spectra[12] of **1a**, **9**, and **10** were in complete accord with the structures determined by X-ray crystallography. For **9**, a single relatively sharp peak at $\delta_{iso} = 13 \pm 1.5$ ppm was observed, whereas, for **10**, a sharp peak at $\delta_{iso} = 13 \pm 1.5$ ppm for the four-coordinate boron was

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(9) (a) Haubold, W.; Hrebicek, J.; Sawitzki, G. *Z. Naturforsch.* **1984**, *39b*, 1027. (b) For mono adducts of B_2X_4 (X = halide) see: Keller, W.; Sneddon, L. G.; Einholz, W.; Gemmler, A. *Chem. Ber.* **1992**, *125*, 2343. Haubold, W.; Kraatz, U.; Einholz, W. *Z. Anorg. Allg. Chem.* **1991**, *592*, 35.

(10) (a) Anal. Calcd for $C_{24}H_{22}N_2O_4B_2$ (**9**): C, 67.98; H, 5.23. Found: C, 67.71; H, 5.39. (b) Anal. Calcd for $C_{18}H_{15}NO_4B_2$ (**10**): C, 65.33; H, 4.57. Found: C, 65.58; H, 4.70.

(11) (a) Crystal data for **9**: formula = $C_{24}H_{22}N_2O_4B_2 \cdot 2C_6H_7N$, fw = 610.3, monoclinic, space group $P2_1/c$ (No. 14), a = 13.991(3) Å, b = 10.261(2) Å, c = 11.376(3) Å, β = 104.48(2)°, V = 1581.2(5) Å^3, Z = 2, ϱ = 1.282 g cm^{-3}, T = 200 K, $F(000)$ = 644. Anisotropic refinement of all non-hydrogen atoms (H refined using riding model with isotropic thermal parameters, 227 variables) using 2281 reflections with $F > 6.0\sigma(F)$ from 3125 unique data (3125 collected) gave R = 0.0368 and R_w = 0.0349. (b) Crystal structure data for **10**: formula = $C_{18}H_{15}NO_4B_2$, fw = 330.9, triclinic, space group $P\bar{1}$ (No. 2), a = 9.358(1) Å, b = 9.874(1) Å, c = 10.011(1) Å, α = 88.60(1)°, β = 84.09(1)°, γ = 64.02(1)°, V = 826.9(2) Å^3, Z = 2, ϱ = 1.329 g cm^{-3}, T = 180 K, $F(000)$ = 344. Refinements as above (242 variables) using 2479 reflections with $F > 6.0\sigma(F)$ from 3270 unique data (3270 collected) gave R = 0.0350 and R_w = 0.0340.

(12) The solid-state ^{11}B shifts we report are "true" ^{11}B δ_{iso}'s that have been corrected for quadrupole effects; see: Samoson, A. *Chem. Phys. Lett.* **1985**, *119*, 29.

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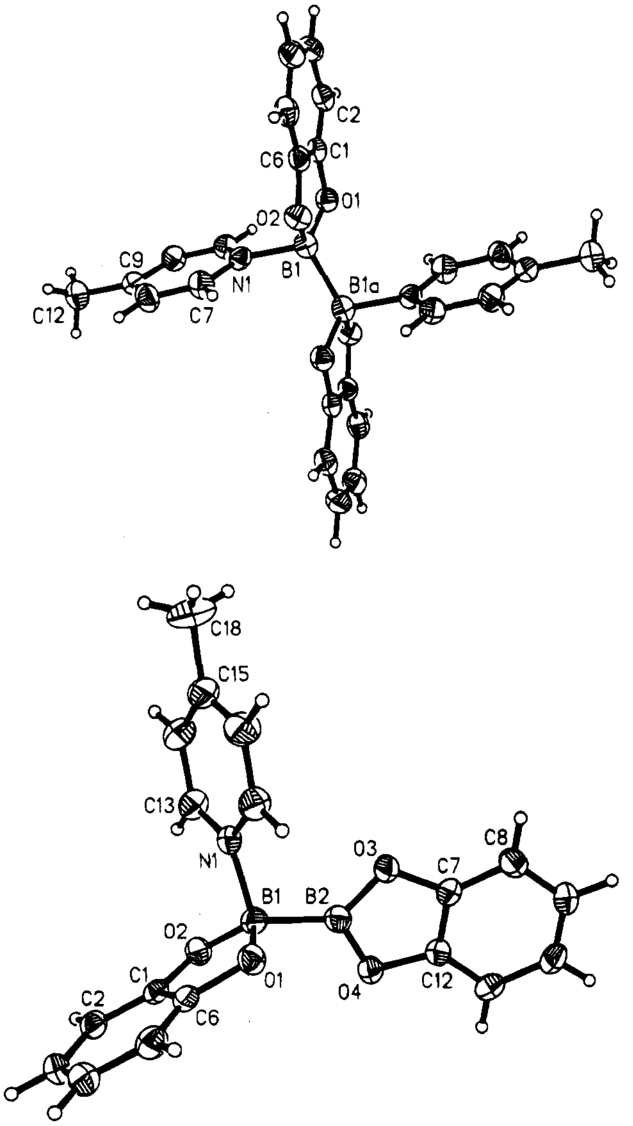
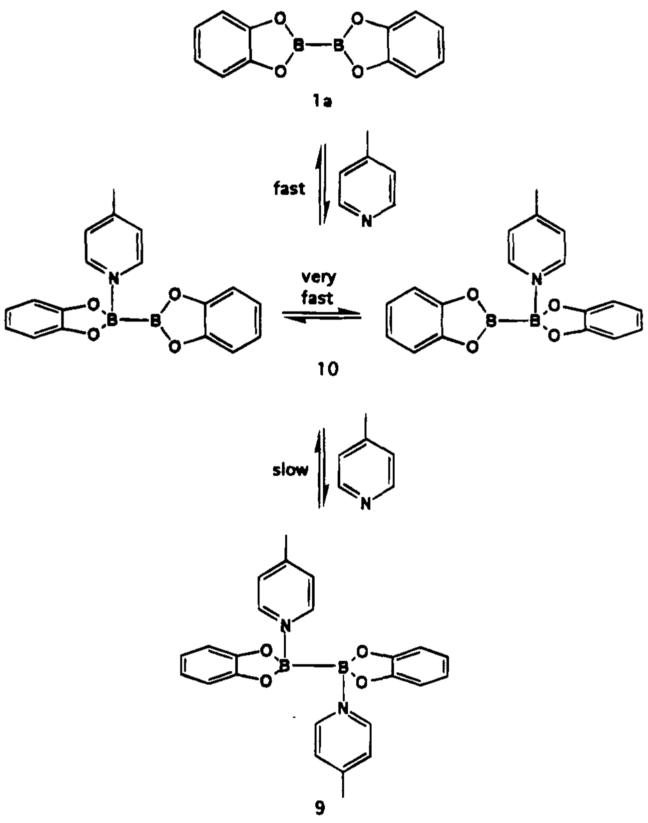


Figure 1. ORTEP diagrams for **9** (top) and **10** (bottom). Selected bond distances (Å) follow. Data for **9**: B1–B1a = 1.713(4), B1–N1 = 1.659(2), B1–O1 = 1.489(2), B1–O2 = 1.498(2), O1–C1 = 1.370(2), O2–C6 = 1.368(2), C1–C2 = 1.372(2), C2–C3 = 1.403(3), C3–C4 = 1.378(3), C4–C5 = 1.401(2), C5–C6 = 1.373(3), C1–C6 = 1.394(2). For **10**: B1–B2 = 1.706(3), B1–N1 = 1.644(2), B1–O1 = 1.489(3), B1–O2 = 1.471(2), B2–O3 = 1.402(2), B2–O4 = 1.398(2), O1–C6 = 1.368(2), O2–C1 = 1.370(2), O3–C7 = 1.387(2), O4–C12 = 1.388(2), C1–C2 = 1.374(2), C2–C3 = 1.396(3), C3–C4 = 1.379(3), C4–C5 = 1.395(3), C5–C6 = 1.372(2), C1–C6 = 1.393(3), C7–C8 = 1.371(3), C8–C9 = 1.393(2), C9–C10 = 1.384(2), C10–C11 = 1.390(3), C11–C12 = 1.380(2), C7–C12 = 1.377(2).

accompanied by a very broad resonance at $\delta_{\mathrm{iso}} = 32 \pm 1.5$ ppm for the three-coordinate boron (cf. $\delta_{\mathrm{iso}} = 32 \pm 1.5$ ppm for **1a**). In solution, several exchange processes and equilibria were clearly evident (Scheme 1). Both ^{1}H and ^{11}B{^{1}H} NMR spectra of **1a** in the presence of 0, 0.5, 1.0, 1.5, 2.0, 3.0, 5.0, 7.0, and 10.0 molar equiv of 4-picoline were recorded at room temperature, and a variable-temperature (190–300 K) ^{1}H NMR study was conducted on a 1:1 **1a**:4-picoline solution in CDCl$_3$.

At room temperature, in the presence of 0.5 equiv of 4-picoline, a single resonance at 26 ppm was observed in the ^{11}B{^{1}H} NMR spectrum (cf. 31.6 ppm for pure **1a**) indicative of fast exchange processes involving **1a** and *both* boron sites in **10**. As the picoline concentration is increased, this resonance continues to shift upfield, while decreasing in intensity relative to a signal at 6 ppm due to **9**, which appears at picoline:**1a** ratios of ca. 1.0 or larger. The signal due to **9** dominates once the picoline:**1a** ratio reaches 2:1. The analogous room-temperature ^{1}H NMR spectra indicate discrete and sharp catecholate resonances for **9**, but only one set of catecholate resonances for **(10 ↔ 1a)**. Thus, exhange of 4-picoline between **1a** and **10** *and* between the two boron sites in **10** must be fast, whereas exchange processes involving **9** are relatively slow. The variable-temperature 500 MHz ^{1}H NMR study of the 1:1 solution of 4-picoline:**1a** confirmed these observations and also indicated that intramolecular picoline exchange between the two borons in **10** is faster than intermolecular exhange between **1a** and **10**. Thus, at 190 K, discrete catecholate resonances for **1a**, **9**, and **10** were observed, yet those due to the two distinct environments in **10** remained broadened.

Scheme 1



No significant changes in the ^{11}B{^{1}H} NMR spectra of **1a** were observed in the presence of a large excess of PMe$_3$, PEt$_3$, PPh$_3$, or dmpe indicating that these ligands do not bind significantly to **1a**. In addition, no shifts in the ^{11}B NMR resonances of **2** or **4** were observed in the presence of 10 mol equiv of 4-picoline, indicative of the lower effective Lewis acidity of these diboron compounds *vs* **1a**.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic thermal parameters, bond distances and angles, and data collection and refinement parameters for **9** and **10** (15 pages). Ordering information is given on any current masthead page.

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