Oxidative Addition of B−B Bonds by Rhodium(I) Phosphine Complexes: Molecular Structures of B_2cat_2 (cat = 1,2-$O_2C_6H_4$) and Its 4-Bu^t and 3,5-Bu^t_2 Analogs[1]

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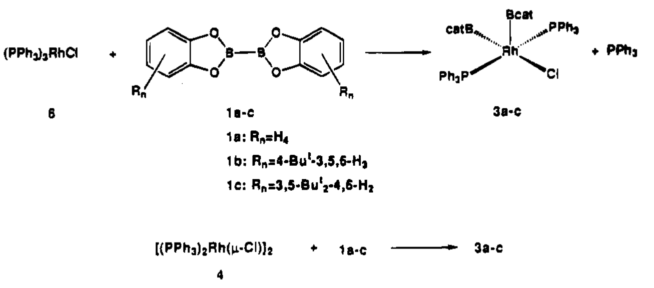
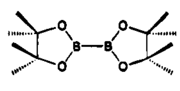
Although B_2X_4 compounds (X = halide) are known[2] to add to alkenes and alkynes, difficulties in handling these reactive reagents have precluded their use in organic synthesis. The $B_2(OR)_4$ ester (**1**) and $B_2(NR_2)_4$ amide (**2**) analogs are much more stable, yet they fail to add to C−C multiple bonds under normal conditions.[3] In connection with our work on Rh-catalyzed alkene hydroboration,[4,5] we reported[4a,6] that the novel bis(boryl) complex $[(PPh_3)_2RhCl(Bcat)_2]$ (**3a**) is formed slowly (days) via reaction of $[(PPh_3)_2Rh(\mu\text{-}Cl)]_2$ (**4**) with excess HBcat (cat = 1,2-$O_2C_6H_4$). Rapid formation of $[(PPh_3)_2Rh(Cl)(H)(Bcat)]$ (**5**) was followed by a slow second step with loss of H_2, resulting in **3a**. Catalytic diboration of alkenes requires the oxidative addition of B−B bonds in compounds of type **1**, a process which had not been reported previously. While our work was in progress, Suzuki reported[7] the Pt(0)-catalyzed addition of $B_2(pin)_2$ (**1d**;[8] pin = $OCMe_2CMe_2O$) to alkynes; however, this catalyst system was ineffective for alkenes, and the Rh complex, $[(PPh_3)_3RhCl]$ (**6**), was incapable of catalyzing the addition of **1d** to alkynes. Suzuki also reported ^{31}P and ^{11}B NMR evidence suggesting the formation of a Pt bis(boryl) complex upon reaction of 10 equiv of **1d** with $Pt(PPh_3)_4$. We recently developed[9] several Rh(I) and Au(I) systems capable of catalyzing the addition of B_2cat_2 (**1a**)[10] to vinylarenes, generating a variety of products depending upon the nature of the catalyst. In order to develop improved catalytic diboration processes, more data are required on the molecular and electronic structures of $B_2(OR)_4$ compounds and on their oxidative addition to metal centers. We report herein the molecular structures of $B_2(1,2\text{-}O_2C_6H_4)$ (**1a**), $B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2$ (**1b**), and $B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2C_6H_2)_2$ (**1c**) and preliminary studies of the oxidative addition of these diboron compounds to the Rh(I) centers in **4** and **6**.

Compounds **1a**−**d** and $B_2(OCH_2CMe_2CH_2O)_2$ (**1e**) were prepared[11] via treatment of $B_2(NMe_2)_4$ with the appropriate diols in the presence of 4 equiv of HCl. Previously, only **1d** had been characterized[8] by X-ray diffraction and $B_2(OMe)_4$ (**1f**),[12] by electron diffraction in the gas phase. In the solid state,[13] **1a** is planar and resides on a crystallographic inversion center which constrains the dihedral angle between the two BO_2 units to be

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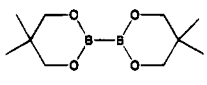
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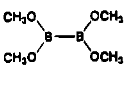
1f

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[1] This work was presented in part at the 5th International Conference on the Chemistry of the Platinum Group Metals, St. Andrews, Scotland, July 11−16, 1993.

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[11] Spectroscopic data. For **1a**: ^1H NMR δ 7.15−7.25 (m, 4H), 7.35−7.40 (m, 4H); $^{13}C\{^1H\}$ NMR δ 113.2, 123.5, 147.8; $^{11}B\{^1H\}$ NMR δ 31.6. Anal. Calcd for $C_{12}H_8O_4B_2$: C, 60.61; H, 3.39. Found: C, 60.77; H, 3.19. For **1b**: ^1H NMR δ 1.29 (s, 18H), 7.02−7.13 (multiplets, 6H); $^{13}C\{^1H\}$ NMR δ 31.7, 34.9, 110.2, 112.0, 120.3, 145.4, 147.3, 147.7; $^{11}B\{^1H\}$ NMR δ 31.9. Anal. Calcd for $C_{20}H_{24}O_4B_2$: C, 68.63; H, 6.91. Found: C, 68.77; H, 7.05. For **1c**: ^1H NMR δ 1.35 (s, 18H), 1.50 (s, 18H), 7.13 (d, J = 2 Hz, 2H), 7.28 (d, J = 2 Hz, 2H); $^{13}C\{^1H\}$ NMR δ 29.9, 31.9, 34.5, 35.0, 107.6, 116.4, 134.9, 144.0, 145.6, 148.3; $^{11}B\{^1H\}$ NMR δ 31.6. Anal. Calcd for $C_{28}H_{40}O_4B_2$: C, 72.75; H, 8.70. Found: C, 72.90; H, 8.75. For **1e**: ^1H NMR δ 0.91 (s, 12H), 3.35 (s, 8H); $^{13}C\{^1H\}$ NMR δ 22.1, 31.7, 71.6; $^{11}B\{^1H\}$ NMR δ 28.4. Anal. Calcd for $C_{10}H_{20}O_4B_2$: C, 53.15; H, 8.90. Found: C, 52.95; H, 9.00.

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[13] (a) Crystal structure data for **1a** (from CH_3CN): formula = $C_{12}H_8B_2O_4$, fw = 237.8, monoclinic, space group $P2_1/n$ (nonstandard No. 14), a = 4.746(1) Å, b = 16.427(3) Å, c = 7.053(2) Å, β = 98.59(2)°, V = 543.7(2) Å^3, Z = 2, ϱ = 1.453 g cm^{-3}, T = 200 K, $F(000)$ = 244. Anisotropic refinement of all non-hydrogen atoms (H refined with isotropic thermal parameters; 99 variables) using 1286 reflections with $F > 6.0\sigma(F)$ from 1594 unique data (1594 collected) gave R = 0.0385 and R_w = 0.0358. (b) Crystal structure data for **1b** (from THF): formula = $C_{20}H_{24}B_2O_4$, fw = 350.0, monoclinic, space group $P2_1/c$ (No. 14), a = 6.847(1) Å, b = 18.871(5) Å, c = 15.270(2) Å, β = 93.16(2)°, V = 1970.1(6) Å^3, Z = 4, ϱ = 1.180 g cm^{-3}, T = 200 K, $F(000)$ = 744. Refinement as above (260 variables) using 3261 reflections with $F > 6.0\sigma(F)$ from 4769 unique data (5140 collected) gave R = 0.0495 and R_w = 0.0497. (c) Crystal structure data for **1c** (from THF): formula = $C_{28}H_{40}B_2O_4$, fw = 462.2, triclinic, space group $P\bar{1}$ (No. 2), a = 9.478(4) Å, b = 10.355(4) Å, c = 15.082(7) Å, α = 105.71(3)°, β = 100.31(4)°, γ = 94.58(3)°, V = 1389.0(10) Å^3, Z = 2, ϱ = 1.105 g cm^{-3}, T = 298 K, $F(000)$ = 500. Refinement (riding model for isotropic H atoms 361 variables) using all 4897 unique F^2 data (8001 collected) gave R_w = 0.1414. The conventional R = 0.0446 based on F values for 3575 data with $F^2 > 2\sigma(F^2)$.

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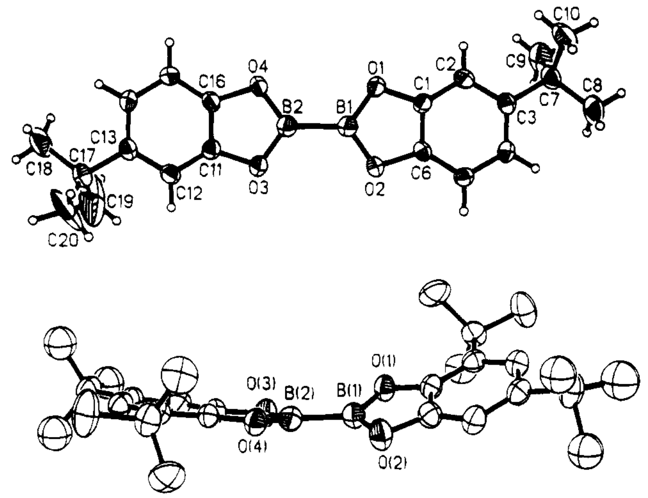

Figure 1. ORTEP diagrams for **1b** (top) and **1c** (bottom). Selected bond distances (Å) and angles (deg) follow. For **1b**: B1−B2 = 1.687(3), B1−O1 = 1.389(3), B1−O2 = 1.381(3), B2−O3 = 1.391(3), B2−O4 = 1.379(3), O1−B1−O2 = 111.3(2), O1−B1−B2 = 124.6(2), O2−B1−B2 = 124.1(2), O3−B2−O4 = 111.2(2), O3−B2−B1 = 124.2(2), O4−B2−B1 = 124.5(2). For **1c**: B1−B2 = 1.684(3), B1−O1 = 1.385(3), B1−O2 = 1.381(3), B2−O3 = 1.384(3), B2−O4 = 1.385(3), O1−B1−O2 = 111.1(2), O1−B1−B2 = 124.4(2), O2−B1−B2 = 123.8(2), O3−B2−O4 = 110.8(2), O3−B2−B1 = 126.9(2), O4−B2−B1 = 121.8(2).

0°. The B−B bond distance (1.678(3) Å) is shorter than those in **1d** (1.711(6) Å) and **1f** (1.720(6) Å). The packing is dominated by intermolecular π-stacking, with the separation between adjacent planes being 3.30 Å. $B_2(OR)_4$ compounds contain an 8-π-electron 6-atom system, which results in a π-bond order of 0, and thus a net B−B bond order of 1 arising from the σ-bond alone. In **1a−c**, the π-systems are further delocalized into the C_6, rings resulting in small but significant deviations of the C−C bond lengths from those of benzene. The Bu^t-substituted analogs **1b,c** were prepared[11] in order to improve solubility, allowing us to explore catalytic reactions in a wider range of solvents. The solid-state structure[13] of **1b** (Figure 1) reveals a dihedral angle between the two BO_2 planes of *ca.* 17°. This loss of planarity is presumably due to the presence of the bulky Bu^t groups which disrupt the graphitic π-stacking found for **1a**. In **1c** (Figure 1), the angle between the planes defined by B1, O1, C6, C1, O2 and B2, O3, C20, C15, O4 is 31.8°. The similarity of the B−B bond distances in **1b** (1.687(3) Å), **1c** (1.684(3) Å),[13] and **1a**, despite the range of dihedral angles, is consistent with a π-bond order of 0 and an insignificant barrier to B−B bond rotation. Two X-ray data sets were collected on **1e**, confirming its formulation; however, 3-fold rotational disorder prevented our obtaining highly accurate bond distances and angles.

Reaction of **1a** with **4** or **6**, in a 1.2:1 B_2:Rh molar ratio in THF or CH_2Cl_2 at room temperature, led to a discharge of the color of the Rh(I) compounds and the formation of **3a**[4a,6,14] in quantitative yield as shown by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectroscopy. No other phosphorus-containing species were observed, with the exception of free PPh_3 in the reaction with **6**. Reaction of **1b** or **1c** with **4** or **6** proceeded similarly, yielding $[(PPh_3)_2RhCl(B\text{-}1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2]$ (**3b**) or $[(PPh_3)_2RhCl(B\text{-}1,2\text{-}O_2\text{-}3,5\text{-}Bu^t{}_2C_6H_2)_2]$ (**3c**), respectively, in quantitative yield. Reactions involving **4** were generally found to be slightly faster than those with **6**; however, the most noticeable differences were found for the relative reactivities of **1a−e**. Reaction of **1a** with **4** in CH_2Cl_2 was complete in *ca.* 10 min, whereas the analogous reaction involving **1b** took *ca.* 1.25 h. Interestingly, no reaction was observed when pure **1d** or **1e** was treated with **6** at room temperature. Clearly, the reactivity of the *alkoxy*boron dimers is considerably lower than that of the catecholate analogs. No reaction was observed between **6** and $B_2(NMe_2)_4$ under the above conditions.

The molecular structure of **3a** was determined[6] previously. In the solid state, **3a** is a distorted square pyramid with *trans* PPh_3 groups, one Bcat ligand in an axial site, and the other lying *trans* to Cl in an equatorial site. The $^{31}P\{^1H\}$ NMR spectra of **3a** (33.6 ppm, d, J_{Rh-P} = 115 Hz), **3b** (33.7 ppm, d, J_{Rh-P} = 115 Hz), and **3c** (34.3 ppm, d, J_{Rh-P} = 116 Hz) are consistent with this structure. The observation of a single very broad resonance for the two boryl ligands in the $^{11}B\{^1H\}$ NMR spectra of **3a** (39.9 ppm), **3b** (38.9 ppm), and **3c** (42.6 ppm) indicates either that the signals for the two borons are overlapped or that the two boryl groups are equivalent on the NMR time scale. Both the ^1H and $^{13}C\{^1H\}$ NMR spectra[14] of **3a−c** are consistent with a single type of boryl group at room temperature, and there was no indication of a second *tert*-butylcatecholate environment in a $^{13}C\{^1H\}$ NMR spectrum of **3b** recorded at −70 °C. Clearly, any dynamic exchange process must have a very low barrier associated with it. Consistent with this is the fact that, in the solid-state, the related mono(boryl) complex $[(PPr^i{}_3)_2Rh(H)(Cl)(Bcat)]$[15] is a distorted trigonal bipyramid with axial phosphines.

It is interesting that the aryloxydiboron compounds **1a−c**, which have *shorter* B−B bonds than their alkoxy analogs **1d−f**, are nonetheless easier to oxidatively add to Rh(I) centers. In order to address this point, further studies[16] of the molecular and electronic structures of $B_2(OR)_4$ compounds, and their oxidative addition to other metal centers, are in progress and will be reported in due course.

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Supplementary Material Available: An ORTEP diagram of **1a** and tables of atomic coordinates, anisotropic thermal parameters, bond distances and angles, and data collection and refinement parameters for **1a−c** (18 pages). Ordering information is given on any current masthead page.

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(14) $^{13}C\{^1H\}$ NMR data for **3a**: δ 111.1, 121.3, 128.2 (t, para C of PPh_3), 130.4 (s, meta C of PPh_3), 132.4 (t, ipso C of PPh_3), 134.9 (t, ortho C of PPh_3), 149.5. NMR data for **3b**: ^1H δ 1.27 (s, 18H), 6.60−6.85 (m, 6H), 7.21−7.33 (m, 18H), 7.69−7.78 (m, 12H); $^{13}C\{^1H\}$ δ 31.9, 34.9, 108.8, 110.0, 117.8, 128.3 (t), 130.4, 132.6 (t), 135.0 (t), 145.1, 147.3, 149.5. NMR data for **3c**: ^1H δ 1.07 (s, 18H), 1.30 (s, 18H), 6.66 (d, J = 2 Hz, 2H), 6.82 (d, J = 2 Hz, 2H), 7.21−7.35 (m, 18H), 7.72−7.79 (m, 12H); $^{13}C\{^1H\}$ δ 30.0, 32.0, 34.2, 35.0, 106.7, 115.2, 128.4 (t), 130.4, 132.6 (t), 133.6, 135.1 (t), 144.3, 145.3, 149.7.

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