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Synthesis and Characterization of Rhodium(I) Boryl and Rhodium(III) Tris(Boryl) Compounds: Molecular Structures of $[(PMe_3)_4Rh(B(cat))]$ and *fac*-$[(PMe_3)_3Rh(B(cat))_3]$ (cat = 1,2-$O_2C_6H_4$)

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Transition metal monoboryl ($M-BR_2$) complexes[1] have received considerable attention due to their role in the metal-catalyzed hydroboration[2] of unsaturated organic substrates. Recently, the first well-characterized polyboryl complexes $M(BR_2)_n$ ($n = 2,3$) have been isolated,[3−5] particularly from the oxidative addition[4,5] of $B_2(cat)_2$ (cat = 1,2-$O_2C_6H_4$) (**1**) and its analogues to low-valent unsaturated metal fragments. This is of importance with regard to the metal-catalyzed diboration of alkynes[5] and alkenes[6] and the related formation of ArBpin (Ar = aryl, pin = $OCMe_2CMe_2O$) compounds[7] from ArX + $B_2(pin)_2$ catalyzed by a Pd system.

In order to study the reactivity of the M−B bond in low-valent, electron-rich, late metal boryl complexes, and to examine the reversibility of the B−B bond oxidative addition process, we sought to prepare a rhodium(I) boryl complex; the only previous example[8] being the poorly characterized species $[(PPh_3)_3Rh(BBr_2)]$. Our previous attempts to prepare Rh(I)−B(cat) compounds via reactions of $[(PMe_3)_4RhH]$ or $[({}^iPr_2PCH_2CH_2P^iPr_2)Rh(\eta^3\text{-2-Me-allyl})]$ with HB(cat)[1c,9] resulted in the formation of compounds such as $[(PMe_3)_4Rh]^+$, $[(PMe_3)_4Rh(H)_2]^+$ and the zwitterion $[(dippe)Rh(\eta^6\text{-(cat)}B(cat))]$. We reasoned that reaction of **1** with $[(PMe_3)_4RhMe]$ (**2**), however, would likely lead to $[(PMe_3)_4Rh(B(cat))]$ (**3**) via oxidative addition of the B−B bond followed by rapid reductive elimination of MeB(cat) (**4**) (eq 1).

$$\underset{\mathbf{2}}{[(PMe_3)_4RhMe]} + \underset{\mathbf{1}}{B_2(cat)_2} \xrightarrow[-PMe_3]{} [(PMe_3)_3Rh(Me)(B(cat))_2] \quad (1)$$

$$\xrightarrow[-MeB(cat)(\mathbf{4})]{+PMe_3} \underset{\mathbf{3}}{[(PMe_3)_4Rh(B(cat))]}$$

Indeed, when this reaction was conducted using a 1:1 molar ratio of **1**:**2** in heptane, **3** and **4** were formed rapidly in essentially quantitative yield[10] as evidenced by ^1H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The presence of **4** in solution was confirmed additionally by ambient temperature vacuum transfer of all volatiles to a separate vessel and subsequent examination of these by GC/MS.

Compound **3** is fluxional in solution as evidenced by the appearance of one doublet (−21.9 ppm, $J_{Rh-P} = 137$ Hz) in the room temperature $^{31}P\{^1H\}$ NMR spectrum which displays a sharp doublet of doublets (−22.0 ppm, $J_{Rh-P} = 157$, $^2J_{P-P} = 48$ Hz, 3P) and a broader overlapped doublet of quartets (−13.2 ppm, $J_{Rh-P} = 91$, $^2J_{P-P} = 48$ Hz, 1P) at 193 K. The low-temperature limiting spectrum indicates a trigonal bipyramidal geometry with the B(cat) ligand occupying an axial site. This structure was confirmed by single-crystal X-ray diffraction[11] (Figure 1, top). That the B(cat) group prefers an axial rather

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(10) NMR spectroscopic data for **3** in C_6D_6: $^{11}B\{^1H\}$ δ 49.0 (br); ^1H δ 7.11 (m, 2H), 6.86 (m, 2H), 1.28 (s, 36H); $^{13}C\{^1H\}$ δ 150.6, 120.8, 110.7 (cat), 26.9 (br, PMe_3). The isolated yields were 92−99%, but the material always contained a small amount (*ca.* 2% by NMR) of $[(PMe_3)_4Rh(H)]$ due to its considerable moisture sensitivity. For MeB(cat): $^{11}B\{^1H\}$ δ 35.2 (s); ^1H δ 6.99 (m, 2H), 6.79 (m. 2H), 0.46 (s, 3H); MS-EI *m/z* 134 (M^+) with expected isotope pattern.

(11) Crystal data for **3**: $C_{18}H_{40}BO_2P_4Rh$, $M_r = 526.10$, monoclinic, $P2_1/c$, $a = 16.7763(12)$ Å, $b = 9.8236(7)$ Å, $c = 16.3714(12)$ Å, $\beta = 103.728(2)°$, $V = 2621.0(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.333$ g cm^{-3}, $\mu = 0.91$ mm^{-1} (Mo Kα, $\lambda = 0.710\ 73$ Å), $F(000) = 1096$, $T = 160$ K. Siemens SMART CCD, crystal size 0.50 × 0.38 × 0.14 mm, $\theta_{max} = 26.35°$, 14 698 reflections measured, 5342 unique ($R_{int} = 0.0323$), semiempirical absorption correction (transmission 0.540−0.647). Structure solution by direct methods, refinement on F^2 with weighting $w^{-1} = \sigma^2(F_o^2) + (0.0323P)^2 + 2.0805P$, where $P = (F_o^2 + 2F_c^2)/3$, anisotropic displacement parameters, riding isotropic hydrogen atoms. Final $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.0746$ for all data, conventional $R = 0.0278$ on F values of 4901 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.161$ on F^2 for all data, and 248 parameters. Final difference map between +0.74 and −1.11 e Å^{-3}.

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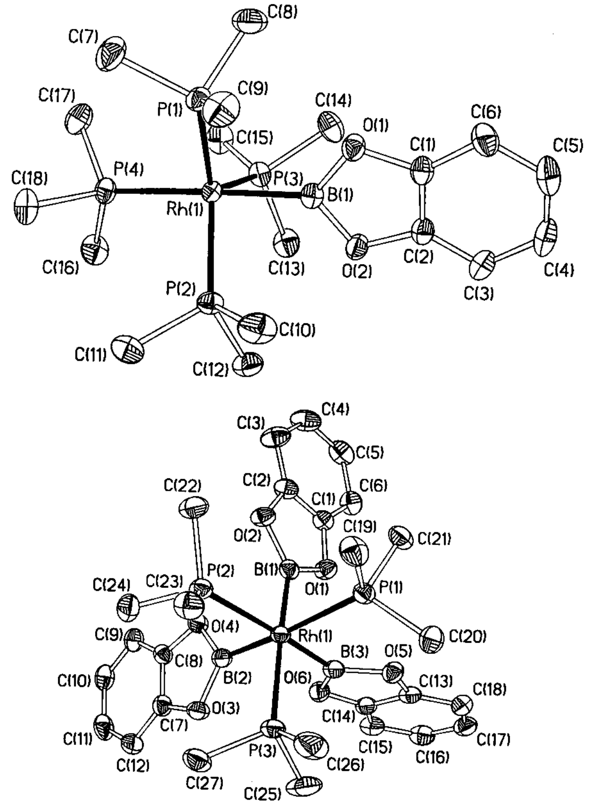

Figure 1. Top: view of the molecular structure of $[(\mathrm{PMe_3})_4\mathrm{Rh(B(cat))}]$ (**3**) with thermal elipsoids at 50% probablility and H atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−B(1) 2.047(2), Rh(1)−P(1) 2.3049(6), Rh(1)−P(2) 2.2891(6), Rh(1)−P(3) 2.3096(6), Rh(1)−P(4) 2.3404(6), B(1)−Rh(1)−P(1) 87.32(7), B(1)−Rh(1)−P(2) 83.07(7), B(1)−Rh(1)−P(3) 80.39(7), B(1)−Rh(1)−P(4) 174.74(7). Bottom: view of the molecular structure of $[(\mathrm{PMe_3})_3\mathrm{Rh(B(cat))_3}]$ (**5**) as above. Selected bond distances (Å) and angles (deg): Rh(1)−B(1) 2.055(4), Rh(1)−B(2) 2.053(4), Rh(1)−B(3) 2.061(4), Rh(1)−P(1) 2.3913(8), Rh(1)−P(2) 2.3906(9), Rh(1)−P(3) 2.3920(9); B−Rh−B 79.34(14)−82.05(14), P−Rh−P 94.42(3)−99.69(3).

than equatorial site suggests[12] that it is a strong σ-donor and a poor π-acceptor (cf. $[(\mathrm{PMe_3})_4\mathrm{Rh(C{\equiv}CPh)}]$);[13] if B(cat) were a strong π-acceptor, it would be expected to occupy an equatorial site and to lie perpendicular to the equatorial plane in such a $\mathrm{d^8\text{-}ML_4{-}B(cat)}$ complex in order to maximize Rh→B π-bonding.

Direct reaction of **2** with 2 equiv of **1** generates the triboryl complex *fac*-$[(\mathrm{PMe_3})_3\mathrm{Rh(B(cat))_3}]$ (**5**)[14] in 95% yield with loss of one $\mathrm{PMe_3}$ group and formation of **4** (eq 2). Reaction of isolated **3** with 1 equiv of **1** also gives **5** cleanly by ^{31}P and ^{1}H NMR. The only previously reported[3b] tris(boryl) complexes are $[(\eta^6\text{-arene})\mathrm{Ir(B(cat))_3}]$ (**6**) derivatives, one of which was found to react with 3 equiv of $\mathrm{PEt_3}$, yielding *fac*-$[(\mathrm{PEt_3})_3\mathrm{Ir(B(cat))_3}]$ (**7**) analogous to **5**. Compound **5** is the first structurally characterized[15] phosphine or Rh containing tris(boryl) complex (Figure 1, bottom). The *fac*-arrangement of the three B(cat) groups is evidence of their very strong *trans*-influence which is most likely a reflection of their strong σ-donating ability. In fact, there are, as yet, no well characterized[16] bis- or tris(boryl) complexes in which two boryl groups occupy mutually *trans*-coordination sites.

$$\underset{\mathbf{2}}{[(\mathrm{PMe_3})_4\mathrm{RhMe}]} + \underset{\mathbf{1}}{\mathrm{B_2(cat)_2}} \xrightarrow[-\mathrm{MeB(cat)}\ (\mathbf{4})]{} \underset{\mathbf{3}}{[(\mathrm{PMe_3})_4\mathrm{Rh(B(cat))}]} \tag{2}$$

$$\xrightarrow[-\mathrm{PMe_3}]{+\mathrm{B_2(cat)_2}} \underset{\mathbf{5}}{fac\text{-}[(\mathrm{PMe_3})_3\mathrm{Rh(B(cat))_3}]}$$

In order to examine the possibility that the second B−B bond oxidative addition (**3** → **5**) might be reversible, **5** was reacted with one equiv of **2** in the presence of one drop (excess) of $\mathrm{PMe_3}$ giving **3** + **4** in quantitative yields (eq 3). The simplest

$$\underset{\mathbf{5}}{fac\text{-}[(\mathrm{PMe_3})_3\mathrm{Rh(B(cat))_3}]} + \underset{\mathbf{2}}{[(\mathrm{PMe_3})_4\mathrm{RhMe}]} + \mathrm{PMe_3} \rightarrow 2\ \underset{\mathbf{3}}{[(\mathrm{PMe_3})_4\mathrm{Rh(B(cat))}]} + \underset{\mathbf{4}}{\mathrm{MeB(cat)}} \tag{3}$$

pathway consistent with eq 3 is the reductive elimination of $\mathrm{B_2(cat)_2}$ from **5** to give the transient complex $[(\mathrm{PMe_3})_3\mathrm{Rh(B(cat))}]$ which is rapidly trapped by $\mathrm{PMe_3}$ forming 1 equiv of **3**, the free $\mathrm{B_2(cat)_2}$ then reacting with **2** as in eq 1 to give a second equivalent of **3** and 1 equiv of **4**.

While studies of the reactivity of **3** and **5** with organic substrates and small molecules are in progress, as are studies of the reaction of **2** with other boron compounds, the preliminary results described herein demonstrate the strong σ-donor ability, strong *trans*-influence, and poor π-acceptor ability of the B(cat) group, and the apparent reversibility of the B−B bond oxidative addition process, and provide a simple route to a novel electron-rich rhodium(I) boryl complex.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **3** and **5**. Access information is given on any current masthead page.

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[14] NMR spectroscopic data for (**5**) in $\mathrm{C_6D_6}$: $^{11}\mathrm{B}\{^{1}\mathrm{H}\}$ δ 46.8 (br); $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ δ −26.2 (br), ^{1}H δ 6.98 (m, 2H), 6.73 (m, 2H), 1.19 (dd, $^{4}J_{\mathrm{Rh-H}} = 1.8$, $^{3}J_{\mathrm{P-H}} = 3.6$ Hz, 9H); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ δ 150.4, 120.9, 111.2 (cat), 22.5 (dd, $^{3}J_{\mathrm{Rh-C}} = 8.5$, $^{2}J_{\mathrm{P-C}} = 18.7$ Hz, $\mathrm{PMe_3}$). Anal. Calcd for $\mathrm{C_{27}H_{39}B_3O_6P_3Rh}$: C, 47.15; H, 5.71. Found: C, 47.80; H, 5.88.

[15] Crystal data for **5**: $\mathrm{C_{27}H_{39}B_3O_6P_3Rh{\cdot}0.5C_7H_8}$, $M_r = 733.90$ triclinic, $P1$, $a = 9.4861(9)$ Å, $b = 11.5356(11)$ Å, $c = 17.8907(18)$ Å, $\alpha = 73.055(3)°$, $\beta = 83.211(2)°$, $\gamma = 68.390(2)°$, $V = 1741.0(3)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.400$ g cm^{-3}, $\mu = 0.668$ mm^{-1} (Mo Kα, $\lambda = 0.710\,73$ Å), $F(000) = 758$, $T = 160$ K. Procedures as for **3**, crystal size 0.48 × 0.40 × 0.38 mm, $\theta_{\max} = 25.74°$, 7712 reflections measured, 5643 unique ($R_{\mathrm{int}} = 0.0354$), transmission 0.672−0.936. Weighting $w^{-1} = \sigma^2(F_o^2) + (0.0632P)^2 + 2.1542P$, geometrical and displacement parameter restraints on toluene molecule disordered over inversion center. Final $R_w = 0.1023$ for all data, conventional $R = 0.0375$ on F values of 5433 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.050$ for all data, 416 parameters, and 164 restraints. Final difference map between +0.96 and −1.22 e Å^{-3}.

[16] For some early work on Co−bis(boryl) complexes see: Schmid, G.; Nöth, H. *Chem. Ber.* **1967**, *100*, 2899.