

Preliminary communication

Synthesis and molecular structure of the paramagnetic Co(II) bis(boryl) complex $[\text{Co}(\text{PMe}_3)_3(\text{Bcat})_2]$ (cat = 1,2-O₂C₆H₄)

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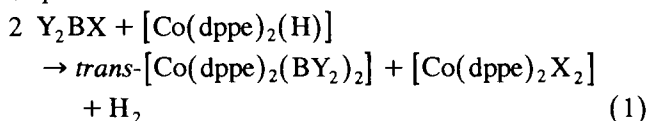
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Abstract

The B–B bonded compound B₂cat₂ (cat = 1,2-O₂C₆H₄) reacts with $[\text{Co}(\text{PMe}_3)_4]$ via oxidative addition of the B–B bond to Co(0) yielding the paramagnetic, formally 17-electron Co(II) *cis*-bis(boryl) complex $[\text{Co}(\text{PMe}_3)_3(\text{Bcat})_2]$. This complex has an unusually small B–Co–B angle of 67.9(4)° and short B–B separation of 2.185 Å, and, although it can be described as a distorted square pyramid, the geometry of the trigonal-pyramidal $[\text{Co}(\text{PMe}_3)_3]$ fragment is similar to that in the Co(I) complex $[\text{Co}(\text{PMe}_3)_3\text{Cl}]$, which has also been characterized by single-crystal X-ray diffraction.

Keywords: Cobalt; Boron; Boryl; Oxidative addition; Paramagnetic; Phosphine

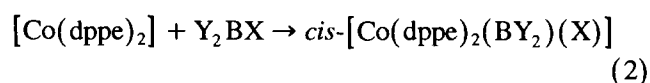
There have been several recent reports of transition metal catalyzed additions of B–B bonds in (RO)₂B–B(OR)₂ compounds to alkenes [1] and alkynes [2]. A key step in this process is the oxidative addition of the B–B bond to a low valent late transition metal center. In this regard, we and others have recently reported B–B oxidative addition to Rh(I) [3] and Pt(0) [2] centers and have been examining the chemistry of the resulting polyboryl complexes [2–4]. We were intrigued by several early reports [5] of Co(II) bis(boryl) complexes from the 1960s. Thus, Schmid and Nöth reported [5a,b,d] that reaction of Y₂BX with $[\text{Co}(\text{dppe})_2(\text{H})]$ (dppe = Ph₂PCH₂CH₂PPh₂) gave the formally 19-electron Co(II) bis(boryl) complexes *trans*- $[\text{Co}(\text{dppe})_2(\text{BY}_2)_2]$ (Eq. 1).



X = Cl, Br, I; Y = Br, I, Ph; Y₂B = PhClB;

Y₂B = C₁₂H₈B

In addition, they found [5c] that the Co(0) complex $[\text{Co}(\text{dppe})_2]$ reacted with Y₂BX to provide *cis*- $[\text{Co}(\text{dppe})_2(\text{BY}_2)(\text{X})]$ (Eq. 2).



Y₂BX = Ph₂BCl, BCl₃, BBr₃, BI₃

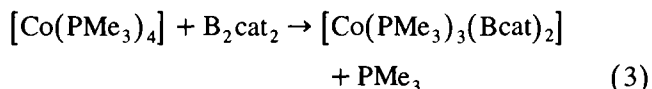
Although the above bis(boryl) compounds were widely utilized [5b,d] as boryl transfer agents to prepare numerous other metal boryl complexes, none of them were ever structurally characterized, and their true nature remains unknown. The only structurally characterised [6] cobalt boryl complex is $[\text{Co}(\text{dppm})(\text{CO})_2(\mu\text{-dppm})(\text{BH}_2)]$ in which the boryl ligand is coordinated by one arm of the bridging dppm ligand, and the Co–B distance is 2.227(6) Å.

While studying the synthesis, molecular and electronic structures [3,7a,b] and the reactivity with Lewis bases [7c] and transition metals [1,2b,3] of B₂cat₂ (cat = 1,2-O₂C₆H₄) **1**, we carried out the reaction [8] of **1** with the Co(0) complex $[\text{Co}(\text{PMe}_3)_4]$ [9] and found that the B–B bond undergoes oxidative addition to Co yield-

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ing the yellow, formally Co(II), 17-electron complex $[\text{Co}(\text{PMe}_3)_3(\text{Bcat})_2]$ **2** in 60% yield (Eq. 3).



Consistent with the complex being paramagnetic, no resonances were observed in either the $^{11}\text{B}\{^1\text{H}\}$ or $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2**. Elemental analysis was consistent with the presence of three PMe_3 ligands in addition to the two Bcat groups. Single crystals [10] suitable for X-ray diffraction were grown from hexane. The molecular structure of **2** is shown in Fig. 1. The Co1–B1 distance = 1.945(11) and Co1–B2 = 1.970(11) Å. The Co–P distances, which average 2.214(3) Å, (Co1–P1 = 2.203(3), Co1–P2 = 2.233(3) and Co1–P3 = 2.205(3) Å) show a small variation with Co1–P2 being 0.03 Å longer than the other two which are quite similar. It seems likely that the slight lengthening of the Co1–P2 bond is due to the fact that the PMe_3 group involving P2 is more sterically hindered than the other two PMe_3 groups.

Of particular interest is the B1–Co1–B2 angle of $67.9(4)^\circ$ which gives rise to a B1–B2 separation of only 2.185 Å. Although a small B1–Pt1–B2 angle of $77.1(2)^\circ$ has been observed [2b] ($77.8(7)^\circ$ in Ref. [2c]) in the solid-state structure of *cis*-[Pt(PPh₃)₂(Bcat)₂], none as small as 67.9° has been found previously. The B–B bond distance [3] in B_2cat_2 of 1.678(3) Å is at the short end of the usual range for a B–B bond [11] and the B–B separation in **2** is only 0.507 Å longer than this

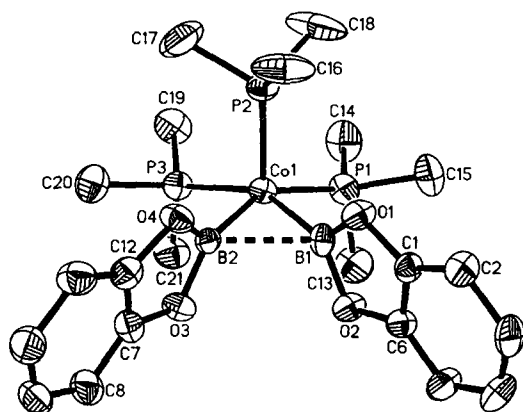


Fig. 1. Projection of the molecular structure of **2** showing the atom numbering scheme and illustrating the distorted square-pyramidal description of the coordination environment. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$) for **2**: Co1–B1 = 1.945(11), Co1–B2 = 1.970(11), Co1–P1 = 2.203(3), Co1–P2 = 2.233(3), Co1–P3 = 2.205(3), B1–O1 = 1.422(12), B1–O2 = 1.426(12), B2–O3 = 1.428(12), B2–O4 = 1.437(12), B1–Co1–B2 = $67.9(4)$, P1–Co1–P2 = $104.3(1)$, P1–Co1–P3 = $104.0(1)$, P1–Co1–B1 = $89.0(3)$, P1–Co1–B2 = $148.8(3)$, P2–Co1–P3 = $101.1(1)$, P2–Co1–B1 = $100.5(3)$, P2–Co1–B2 = $100.4(3)$, P3–Co1–B1 = $151.3(3)$ and P3–Co1–B2 = $89.4(3)$.

value suggesting the possibility of some remaining B–B interaction. Thus, the B1–B2 separation in **2** is only 0.212 Å longer than that for the peripheral B4'–B1 bond in decaborane(14) which was shown [12] to be 1.973 Å from a neutron diffraction study of $^{11}\text{B}_{10}^2\text{H}_{14}$ carried out at -160°C . The sum of the angles about B1 (359.3°) and B2 (359.5°) in **2** indicate clearly a trigonal planar environment about each boron, yet conjugation with the catecholato π -system will introduce electron density into the boron p_z -orbitals. The angles between the Co1–B1–B2 plane and B1–O1–O2 (88.8°) and B2–O3–O4 (86.5°) planes are quite similar, thus the two Bcat π -systems are facing each other with the closest approach being that of the two boron p_z -orbitals.

It is possible to describe the overall structure as a distorted square pyramid with P2 at the apical site and Co1 lying 0.0427 Å above the least-squares plane defined by P1, P3, B1 and B2 (deviations of these four atoms are 0.015, -0.015 , -0.024 and 0.024 Å respectively). However, the close approach of the two boron atoms suggests the possibility that the (Bcat)₂ unit should be considered as a single ligand. Interestingly, the geometry of the $[\text{Co}(\text{PMe}_3)_3]$ fragment in **2** (Fig. 2, top) is quite similar to that found in the Co(I) complex

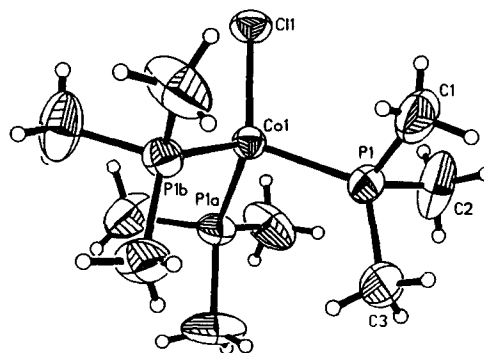
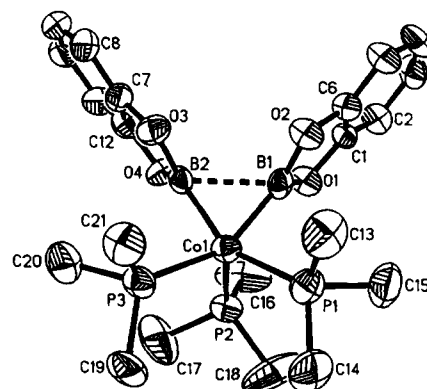


Fig. 2. Projection of the molecular structure of **2** (top) with hydrogen atoms omitted for clarity illustrating the distorted tetrahedral description of the coordination environment. Projection of the molecular structure of **3** (bottom). Selected bond distances (Å) and angles ($^\circ$) for **3**: Co1–P1 = 2.232(1), Co1–C11 = 2.226(2), C11–Co1–P1 = $114.1(1)$ and P1–Co1–P1A = $104.5(1)$.

[Co(PMe₃)₃Cl] **3** which has been structurally characterized previously at room temperature [13], and in this study [14], at 200 K (Fig. 2, bottom). The two structures of **3** are similar, and as the present one is more accurate, it is included here and used in the following discussion. In compound **3**, the Co1 and Cl1 atoms lie on a crystallographic 3-fold axis so that there is only one unique PMe₃ group. The Co1–P1 distance of 2.232(1) Å is only 0.018 Å longer than the average value in **2**, whereas the P–Co–P angles in **3** are all 104.5(1)° which is quite similar to the average P–Co–P angle of 103.1(1)° in **2**. Thus, complex **2** could be considered to have a distorted tetrahedral geometry in which the two boryl ligands occupy a single coordination site [15]. The degree of interaction between the two Bcat groups is not clear at this time; however, complex **2** may be viewed as lying part way along an oxidative addition reaction coordinate, with some B–B interaction still present.

Further studies of the electronic structure and reactivity of **2** are in progress and will be reported in due course.

Tables of atomic coordinates, anisotropic thermal parameters, bond distances and angles for complexes **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre. Structure factors are available from the authors.

Acknowledgements

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- [8] In an N₂-filled glove box, a scintillation vial was charged with [Co(PMe₃)₄] **1** (100 mg, 0.275 mmol), B₂cat₂ (65 mg, 0.277 mmol) and THF (4 ml) resulting in a brown solution. After stirring at room temperature over night, the solution lightened to a yellow-brown color, and the solvent was removed in vacuo yielding 150 mg of a brown solid. Recrystallization from hot hexane gave 92 mg of yellow crystals of **2** in 60% yield (Found: C, 48.23; H, 6.55. Calc. for C₂₁H₃₅B₂CoO₄P₃: C, 48.00; H, 6.67%).
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- [10] Crystal data for **2**: C₂₁H₂₃B₂CoO₄P₃, 0.11 × 0.25 × 0.34 mm, *M* = 525.0, orthorhombic, space group Pbc_a, *a* = 17.127(5), *b* = 15.303(4), *c* = 20.545(6) Å, *U* = 5385(2) Å³, *Z* = 8, *D_c* = 1.295 g cm⁻³, *μ* = 8.39 cm⁻¹, *F*(000) = 2200, *R* = 0.0687, *R_w* = 0.0473 for 280 parameters and 2053 unique observed [*F* > 6.0σ(*F*)] data (2θ_{max} = 52°), *w*⁻¹ = σ²(*F*), measured at room temperature.
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- [14] Crystal data for **3**: C₉H₂₇ClCoP₃, crystal size = 0.11(100) mm (distances from a common centre), *M* = 322.6, cubic, space group Pa $\bar{3}$, *a* = 15.345(2) Å, *U* = 3613.4(16) Å³, *Z* = 8, *D_c* = 1.186 g cm⁻³, *μ* = 13.37 cm⁻¹, *F*(000) = 1360, *R* = 0.0361, *R_w* = 0.0322 for 52 parameters and 632 unique observed [*F* > 6.0σ(*F*)] data (2θ_{max} = 50°), *w*⁻¹ = σ²(*F*), measured at 200 K.
- [15] For studies of metal complexes of the (η²-B₂H₅)⁻ ligand see, for example: T.J. Coffy, G. Medford, J. Plotkin, G.J. Long, J.C. Huffman and S.G. Shore, *Organometallics*, **8** (1989) 2404, and references contained therein. These complexes, which can be regarded as containing the protonated (η²-B₂H₄)²⁻ ligand (isoelectronic with ethylene) have three center B–M–B bonds. In [Fe(η⁵-C₅H₅)(CO)₂(η²-B₂H₅)], for example, the Fe–B distances average 2.217(3) Å and the B–B distance is 1.773(8) Å, i.e. the M–B distance is considerably longer and the B–B distance shorter than that in **2**.