Synthesis and reactivity of cobalt boryl complexes

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The reaction between [Co(PMe$_3$)$_4$] and B$_2$(4-Mecat)$_2$ (4-Mecat = 1,2-O$_2$-4-MeC$_6$H$_3$) or between [Co(PMe$_2$Ph)$_4$] and B$_2$(cat)$_2$ (cat = 1,2-O$_2$C$_6$H$_4$) affords the paramagnetic Co(II) bisboryl complexes [Co(PMe$_3$)$_3${B(4-Mecat)}$_2$] and [Co(PMe$_2$Ph)$_3${B(cat)}$_2$] respectively, both of which have been structurally characterised. ESR data and preliminary diboration and boryl transfer reactivity studies are also presented. The reaction between [CoMe(PMe$_3$)$_4$] and B$_2$(cat)$_2$ affords the Co(I) monoboryl complex [Co(PMe$_3$)$_4${B(cat)}].

Transition metal boryl compounds[1] continue to attract attention not least because of their involvement in various metal catalysed diboration and other borylation reactions.[2] Boryl complexes have now been characterised for many metals,[1] one of the more unusual of which is cobalt since many are reported to be paramagnetic. Nöth and Schmid were the first to study cobalt boryl complexes and in early work reported the 19-electron Co(II) species *trans*-[Co(dppe)$_2$(BR$_2$)$_2$] (R = Ph, Br, I and derivatives with 1,2-(PMe$_2$)$_2$C$_6$H$_4$ and 9-borafluorenyl),[3] *cis*-[Co(dppe)$_2$(BPh$_2$)X] and *cis*-[Co(dppe)$_2$(BX$_2$)X] (X = halide)[4] together with the diamagnetic Co(I) complexes [Co(CO)$_4$(BR$_2$)] (R = Cl, Ph, NMe$_2$ and related phosphine substituted derivatives)[5] and the dimethylglyoxime compounds [Co(dmg-BR$_2$)$_2$(BX$_2$)(L)] (R = Ph, Bu; X = Ph, Cl, NMe$_2$; L = PPh$_3$, AsPh$_3$, pyridine);[6] much of this work they subsequently reviewed.[7] It was also reported that the complex *trans*-[Co(dppe)$_2$(BPh$_2$)$_2$] could be reduced with sodium to the 20-electron diamagnetic anion *trans*-[Co(dppe)$_2$(BPh$_2$)$_2$]$^-$.[3,7] Unfortunately, there were very little spectroscopic data reported for any of these species and none were structurally characterised so their true nature remains ambiguous. In later work, the complexes [Co(CO)$_4${BH$_2$(thf)}][8] and [Co(CO)$_2$(η^1-dppm)(μ-dppm)(BH$_2$)][9] were described. Of particular interest were the reports that the purported paramagnetic Co(II) bisboryls apparently acted as efficient and versatile boryl transfer reagents in which the boryl group could be transferred to a range of other transition metal (*e.g.* Cu, Ag, Au, Rh, Fe, Ni, Mn) or main group metal (*e.g.* Sn, Pb) centres by reaction with the corresponding metal halide.[3,7,10] Despite this interest, the first structurally characterised cobalt boryl containing an unsupported Co–B bond was the Co(II) complex [Co(PMe$_3$)$_3${B(cat)}$_2$] (**1**)[11] (cat = 1,2-O$_2$C$_6$H$_4$), obtained by us in 1996 from the reaction between [Co(PMe$_3$)$_4$][12] and B$_2$(cat)$_2$,[13] which also exhibited an unusually short B–B interaction (2.185 Å). Herein we describe some preliminary results on the further chemistry and reactivity of phosphine–cobalt boryls.

The reaction between [Co(PMe$_3$)$_4$] and B$_2$(4-Mecat)$_2$ (4-Mecat = 1,2-O$_2$-4-MeC$_6$H$_3$)[13b] or between [Co(PMe$_2$Ph)$_4$][12] and B$_2$(cat)$_2$ afforded the complexes [Co(PMe$_3$)$_3${B(4-Mecat)}$_2$] (**2**) and [Co(PMe$_2$Ph)$_3${B(cat)}$_2$] (**3**) respectively,† albeit in low isolated yields and together with other unidentified products; both **2** and **3** were characterised by X-ray crystallography.‡ A view of the molecular structure of **3** is shown in Fig. 1. Compounds **1**,[11] **2** (two crystallographically independent molecules) and **3** adopt square-based pyramidal structures with a phosphine in the apical site and *cis*, basal boryl groups.[14] All have similar Co–B distances [**1**, 1.945(11), 1.970(11); **2**, 1.947(6), 1.966(5), 1.954(6), 1.960(6); **3**, 1.948(3), 1.955(3) Å], B–Co–B angles [**1**, 67.9(4); **2**, 68.8(2), 68.1(2); **3**, 71.19(12)°] and B–B distances [**1**, 2.185; **2**, 2.211, 2.192; **3**, 2.271 Å] indicating that the acute B–Co–B angle and short B–B distance in particular are fundamental features for this type of Co(II) bisboryl complex. A molecular orbital analysis, on the basis of DFT calculations,[15] for the model complex [Co(PH$_3$)$_3${B(O$_2$C$_2$H$_2$)}$_2$] does reveal the presence of a three-centre CoB$_2$ interaction (Fig. 2) consistent with some degree of weak B–B bonding involving one of the Co d orbitals and the in-phase

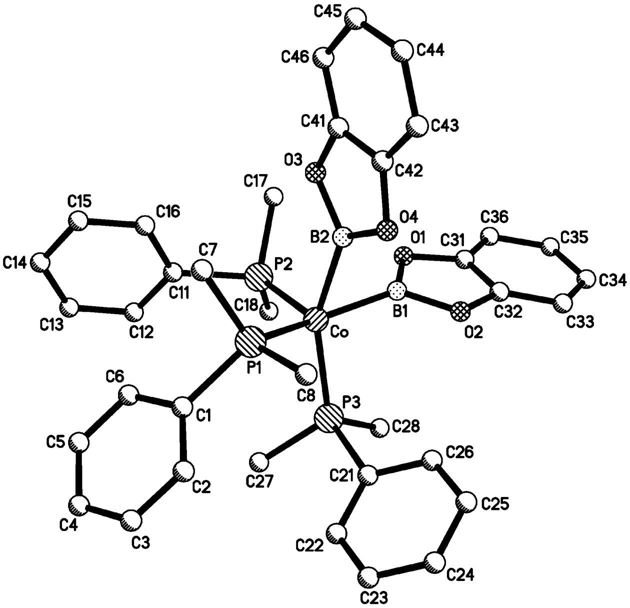

Fig. 1 A view of the molecular structure of **3** showing the atom numbering scheme. Selected bond length (Å) and angle data (°) include: Co(1)–B(1) 1.948(3), Co(1)–B(2) 1.955(3), Co(1)–P(1) 2.2237(7), Co(1)–P(2) 2.2510(7), Co(1)–P(3) 2.2067(7); B(1)–Co(1)–B(2) 71.19(12).

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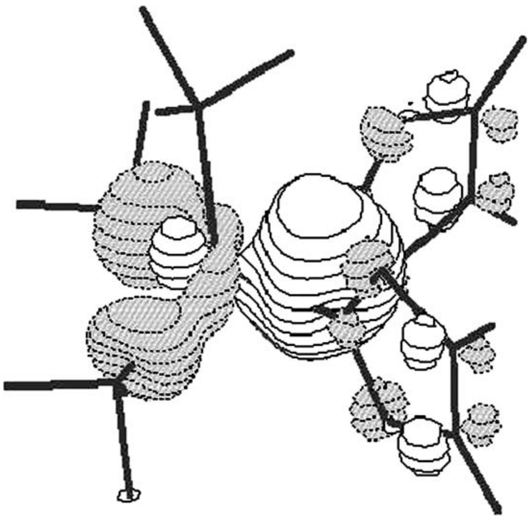


Fig. 2 A spatial plot of the three-centre, two-electron bonding molecular orbital showing the weak interaction between Co and the two boron centres.

combination of the two 'empty' boron p orbitals from the two $B(O_2C_2H_2)$ ligands which is consistent with these observed structural features.

Compounds **1–3** are paramagnetic and exhibit ESR spectra which are broad at room temperature and well-defined at low temperature. Preliminary analysis of the spectrum of **2** (Fig. 3)[§] presented here (g_x and $g_y > g_e$, $g_z \approx g_e$) is consistent with the presence of a single unpaired electron in a d_{z^2} orbital in accord with both the observed structure and the results of the DFT calculations.[14] The high field component shows significant coupling to cobalt (^{59}Co, 100%, $I = -7/2$), whilst the lower field features show coupling to two equivalent phosphorus nuclei. No appreciable coupling was observed to ^{11}B.

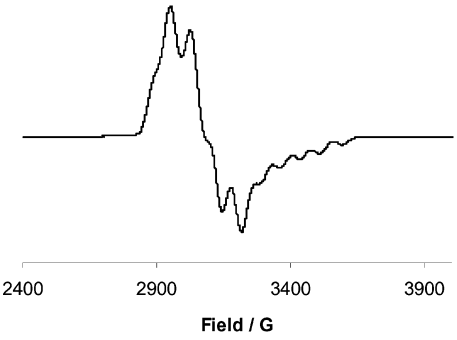


Fig. 3 The ESR spectrum of **2** recorded at 120 K. Selected data include: $A_1(2P) \approx 60$ G, $A_2(2P) \approx 75$ G, $A_3(Co) = 80$ G, $g_1 = 2.239$, $g_2 = 2.110$, $g_3 = 1.985$, $g_{iso} = 2.116$.

Since the Co(II) bisboryls are paramagnetic, it was not expected that they would exhibit observable ^{11}B or ^{31}P NMR signals. However, routine monitoring of reaction solutions by ^{11}B NMR consistently showed the presence of a broad signal around 50 ppm. It was considered likely that such a signal was due to the presence of either a diamagnetic Co(I) or Co(III) boryl species, most likely either $[Co(PMe_3)_4\{B(cat)\}]$ (**4**) or *fac*-$[Co(PMe_3)_3\{B(cat)\}_3]$ (**5**) by analogy with the known corresponding rhodium species.[16] Accordingly, and guided by the analogous rhodium chemistry, the reaction shown in eqn (1) was carried out which resulted in the production and isolation of the Co(I) species **4** and MeB(cat).[¶,17] The signal observed for **4** (52.5 ppm) was identical to that seen in reaction solutions from which **1** was obtained, and the presence of MeB(cat) (δ ^{11}B 34.8) was confirmed by comparison with previous data.[16]

$$[CoMe(PMe_3)_4] + B_2(cat)_2 \rightarrow [Co(PMe_3)_4\{B(cat)\}] + MeB(cat) \qquad (1)$$

The structure of **4** was established by X-ray crystallography, the results of which are shown in Fig. 4.[*] The 18-electron Co(I) compound **4** adopts the expected[14,16] trigonal bipyramidal geometry with the high *trans*-influence boryl group in an axial site. Also by analogy with the rhodium system, the synthesis of the Co(III) trisboryl complex **5** was attempted according to eqn (2). Prolonged reaction in toluene revealed the presence of a new ^{11}B NMR signal at 50.1 ppm assumed to be due to compound **5**, although the reaction did not proceed to completion and the trisboryl species was not isolated.

$$[Co(PMe_3)_4\{B(cat)\}] + B_2(cat)_2 \rightarrow [Co(PMe_3)_3\{B(cat)\}_3]+PMe_3 \qquad (2)$$

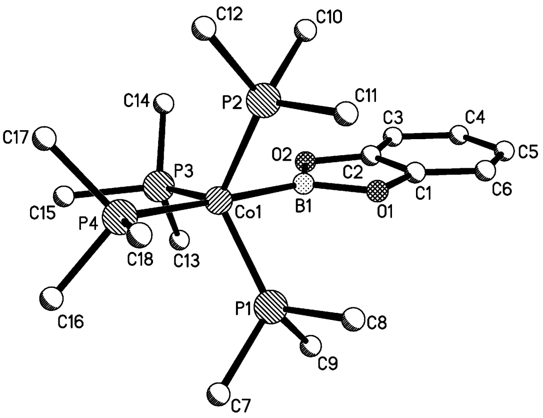
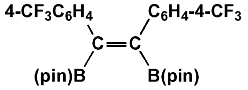


Fig. 4 A view of the molecular structure of **4** showing the atom numbering scheme. Selected bond length (Å) and angle data (°) include: Co(1)–B(1) 1.949(2), Co(1)–P(1) 2.1527(5), Co(1)–P(2) 2.1686(5), Co(1)–P(3) 2.1687(5), Co(1)–P(4) 2.1859(5); B(1)–Co(1)–P(4) 174.04(6).

Preliminary reactivity studies involving both diboration catalysis and boryl transfer were also carried out. With regard to diboration, the reaction between $B_2(cat)_2$ and the alkyne 4-$CF_3C_6H_4C{\equiv}CC_6H_4$-4-$CF_3$ in THF in the presence of 5 mol% $[Co(PMe_3)_4]$ at 80 °C for 24 h afforded good yields of the diboration product $(4\text{-}CF_3C_6H_4)\{B(cat)\}C{=}C\{B(cat)\}(C_6H_4\text{-}4\text{-}CF_3)$.[††] Analysis of the reaction mixture by GC-MS (after treatment with pinacol to make the bis-B(pin) derivative which is more easily analysed by GC-MS) showed not only the expected *cis* isomer **6**[18] but also a small amount of a compound with the same mass and similar fragmentation pattern which we assign to the *trans* isomer **7**, as it also gave a singlet in the ^{19}F NMR spectrum and in the B(pin) region of the ^{1}H NMR spectrum. *Trans*-diboration of alkynes has not been observed previously (although we note an example of metal catalysed *trans*-hydroboration[19]) and its appearance in this system is most likely associated with the paramagnetic nature of the catalyst although the detailed mechanism and reaction pathway remain to be elucidated. The structure of the *cis* isomer, **6**, was confirmed by X-ray crystallography as a mixed B(pin)/B(cat) species.‡‡



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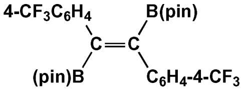

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Boryl transfer was investigated initially by carrying out reactions between equimolar amounts of $B_2(cat)_2$, $[Co(PMe_3)_4]$ and a 4-substituted aryl bromide ($4\text{-}BrC_6H_4X$) in THF at room temperature and analysing the reaction solution after 24 h by GC-MS. For the arenes examined where X = H, CH_3 and CF_3, the corresponding borylation products 4-{B(cat)}C_6H_4X were observed in all cases. In addition, the bisborylated product 1,2-$\{B(cat)\}_2C_6H_4$ was observed in the reaction with *ortho*-dibromobenzene. Interestingly, the reaction between bromobenzene and isolated **1** under similar conditions afforded PhB(cat), whereas reaction with 4-iodotoluene at 80 °C gave 4-tolylB(cat), confirmed by single crystal X-ray diffraction.

In conclusion, these studies have shown that paramagnetic Co(II) bisboryls can be formed from Co(0) precursors and diborane(4) compounds, if somewhat unselectively and in low isolated yields, but that Co(I), and possibly Co(III), species are also formed. Preliminary reactivity studies have also demonstrated that alkyne diboration takes place and that borylation of aryl bromides, including dibromobenzene, is also possible albeit with low selectivity and in modest yields. Further studies are in progress to examine much of this chemistry in more detail.

Acknowledgements

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Notes and references

† Preparation of **2**: A sample of $B_2(4\text{-}Mecat)_2$[13b] (0.070 g, 0.26 mmol) was added to a solution of $[Co(PMe_3)_4]$[12] (0.100 g, 0.28 mmol) in toluene (4 cm^3) and the resulting mixture was stirred overnight at room temperature. After removal of all volatiles *in vacuo*, the solid residues were extracted with hexane and filtered. Slow evaporation of the solvent from the filtrate afforded yellow crystals of **2** (0.03 g, 21%) one of which was suitable for X-ray crystallography. Preparation of **3**: A sample of $B_2(cat)_2$ (0.043 g, 0.18 mmol) was added to a deep red solution of $[Co(PMe_2Ph)_4]$[12] (0.110 g, 0.18 mmol) in THF (3 cm^3) and the resulting mixture was stirred at 60 °C for 1 h. After standing overnight at room temperature, a small quantity of blue crystals precipitated which have not been identified. The remaining red supernatant liquid was separated, all volatiles were removed *in vacuo* and the solid residues extracted with hot hexane which afforded a small quantity of orange crystals of **3** on cooling, one of which was suitable for X-ray crystallography. Satisfactory analytical data were not obtained due to the persistent presence of traces of unidentified side products in both cases.

‡ Crystal data for **2**: $C_{23}H_{39}B_2CoO_4P_3$, $M = 553.00$, triclinic, $a = 12.3126(12)$, $b = 16.2340(16)$, $c = 16.3156(16)$ Å, $\alpha = 110.985(2)$, $\beta = 91.761(2)$, $\gamma = 108.279(2)°$, $V = 2853.4(5)$ Å^3, $T = 173(2)$ K, space group $P\bar{1}$, $Z = 4$, $\mu = 0.795$ mm^{-1}, $R_{int} = 0.0560$ (for 30 455 measured reflections), $R1 = 0.0487$ [for 6776 unique reflections with $I > 2\sigma(I)$], $wR2 = 0.1206$ (for all 12 934 unique reflections). Compound **2** contains two crystallographically distinct molecules one of which shows disorder in the position of the methyl substituent on the B(cat) ligand. Crystal data for **3**: $C_{36}H_{41}B_2CoO_4P_3$, $M = 711.15$, monoclinic, $a = 13.2266(6)$, $b = 16.0716(7)$, $c = 33.7307(15)$ Å, $\beta = 96.30(1)°$, $V = 7126.9(6)$ Å^3, $T = 120(2)$ K, space group $C2/c$, $Z = 8$, $\mu = 0.654$ mm^{-1}, $R_{int} = 0.0523$ (for 33 424 measured reflections), $R1 = 0.0480$ [for 6062 unique reflections with $I > 2\sigma(I)$], $wR2 = 0.0962$ (for all 7749 unique reflections).

§ ESR spectra were recorded by Dr Damien Murphy of the University of Cardiff as toluene glasses at 120 K in a 4119HS cavity on a Bruker EMX X-band spectrometer operating at 100 kHz field modulation.

¶ Preparation of **4**: A sample of $B_2(cat)_2$ (0.016 g, 0.067 mmol) was added to an orange-red solution of $[CoMe(PMe_3)_4]$[17] (0.027 g, 0.071 mmol) in hexane (0.6 cm^3) resulting in a light yellow solution and a small amount of an unidentified green precipitate. The solution was filtered and concentrated *in vacuo* resulting in the appearance of a small quantity of yellow crystals of **4** after a few days, one of which was suitable for X-ray crystallography. NMR (hexane/THF): ^{11}B δ 52.5, **4**; 34.8, MeB(cat). Satisfactory analytical data were not obtained due to persistent traces of unidentified side products.

* Crystal data for **4**: $C_{18}H_{40}BCoO_2P_4$, $M = 482.12$, monoclinic, $a = 16.6032(12)$, $b = 9.7012(7)$, $c = 16.1590(12)$ Å, $\beta = 104.3940(10)°$, $V = 2521.0(3)$ Å^3, $T = 173(2)$ K, space group $P2_1/c$, $Z = 4$, $\mu = 0.945$ mm^{-1}, $R_{int} = 0.0343$ (for 15 951 measured reflections), $R1 = 0.0294$ [for 4639 unique reflections with $I > 2\sigma(I)$], $wR2 = 0.0737$ (for all 5793 unique reflections).

†† To a stirred solution of $B_2(cat)_2$ (0.061 g, 0.27 mmol) in THF (2.5 cm^3), a sample of $4\text{-}CF_3C_6H_4C{\equiv}CC_6H_4\text{-}4\text{-}CF_3$ (0.080 g, 0.25 mmol) was added followed by $[Co(PMe_3)_4]$ (0.004 g, 0.011 mmol). The reaction mixture was then stirred at 80 °C and samples were taken after 24 and 48 h for GC-MS analysis. The samples were treated with excess pinacol before analysing by GC-MS.

‡‡ Crystal data for **6**: $C_{28}H_{24}B_2F_6O_4$, $M = 560.09$, monoclinic, $a = 11.588(1)$, $b = 13.554(1)$, $c = 26.571(3)$ Å, $\beta = 101.58(1)°$, $V = 4088.4(7)$ Å^3, $T = 120(2)$ K, space group $P2/c$, $Z = 6$, $\mu = 0.116$ mm^{-1}, $R_{int} = 0.0467$ (for 45 186 measured reflections), $R1 = 0.0874$ [for 6654 unique reflections with $I > 2\sigma(I)$], $wR2 = 0.2090$ (for all 9403 unique reflections). The structure of **6** contains one molecule that has ordered B(pin) and B(cat) groups and a second molecule which sits on a 2-fold axis and is thus disordered with exact 1 : 1 disorder in the positions of the B(cat)/B(pin) substituents. Both molecules also show disorder in their CF_3 groups. CCDC reference numbers 290418–290421. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516594f

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