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Synthesis and structures of carbonyl adducts of the boranes $B(BX_2)_3$ (X = F, Cl)

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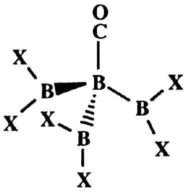
The borane carbonyl adduct $(Cl_2B)_3BCO$ has been prepared and characterised by spectroscopic methods and X-ray crystallography and is compared with the fluorine analogue $(F_2B)_3BCO$ which has also been structurally characterised by X-ray crystallography.

In recent years the study of carbon monoxide as a ligand has attracted renewed attention largely as a result of the discovery and characterisation of many so-called 'non-classical metal carbonyls' for which metal to CO π-backbonding is thought to be absent or at least much reduced in comparison with more classical species.[1] These compounds merit comparison with the few known boron carbonyl complexes such as the borane carbonyls H_3BCO,[2]† B_4H_8CO,[4] and $(F_2B)_3BCO$ **1** prepared by



1, X = F; **2**, X = Cl

Timms,[5,6] the related silicon containing species $(Cl_3Si)_2(Cl_2B)BCO$,[7] and the osmium cluster complex $[Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}BCO)]$ prepared by Shore *et al.*[8] Herein we report the X-ray structure of **1** and the preparation and X-ray structure of the chloro analogue $(Cl_2B)_3BCO$ **2**.

Compound **2** was prepared by two methods. In the first instance, BCl_3 was passed through a column of boron granules contained in a graphite tube inductively heated to *ca.* 2000 °C under high vacuum, using an apparatus slightly modified from that described for the preparation of BF.[5,6] The hot vapour emerging from the graphite tube, believed to be a mixture of BCl and BCl_3 in a mole ratio of about 1 : 3, was then condensed on the liquid nitrogen cooled walls of the surrounding vacuum vessel. When the condensate was allowed to warm to room temperature with continuous pumping through a cold trap, a mixture of BCl_3 and B_2Cl_4 was collected; no B_4Cl_4 was detected in contrast to earlier studies involving BCl.[9] However, when a similar experiment was carried out in which the condensate was allowed to warm to room temperature in the presence of a 3×10^4 Pa pressure of CO, the resulting volatiles comprised not only BCl_3 and B_2Cl_4 but also the white crystalline solid **2**.

Spectroscopic data for **2** were consistent with the formula $(Cl_2B)_3BCO$‡ which was confirmed by X-ray crystallography (*vide infra*). The formation of **2** in the above experiment may involve the intermediacy of $(Cl_2B)_2BCl$, just as the condensation of BF is known to yield $(F_2B)_2BF$ which, in the presence of CO, gives **1** and B_2F_4.[5] Compound **2** was also prepared in a more direct manner and in essentially quantitative yield by treating **1** (prepared as described in ref. 5) with an excess of BCl_3 vapour for a few minutes at room temperature.

The structures of both **1** and **2** were determined by X-ray crystallography.§ Compound **1** crystallises with two molecules in the asymmetric unit one of which is shown in Fig. 1. Compound **2** resides on a crystallographic C_3 axis and part of the crystal structure is shown in Fig. 2. On a molecular level, the structures are very similar and also similar to that reported for the PF_3 analogue of **1**, $(F_2B)_3BPF_3$.[11] The central boron atoms in each structure are all within a degree of being tetrahedral and the B–B bond lengths [1.677(5)–1.690(5) Å for **1** and 1.694(7)

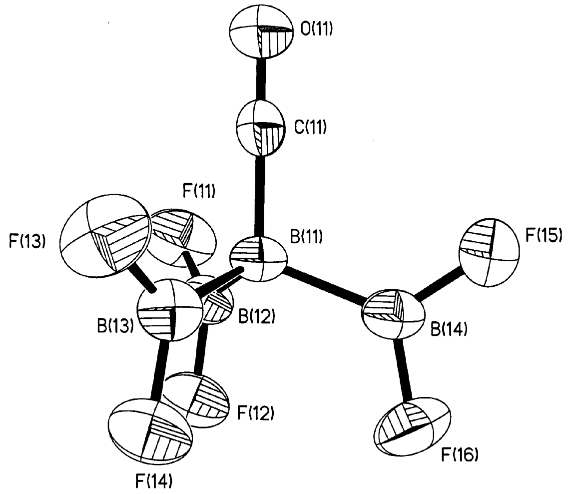


Fig. 1 A view of one of the crystallographically independent molecules of **1**. Ellipsoids are drawn at the 40% level. Bond lengths (Å) and angles (°) for the molecule shown: C(11)–O(11) 1.117(3), C(11)–B(11) 1.522(5), B(11)–B(12) 1.677(5), B(11)–B(13) 1.690(5), B(11)–B(14) 1.681(5), B(12)–F(11) 1.310(4), B(12)–F(12) 1.311(4), B(13)–F(13) 1.317(4), B(13)–F(14) 1.305(4), B(14)–F(15) 1.315(4), B(14)–F(16) 1.302(4); O(11)–C(11)–B(11) 178.8(3), C(11)–B(11)–B(12) 109.6(3), C(11)–B(11)–B(13) 109.3(3), C(11)–B(11)–B(14) 110.5(3), B(12)–B(11)–B(13) 109.5(3), B(12)–B(11)–B(14) 109.9(3), B(13)–B(11)–B(14) 108.0(3), B(11)–B(12)–F(11) 124.9(3), B(11)–B(12)–F(12) 121.1(3), F(11)–B(12)–F(12) 114.0(3), B(11)–B(13)–F(13) 124.3(3), B(11)–B(13)–F(14) 121.8(3), F(13)–B(13)–F(14) 113.9(3), B(11)–B(14)–F(15) 125.0(3), B(11)–B(14)–F(16) 121.5(4), F(15)–B(14)–F(16) 113.5(3).

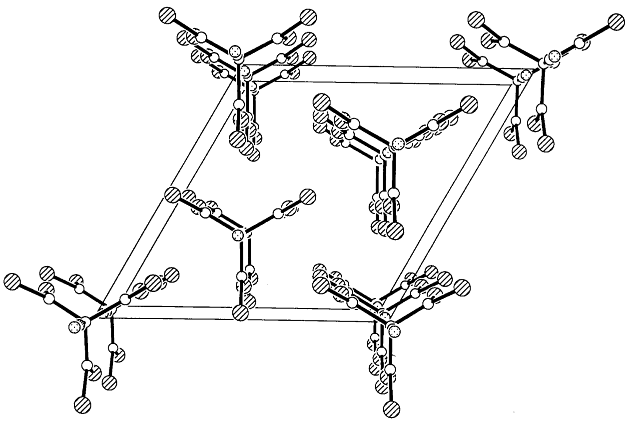


Fig. 2 The crystal structure of **2** viewed down the *c* axis. Bond lengths (Å) and angles (°): C(1)–O(1) 1.091(14), B(1)–C(1) 1.544(15), B(1)–B(2) 1.694(7), B(2)–Cl(1) 1.748(7), B(2)–Cl(2) 1.748(7), O(1)–C(1)–B(1) 180, C(1)–B(1)–B(2) 107.3(4), B(2)–B(1)–B(2a) 111.5(4), B(1)–B(2)–Cl(1) 122.0(5), B(1)–B(2)–Cl(2) 121.9(5), Cl(1)–B(2)–Cl(2) 116.1(4).

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Å for **2**] are of the same order as those observed in $(F_2B)_3BPF_3$ [1.677(15) Å][11] and B_2F_4 [1.67(4) Å].[12] The B–F bonds in **1** range from 1.302(4) to 1.317(4) Å [*cf.* 1.30, 1.32(3) and 1.305(15) for BF_3,[13] B_2F_4[12] and $(F_2B)_3BPF_3$[11] respectively] whilst the two B–Cl bond lengths in **2** [1.748(7) Å] are similar to other B–Cl bond distances for trigonal planar boron.[14] Both **1** and **2** have C_{3v} symmetry, crystallographically constrained in the latter case, such that the three BX_2 planes lie parallel to the BCO axis. Despite the similarity in the molecular structures, however, **1** and **2** pack differently in the solid state. Thus, although there are no close intermolecular contacts in either structure, **1** [and $(F_2B)_3BPF_3$] crystallises in a centrosymmetric space group $P2_1/n$ [*Pnma* for $(F_2B)_3BPF_3$] whereas **2** crystallises in the polar space group $R3m$ with all BCO vectors aligned along the crystallographic *c* axis.

The CO stretching frequencies for **1** (2162 cm^{-1})[5] and **2** (2176 cm^{-1}) are both higher than that of free CO (2143 cm^{-1}) but are close to those observed in many non-classical metal carbonyls[1] and in $(Cl_3Si)_2(Cl_2B)BCO$.[7] Such values are often characteristic of non-classical carbonyls and are associated with increased σ-donation and little if any π-donation into the CO π*-orbitals[1,3] (electrostatic effects are also thought to be important[3]). As expected, both **1** and **2** have C–O bond lengths which appear to be shorter than CO itself [**1**, 1.117(3), 1.116(3) Å; **2**, 1.091(14) Å; CO, 1.1281 Å]. However, given the relatively large esds involved, such comparisons must be made with due caution.

In conclusion, we note that the synthesis of **2** and the structures of **1** and **2** provide a significant contribution to what is known about CO adducts of boron and to the study of non-classical CO complexes in general. Both **1** and **2** are stable to CO loss and future studies, both theoretical and experimental, will address the magnitude of the B–C bond dissociation energy.

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Notes and references

† A recent and comprehensively referenced theoretical analysis of the bonding and stability of the compounds H_3BCO, F_3BCO and $(C_6F_5)_3BCO$ has been carried out by Berke and Erker *et al.*[3] where the analogy between borane carbonyls and non-classical metal carbonyls is also addressed.

‡ *Spectroscopic data* for **2**: ^{11}B NMR (CD_2Cl_2) δ 68.2 [br s, 3B, $(Cl_2B)_3BCO$], −20.7 [br s, 1B, $(Cl_2B)_3BCO$] (referenced to $BF_3\cdot Et_2O$). IR (thin film on AgCl window) ν(CO) 2176 cm^{-1}. Mass spectrum (EI), *m/z* 166 (B_3Cl_3CO), 221 (B_4Cl_5), 249 (B_4Cl_5CO) all with correct isotope patterns.

§ A suitable single crystal of **1** was prepared inside a Lindemann tube by condensing its vapour into the tube, sealing it under vacuum and cycling the temperature between 20 and 35 °C. A colourless needle crystal of **2** was grown under vacuum at 4 °C and transferred and sealed under nitrogen in a Lindemann tube prior to mounting on the diffractometer. Both compounds are pyrophoric.

Crystal data: for **1**: CB_4F_6O, $M = 185.25$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.909(3)$, $b = 11.518(3)$, $c = 11.098(3)$ Å, $\beta = 90.548(18)°$, $U = 1394.4(6)$ Å^3, $Z = 8$, $D_c = 1.765$ Mg m^{-3}, $\lambda = 0.71073$ Å, μ(Mo-Kα) $= 0.218$ mm^{-1}, $F(000) = 704$, $T = 292(2)$ K.

For **2**: CB_4Cl_6O, $M = 283.95$, rhombohedral on hexagonal axes, space group $R3m$ (no. 160), $a = 11.150(5)$, $c = 7.586(4)$ Å, $U = 816.8(7)$ Å^3, $Z = 8$, $D_c = 1.732$ Mg m^{-3}, $\lambda = 0.71073$ Å, μ(Mo-Kα) $= 1.520$ mm^{-1}, $F(000) = 1700$, $T = 292(2)$ K.

Data for both structures were collected on a Siemens SMART diffractometer over the range $2.55 < \theta < 27.51°$ for **1** and $3.42 < \theta < 27.51°$ for **2**. The structures were solved by direct methods using SHELXL97[10] and refined by least squares methods against all 2363 F^2 values with $F^2 > -3\sigma(F^2)$ to $wR2 = 0.1102$ [$R1 = 0.0419$ for 1117 data with $F^2 > 2\sigma(F^2)$] for **1** and all 316 F^2 values with $F^2 > -3\sigma(F^2)$ to $wR2 = 0.0939$ [$R1 = 0.0391$ for 280 data with $F^2 > 2\sigma(F^2)$].

Both crystals suffered significant degradation during the later stages of data collection owing to the propensity of the two compounds to sublime at room temperature and for this reason only the first set of frames in each data set were used in solving the structures. Because of the extreme sensitivity of both compounds they were mounted in Lindemann tubes rather than in frozen oil drops which, owing to the nature of the diffractometer cooling apparatus, precluded data collection at low temperature.

CCDC 182/1824. See http://www.rsc.org/suppdata/cc/b0/b007484p/ for crystallographic files in .cif format.

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