Syntheses and Crystal Structures of [Cr(CO)$_5$(B$_2$H$_4$·2PMe$_3$)] and [Cr(CO)$_4$(B$_2$H$_4$·2PMe$_3$)]: the First Example of a Single Hydrogen Bridge Bond between a Metal and a Polyborane

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The two novel complexes [Cr(CO)$_5$(B$_2$H$_4$·2PMe$_3$)] (**2**) and [Cr(CO)$_4$(B$_2$H$_4$·2PMe$_3$)] (**3**) containing B$_2$H$_4$·2PMe$_3$ (**1**), have been synthesized by photochemical reaction of Cr(CO)$_6$ with (**1**), (**2**) being the first complex that contains a polyborane co-ordinated to metal only through a single M–H–B linkage; *X*-ray crystal structures of compounds (**2**) and (**3**) are reported.

Bis(trimethylphosphine)–diborane(4) (**1**) is known to function as a bidentate ligand through two vicinal hydrogen atoms, but the central metal atoms of all the complexes so far reported are limited to d^{10} metal ions.[1—4] Here we report the syntheses and *X*-ray crystal structures of [Cr(CO)$_5$(B$_2$H$_4$·2PMe$_3$)] (**2**) and [Cr(CO)$_4$(B$_2$H$_4$·2PMe$_3$)] (**3**). These are the first complexes in which (**1**) is co-ordinated to a d^6 metal ion, and moreover, (**2**) is the first complex in which a polyborane is co-ordinated to metal through a single M–H–B linkage.

A mixture of Cr(CO)$_6$ and (**1**) (1 : 1 molar ratio) in toluene was irradiated for 90 min with a 450 W medium pressure Hg lamp at 0 °C with stirring. The solvent was then removed under vacuum and extraction with hexane afforded yellow crystals of [Cr(CO)$_5$(B$_2$H$_4$·2PMe$_3$)] (**2**) (24%), and further extraction with CH$_2$Cl$_2$ yielded another yellow solid, [Cr(CO)$_4$(B$_2$H$_4$·2PMe$_3$)] (**3**) (64%). ^{1}H NMR spectral analysis of the reaction showed that only (**2**) was formed at the first stage, and that (**2**) was then converted to (**3**) both thermally and photochemically.

$$\underset{}{\mathrm{Cr(CO)_6}} + \underset{(\mathbf{1})}{\mathrm{B_2H_4{\cdot}2PMe_3}} \xrightarrow{h\nu} \underset{(\mathbf{2})}{[\mathrm{Cr(CO)_5(B_2H_4{\cdot}2PMe_3)}]}$$

$$\xrightarrow{h\nu,\,\Delta} \underset{(\mathbf{3})}{[\mathrm{Cr(CO)_4(B_2H_4{\cdot}2PMe_3)}]}$$

The structure of (**3**), determined by single crystal *X*-ray diffraction,[†] is shown in Figure 1. B$_2$H$_4$·2PMe$_3$ acts as a bidentate ligand and its conformation is eclipsed (*anticlinal*), as in the cases of the previously reported complexes, [ZnCl$_2$(B$_2$H$_4$·2PMe$_3$)][1] and [Cu(B$_2$H$_4$·2PMe$_3$)$_2$]I.[4] However, the deviations of the bridging hydrogen atom positions from the M–B–B plane (0.28 and −0.44 Å) are much larger than those in the zinc and copper complexes. Furthermore, the B–B bond length for (**3**) [1.748(11) Å] is shorter than those in the zinc [1.814(6) Å] and copper [1.80(2), 1.81(2) Å] complexes, and is comparable with that in the free B$_2$H$_4$·2PMe$_3$ [1.740(7) Å].[5] This may be due to the difference of the co-ordination geometry around the metals: Zn^{II} and Cu^{I} are tetrahedral and Cr^0 in (**3**) is octahedral.

The structure of (**2**) has also been determined by single crystal *X*-ray diffraction,[†] and is shown in Figure 2. In this complex B$_2$H$_4$·2PMe$_3$ acts as a unidentate ligand, bonding through only one hydrogen atom. Although the co-ordination mode of borane complexes through a single M–H–B linkage has been reported for several BH$_4^-$ complexes,[6] this is the first example among the polyborane complexes. The Cr–H(1b)–B(1) angle is bent to 141(8)°, and the positions of both H(1b) and B(1) are appreciably distorted from the idealized octahedral geometry, whereas the carbonyl carbon atoms are regular. These features indicate that the Cr–H–B three-centre bonding is 'closed' as in the case of Cu–H–BH$_3$ complexes.[7] Although the ligand acts in a unidentate mode, it also adopts an eclipsed

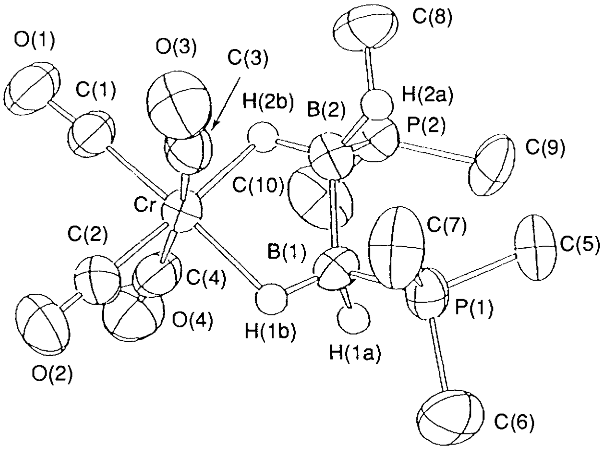


Figure 1. Molecular structure of the complex (**3**). Selected interatomic distances (Å): Cr–H(1b) 1.91(6), Cr–H(2b) 1.90, Cr···B(1) 2.413(7), Cr···B(2) 2.412(8), Cr–C(1) 1.815(7), Cr–C(2) 1.820(8), Cr–C(3) 1.874(6), Cr–C(4) 1.918(7), B(1)–B(2) 1.748(11), B(1)–H(1a) 1.00(6), B(1)–H(1b) 1.18(6), B(2)–H(2a) 1.19(7), B(2)–H(2b) 1.10, B(1)–P(1) 1.912(7), B(2)–P(2) 1.930(8). Selected interatomic angles (°): H(1b)–Cr–H(2b) 95.0, B(1)···Cr···B(2) 42.5(3), H(1b)–Cr–C(1) 175.2(17), H(1b)–Cr–C(2) 87.3(17), H(1b)–Cr–C(3) 95.6(17), H(1b)–Cr–C(4) 88.5(17), H(2b)–Cr–C(1) 88.7, H(2b)–Cr–C(2) 177.2, H(2b)–Cr–C(3) 96.8, H(2b)–Cr–C(4) 90.6, Cr–H(1b)–B(1) 100(4), Cr–H(2b)–B(2) 103.5.

[†] *Crystal data* for (**3**): C$_{10}$H$_{22}$B$_2$CrO$_4$P$_2$, M = 341.85, orthorhombic, space group $P2_1nb$ (variant of No. 33), a = 9.416(1), b = 21.068(3), c = 9.112(1) Å, U = 1807.6(4) Å^3, Z = 4, D_c = 1.26 g cm^{-3}, $F(000)$ = 712, μ(Mo-K_α) = 8.4 cm^{-1}, crystal size *ca.* 0.4 × 0.2 × 0.1 mm, $3 < 2\theta < 60°$. Final R = 0.051 (R_W = 0.076) for 3024 unique reflections [with $|F_o| > 3\sigma(F_o)$]. For (**2**): C$_{11}$H$_{22}$B$_2$CrO$_5$P$_2$, M = 369.86, monoclinic, space group $P2_1/n$ (variant of No. 14), a = 18.510(4), b = 10.669(3), c = 10.278(1) Å, β = 93.79(3)°, U = 2025.4(9) Å^3, Z = 4, D_c = 1.57 g cm^{-3}, $F(000)$ = 768, μ(Mo-K_α) = 7.6 cm^{-1}, crystal size *ca.* 0.4 × 0.4 × 0.15 mm, $3 < 2\theta < 55°$. Final R = 0.079 (R_W = 0.108) for 2153 unique reflections [with $|F_o| > 3\sigma(F_o)$]. The intensity data were collected on a Rigaku AFC-6A automated four-circle diffractometer using monochromated Mo-K_α radiation. The structures of (**2**) and (**3**) were solved by Patterson and Fourier methods. All non-hydrogen atoms were located and refined anisotropically. The hydrogen atoms bonded to boron atoms were located from the difference maps and isotropic thermal parameters, except for H(2b) in both cases, were included in the refinement [the co-ordinates of H(2b) for both (**2**) and (**3**) were fixed]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

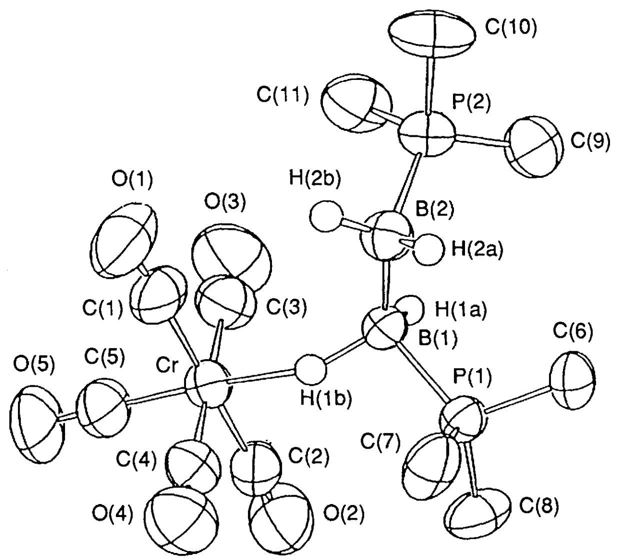
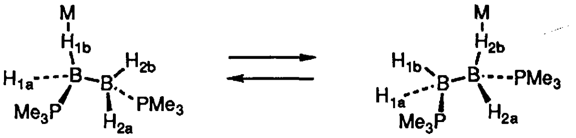


Figure 2. Molecular structure of the complex (**2**). Selected interatomic distances (Å): Cr–H(1b) 1.76(8), Cr···H(1a) 3.34(7), Cr···H(2b) 3.92, Cr···B(1) 2.876(8), Cr···B(2) 3.922(9), Cr–C(1) 1.893(10), Cr–C(2) 1.876(8), Cr–C(3) 1.913(13), Cr–C(4) 1.876(12), Cr–C(5) 1.835(9), B(1)–B(2) 1.759(12), B(1)–H(1a) 1.40(9), B(1)–H(1b) 1.28(8), B(2)–H(2a) 1.20(7), B(2)–H(2b) 1.13, B(1)–P(1) 1.920(10), B(2)–P(2) 1.881(10). Selected interatomic angles (°): H(1b)–Cr–C(1) 89(3), H(1b)–Cr–C(2) 93(3), H(1b)–Cr–C(3) 97(3), H(1b)–Cr–C(4) 82(3), H(1b)–Cr–C(5) 171(3), B(1)···Cr–C(1) 90.4(3), B(1)···Cr–C(2) 90.8(3), B(1)···Cr–C(3) 81.1(4), B(1)···Cr–C(4) 98.2(4), B(1)···Cr–C(5) 172.7(3), Cr–H(1b)–B(1) 141(8), H(1b)–B(1)–B(2) 110(3).

(*anticlinal*) conformation in contrast to the staggered (*trans*) conformation of free (**1**).[5]

The ^1H NMR spectrum‡ of (**3**) in CD_2Cl_2 consists of a doublet resonance at δ 1.31 (PMe_3) and two very broad singlet resonances at δ −0.2 and −8.6, and the integrated intensity ratios of these resonances are 9:1:1. Of the two broad



resonances, that at higher field is assigned to the Cr–H–B bridging hydrogens and that at lower field to the terminal BH hydrogens. This result indicates that (**3**) retains the solid state structure in solution. However, the ^1H NMR spectrum‡ of (**2**) in $C_6D_5CD_3$ consists of one 'triplet' due to virtual coupling at δ 0.84 (PMe_3) and two very broad resonances at δ 0.2 and −6.3, and the integrated intensity ratios of these resonances are also 9:1:1.§ This result is inconsistent with the solid state structure determined by *X*-ray crystallography, and indicates the occurrence of a fast exchange process between H(1b) and H(2b). H(1a) and H(2a) do not take part in this exchange.

Formation of $B_2H_4{\cdot}2PMe_3$ complexes was also observed for the reactions of molybdenum and tungsten carbonyls and we have succeeded in the isolation of both types of complexes, with the exception of $[Mo(CO)_5(B_2H_4{\cdot}2PMe_3)]$.

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‡ *Spectral data* for (**2**): ^1H NMR (200 MHz, $C_6D_5CD_3$) δ 0.84 (t, 18H, Me), 0.2 [br. s, 2H, H(1a) and H(2a)], −6.3 [br. s, 2H, H(1b) and H(2b)]; IR (KBr disk) ν(BH) 2348, 2325, 2250 cm^{-1}, ν(CO) 2080, 1982, 1938, 1920, 1884 cm^{-1}; IR (C_6D_6) ν(CO) 1980, 1932, 1898 cm^{-1}. For (**3**): ^1H NMR (200 MHz, CD_2Cl_2) δ 1.31 (d, 18H, $^2J_{PH}$ 10.7 Hz, Me), −0.2 [br. s, 2H, H(1a) and H(2a)], −8.6 [br. s, 2H, H(1b) and H(2b)]; $^{11}B\{^1H\}$ NMR (28.8 MHz, CD_2Cl_2) δ −41.6 (br. s); $^{31}P\{^1H\}$ NMR (36.3 MHz, CD_2Cl_2) δ 8.4 (br. d); IR (KBr disk) ν(BH) 2343 cm^{-1}, ν(CO) 2015, 1917, 1862, 1832 cm^{-1}; IR (C_6D_6) ν(CO) 2010, 1930, 1890, 1852 cm^{-1}.

§ Due to its thermal instability, $^{11}B\{^1H\}$ NMR spectral data for (**2**) are not available. However, as a preliminary result, we have a $^{11}B\{^1H\}$ NMR spectrum (28.8 MHz, $C_6D_5CD_3$) for $[W(CO)_5(B_2H_4{\cdot}2PMe_3)]$ which is more stable than (**2**). It gives a broad singlet signal with the chemical shift, −38.1 ppm. This value is just between those for the bidentate complex $[W(CO)_4(B_2H_4{\cdot}2PMe_3)]$ (−40.6 ppm) and for the free ligand (−37.4 ppm).