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Synthesis and Structure of a Dichromatetraborane Derivative $[\{(OC)_4Cr\}_2(\eta^4\text{-}H,H',H'',H'''\text{-}BH_2BH_2\cdot PMe_2CH_2PMe_2)]$

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A number of metallaboranes[1] containing an anionic borane as the ligand are known. In contrast, only a few examples have been reported for transition metal complexes having a neutral borane−Lewis base adduct. We previously reported the syntheses of metal complexes of $BH_3\cdot PMe_3$, $[M(\eta^1\text{-}HBH_2\cdot PMe_3)(CO)_5]$ (**1**, M = Cr, W). In **1**, trimethylphosphineborane coordinates to the metal center through a B−H−M bridge.[2] The trimethylphosphineborane ligand in **1** so readily dissociates in solution or under a vacuum that study on the details of reactivity of **1** was difficult. To better investigate the properties of the borane complexes while avoiding this difficulty, we have attempted to stabilize the complexes having M−H−B linkages by forming a chelate ring through two M−H−B bonds. In this work, a diphosphine−bisborane adduct, $BH_3\cdot PMe_2CH_2PMe_2\cdot BH_3$ (**2**), was used as a precursor of the chelate ligand.[3] However, when $[Cr(CO)_6]$ was irradiated in the presence of **2**, an unexpected product, a dichromatetraborane derivative $[\{(OC)_4Cr\}_2(\eta^4\text{-}H,H',H'',H'''\text{-}BH_2\text{-}BH_2\cdot PMe_2CH_2PMe_2)]$ (**3**), was isolated.

A 1:1 mixture of $[Cr(CO)_6]$ and **2** was photolyzed in toluene under vacuum using a medium-pressure Hg lamp for 11 h at 0 °C, with periodical removal of the evolved gas, to provide an orange solution. Concentration and cooling of the filtered solution afforded $\mathbf{3}\cdot 2C_7H_8$ as orange-yellow, air-sensitive crystals in low yield (ca. 1%).[4] Characterization of **3** was achieved by NMR and IR spectroscopy as well as X-ray structural analysis. The Cr−*H*−B protons are observed at −8.5 ppm as a broad quartet in the ^{1}H NMR spectrum. The IR spectrum of **3** exhibits eight bands in the terminal CO stretching region. It is interpreted as the symmetrical and antisymmetrical combinations of two $Cr(CO)_4$ moieties having a C_{2v} local symmetry, for which appearance of four bands is expected.

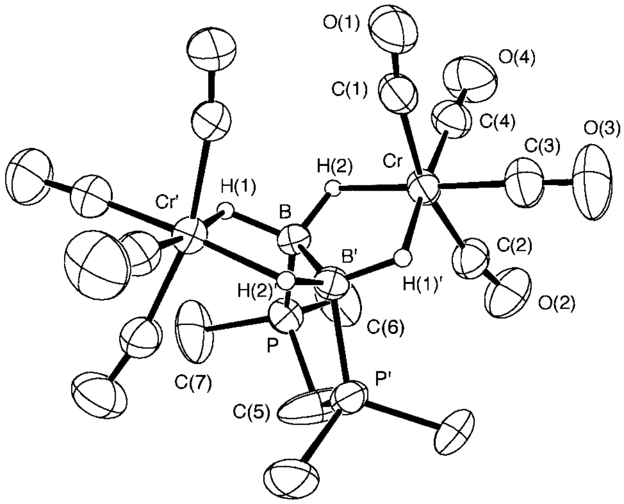

Figure 1. Molecular structure of $[\{(OC)_4Cr\}_2(\eta^4\text{-}H,H',H'',H'''\text{-}BH_2\text{-}BH_2\cdot PMe_2CH_2PMe_2)]$ (**3**). Selected bond lengths (Å) and angles (deg): Cr−H(1)′ 1.84(6), Cr−H(2) 1.83(7), B−B′ 1.733(13), B−H(1) 1.27(6), B−H(2) 1.23(7), B−P 1.932(7), Cr···B 2.414(7), Cr···B′ 2.419(7), Cr···Cr′ 4.111(2), O(1)···O(1)′ 2.903(11), O(2)···C(6) 3.476(11), O(2)···C(7)′ 3.539(12); H(1)′−Cr−H(2) 103(3), Cr−H(1)′−B′ 101(5), Cr−H(2)−B 103(6), H(2)−B−B′ 116(3), H(1)−B−B′ 117(3), B′−B−P 108.8(2), C(1)−Cr−C(2) 165.2(3), Cr−C(1)−O(1) 169.6(6), Cr−C(2)−O(2) 169.3(7), H(1)′−Cr−C(3) 83(2), H(2)−Cr−C(4) 84(2), C(3)−Cr−C(4) 91.2(4).

The molecular structure of **3** is shown in Figure 1.[5] The molecule has a crystallographic C_2 axis through the midpoint of the B−B bond and the C(5) atom. The cyclic diborane(4)−diphosphine adduct $B_2H_4\cdot PMe_2CH_2PMe_2$ coordinates to each of the two $Cr(CO)_4$ fragments in a bidentate fashion through vicinal BH's. Thus, the cyclic diborane acts as a tetradentate ligand on the whole. Two chromium atoms and two boron atoms make a butterfly framework. The positions of the hydrogen atoms bound to boron are located and refined. The interatomic distances between Cr−H(1) and Cr−H(2) are 1.84(6) and 1.83(7) Å, respectively. The bond lengths of B−H(1) and B−H(2) are 1.27(6) and 1.23(7) Å; the B−B′ bond distance is 1.733(13) Å. These are typical values for such bonds.[6,7] The geometry around each of the chromium atoms is largely distorted from the regular octahedron. The axial carbonyls (bridging hydrogens are lying in the equatorial plane) are bent away from the center of the molecule (Cr−C(1)−O(1) = 169.6(6)°, C(1)−Cr−C(2) = 165.2(3)°, Cr−C(2)−O(2) = 169.3(7)°) due to the steric repulsions

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(3) $BH_3\cdot PMe_2CH_2PMe_2\cdot BH_3$ (**2**) was synthesized by the reaction of B_2H_6 with bis(dimethylphosphino)methane under vacuum in 96% yield. Data for **2**: ^{1}H NMR (500 MHz, C_6D_6) δ 1.21 (br, $^2J_{PH} \cong 13$ Hz, $^1J_{BH} \cong 100$ Hz, 6H, BH), 1.02 (t, $^2J_{PH} = 11.4$ Hz, 2H, CH), 0.88 (d, $^2J_{PH} = 10$ Hz, 12H, PMe_2); ^{11}B NMR (160.35 MHz, C_6D_6) δ −36.2 (dq, $^1J_{PB} = 54.3$ Hz, $^1J_{BH} = 97.1$ Hz); ^{31}P{^{1}H} NMR (202.35 MHz, C_6D_6) δ 4.87 (q, $^1J_{PB} = 53.3$ Hz); IR (KBr) ν (BH) = 2377.8 (s), 2364.3 (s), 2339.2 (s), 2276.6 (w), 2253.4 (w) cm^{-1}. Anal. Calcd for $C_5H_{20}P_2B_2$: C, 36.67; H, 12.31. Found: C, 36.46; H, 12.02.

(4) Spectral data for **3**: ^{1}H NMR (500 MHz, C_6D_6) δ −8.5 (br, 4H, BH), 0.67 (vt, $J_{PH} = 5.5$ Hz, 12H, PMe_2), 1.22 (t, $^2J_{PH} = 11.3$ Hz, 2H, CH); ^{11}B{^{1}H} NMR(160.35 MHz, C_6D_6) δ −34.1 (br); ^{31}P{^{1}H} NMR (202.35 MHz, C_6D_6) δ 14.5(br); IR (KBr) ν (CO) 2029.7 (m), 2006.6 (m), 1941.0 (m), 1899.5 (s), 1887.0 (s), 1870.6 (s), 1848.4 (s), 1826.3(m) cm^{-1}.

(5) Crystal data for $\mathbf{3}\cdot 2C_7H_8$: orange-yellow crystals, crystal size 0.3 × 0.3 × 0.5 mm, monoclinic, space group *C*2/*c* (No. 15); $a = 21.096(5)$ Å, $b = 10.071(3)$ Å, $c = 17.565(2)$ Å, $\beta = 117.68(1)°$; $V = 3304.8(12)$ Å^3; $Z = 4$. Data collection: Mo Kα, 1.25 kW, 273 K, $2\theta = 5−60°$, 5319 independent reflections. A full-matrix least-squares refinement was carried out on $|F_o|^2$ with 2146 reflection having $|F_o| > 3\sigma(F_o)$. The structure was solved by the heavy atom method; 194 parameters. Positions of non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms bound to boron were determined by difference Fourier synthesis and were refined isotropically. The other hydrogens were not found. $R = 0.076$.

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between O(1) and O(1)′ (O(1)···O(1)′ = 2.903(11) Å), O(2) and C(6) (O(2)···C(6) = 3.476(11) Å), and O(2) and C(7)′ (O(2)···C(7)′ = 3.539(12) Å). These distances are in agreement with the sum of the van der Waals radii of two oxygen atoms (3.04 Å), and of a methyl group and an oxygen atom (3.52 Å). The conformation around the B−B bond is eclipsed (*synperiplanar*) because the phosphine units are tightly bound by the methylene bridge. This allows the cyclic diborane to use the four hydrogen atoms as donors. This coordination mode makes a contrast to that of noncyclic bis(trimethylphosphine)diborane(4), which acts only as a bidentate ligand with an eclipsed (*anticlinal*) conformation in $[M(CO)_4(B_2H_4 \cdot 2PMe_3)]$ (M = Cr, Mo, W)[6] and $[ZnCl_2(B_2H_4 \cdot 2PMe_3)]$.[8] The anisotropic thermal ellipsoid of C(5) spreads laterally, probably due to the disorder between two envelope conformers of the five-membered ring composed of the two boron atoms and the diphosphine. For structurally characterized complexes including a multidentate diborane species with an eclipsed conformation along the B−B σ bond, $[\{(OC)_4Mn\}(\eta^6\text{-}B_2H_6)\{Mn(CO)_3\}_2(\mu\text{-}H)]$,[9] $[(C_5Me_4R)M(B_2H_6)]_2$ (R = Me, Et; M = Nb, Ta),[10,11] $[\{Cp^*Mo(\mu\text{-}Cl)\}_2(B_2H_6)]$,[12] and $[\{(p\text{-tolyl})NCHN(p\text{-tolyl})\}_2Ta(B_2H_6)]_2$[13] are known. The $B_2H_6^{2-}$ ligand in these compounds is isoelectronic with the cyclic diborane unit in **3** as well as with ethane. It works as a hexadentate ligand in the Mn complex and a tetradentate ligand in the Nb, Ta, and Mo complexes.

The complex **3** can also be depicted as a dichromatetraborane derivative, with the wing-tip BH_2^+ groups in tetraborane(10) replaced by $Cr(CO)_4$ fragments, which are isolobal with BH_2^+,[14] and the two terminal hydrides attaching to the basal boron atoms replaced by isoelectronic phosphine ligands. The Cr_2B_2 butterfly with the dihedral angle of 130.3° is much wider than those in parent tetraborane(10) (117.4°)[15] and a related chromatetraborane $[Cr(CO)_4(B_3H_8)]^-$ (118.5°),[16] as a result of steric hindrance between the $Cr(CO)_4$ moieties as mentioned above. In other metallaboranes with a tetraborane(10)-like structure, the corresponding dihedral angle is in the range 118−128°.[17]

Much attention is currently focused on metal-mediated dehydrogenative condensation reactions of main-group-element hydrides, especially hydrosilanes.[18] Although the yield of **3** is low, the occurrence of intramolecular B−B bond formation via a dehydrogenative coupling of two phosphineborane moieties in **2** is remarkable. It should be noted that irradiation of **2** in the absence of $[Cr(CO)_6]$ did not give any B−B coupling products. We have reported photoinduced dehydrogenation of borane−secondary amine and borane−primary amine adducts in the presence of $[Cr(CO)_6]$, which produce aminoboranes $[BH_2NR_2]_n$ (n = 2, 3; R = Me, *t*-Bu) and trimethylborazine $[BHNMe]_3$, respectively, accompanied with evolution of H_2.[2] During the formation of the complexes, including a $B_2H_6^{2-}$ ligand mentioned above, a 2c−2e B−B bond formation occurs via a dehydrogenative coupling of BH_4^- ions.[9−13] We also note that the formation of an electron-deficient dichromaborane $[(Cp^*Cr)_2B_4H_8]$, which was prepared from $[Cp^*CrCl]_2$ with $BH_3 \cdot THF$ by Fehlner et al., involves condensation of boranes.[19] The present work is the first example of B−B bond formation from phosphineboranes.

When the photoreaction was monitored in C_6D_6 using ^1H NMR spectroscopy, formation of another borane complex was observed. The broad quartet found at −3.5 ppm with strong intensity is assignable to the BH protons of $[(OC)_5Cr(\eta^1\text{-}HBH_2 \cdot PMe_2CH_2PMe_2 \cdot BH_3)]$ (**6**), in which the diphosphine−bisborane adduct **2** coordinates to $Cr(CO)_5$ through a single B−H−Cr bridge. The chemical shift of the signal suggests that the bridging hydrogen and the terminal hydrogens in the coordinating borane moiety are mutually exchanging their positions faster than the NMR time scale as found in **1**.[2] Attempts to isolate **6**, however, gave only free **2**. This is attributed to the lability of **6**.

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Supporting Information Available: A crystallographic file for $\mathbf{3} \cdot 2C_7H_8$, in CIF format, a reaction scheme, and a schematic drawing of the structures of $[M(CO)_4(B_2H_4 \cdot 2PMe_3)]$ (M = Cr, Mo, W) and $[ZnCl_2(B_2H_4 \cdot 2PMe_3)]$ are available on the Internet only. Access information is given on any current masthead page.

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