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Syntheses and Structures of $[M(CO)_5\{B_2H_4\cdot 2P(CH_3)_3\}]$ and $[M(CO)_4\{B_2H_4\cdot 2P(CH_3)_3\}]$ (M = Cr, Mo, W)

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Photochemical reactions of $M(CO)_6$ (M = Cr, Mo, W) with $B_2H_4\cdot 2P(CH_3)_3$ (**1**) gave two types of new complexes: $[M(CO)_5\{B_2H_4\cdot 2P(CH_3)_3\}]$ (**2**) (M = Cr, W) and $[M(CO)_4\{B_2H_4\cdot 2P(CH_3)_3\}]$ (**3**) (M = Cr, Mo, W). Structures of both types of complexes were characterized by spectroscopic measurements as well as X-ray structure analyses. $B_2H_4\cdot 2P(CH_3)_3$ acts as a unidentate ligand in **2**, whereas it acts as a bidentate chelate in **3**. Both **2** and **3** are the first examples of the coordination of **1** to metals other than d^{10} metals, and moreover complexes **2** are the first examples of complexes with a single M–H–B attachment between polyboranes and metals. Crystals of $[Cr(CO)_5\{B_2H_4\cdot 2P(CH_3)_3\}]$ (**2a**) belong to the monoclinic space group $P2_1/n$, with $a = 18.510$ (4) Å, $b = 10.669$ (3) Å, $c = 10.278$ (2) Å, $\beta = 93.79$ (3)°, $V = 2025.3$ (9) Å^3, $Z = 4$, and $R(F_o) = 0.079$ for 2153 reflections with $|F_o| \geq 3\sigma(F_o)$. Those of $[W(CO)_5\{B_2H_4\cdot 2P(CH_3)_3\}]$ (**2c**) are isomorphous with **2a**: $a = 18.613$ (3) Å, $b = 10.581$ (2) Å, $c = 10.363$ (3) Å, $\beta = 93.61$ (2)°, $V = 2036.9$ (7) Å^3, $Z = 4$, and $R(F_o) = 0.048$ for 1323 reflections with $|F_o| \geq 3\sigma(F_o)$. Crystals of $[Cr(CO)_4\{B_2H_4\cdot 2P(CH_3)_3\}]$ (**3a**) belong to the orthorhombic space group $P2_1nb$, with $a = 9.416$ (1) Å, $b = 21.068$ (3) Å, $c = 9.112$ (1) Å, $V = 1807.6$ (4) Å^3, $Z = 4$, and $R(F_o) = 0.051$ for 1808 reflections with $|F_o| \geq 3\sigma(F_o)$. Those of $[W(CO)_4\{B_2H_4\cdot 2P(CH_3)_3\}]$ (**3c**) are isomorphous with **3a**: $a = 9.425$ (1) Å, $b = 21.141$ (5) Å, $c = 9.177$ (1) Å, $V = 1828.6$ (6) Å^3, $Z = 4$, and $R(F_o) = 0.060$ for 1666 reflections with $|F_o| \geq 3\sigma(F_o)$.

Introduction

Although there is great variety in the binding modes between transition metals and borane ligands,[1] the single M–H–B attachment has been hitherto known only for BH_4^- complexes. Only six examples have been structurally characterized, i.e. $[Cu(\eta^1\text{-}BH_4)(PMePh_2)_3]$,[2-4] $[Cu(\eta^1\text{-}BH_4)\{(PPh_2CH_2)_3CMe\}]$,[5,6] $[FeH(\eta^1\text{-}BH_4)(dmpe)_2]$,[7,8] $[Hf_2\{N(SiMe_2CH_2PMe_2)_2\}_2H_3(BH_4)_3]$,[9] and $[V(\eta^1\text{-}BH_4)_2(dmpe)_2]$,[10] where dmpe denotes bis(dimethylphosphino)ethane. There are no examples of complexes which contain the single M–H–B linkage between polyboranes and transition metals.

Bis(trimethylphosphine)–diborane(4), $B_2H_4\cdot 2P(CH_3)_3$, is known to coordinate to metals through two vicinal hydrogen atoms, and five complexes are described in the literature, i.e. $[ZnCl_2\{B_2H_4\cdot 2P(CH_3)_3\}]$,[11,12] $[CuX(PPh_3)\{B_2H_4\cdot 2P(CH_3)_3\}]$,[11,12] $[CuX\{B_2H_4\cdot 2P(CH_3)_3\}]$,[12] $[Cu\{B_2H_4\cdot 2P(CH_3)_3\}_2]X$ (X = halogen),[13] and $[Ni(CO)_2\{B_2H_4\cdot 2P(CH_3)_3\}]$.[12,14] The $B_2H_4\cdot 2P(CH_3)_3$ ligand in these complexes acts in a bidentate mode, and all of the central metals of these complexes have a d^{10} electron configuration. Here we report the syntheses and structures of two types of complexes in which the $B_2H_4\cdot 2P(CH_3)_3$ ligand is coordinated to group 6 metals.[15] One type of complex contains a bidentate $B_2H_4\cdot 2P(CH_3)_3$ ligand, and the other type of complex, a unidentate $B_2H_4\cdot 2P(CH_3)_3$ ligand. The latter complexes are the first examples of a single M–H–B linkage between metal and polyborane. The complexes reported in this work are also the first ones in which $B_2H_4\cdot 2P(CH_3)_3$ is coordinated to d^6 metal atoms.

Experimental Section

General Procedures and Equipment. Conventional vacuum-line techniques were used for handling volatile compounds. Air- and moisture-sensitive solids were handled in clear plastic bags filled with dry nitrogen. All solvents were purified by distillation over appropriate drying agents under nitrogen. $B_2H_4\cdot 2P(CH_3)_3$ (**1**) was prepared by the reaction of $B_3H_7\cdot THF$ with excess $P(CH_3)_3$.[16] ^1H NMR spectra were measured on a Varian XL-200 instrument, infrared spectra were recorded on a JASCO IR-810 infrared spectrometer, mass spectra were obtained on a Hitachi M-52 mass spectrometer, and electronic spectra were recorded on a Shimadzu UV-260 spectrophotometer.

Synthesis of $[Cr(CO)_n\{B_2H_4\cdot 2P(CH_3)_3\}]$ (n = 5 (2a), 4 (3a)). A mixture of 57 mg (0.32 mmol) of **1** and 71 mg (0.32 mmol) of $Cr(CO)_6$ was placed in a Pyrex reaction tube, to which toluene was added by vacuum distillation. The mixture was irradiated with a 450-W medium-pressure Hg lamp (Ushio UV-450) while being stirred at room temperature. After 90 min of irradiation, the solvent was removed under vacuum. The residue was maintained under high vacuum at room temperature for 4 h to sublime unreacted **1** and $Cr(CO)_6$. Extraction from the residue with 10 mL of hexane followed by removal of the solvent gave yellow crystals of $[Cr(CO)_5\{B_2H_4\cdot 2P(CH_3)_3\}]$ (**2a**) (28 mg, 24%). Further extraction with 3 mL of dichloromethane followed by removal of the solvent gave $[Cr(CO)_4\{B_2H_4\cdot 2P(CH_3)_3\}]$ (**3a**) (68 mg, 64%) as a yellow crystalline solid. Anal. Calcd for **2a**, $C_{11}H_{22}B_2CrO_5P_2$: C, 35.72; H, 6.00. Found: C, 36.29; H, 6.50. ^1H NMR (200 MHz, $C_6D_5CD_3$): δ 0.84 (vt,[17] 18 H, CH_3), 0.2 (br s, 2 H), −6.3 (br s, 2 H). IR (KBr disk), cm^{-1}: ν(BH) 2348 (m), 2325 (m), 2250 (w), $\delta(BH_2)$ 1136 (w), ν(CO) 2080 (m), 1982 (s), 1920 (vs, br), 1884 (vs). MS (EI, 13.5 eV): m/z 342 ($M^+ - CO$, 0.7), 176 ($^{11}B_2H_2\cdot 2P(CH_3)_3^+$, 41), 76 ($P(CH_3)_3^+$, 100). UV–vis ($CH_2Cl_2$), λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 411 (2400). Anal. Calcd for **3a**, $C_{10}H_{22}B_2CrO_4P_2$: C, 35.14; H, 6.49. Found: C, 35.10; H, 6.65. ^1H NMR (200 MHz, CD_2Cl_2): δ 1.31 (d, 18 H, CH_3), −0.2 (br s, 2 H), −8.6 (br s, 2 H). IR (KBr disk), cm^{-1}: ν(BH) 2343 (m), ν(CO) 2015 (s), 1917 (s), 1862 (vs), 1832 (vs). MS (EI, 13.5 eV): m/z 342 (M^+, 3), 176 ($^{11}B_2H_2\cdot 2P(CH_3)_3$, 27), 76 ($P(CH_3)_3^+$, 100). UV–vis ($CH_2Cl_2$), λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 402 (1130), 422 (1100).

Synthesis of $[Mo(CO)_4\{B_2H_4\cdot 2P(CH_3)_3\}]$ (3b). Almost the same procedure as that used for the preparation of the chromium compounds was followed, using 70 mg (0.39 mmol) of **1** and 103 mg (0.39 mmol) of

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Table I. Crystallographic Data for $[Cr(CO)_5\{B_2H_4 \cdot 2P(CH_3)_3\}]$ (**2a**), $[W(CO)_5\{B_2H_4 \cdot 2P(CH_3)_3\}]$ (**2c**), $[Cr(CO)_4\{B_2H_4 \cdot 2P(CH_3)_3\}]$ (**3a**), and $[W(CO)_4\{B_2H_4 \cdot 2P(CH_3)_3\}]$ (**3c**)

	2a	**2c**	**3a**	**3c**
formula	$C_{11}H_{22}B_2CrO_5P_2$	$C_{11}H_{22}B_2O_5P_2W$	$C_{10}H_{22}B_2CrO_4P_2$	$C_{10}H_{22}B_2O_4P_2W$
fw	369.86	501.71	341.85	473.70
space group	$P2_1/n$	$P2_1/n$	$P2_1nb$	$P2_1nb$
a/Å	18.510 (4)	18.613 (3)	9.416 (1)	9.425 (1)
b/Å	10.669 (3)	10.581 (2)	21.068 (3)	21.141 (5)
c/Å	10.278 (2)	10.363 (3)	9.112 (1)	9.177 (1)
β/deg	93.79 (3)	93.61 (2)		
V/Å^3	2025.3 (9)	2036.9 (7)	1807.6 (4)	1828.6 (6)
Z	4	4	4	4
ρ_{calcd}/g cm^{-3}	1.21	1.64	1.26	1.72
μ(Mo Kα)/cm^{-1}	7.57	59.6	8.38	66.3
cryst size/mm	0.4 × 0.4 × 0.15	0.3 × 0.2 × 0.2	0.4 × 0.2 × 0.1	0.25 × 0.13 × 0.07
T/°C	20	20	20	20
λ/Å	0.71073	0.71073	0.71073	0.71073
no. of unique data	5916	2056	3024	3064
no. of data used with $\|F_o\| \geq 3\sigma(F_c)$	2153	1323	1808	1666
$R(F_o)^a$	0.079	0.048	0.051	0.060
$R_w(F_o)^b$	0.108	0.048	0.076	0.060

$^a R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(F_o) + aF_o^2]^{-1}$, where $a = 0.0025$ (**2a**) and 0.005 (**3a**), and unit weighting schemes were applied for **2c** and **3c**.

$Mo(CO)_6$. However, no hexane-soluble species was detected in this case, and extraction with 3 mL of dichloromethane gave pale-yellow crystalline $[Mo(CO)_4\{B_2H_4 \cdot 2P(CH_3)_3\}]$ (**3b**) (141 mg, 93%) as the sole product. Anal. Calcd for $C_{10}H_{22}B_2MoO_4P_2$: C, 31.13; H, 5.75. Found: C, 30.78; H, 5.96. ^1H NMR (200 MHz, CD_2Cl_2): δ 1.32 (d, 18 H, CH_3), 0.0 (br s, 2 H), −6.4 (br s, 2 H). IR (KBr disk), cm^{-1}: ν(BH) 2347 (m), ν(CO) 2022 (s), 1924 (vs), 1868 (vs), 1830 (vs). MS (EI, 13.5 eV): m/z 388 (M^+ ($C_{10}H_{22}{}^{11}B_2{}^{98}MoO_4P_2{}^+$), 0.8), 176 ($^{11}B_2H_2 \cdot 2P(CH_3)_3{}^+$, 15), 76 ($P(CH_3)_3{}^+$, 100). UV–vis ($CH_2Cl_2$), λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 380 (1720), 400 (sh).

Synthesis of $[W(CO)_n\{B_2H_4 \cdot 2P(CH_3)_3\}]$ (n = 4 (3c), 5 (2c)). Almost the same procedure as that used for the preparation of the chromium compounds was followed, using 66 mg (0.37 mmol) of **1** and 132 mg (0.37 mmol) of $W(CO)_6$. After removal of unreacted species by sublimation, 2 mL of toluene and then 10 mL of hexane were added to the residue. After the solution thus obtained was filtered, removal of the solvent from the filtrate afforded yellow crystals of **2c** (93 mg, 48%). Further extraction of the residue with 3 mL of dichloromethane gave **3c** as a yellow crystalline solid (91 mg, 50%). Anal. Calcd for **2c**, $C_{11}H_{22}B_2O_5P_2W$: C, 26.33; H, 4.42. Found: C, 26.91; H, 4.41. ^1H NMR (200 MHz, $C_6D_5CD_3$): δ 0.86 (vt, 18 H, CH_3), 0.1 (br s, 2 H), −3.9 (br s, 2 H). IR (KBr disk), cm^{-1}: ν(BH) 2347 (m), 2318 (m), 2245 (w), δ(BH_2) 1132 (w), ν(CO) 2069 (m), 1981 (s), 1932 (vs), 1912 (vs), 1879 (vs). MS (EI, 25 eV): m/z 474 (M^+ − CO ($C_{10}H_{22}{}^{11}B_2O_4P_2{}^{184}W^+$), 5), 176 ($^{11}B_2H_2 \cdot 2P(CH_3)_3{}^+$, 43), 76 ($P(CH_3)_3{}^+$, 100). UV–vis ($CH_2Cl_2$), λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 385 (1600). Anal. Calcd for **3c**, $C_{10}H_{22}B_2O_4P_2W$: C, 25.36; H, 4.68. Found: C, 25.43; H, 4.68. ^1H NMR (200 MHz, CD_2Cl_2): δ 1.34 (d, 18 H, CH_3), 0.3 (br s, 2 H), −6.7 (br s, 2 H). IR (KBr disk), cm^{-1}: ν(BH) 2350 (m), ν(CO) 2015 (s), 1907 (s), 1860 (vs), 1829 (vs). MS (EI, 25 eV): m/z 474 (M^+ ($C_{10}H_{22}{}^{11}B_2O_4P_2{}^{184}W^+$), 5), 176 ($^{11}B_2H_2 \cdot 2P(CH_3)_3{}^+$, 7), 76 ($P(CH_3)_3{}^+$, 100). UV–vis ($CH_2Cl_2$), λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 373 (1470), 392 (1560), 427 (720).

X-ray Crystal Structure Analyses of 2a, 2c, 3a, and 3c. The crystals used for X-ray structure analyses were prepared as follows: **2a**, cooling a hexane solution of **2a** to −20 °C; **3a** and **3c**, slow diffusion of pentane into dichloromethane solutions of the compounds; **2c**, cooling a hexane solution of **2c** to −45 °C. A crystal of **2a** was sealed in a thin-wall glass capillary under nitrogen, while the crystals of **2c**, **3a**, and **3c** were coated with cyanoacrylate resin. The intensity data were collected on a Rigaku AFC-6A automated four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The reflection data were corrected with Lorentz and polarization factors but not for absorption and extinction. Crystallographic and experimental data are listed in Table I. As the crystals of **2c** decomposed rapidly upon the exposure of X-rays, only the data with $2\theta < 40°$ were collected.

The structures were solved by heavy-atom methods. All the non-hydrogen atoms were located and refined by block-diagonal least-squares methods applying anisotropic temperature factors. In the cases of **2a** and **3a**, positions of hydrogen atoms attaching to boron atoms were deduced from difference Fourier syntheses and refined with isotropic temperature factors, except for H(2b). The parameters of H(2b) for both **2a** and **3a** diverged when the weighting schemes shown in the Table I were applied, although they converged when unit-weighting schemes were applied. Thus, the positions of H(2b) for both **2a** and **3a** were fixed at the positions deduced from the difference Fourier maps. The coordinates of hydrogen atoms attached to boron atoms for **2c** and **3c** were fixed at positions calculated by assuming regular tetrahedral geometries around the boron atoms with a B–H bond length of 1.08 Å. In the cases of **3a** and **3c**, whose space groups are noncentrosymmetric, the chirality which gave lower R values was adopted (0.051 vs 0.052 for **3a** and 0.060 vs 0.062 for **3c**).

Atomic scattering factors for non-hydrogen atoms and hydrogen atoms were taken from refs 19 and 20, respectively. The calculations were performed on a Nippon Electric Co. ACOS-2000 computer at the Computer Center of Tohoku University using the Universal Program System UNICS III.[21]

Results and Discussion

Syntheses and Characterization. $[M(CO)_5\{B_2H_4 \cdot 2P(CH_3)_3\}]$ (M = Cr (**2a**), W (**2c**)) and $[M(CO)_4\{B_2H_4 \cdot 2P(CH_3)_3\}]$ (M = Cr (**3a**), Mo (**3b**), W (**3c**)) were prepared by the photochemical reactions of $M(CO)_6$ in the presence of **1**; they are pale-yellow to orange-yellow crystalline solids. $[Mo(CO)_5\{B_2H_4 \cdot 2P(CH_3)_3\}]$ (**2b**) could not be isolated, but its formation was confirmed by ^1H NMR spectroscopy.[22] Complexes **2** are less stable than **3** and oxidize slowly in air even in the solid state, but complexes **3** are stable to air in the solid state (solutions of **3**, however, oxidize readily in air).

The X-ray analyses revealed that complexes **2** and **3** contain unidentate **1** and bidentate **1**, respectively (vide infra). The difference of the coordination modes of **1** in **2** and **3** is apparent from infrared spectroscopy. Infrared spectra of **3** resemble those of the complexes $[ZnCl_2\{B_2H_4 \cdot 2P(CH_3)_3\}]$[11,12] and $[Cu\{B_2H_4 \cdot 2P(CH_3)_3\}_2]X$[13] in the region characteristic of the $B_2H_4 \cdot 2P(CH_3)_3$ ligand: Each complex shows only one absorption band around 2350 cm^{-1}, which is assignable to the B–H(terminal) stretching. On the other hand, both **2a** and **2c** show three B–H(terminal) stretching absorption bands at 2350–2240 cm^{-1} and also a BH_2 deformation absorption band around 1130 cm^{-1}. The latter band was not observed for the zinc and copper complexes and **3**. It was not possible to observe B–H–M stretching absorptions for either **2** or **3**, because of the strong carbonyl stretching absorption in the 2100–1800-cm^{-1} region.

Mass spectra of **2a** and **2c** did not show any parent ion peak $M(CO)_5\{B_2H_4 \cdot 2P(CH_3)_3\}^+$. The highest mass peak corresponded

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Table II. Final Atomic Parameters for $[Cr(CO)_5\{B_2H_4{\cdot}2P(CH_3)_3\}]$ (**2a**)[a]

atom	*x*	*y*	*z*	B_{eqv}/Å^2 [b]
Cr	4053.1 (6)	2658.1 (12)	6001.1 (12)	5.5
P(1)	2833 (1)	208 (2)	3747 (2)	4.5
P(2)	1279 (1)	2474 (2)	5682 (2)	5.1
B(1)	2730 (4)	1438 (8)	5087 (7)	4.3
B(2)	2040 (5)	2491 (8)	4557 (8)	4.8
O(1)	3389 (4)	5232 (7)	5482 (8)	11.3
O(2)	4772 (3)	193 (6)	6652 (7)	9.3
O(3)	3388 (4)	2502 (9)	8604 (7)	11.9
O(4)	4762 (4)	2813 (7)	3475 (7)	10.4
O(5)	5345 (3)	3971 (7)	7243 (8)	10.7
C(1)	3623 (5)	4245 (9)	5665 (9)	7.7
C(2)	4488 (4)	1103 (7)	6391 (8)	6.0
C(3)	3600 (5)	2560 (9)	7617 (9)	7.6
C(4)	4487 (5)	2753 (8)	4405 (9)	6.8
C(5)	4842 (5)	3469 (9)	6781 (9)	7.3
C(6)	1991 (4)	−574 (8)	3270 (8)	6.0
C(7)	3115 (5)	879 (8)	2250 (7)	7.1
C(8)	3462 (5)	−1067 (8)	4157 (8)	7.3
C(9)	549 (5)	3540 (10)	5186 (9)	8.8
C(10)	855 (5)	941 (9)	5828 (9)	7.6
C(11)	1561 (5)	2946 (11)	7343 (8)	7.8
atom	*x*	*y*	*z*	B_{iso}/Å^2
H(1a)	262 (4)	79 (7)	624 (6)	6.8 (17)
H(1b)	335 (4)	197 (8)	501 (7)	7.9 (20)
H(2a)	183 (3)	234 (5)	345 (5)	4.0 (13)
H(2b)[c]	216	349	430	8.8

[a] Coordinates for non-hydrogen atoms are multiplied by 10^4, and those for hydrogen atoms, by 10^3. [b] The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eqv} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac \cos \beta)$. The B_{ij}'s are defined by $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$. [c] The coordinates for H(2b) were fixed at those found in the difference Fourier map.

Table III. Final Atomic Parameters for $[W(CO)_5\{B_2H_4{\cdot}2P(CH_3)_3\}]$ (**2c**)[a]

atom	*x*	*y*	*z*	B_{eqv}/Å^2 [b]
W	4062.3 (5)	2648.0 (8)	6033.7 (9)	4.7
P(1)	2822 (3)	115 (5)	3768 (5)	4.2
P(2)	1286 (3)	2462 (6)	5641 (5)	4.7
B(1)	2721 (12)	1379 (21)	5078 (22)	3.8
B(2)	2065 (12)	2479 (23)	4525 (19)	4.1
O(1)	3345 (12)	5321 (18)	5522 (22)	11.6
O(2)	4845 (9)	68 (16)	6675 (17)	7.8
O(3)	3342 (11)	2434 (27)	8696 (17)	12.5
O(4)	4807 (12)	2903 (20)	3393 (20)	11.6
O(5)	5382 (9)	4053 (17)	7330 (19)	8.9
C(1)	3582 (13)	4338 (23)	5693 (23)	6.8
C(2)	4552 (13)	1024 (21)	6373 (25)	6.5
C(3)	3570 (12)	2431 (34)	7749 (28)	9.6
C(4)	4575 (13)	2800 (26)	4354 (28)	8.1
C(5)	4886 (12)	3526 (23)	6859 (26)	6.9
C(6)	1970 (11)	−631 (20)	3326 (21)	5.1
C(7)	3135 (13)	788 (21)	2283 (20)	6.1
C(8)	3437 (13)	−1168 (20)	4186 (23)	6.1
C(9)	549 (12)	3519 (26)	5120 (25)	7.6
C(10)	860 (13)	922 (23)	5821 (23)	6.6
C(11)	1569 (13)	2969 (28)	7295 (21)	7.3
atom	*x*	*y*	*z*	B_{iso}/Å^2
H(1a)	2560	938	5954	6.0
H(1b)	3229	1855	5280	6.0
H(2a)	1867	2237	3554	6.0
H(2b)	2299	3413	4517	6.0

[a] Coordinates are multiplied by 10^4. [b] The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eqv} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac \cos \beta)$. The B_{ij}'s are defined by $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$. [c] The coordinates for hydrogen atoms were fixed at the calculated positions.

Table IV. Interatomic Distances (Å) for $[M(CO)_5\{B_2H_4{\cdot}2P(CH_3)_3\}]$ (M = Cr (**2a**), W (**2c**))

	M = Cr	M = W		M = Cr	M = W
M–H(1b)	1.76 (8)	1.89	B(2)–P(2)	1.881 (10)	1.91 (3)
M···H(1a)	3.34 (7)	3.33	B(2)–H(2a)	1.20 (7)	1.08
M···H(2b)	3.92	3.64	B(2)–H(2b)	1.13	1.08
M···B(1)	2.876 (8)	2.95 (2)	C(1)–O(1)	1.149 (12)	1.14 (3)
M···B(2)	3.922 (9)	3.95 (2)	C(2)–O(2)	1.129 (10)	1.18 (3)
M–C(1)	1.893 (10)	2.02 (3)	C(3)–O(3)	1.112 (17)	1.09 (5)
M–C(2)	1.876 (8)	1.97 (2)	C(4)–O(4)	1.115 (16)	1.12 (5)
M–C(3)	1.913 (13)	2.06 (4)	C(5)–O(5)	1.149 (12)	1.16 (3)
M–C(4)	1.876 (12)	2.04 (4)	P(1)–C(6)	1.807 (8)	1.81 (2)
M–C(5)	1.835 (9)	1.95 (3)	P(1)–C(7)	1.805 (11)	1.82 (3)
B(1)–B(2)	1.759 (12)	1.76 (3)	P(1)–C(8)	1.822 (9)	1.81 (2)
B(1)–P(1)	1.920 (10)	1.92 (3)	P(2)–C(9)	1.813 (11)	1.83 (3)
B(1)–H(1a)	1.40 (9)	1.08	P(2)–C(10)	1.825 (10)	1.83 (3)
B(1)–H(1b)	1.28 (8)	1.08	P(2)–C(11)	1.823 (14)	1.84 (4)

Table V. Bond Angles (deg) for $[M(CO)_5\{B_2H_4{\cdot}2P(CH_3)_3\}]$ (M = Cr (**2a**), W (**2c**))

	M = Cr	M = W
H(1b)–M–C(1)	89 (3)	88.7
H(1b)–M–C(2)	92 (3)	92.6
H(1b)–M–C(3)	97 (3)	84.8
H(1b)–M–C(4)	82 (3)	95.6
H(1b)–M–C(5)	171 (3)	176.9
B(1)···M–C(1)	90.4 (3)	89.3 (8)
B(1)···M–C(2)	90.8 (3)	92.0 (8)
B(1)···M–C(3)	81.1 (4)	80.0 (13)
B(1)···M–C(4)	98.2 (4)	100.4 (11)
B(1)···M–C(5)	172.7 (3)	172.9 (9)
C(1)–M–C(2)	178.1 (4)	178.6 (10)
C(1)–M–C(3)	90.2 (5)	91.9 (14)
C(1)–M–C(4)	89.5 (5)	90.4 (13)
C(1)–M–C(5)	88.3 (4)	89.0 (10)
C(2)–M–C(3)	88.5 (5)	88.6 (13)
C(2)–M–C(4)	91.8 (4)	89.1 (12)
C(2)–M–C(5)	90.3 (4)	89.7 (10)
C(3)–M–C(4)	179.3 (5)	177.7 (16)
C(3)–M–C(5)	91.6 (5)	93.2 (14)
C(4)–M–C(5)	89.0 (5)	86.5 (13)
M–C(1)–O(1)	177.1 (9)	176 (2)
M–C(2)–O(2)	177.2 (7)	175 (2)
M–C(3)–O(3)	174.6 (12)	172 (4)
M–C(4)–O(4)	178.1 (11)	175 (3)
M–C(5)–O(5)	178.3 (8)	179 (2)
M–H(1b)–B(1)	141 (8)	167
P(1)–B(1)–B(2)	108.6 (6)	109 (2)
P(1)–B(1)–H(1a)	107 (4)	110
P(1)–B(1)–H(1b)	97 (3)	110
B(2)–B(1)–H(1a)	116 (4)	110
B(2)–B(1)–H(1b)	110 (3)	110
H(1a)–B(1)–H(1b)	117 (5)	109
P(2)–B(2)–B(1)	111.2 (6)	110 (2)
P(2)–B(2)–H(2a)	112 (3)	110
P(2)–B(2)–H(2b)	109	110
B(1)–B(2)–H(2a)	113 (3)	110
B(1)–B(2)–H(2b)	122	110
H(2a)–B(2)–H(2b)	88	109

to that of $M(CO)_4\{B_2H_4{\cdot}2P(CH_3)_3\}^+$, followed by peaks due to the successive loss of the four CO groups. Thus, their spectra resembled those of **3a** and **3c** except for the observation that the relative intensities of the liberated borane ligand were stronger than those for **3**. This phenomenon was also observed in the unidentate complexes $[M(CO)_5(L\text{-}L)]$ (M = Cr, Mo, W; L-L = a potentially bidentate ligand such as bis(dimethylphosphino)ethane).[23]

^{1}H NMR spectra of **2** show only one kind of methyl resonance and two BH hydrogen resonances, which indicate the existence of some fluxional process in **2**.[24] ^{1}H NMR spectra of **3** also show one kind of methyl resonance and two BH hydrogen resonances, and these features are consistent with the bidentate ligation of **1** in **3**.

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(23) Connor, J. A.; Day, J. P.; McEwen, G. K. *J. Chem. Soc., Dalton Trans.* **1973**, 347–354.

(24) Katoh, K.; Shimoi, M.; Ogino, H.; Kodama, G. To be published.

Table VI. Final Atomic Parameters for $[Cr(CO)_4\{B_2H_4{\cdot}2P(CH_3)_3\}]$ (**3a**)[a]

atom	x	y	z	$B_{eqv}/Å^2$ [b]
Cr	0	1145.0 (4)	907.5 (9)	3.5
P(1)	−252 (2)	2020.6 (7)	4683 (2)	4.0
P(2)	3240 (2)	783.5 (7)	3438 (2)	3.8
B(1)	214 (8)	1293 (3)	3525 (7)	3.7
B(2)	1859 (9)	1370 (3)	2653 (8)	3.7
O(1)	1020 (8)	795 (3)	−2083 (5)	6.4
O(2)	−2931 (7)	1161 (4)	−322 (7)	7.1
O(3)	34 (9)	2487 (3)	−267 (6)	6.9
O(4)	−511 (9)	−263 (2)	1370 (7)	6.8
C(1)	651 (9)	939 (3)	−906 (7)	4.4
C(2)	−1797 (9)	1153 (3)	172 (8)	5.0
C(3)	51 (9)	1994 (3)	298 (7)	4.5
C(4)	−248 (9)	256 (3)	1286 (7)	4.9
C(5)	1125 (11)	2257 (4)	5909 (8)	5.5
C(6)	−1779 (12)	1877 (5)	5887 (11)	6.9
C(7)	−622 (13)	2732 (4)	3619 (9)	6.8
C(8)	4916 (11)	840 (4)	2461 (9)	6.3
C(9)	3673 (11)	940 (4)	5344 (7)	6.1
C(10)	2770 (11)	−38 (4)	3329 (12)	6.9
atom	**x**	**y**	**z**	**$B_{iso}/Å^2$**
H(1a)	−5 (10)	96 (3)	426 (6)	3.6 (12)
H(1b)	−82 (7)	132 (2)	278 (5)	2.5 (11)
H(2a)	246 (9)	186 (3)	277 (7)	4.8 (17)
H(2b)[c]	190	111	161	5.8

[a] Coordinates for non-hydrogen atoms are multiplied by 10^4, and those for hydrogen atoms, by 10^3. [b] The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eqv} = {}^4/_3(B_{11a}{}^2 + B_{22}b^2 + B_{33}c^2)$. The B_{ij}'s are defined by $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$. [c] The coordinates for H(2b) were fixed at those found in the difference Fourier map.

Table VII. Final Atomic Parameters for $[W(CO)_4\{B_2H_4{\cdot}2P(CH_3)_3\}]$ (**3c**)[a]

atom	x	y	z	$B_{eqv}/Å^2$ [b]
W	0	1148.3 (4)	837.7 (9)	3.5
P(1)	−185 (12)	2021 (3)	4718 (7)	3.9
P(2)	3293 (8)	774 (3)	3429 (7)	3.7
B(1)	253 (25)	1328 (14)	3566 (22)	3.2
B(2)	1892 (34)	1381 (14)	2709 (30)	3.7
O(1)	1058 (25)	748 (11)	−2265 (21)	6.5
O(2)	−3049 (21)	1223 (13)	−476 (24)	7.2
O(3)	191 (43)	2528 (8)	−382 (19)	5.8
O(4)	−607 (26)	−293 (10)	1446 (29)	7.5
C(1)	651 (27)	890 (14)	−1106 (26)	4.5
C(2)	−1963 (36)	1167 (29)	−20 (29)	11.5
C(3)	135 (43)	2034 (14)	81 (20)	5.7
C(4)	−267 (47)	228 (17)	1405 (33)	7.3
C(5)	1245 (34)	2275 (12)	5979 (35)	5.3
C(6)	−1654 (40)	1895 (14)	5965 (39)	6.3
C(7)	−565 (39)	2711 (14)	3521 (36)	6.5
C(8)	4876 (49)	816 (16)	2501 (34)	6.5
C(9)	3698 (32)	883 (17)	5363 (28)	5.7
C(10)	2756 (37)	−33 (14)	3145 (52)	7.6
atom	**x**	**y**	**z**	**$B_{iso}/Å^2$**
H(1a)	248	910	4243	5.9
H(1b)	−556	1280	2739	5.9
H(2a)	2307	1852	2870	5.9
H(2b)	1746	1302	1556	5.9

[a] Coordinates are multiplied by 10^4. [b] The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eqv} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2)$. The B_{ij}'s are defined by $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$. [c] The coordinates for hydrogen atoms were fixed at the calculated positions.

Table VIII. Interatomic Distances (Å) for $[M(CO)_4\{B_2H_4{\cdot}2P(CH_3)_3\}]$ (M = Cr (**3a**), W (**3c**))

	M = Cr	M = W		M = Cr	M = W
M–H(1b)	1.91 (6)	1.84	B(1)–P(1)	1.912 (7)	1.85 (3)
M–H(2b)	1.90	1.80	B(1)–H(1a)	1.00 (6)	1.08
M···B(1)	2.413 (7)	2.54 (2)	B(1)–H(1b)	1.18 (6)	1.08
M···B(2)	2.412 (8)	2.52 (3)	B(2)–P(2)	1.930 (8)	1.96 (3)
M–C(1)	1.815 (7)	1.96 (3)	B(2)–H(2a)	1.19 (7)	1.08
M–C(2)	1.820 (8)	2.01 (4)	B(2)–H(2b)	1.10	1.08
M–C(3)	1.874 (6)	2.00 (3)	P(1)–C(5)	1.782 (9)	1.86 (3)
M–C(4)	1.918 (7)	2.03 (4)	P(1)–C(6)	1.833 (11)	1.82 (4)
C(1)–O(1)	1.168 (9)	1.17 (4)	P(1)–C(7)	1.819 (9)	1.86 (3)
C(2)–O(2)	1.159 (11)	1.11 (4)	P(2)–C(8)	1.816 (10)	1.72 (4)
C(3)–O(3)	1.159 (9)	1.13 (3)	P(2)–C(9)	1.814 (8)	1.83 (3)
C(4)–O(4)	1.124 (9)	1.15 (4)	P(2)–C(10)	1.788 (8)	1.80 (3)
B(1)–B(2)	1.748 (11)	1.74 (4)			

When complexes **2a** and **2c** were dissolved in THF or CH_3CN, they liberated $B_2H_4{\cdot}2P(CH_3)_3$ to form $[M(CO)_5(THF)]$ or $[M(CO)_5(CH_3CN)]$, whereas complexes **3a**, **3b**, and **3c** did not liberate $B_2H_4{\cdot}2P(CH_3)_3$ into the solvents. This result means that the coordination of $B_2H_4{\cdot}2P(CH_3)_3$ to metals in **2** is very weak and that the choice of solvent for the photochemical reaction is an important factor for the preparation of **2**.

X-ray Crystal Structures of $[M(CO)_5\{B_2H_4{\cdot}2P(CH_3)_3\}]$ (M = Cr (2a), M = W (2c)). The final atomic coordinates and equivalent isotropic temperature factors for **2a** and **2c** are listed in Tables II and III, respectively. The interatomic distances and angles for both complexes are given in Tables IV and V, respectively. Figure 1 shows the ORTEP diagrams of **2a** and **2c**. As the structures of **2a** and **2c** are almost identical, the structures of the complexes are explained using the chromium complex **2a**.

The distances between chromium and hydrogen atoms (Cr–H(1b) = 1.76 (8) Å, Cr···H(1a) = 3.34 (7) Å, Cr···H(2a) = 4.75 (6) Å, and Cr···H(2b) = 3.92 Å) clearly indicate that $B_2H_4{\cdot}2P(CH_3)_3$ coordinates to chromium through only one B–H–M bridge bond. The distances of Cr···B (Cr···B(1) = 2.876 (8) Å and Cr···B(2) = 3.922 (9) Å) show that there is no *direct* interaction between the chromium and boron atoms. Such a single B–H–M binding mode has hitherto been known only for some BH_4^- complexes,[2–10] and **2a** and **2c** are the first examples of polyborane complexes with a single B–H–M linkage. The Cr–H(1b)–B(1) angle is nonlinear, apparently bent to 141 (8)°. Such bending, also observed in unidentate BH_4^- complexes,[4–6,8–10] indicates that the M–H–B linkage is a three-center two-electron bond.

Figure 2 shows an alternative view of **2a**. It is clear from this figure that the $B_2H_4{\cdot}2P(CH_3)_3$ ligand in this complex also adopts an eclipsed (anticlinal) conformation as observed for the previously reported complexes $[ZnCl_2\{B_2H_4{\cdot}2P(CH_3)_3\}]$[11] and $[Cu\{B_2H_4{\cdot}2P(CH_3)_3\}_2]I$,[13] which contain bidentate $B_2H_4{\cdot}2P(CH_3)_3$ ligands, in contrast to the staggered (trans) conformation of free **1**.[25] Since the eclipsed conformation of the $B_2H_4{\cdot}2P(CH_3)_3$ ligand in the reported complexes is thought to derive from the chelate coordination mode, the adoption of the same conformation in **2** was surprising. However, if the $B_2H_4{\cdot}2P(CH_3)_3$ ligand in **2** adopts the staggered conformation like free **1**, the methyl groups attached to P(2) would approach the trans-C carbonyl groups very closely. Thus, steric effects force the ligand to take the eclipsed conformation. In the case of tungsten complex **2c**, although the positions of hydrogen atoms attached to boron atoms were not found in the difference Fourier map and were fixed in calculated positions, the unidentate attachment of $B_2H_4{\cdot}2P(CH_3)_3$ in this complex is also apparent from the W···B distances (W···B(1) = 2.95 (2) Å, W···B(2) = 3.95 (2) Å).

The bond length of Cr–C(trans-H) (1.835 (9) Å) is shorter than those of Cr–C(cis-H) (average 1.890 (15) Å). Such a tendency is also observed in $[Cr(CO)_4(BH_4)]^-$,[26] $[Cr(CO)_4(B_3H_8)]^-$,[27] and $[Cr(CO)_4\{B_2H_4{\cdot}2P(CH_3)_3\}]$ (**3a**). Bridging hydrogen atoms have no π-acceptor ability; thus, the metal dπ electron density predominantly increases in the carbonyl trans to the H atom, and the length of Cr–C(trans-H) becomes shorter than those of Cr–C(cis-H).[27]

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(25) Ruble, J. R. M.S. Thesis, The Ohio State University, 1972.

(26) Darensbourg, M. Y.; Bau, R.; Marks, M. E.; Burch, R. R., Jr.; Deaton, J. C.; Slater, S. *J. Am. Chem. Soc.* **1982**, *104*, 6961–6969.

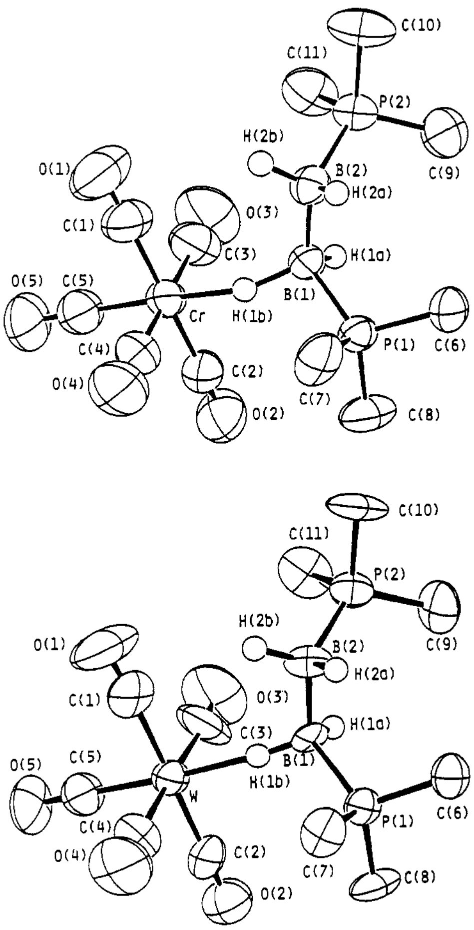

Figure 1. ORTEP diagrams of [Cr(CO)$_5${B$_2$H$_4$·2P(CH$_3$)$_3$}] (**2a**) (upper) and [W(CO)$_5${B$_2$H$_4$·2P(CH$_3$)$_3$}] (**2c**) (lower) with atomic numbering schemes.

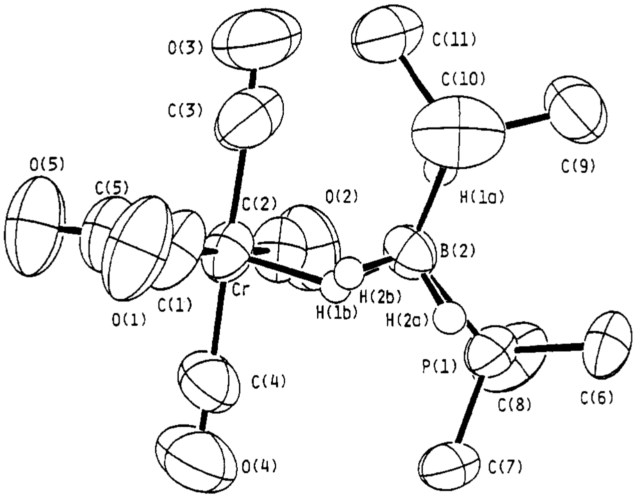

Figure 2. Alternative diagram of **2a**, viewed along the B–B bond axis.

X-ray Crystal Structures of [M(CO)$_4${B$_2$H$_4$·2P(CH$_3$)$_3$}] (M = Cr (3a), M = W (3c)). The final atomic coordinates and equivalent isotropic temperature factors of **3a** and **3c** are given in Tables VI and VII, respectively. Bond lengths and angles of both complexes are collected in Tables VIII and IX, respectively. Figure 3 shows the ORTEP diagrams of **3a** and **3c**. As the structure of **3c** is almost the same as that of **3a**, the structure of the chromium complex is discussed mainly.

B$_2$H$_4$·2P(CH$_3$)$_3$ coordinates to the Cr or W metal atom through two vicinal hydrogen atoms, and the geometry around the metal

Table IX. Bond Angles (deg) for [M(CO)$_4${B$_2$H$_4$·2P(CH$_3$)$_3$}] (M = Cr (**3a**), W (**3c**))

	M = Cr	M = W
B(1)···M···B(2)	42.5 (3)	40.1 (9)
H(1b)–M–H(2b)	95	84
H(1b)–M–C(1)	175.2 (17)	172
H(1b)–M–C(2)	87.3 (17)	96
H(1b)–M–C(3)	95.6 (17)	102
H(1b)–M–C(4)	88.5 (17)	82
H(2b)–M–C(1)	88.7	96
H(2b)–M–C(2)	177.2	168
H(2b)–M–C(3)	96.8	84
H(2b)–M–C(4)	90.6	101
C(1)–M–C(2)	88.9 (4)	86.4 (13)
C(1)–M–C(3)	87.1 (3)	85.7 (12)
C(1)–M–C(4)	88.4 (3)	90.3 (14)
C(2)–M–C(3)	84.6 (3)	84.6 (13)
C(2)–M–C(4)	87.8 (3)	90.3 (14)
C(3)–M–C(4)	171.3 (3)	173.6 (13)
M–H(1b)–B(1)	100 (4)	119
M–H(2b)–B(2)	104	120
M–C(1)–O(1)	177.3 (6)	178 (2)
M–C(2)–O(2)	178.7 (8)	175 (3)
M–C(3)–O(3)	170.6 (6)	178 (3)
M–C(4)–O(4)	171.5 (6)	164 (3)
P(1)–B(1)–B(2)	112.4 (4)	114 (2)
P(1)–B(1)–H(1a)	98 (4)	109
P(1)–B(1)–H(1b)	96 (3)	108
B(2)–B(1)–H(1a)	126 (4)	109
B(2)–B(1)–H(1b)	118 (3)	108
H(1a)–B(1)–H(1b)	102 (5)	109
P(2)–B(2)–B(1)	111.7 (4)	114 (2)
P(2)–B(2)–H(2a)	102 (4)	108
P(2)–B(2)–H(2b)	88	108
B(1)–B(2)–H(2a)	118 (4)	109
B(1)–B(2)–H(2b)	112	109
H(2a)–B(2)–H(2b)	120	109

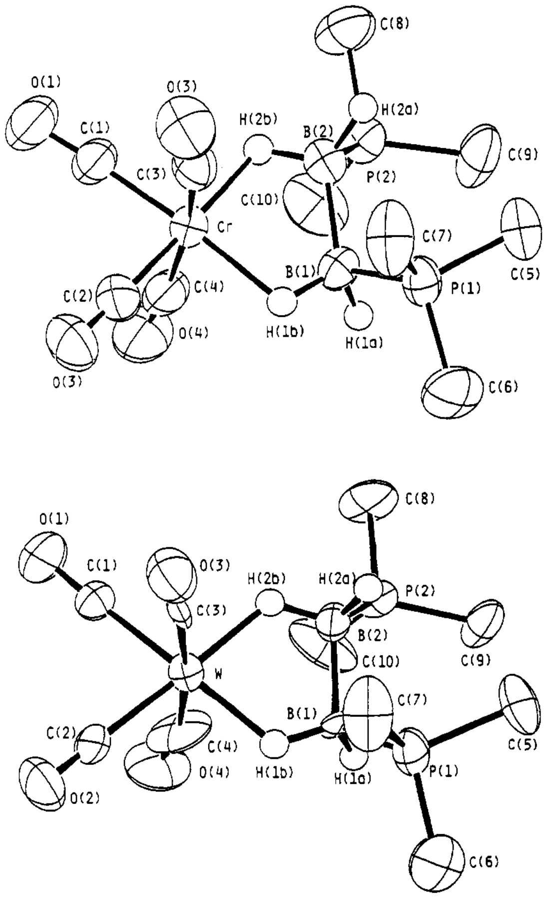

Figure 3. ORTEP drawings of [Cr(CO)$_4${B$_2$H$_4$·2P(CH$_3$)$_3$}] (**3a**) (upper) and [W(CO)$_4${B$_2$H$_4$·2P(CH$_3$)$_3$}] (**3c**) (lower) with atomic numbering schemes.

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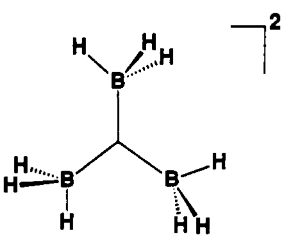
(27) Guggenberger, L. J. *Inorg. Chem.* **1970**, *9*, 367–373.

Chart I



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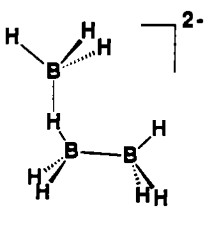

1015

atom is a distorted octahedron. The axial carbonyls are bent away from the borane ligand, C(3)–M–C(4) = 171.3 (3)° (M = Cr) and 174 (1)° (M = W) (such bending is also observed in $[Cr(CO)_4(BH_4)]^-$ [26] and $[Cr(CO)_4(B_3H_8)]^-$ [27]).

The conformation of $B_2H_4{\cdot}2P(CH_3)_3$ in **3a** and **3c** is eclipsed (anticlinal) as in the cases of the previously reported chelate complexes, $[ZnCl_2\{B_2H_4{\cdot}2P(CH_3)_3\}]$[11] and $[Cu\{B_2H_4{\cdot}2P(CH_3)_3\}_2]I$.[13] In contrast to the good planarity of the MH_2B_2 rings in these complexes, the hydrogen atoms of the chromium complex **3a** deviate considerably from the B(1)–Cr–B(2) triangle (+0.28 and –0.44 Å). Due to steric repulsion between the carbonyl and trimethylphosphine groups, the B–B axis is twisted with respect to the C(1)–Cr–C(2) plane: The dihedral angle between the C(1)–Cr–C(2) and B(1)–Cr–B(2) planes is 16°. To make the overlap of orbitals of Cr and $B_2H_4{\cdot}2P(CH_3)_3$ ligand feasible, the bridging hydrogen atoms are located in the C(1)–Cr–C(2) plane (the dihedral angle between the C(1)–Cr–C(2) and H(1b)–Cr–H(2b) planes is only 3.5°). Thus the H(1b) and H(2b) atoms deviate greatly from the B(1)–Cr–B(2) triangle.

It was previously considered that the lengthening of the B–B bond in the zinc and copper complexes in comparison with free **1** was caused by the decrease of electron density at the boron atoms.[12] However, the B–B bond lengths of **1** in **3a** and **3c** (**3a**, 1.748 (11) Å; **3c**, 1.74 (4) Å) are shorter than those in the zinc (1.814 (6) Å)[11] and copper (1.80 (2), 1.81 (2) Å)[13] complexes and comparable with that in free $B_2H_4{\cdot}2P(CH_3)_3$ (1.740 (7) Å).[25] Thus, the B–B bond length is not affected by electronic effects but rather by steric effects deriving from the difference of the geometry around the central metal atoms; i.e., the Cr and W complexes adopt octahedral geometry and the Zn and Cu complexes tetrahedral. The Cr–H(1b)–B(1) and Cr–H(2b)–B(2) angles (100 (4), 104°) are larger than the M–H–B angles in the zinc and copper complexes (about 90°), and the angles of H(1b)–Cr–H(2b) (95°) and B(1)···Cr···B(2) (42.5 (3)°) are smaller than the corresponding angles in the zinc and copper complexes. These results also reflect the difference of the coordination geometries.

The average Cr–C(trans-C) distance is longer than the average Cr–C(trans-H) distance. This is the same tendency as observed in **2a**, as mentioned above.

$B_2H_4{\cdot}2P(CH_3)_3$ Complexes as Metallaboranes. Borane complexes are often regarded as metallaboranes, namely metal-substituted boranes, and this concept is valid for complexes of higher boranes.[28] It is of interest if complexes of the electron-precise $B_2H_4{\cdot}2P(CH_3)_3$ can also be regarded as metallaboranes.

Taking into consideration the electron-counting system of Wade, $M(CO)_5$ fragments of group 6 metals are isoelectronic (and isolobal) with BH_3, and $B_2H_4{\cdot}2P(CH_3)_3$ is isoelectronic with $B_2H_6^{2-}$; thus, the complex $[M(CO)_5\{B_2H_4{\cdot}2P(CH_3)_3\}]$ is isoelectronic with $B_3H_9^{2-}$, which has not yet been reported. The complex may thus be regarded as a model compound for $B_3H_9^{2-}$. Two possible structures were proposed for $B_3H_9^{2-}$, namely 0106 and 1015 according to Lipscomb's styx index method.[29] Complex **2** is isostructural with the 1015 configuration (Chart I). On the other hand, $M(CO)_4$ fragments of group 6 metals are isoelectronic and isolobal with BH_2^+, and $[M(CO)_4\{B_2H_4{\cdot}2P(CH_3)_3\}]$ is isoelectronic and isostructural with $B_3H_6{\cdot}2P(CH_3)_3^+$ [30,31] and $B_3H_8^-$.[32–34] This isoelectronic and isostructural relationship is also valid for other bidentate complexes of $B_2H_4{\cdot}2P(CH_3)_3$, $[ZnCl_2\{B_2H_4{\cdot}2P(CH_3)_3\}]$,[11,12] $[CuX(PPh_3)\{B_2H_4{\cdot}2P(CH_3)_3\}]$,[11,12] $[CuX\{B_2H_4{\cdot}2P(CH_3)_3\}]$,[12] $[Cu\{B_2H_4{\cdot}2P(CH_3)_3\}_2]X$ (X = halogen),[13] and $[Ni(CO)_2\{B_2H_4{\cdot}2P(CH_3)_3\}]$.[12,14] Thus the metallaborane concept is applicable to the complexes containing the unidentate and bidentate $B_2H_4{\cdot}2P(CH_3)_3$ ligands.

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Supplementary Material Available: Tables S1–S8, giving full crystallographic and experimental data and thermal parameters for **2a**, **2c**, **3a**, and **3c** (16 pages); tables of observed and calculated structure factors for **2a**, **2c**, **3a**, and **3c** (19 pages). Ordering information is given on any current masthead page.

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