

# Articles

## Synthesis and Characterization of Group VI Metal Carbonyl Complexes Containing *closo*-1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> and Their Conversion to Metal Carbene Complexes

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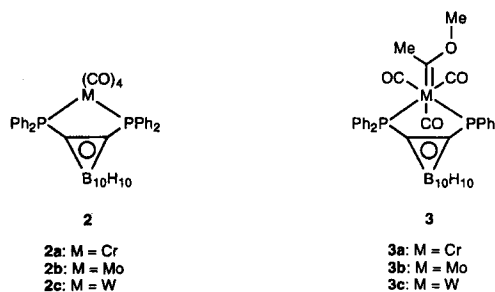
The complexes M(CO)<sub>4</sub>-1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (M=Cr **2a**, Mo **2b**, W **2c**) have been prepared in good yields from readily available *bis*-diphenylphosphino-*o*-carboranyl ligand, *closo*-1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**1**), by direct reaction with Group VI metal carbonyls. The infrared spectra of the complexes indicate that there is an octahedral disposition of chelate *bis*-diphenylphosphino-*o*-carboranyl ligand around the metal atom. The crystal structure of **2a** was determined by X-ray diffraction. Complex **2a** crystallizes in the monoclinic space group *P* 2<sub>1</sub>/*n* with cell parameters *a* = 12.2360(7), *b* = 17.156(1), *c* = 16.2040(6) Å, *V* = 3354.1(3) Å<sup>3</sup>, and *Z* = 4. Of the reflections measured a total of 2514 unique reflections with *F*<sup>2</sup> > 3σ(*F*<sup>2</sup>) was used during subsequent structure refinement. Refinement converged to *R*<sub>1</sub> = 0.066 and *R*<sub>2</sub> = 0.071. Structural studies showed that the chromium atom had a slightly distorted pseudo-octahedral configuration about the metal center with two phosphine groups of *o*-carborane occupying the equatorial plane *cis*-orientation to each other. These metal carbonyl complexes are rapidly converted to the corresponding metal carbene complexes, [(CO)<sub>3</sub>M=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (M = Cr **3a**, Mo **3b**, W **3c**), *via* alkylation with methylolithium followed by O-methylation with CF<sub>3</sub>SO<sub>3</sub>CH<sub>3</sub>.

### Introduction

The preparation and coordination chemistry of symmetrical di(phosphines) has been an area of great interest for a number of years. Of particular interest are the *bis*-phosphino derivatives in which the *o*-carborane nucleus functions as a ligand backbone.<sup>1,2</sup> *o*-Carborane is an interesting backbone because its electron withdrawing power, large size and extensive electronic delocalization confer a rather unusual stability to the molecule. Accordingly, phosphino derivatives of the types *closo*-1,2-(PR<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (R = C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>) have been prepared as well as some chelate complexes.<sup>3-6</sup> They lend themselves to a detailed study of ligand-metal bonding since varying the substituents on the borane portion of the molecule should affect the electronic environment of the phosphorus atoms and the stability of the complexes.

In the present work metal carbonyl complexes in which chelating *bis*-diphenylphosphino-*o*-carboranyl ligand **1** is directly attached to the metal in a σ-bonded fashion are now to be studied. Cluster complexes of transition-metals in which the metal atoms are directly bound are of interest for the evidence they provide the ability of cluster to transmit its influence to the metal. Recent study<sup>7</sup> of *o*-carboranyl metal system in which metal and carborane are separated by one atom, has shown that some metal-carborane interaction occurs in such compounds.

In this paper, we wish to report on progress made towards the syntheses of Group VI metal carbonyl complexes containing *bis*-diphenylphosphino-*o*-carborane **2** and the formation of the corresponding metal carbene complexes **3** is discussed. Due to our interest in the structural features of



Group VI metal carbonyl complexes a single crystal X-ray diffraction determination of **2a** was carried out.

### Experimental

**Methods and Materials.** The majority of solvents were of reagent grade and were used without further purification. Xylene was dried over sodium metal and vacuum distilled. Hexane and benzene were purified by distillation from lithium aluminum hydride, while diethyl ether and THF were further purified by distillation from sodium-benzophenone. Complex **1** was prepared by literature methods.<sup>3</sup> All reactions involving lithio-metal acyl complexes were carried out under argon atmosphere. Silica gel was obtained from J. T. Baker Co. and was dried before use.

**Physical Measurements.** <sup>1</sup>H NMR spectra at 200 MHz and <sup>11</sup>B NMR spectra at 64.2 MHz were obtained on a Bruker AM-200 Fourier transform spectrometer. Selective proton-decoupled carbon-13 NMR spectra (50.3 MHz) were obtained on the Bruker AM-200 spectrometer. All boron-11 chemical shifts were referenced to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (0.0 ppm)

with a negative sign indicating an upfield shift. All proton and carbon chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5%  $C_6D_6$ ) and then referenced to  $Me_4Si$  (0.00 ppm). High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. All melting points were uncorrected. Elemental analyses were obtained from Schwarzkopf Laboratories, Woodside, NY.

**Crystallographic Data for  $[(CO)_4Cr]-closo-1,2-(PPh_2)_2-1,2-C_2B_{10}H_{10}$  (2a).** Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of hexane through a  $CH_2Cl_2$  solution of **2a**. A white opaque crystalline needle was mounted on the top of a glass fiber. This fiber was mounted and transferred to the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections.

**X-ray Data Collection and Structure Solution and Refinement.** Diffraction data were collected on a Rigaku diffractometer with area detector employing graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda=0.7107$  Å). X-ray data were processed, and the structure was solved and refined using the Molecular Structure Corporation teXan<sup>8</sup> package on a Silicon Graphics Indigo R4000 computer. A total of 5782 reflections was measured over the range:  $0 < 2\theta < 49.44^\circ$ ,  $0 < h < 12$ ,  $-18 < k < 18$ ,  $0 < l < 16$ . The intensity data were corrected for Lorentz and polarization effects but not for absorption. Of the reflections measured a total of 2514 unique reflections with  $F^2 > 3\sigma(F^2)$  was used during subsequent structure refinement. The structure was solved by direct method (SIR 88<sup>9</sup>). Refinement was carried out by full-matrix least squares techniques based on  $F$  to minimize the quantity  $\sum w(|F_o| - |F_c|)^2$  with  $w=1/\sigma^2(F)$ . Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included as constant contributions to the structure factors and only cage hydrogen atoms are refined. Refinement converged to  $R_1=0.066$  and  $R_2=0.071$ . Figure 1 is an ORTEP<sup>10</sup> representation of the molecule with 30% probability thermal ellipsoids displayed.

**$Cr(CO)_4-1,2-(PPh_2)_2-1,2-C_2B_{10}H_{10}$  (2a).** Under nitrogen, 2.44 g (4.76 mmol) of **1** in 100 mL of anhydrous xylene was slowly added to a stirred suspension of 1.41 g (6.4 mmol) of  $Cr(CO)_6$  in 50 mL of anhydrous ethyl ether. After stirring for 3 h at reflux temperature, the reaction mixture was rotary evaporated to give a brown oil. The oil was mixed with 50 mL of dry benzene and the resulting mixture was placed atop a 1 in.  $\times$  12 in. column in hexane and was flash-chromatographed with 1:9 diethyl ether-hexane mixture. The yellow band so eluted was rotary evaporated to near dryness and the residue was sublimed at room temperature under high vacuum to give 2.10 g (3.1 mmol, 65%) of bright yellow complex **2a**.  $^{11}B$  NMR (64.2 MHz, ppm,  $C_6D_6$ ): -1.0 (d,  $B_{9,12}$ ,  $J_{BH}=140$  Hz), -4.3 (d,  $B_{8,10}$ ,  $J_{BH}=130$  Hz), -7.4 (d,  $B_{4,5,7,11}$ ,  $J_{BH}=135$  Hz), -8.7 (d,  $B_{3,6}$ ,  $J_{BH}=165$  Hz);  $^1H$  NMR (200.13 MHz, ppm,  $C_6D_6$ ) 7.8 (m,  $C_6H_5$ ), 7.0 (d,  $C_6H_5$ ); exact mass calcd for  $^{11}B_{10}^{12}C_{30}^{1}H_{30}^{31}P_2^{16}O_4^{52}Cr$  678.1599, found 678.1592; Anal. Calcd: C, 53.26; H, 4.47. Found: C, 53.40; H, 4.67. Rf=0.96 by silica gel TLC analysis (benzene); Mp=131-133 °C (dec); IR spectrum (KBr pallet,  $cm^{-1}$ ) 3057 (w), 2624 (s), 2021 (s), 1954 (s), 1906 (s), 1897 (s), 1508 (w), 1431 (w), 1085 (w), 1070 (w), 746 (w), 694 (w), 669 (w), 640 (m), 519 (w), 505 (w).

**$Mo(CO)_4-1,2-(PPh_2)_2-1,2-C_2B_{10}H_{10}$  (2b).** A solution of 1.54 g (3 mmol) of **1** in 100 mL of anhydrous xylene was slowly added under an argon atmosphere to a rapidly stirred suspension of 1.06 g (4 mmol) of  $Mo(CO)_6$  in 50 mL of anhydrous ethyl ether. After stirring for 5 h at reflux temperature, the reaction mixture was evaporated to give a dark oil. The oil was dissolved in 50 mL of benzene and the resulting solution was rotary evaporated onto 2 g of predried silica gel. This mixture was placed on a 1 in.  $\times$  6 in. column in hexane, and a yellow band was eluted from the flash-chromatograph with 1:9 diethyl ether-hexane mixture. An additional 100 mL of eluent was collected. Rotary evaporation of the eluent to 50 mL gave white crystalline needles of complex **2b**. A total of 0.84 g (1.17 mmol, 39%) was collected. The white crystals were sublimed and recrystallized from diethyl ether-hexane mixture.  $^{11}B$  NMR (64.2 MHz, ppm,  $C_6D_6$ ): -1.0 (d,  $B_{9,12}$ ,  $J_{BH}=140$  Hz), -4.7 (d,  $B_{8,10}$ ,  $J_{BH}=130$  Hz), -7.0 (d,  $B_{4,5,7,11}$ ,  $J_{BH}=135$  Hz), -9.0 (d,  $B_{3,6}$ ,  $J_{BH}=160$  Hz);  $^1H$  NMR (200.13 MHz, ppm,  $C_6D_6$ ) 7.8 (d,  $C_6H_5$ ), 7.0 (m,  $C_6H_5$ ); exact mass calcd for  $^{11}B_{10}^{12}C_{30}^{1}H_{30}^{31}P_2^{16}O_4^{96}Mo$  724.1604, found 724.1610; Anal. Calcd: C, 50.01; H, 4.20. Found: C, 50.11; H, 4.29. Rf=0.93 by silica gel TLC analysis (benzene); Mp=126-128 °C (dec); IR spectrum (KBr pallet,  $cm^{-1}$ ) 3058 (w), 2631 (w), 2033 (s), 1964 (s), 1916 (s), 1901 (s), 1431 (w), 1083 (w), 1068 (w), 745 (w), 690 (m), 610 (w), 583 (m), 567 (w), 519 (w), 505 (w).

**$W(CO)_4-1,2-(PPh_2)_2-1,2-C_2B_{10}H_{10}$  (2c).** A solution of 1.54 g (3 mmol) of **1** in 100 mL of xylene was slowly added under an argon atmosphere to a rapidly stirred suspension of 1.41 g (4 mmol) of  $W(CO)_6$  in 50 mL of anhydrous ethyl ether. After stirring for 12 h at reflux temperature, the reaction mixture was evaporated to give a dark oil. The oil was dissolved in 50 mL of benzene and the resulting solution was rotary evaporated onto 2 g of predried silica gel. This mixture was placed on a 1 in.  $\times$  6 in. column in hexane, and a yellow band was eluted from the flash-chromatograph with 1:9 diethyl ether-hexane mixture. An additional 100 mL of eluent was collected. Rotary evaporation of the eluent to 50 mL gave white crystalline needles of complex **2c**. A total of 0.49 g (0.60 mmol, 20%) was collected. The white crystals were sublimed and recrystallized from diethyl ether-hexane mixture.  $^{11}B$  NMR (64.2 MHz, ppm,  $C_6D_6$ ): -1.0 (d,  $B_{9,12}$ ,  $J_{BH}=140$  Hz), -4.6 (d,  $B_{8,10}$ ,  $J_{BH}=130$  Hz), -6.9 (d,  $B_{4,5,7,11}$ ,  $J_{BH}=140$  Hz), -9.2 (d,  $B_{3,6}$ ,  $J_{BH}=155$  Hz);  $^1H$  NMR (200.13 MHz, ppm,  $C_6D_6$ ) 7.8 (d,  $C_6H_5$ ), 7.0 (m,  $C_6H_5$ ); exact mass calcd for  $^{11}B_{10}^{12}C_{30}^{1}H_{30}^{31}P_2^{16}O_4^{184}W$  810.2059, found 810.2049; Anal. Calcd: C, 44.57; H, 3.74. Found: C, 44.66; H, 3.83. Rf=0.94 by silica gel TLC analysis (benzene); Mp=141-143 °C (dec); IR spectrum (KBr pallet,  $cm^{-1}$ ) 3050 (w), 2631 (s), 1958 (s), 1957 (s), 1909 (s), 1897 (s), 1481 (w), 1431 (w), 1080 (w), 1070 (w), 804 (w), 694 (m), 592 (w), 578 (m), 563 (w), 521 (w), 505 (m), 497 (w), 428 (m).

**$[(CO)_3Cr=C(OCH_3)(CH_3)]-1,2-(PPh_2)_2-1,2-C_2B_{10}H_{10}$  (3a).** Anionic chromium acyl complex was prepared by the reaction in vacuum of excess  $CH_3Li$  (1.0 M-1.2 mL, 1.2 mmol) with complex **2a** (0.68 g, 1 mmol) in tetrahydrofuran (25 mL) at -78 °C. The reaction mixture was then allowed to react at 0 °C for 1 h and the solution was stirred for another 2 h at room temperature. The solution

gradually turned dark brown, suggesting the formation of a metal acyl complex.  $^{11}\text{B}$  NMR spectra taken at this point confirmed the exclusive formation of the complex. Methylation with  $\text{CF}_3\text{SO}_3\text{CH}_3$  followed by extraction with hexane gave slightly air-sensitive yellow solid. Subsequent separation was performed on the flash column with hexane to give 0.14 g (0.20 mmol) of **3a**. This corresponds to a 20% yield based on consumed complex **2a**.  $^{11}\text{B}$  NMR (64.2 MHz, ppm,  $\text{C}_6\text{D}_6$ );  $-1.8$  (d,  $\text{B}_{9,12}$ ,  $J_{\text{BH}} = 140$  Hz),  $-6.8$  (d,  $\text{B}_8$ ,  $\text{B}_{10}$ ,  $J_{\text{BH}} = 135$  Hz),  $-10.4$  (d,  $\text{B}_{4,7}$ ,  $\text{B}_{5,11}$ ,  $J_{\text{BH}} = 130$  Hz),  $-12.0$  (d,  $\text{B}_3$ ,  $\text{B}_6$ ,  $J_{\text{BH}} = 150$  Hz);  $^1\text{H}$  NMR (200.13 MHz, ppm,  $\text{C}_6\text{D}_6$ ), 1.6 (s, 3H,  $\text{CH}_3$ ), 3.3 (s, 3H,  $\text{OCH}_3$ ), 7.8 (d,  $\text{C}_6\text{H}_5$ ), 6.9 (m,  $\text{C}_6\text{H}_5$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.3 MHz, ppm,  $\text{C}_6\text{D}_6$ ) 345 (Cr=C), 212, 211 (CO), 132, 130, 120 ( $\text{C}_6\text{H}_5$ ), 64.5 ( $\text{OCH}_3$ ), 55 ( $\text{C}_2\text{B}_{10}$ ), 40 ( $\text{CH}_3$ ); exact mass calcd for  $^{11}\text{B}_{10}^{12}\text{C}_{30}^{1}\text{H}_{30}^{31}\text{P}_2^{16}\text{O}_4^{184}\text{W}_1$  840.2529, found 840.2533; Anal. Calcd: C, 45.84; H, 4.33. Found: C, 45.91; H, 4.52. Rf=0.20 by silica gel TLC analysis (Hexane); Mp=127-128 °C (dec); IR spectrum (KBr pallet,  $\text{cm}^{-1}$ ) 3055 (w), 2574 (s), 2021 (s), 1942 (s, sh), 1910 (s), 1430 (w), 1085 (w), 745 (w), 700 (m), 670 (w), 640 (m), 503 (w).

**[(CO)<sub>3</sub>Mo=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**3b**).** Anionic molybdenum acyl complex was prepared by the reaction in vacuum of excess  $\text{CH}_3\text{Li}$  (1.0 M-1.2 mL, 1.2 mmol) with complex **2b** (0.72 g, 1 mmol) in tetrahydrofuran (25 mL) at  $-78$  °C. The reaction mixture was then allowed to react at 0 °C for 1 h and the solution was stirred for another 2 h at room temperature. The solution gradually turned dark brown, suggesting the formation of a metal acyl complex.  $^{11}\text{B}$  NMR spectra taken at this point confirmed the exclusive formation of the complex. Methylation with  $\text{CF}_3\text{SO}_3\text{CH}_3$  followed by extraction with hexane gave air sensitive yellow solid. Subsequent separation was performed on the flash column with hexane to give 0.17 g (0.23 mmol) of **3b**. This corresponds to a 23% yield based on consumed complex **2b**.  $^{11}\text{B}$  NMR (64.2 MHz, ppm,  $\text{C}_6\text{D}_6$ );  $-1.8$  (d,  $\text{B}_{9,12}$ ,  $J_{\text{BH}} = 140$  Hz),  $-6.8$  (d,  $\text{B}_8$ ,  $\text{B}_{10}$ ,  $J_{\text{BH}} = 135$  Hz),  $-10.4$  (d,  $\text{B}_{4,7}$ ,  $\text{B}_{5,11}$ ,  $J_{\text{BH}} = 130$  Hz),  $-12.0$  (d,  $\text{B}_3$ ,  $\text{B}_6$ ,  $J_{\text{BH}} = 150$  Hz);  $^1\text{H}$  NMR (200.13 MHz, ppm,  $\text{C}_6\text{D}_6$ ), 1.6 (s, 3H,  $\text{CH}_3$ ), 3.3 (s, 3H,  $\text{OCH}_3$ ), 7.8 (d,  $\text{C}_6\text{H}_5$ ), 6.9 (m,  $\text{C}_6\text{H}_5$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.3 MHz, ppm,  $\text{C}_6\text{D}_6$ ) 336 (Mo=C), 215, 210 (CO), 135, 130, 120 ( $\text{C}_6\text{H}_5$ ), 66.2 ( $\text{OCH}_3$ ), 52 ( $\text{C}_2\text{B}_{10}$ ), 38 ( $\text{CH}_3$ ); exact mass calcd for  $^{11}\text{B}_{10}^{12}\text{C}_{30}^{1}\text{H}_{30}^{31}\text{P}_2^{16}\text{O}_4^{96}\text{Mo}_1$  754.2073, found 754.2078; Anal. Calcd: C, 51.2; H, 4.83. Found: C, 51.25; H, 4.92. Rf=0.22 by silica gel TLC analysis (hexane); Mp=120-122 °C (dec); IR spectrum (KBr pallet,  $\text{cm}^{-1}$ ) 3053 (w), 2570 (s), 2020 (s), 1940 (s, sh), 1908 (s), 1430 (w), 1075 (w), 740 (w), 695 (m), 670 (w), 640 (m), 500 (w).

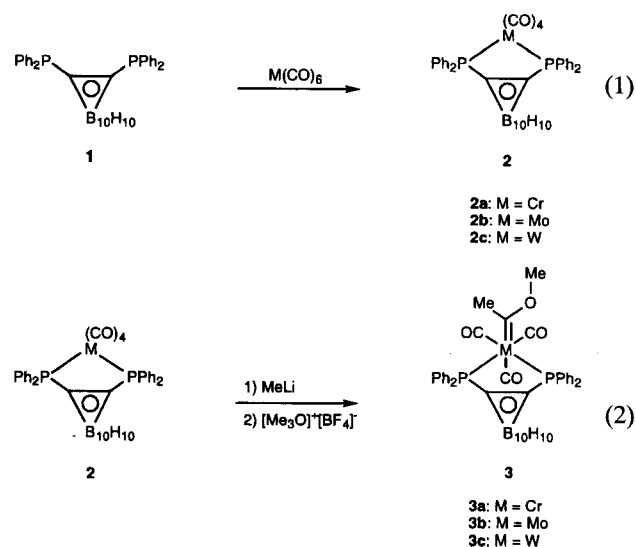
**[(CO)<sub>3</sub>W=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**3c**).** Anionic tungsten acyl complex was prepared by the reaction in vacuum of excess  $\text{CH}_3\text{Li}$  (1.0 M-1.2 mL, 1.2 mmol) with complex **2c** (0.81 g, 1 mmol) in tetrahydrofuran (25 mL) at  $-78$  °C. The reaction mixture was then allowed to react at 0 °C for 1 h and the solution was stirred for another 2 h at room temperature. The solution gradually turned dark brown, suggesting the formation of a metal acyl complex.  $^{11}\text{B}$  NMR spectra taken at this point confirmed the exclusive formation of the complex. Methylation with  $\text{CF}_3\text{SO}_3\text{CH}_3$  followed by extraction with hexane gave air sensitive yellow solid. Subsequent separation was

performed on the flash column with hexane to give 0.23 g (0.27 mmol) of **3c**. This corresponds to a 27% yield based on consumed complex **2c**.  $^{11}\text{B}$  NMR (64.2 MHz, ppm,  $\text{C}_6\text{D}_6$ );  $-1.8$  (d,  $\text{B}_{9,12}$ ,  $J_{\text{BH}} = 140$  Hz),  $-6.8$  (d,  $\text{B}_8$ ,  $\text{B}_{10}$ ,  $J_{\text{BH}} = 135$  Hz),  $-10.4$  (d,  $\text{B}_{4,7}$ ,  $\text{B}_{5,11}$ ,  $J_{\text{BH}} = 130$  Hz),  $-12.0$  (d,  $\text{B}_3$ ,  $\text{B}_6$ ,  $J_{\text{BH}} = 150$  Hz);  $^1\text{H}$  NMR (200.13 MHz, ppm,  $\text{C}_6\text{D}_6$ ) 1.6 (s, 3H,  $\text{CH}_3$ ), 3.3 (s, 3H,  $\text{OCH}_3$ ), 7.8 (d,  $\text{C}_6\text{H}_5$ ), 6.9 (m,  $\text{C}_6\text{H}_5$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.3 MHz, ppm,  $\text{C}_6\text{D}_6$ ) 349 (W=C), 210, 212 (CO), 132, 130, 120 ( $\text{C}_6\text{H}_5$ ), 65.8 ( $\text{OCH}_3$ ), 55 ( $\text{C}_2\text{B}_{10}$ ), 40 ( $\text{CH}_3$ ); exact mass calcd for  $^{11}\text{B}_{10}^{12}\text{C}_{30}^{1}\text{H}_{30}^{31}\text{P}_2^{16}\text{O}_4^{184}\text{W}_1$  840.2529, found 840.2533; Anal. Calcd: C, 45.84; H, 4.33. Found: C, 45.91; H, 4.52. Rf=0.20 by silica gel TLC analysis (Hexane); Mp=127-128 °C (dec); IR spectrum (KBr pallet,  $\text{cm}^{-1}$ ) 3055 (w), 2574 (s), 2021 (s), 1942 (s, sh), 1910 (s), 1430 (w), 1085 (w), 745 (w), 700 (m), 670 (w), 640 (m), 503 (w).

## Results and Discussion

The chelates of metal hexacarbonyls with 1,2-bis(diphenylphosphino)ethane having five membered ring have been obtained by thermal<sup>11</sup> and ultraviolet irradiation methods.<sup>12</sup> Similarly, we have found that the addition of **1** to  $\text{M}(\text{CO})_6$  ( $\text{M}=\text{Cr}, \text{Mo}, \text{W}$ ) proceeds in good yield to give a stable neutral derivatives **2** containing a metal-phosphorus bond (see reaction 1). Subsequent reaction of complexes **2** with 1.2 mol equivalent of methyl lithium gives rise to a corresponding metal acyl complexes. Further methylation of complex with  $\text{CF}_3\text{SO}_3\text{CH}_3$  produces compounds **3** as shown in reaction 2.

Each of the metal carbene complexes was prepared by adaptations of the general methods<sup>13</sup> currently available.



The *o*-carboranyl carbene complexes of Group VI metals are all moderately air stable crystalline solids which are readily soluble in all non-polar solvents (hexane, benzene) and sparingly soluble in polar solvents (ether, acetone). All of these complexes are photo-sensitive but are thermally stable above room temperature.

### Group VI Metal Carbonyl Complexes Containing Bis-diphenylphosphino-*o*-carboranyl Ligand (**2**).

The 1:1 combinations of **1** with a suspension of  $\text{M}(\text{CO})_6$

(M=Cr, Mo, W) in refluxing xylene solution produced Group VI metal carbonyl complexes containing *bis*-diphenylphosphino-*o*-carborane ligand **2** as crystalline air stable white solids. The mass spectral parent ion peak for compounds **2a**, **2b**, and **2c** were observed at *m/e* 678.1587, 724.1620, and 810.2049 corresponding to  $^{11}\text{B}_{10}^{12}\text{C}_{30}^{1}\text{H}_{30}^{31}\text{P}_2^{16}\text{O}_4$ - $^{52}\text{Cr}^+$ ,  $^{11}\text{B}_{10}^{12}\text{C}_{30}^{1}\text{H}_{30}^{31}\text{P}_2^{16}\text{O}_4$ - $^{96}\text{Mo}^+$ , and  $^{11}\text{B}_{10}^{12}\text{C}_{30}^{1}\text{H}_{30}^{31}\text{P}_2^{16}\text{O}_4$ - $^{184}\text{W}^+$ , respectively. Elemental analyses also support these formula. In the infrared spectra of the ligand **1**, the band at about  $1072\text{ cm}^{-1}$  has been assigned to P-C(aromatic) stretch.<sup>14</sup> On complex formation the rise in stretching frequency by  $8\text{--}15\text{ cm}^{-1}$  in the P-C(aromatic) stretch is indicative of the coordination of the donor atoms (phosphorus) to the metal atom. Our complexes **2a-c** gave four absorption bands in the  $2040\text{--}1900\text{ cm}^{-1}$  region, and these are assigned to carbon monoxide groups. The complexes in which two carbon monoxide groups are replaced are of the  $C_{2v}$  class; for this type of complex four infrared active carbonyl stretching modes are expected.<sup>15</sup> The 200 MHz  $^1\text{H}$  NMR spectra of complexes **2a-c** show broad resonances at 7.8–7.0 ppm, which are assigned to the phenyl protons of  $\text{PPh}_2$  groups. The 64.2 MHz  $^{11}\text{B}$  NMR spectra of complexes **2a-c** consist of a set of overlapping doublets of relative intensities 2 : 2 : 4 : 2. This compares favorably with the pattern expected for a 1,2- $\text{R}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  derivative possessing a  $C_{2v}$  symmetry.<sup>16</sup> From this analytical, infrared, and NMR data we propose the structure in reaction 1 for this complex, where the metal atom is bonded to the two phosphorus atoms of *bis*-diphenylphosphino-*o*-carborane through a P(1)-Cr-P(2)  $\sigma$ -bond.

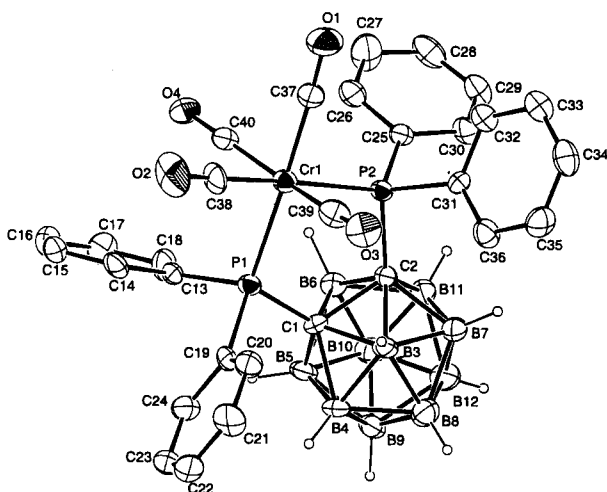
The molecular structure of **2a** was determined by single crystal X-ray diffraction analysis, and a view of the molecule is shown in Figure 1. Details of the crystal structure determination of complex **2a** are shown in Table 1. The final atomic positions and selected bond distances and angles are listed in Table 2-4. The molecule has  $C_{2v}$  symmetry with the chromium atom having a pseudo-octahedral geometry. The Cr-P bond distances are the same: 2.346(3) Å and 2.346(3) Å for the Cr(1)-P(1) and Cr(1)-P(2), respectively. The Cr-P distances of two *cis*-chelating phosphines are shorter than those found in pentacarbonyl(triphenylphos-

**Table 1.** Summary of Structure Determination of Compound **2a**

Formula:	$\text{CrB}_{10}\text{C}_{30}\text{H}_{30}\text{O}_4\text{P}_2$
Formula Weight:	676.61
Crystal Class:	monoclinic
Space group:	$P2_1/n$ (#14)
Z:	4
Cell constants:	
a	12.2360(7) Å
b	17.156(1) Å
c	16.2040(6) Å
$\beta$	99.585(3) $^\circ$
V	3354.1(3) Å <sup>3</sup>
$\mu$	0.472 $\text{cm}^{-1}$
crystal size, mm	0.2 × 0.08 × 0.05
$D_{\text{calc}}$	1.340 $\text{g}/\text{cm}^3$
F(000)	1384.00
Radiation:	Mo-K $\alpha$ ( $\lambda=0.7170$ Å)
$\Theta$ range	2.0–24.72 $^\circ$
h, k, l collected	+12, 18, +16
No. reflections measured:	21845
No. unique reflections:	5782
No. reflections used in refinement	2514 [ $F_o^2 > 3.0 \sigma(F_o^2)$ ]
No. parameters	464
Data/Parameter Ratio	5.4
$R_1$ :	0.066
$R_2$ :	0.071
GOF:	1.99

$$^a R_1 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; R_2 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

phine)chromium(0),  $\text{Cr}(\text{CO})_5(\text{PPh}_3)$  [2.422(4) Å].<sup>17</sup> The average Cr-CO distance, 1.86(1), is slightly shorter than the value displayed by  $\text{Cr}(\text{CO})_6$  [1.909(3) Å].<sup>18</sup> The average carbonyl C-O distance is 1.15(1) Å and this value is equal to that found in  $\text{Cr}(\text{CO})_5(\text{PPh}_3)$  [1.147 Å]. The geometries of two tertiary phosphine ligands are the same, with average C-P-C angle of  $103.0^\circ$  ( $103.0^\circ$  in the free  $\text{PPh}_3$ ).<sup>19</sup> The Cr(1)-P(1)-C(1) and Cr(1)-P(2)-C(2) angles are  $111.5(2)^\circ$  and  $110.8(2)^\circ$ , respectively. The average P-C distance is 1.858(8) Å, *i. e.*, close to that normally found for  $\text{PPh}_3$  as a ligand to transition metals (1.828 Å).<sup>20</sup> The set of atoms Cr(1), P(1), P(2), C(1), and C(2) forms well-defined metallacycle and displacements from the least-squares plane are as follows: Cr(1), -0.0088; P(1), 0.0181; P(2), 0.0209; C(1), -0.0848; C(2), -0.1737. The *bis*-diphenylphosphino-*o*-carborane unit contains two carbon framework atoms each of which are located on the edge at the C(1) and C(2) cage positions, respectively. The inter-cage boron-boron (1.72–1.82 Å) and boron-carbon (1.69–1.75 Å) distances are normal, and the carbon-carbon distance between the only adjacent carbons, C(1)-C(2) 1.69(1) Å, is also in the range previously observed in other *o*-carborane cage systems.<sup>7</sup> There are two exo-polyhedral diphenylphosphine groups substituted on both carbon C(1) and C(2). The P(1)-C(1) and P(2)-C(2) bond distances are found to be 1.906(8) Å and 1.901(8) Å, respectively. The remaining carbon-carbon distances (1.34–1.42 Å) on the phenyl groups of two diphenylphosphines appear normal.



**Figure 1.** ORTEP drawing of **2a** showing the atom-labeling scheme and 30% probability thermal ellipsoids.

**Table 2.** Refined Positional Parameters and B(eq) for Compound 2a

Atom	x	y	z	B(eq)
Cr1	0.4431(1)	0.19057(8)	0.05421(8)	3.12(3)
P1	0.4695(2)	0.2811(1)	0.1642(1)	2.75(5)
P2	0.6128(2)	0.2314(1)	0.0194(1)	2.62(5)
O1	0.4308(7)	0.0616(4)	-0.0713(4)	6.9(2)
O2	0.2125(6)	0.1506(5)	0.0793(5)	8.5(3)
O3	0.3260(6)	0.2897(4)	-0.0858(4)	5.7(2)
O4	0.5048(6)	0.0623(4)	0.1835(4)	6.0(2)
C1	0.5995(7)	0.3421(4)	0.1631(5)	2.9(2)
C2	0.6687(6)	0.3193(5)	0.0845(5)	2.7(2)
C14	0.3764(7)	0.2051(5)	0.2821(5)	3.7(2)
C15	0.3707(8)	0.1600(5)	0.3511(6)	3.8(2)
C16	0.4650(10)	0.1397(6)	0.4048(6)	4.7(3)
C17	0.5668(8)	0.1642(6)	0.3902(6)	4.8(3)
C18	0.5723(8)	0.2102(6)	0.3197(6)	4.5(3)
C19	0.3685(7)	0.3574(5)	0.1781(5)	3.2(2)
C20	0.2896(8)	0.3809(6)	0.1111(6)	4.4(3)
C21	0.2131(8)	0.4378(6)	0.1240(7)	5.6(3)
C22	0.2131(10)	0.4700(6)	0.2009(9)	6.1(3)
C23	0.2915(10)	0.4465(6)	0.2669(7)	5.4(3)
C24	0.3682(8)	0.3907(5)	0.2560(6)	4.2(3)
C25	0.7363(7)	0.1699(5)	0.0309(5)	3.0(2)
C26	0.7413(8)	0.1024(6)	0.0774(6)	4.5(3)
C27	0.8370(10)	0.0565(7)	0.0889(7)	6.3(3)
C28	0.9248(8)	0.0776(7)	0.0519(7)	5.3(3)
C29	0.9198(8)	0.1416(6)	0.0040(6)	4.7(3)
C30	0.8250(7)	0.1879(5)	-0.0092(5)	3.7(2)
C31	0.6006(6)	0.2603(5)	-0.0915(5)	2.6(2)
C32	0.6168(7)	0.2015(5)	-0.1474(5)	3.6(2)
C33	0.5968(7)	0.2161(6)	-0.2337(6)	4.2(3)
C34	0.5586(8)	0.2872(7)	-0.2639(6)	5.0(3)
C35	0.5396(8)	0.3454(6)	-0.2096(6)	4.8(3)
C36	0.5611(8)	0.3306(6)	-0.1229(5)	4.3(3)
C37	0.4371(8)	0.1117(6)	-0.0242(6)	4.1(3)
C38	0.3011(8)	0.1669(6)	0.0713(6)	4.5(3)
C39	0.3743(8)	0.2546(6)	-0.0309(6)	4.4(3)
C40	0.4882(8)	0.1128(6)	0.1357(6)	3.9(3)
B3	0.5840(9)	0.4018(6)	0.0761(7)	3.4(3)
B4	0.5997(9)	0.4414(6)	0.1778(6)	3.4(3)
B5	0.6860(9)	0.3789(6)	0.2468(7)	3.9(3)
B6	0.7244(8)	0.2982(6)	0.1856(6)	3.1(3)
B7	0.7217(9)	0.4025(6)	0.0479(7)	3.9(3)
B8	0.679(1)	0.4814(7)	0.1044(8)	4.5(3)
B9	0.7393(9)	0.4656(6)	0.2119(7)	4.0(3)
B10	0.818(1)	0.3768(7)	0.2176(8)	4.4(3)
B11	0.8049(10)	0.3414(6)	0.1135(7)	3.7(3)
B12	0.813(1)	0.4407(7)	0.1304(8)	4.7(3)

Cage hydrogen atoms were refined.  $B_{eq} = 8/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$ .

**Metal-Carbene Complexes Containing Bis-diphenyl phosphino-O-carboranyl Ligand (3).** The complexes **3** were prepared according to the reaction 2. Thus, anionic metal acyl complexes were prepared by the reaction of excess  $\text{CH}_3\text{Li}$  with **2** at  $-78^\circ\text{C}$ . Further reaction at room temperature produced the exclusive formation of metal acyl complexes.  $^{11}\text{B}$  NMR spectra taken at this point in-

**Table 3.** Selected Bond Distances (Å) in Compound 2a

Atom	Atom	Distance	Atom	Atom	Distance
CR1	P1	2.346(3)	CR1	P2	2.346(3)
CR1	C37	1.85(1)	CR1	C38	1.850(9)
CR1	C39	1.85(1)	CR1	C40	1.89(1)
P1	C1	1.906(8)	P1	C13	1.827(8)
P1	C19	1.841(8)	P2	C2	1.901(8)
P2	C25	1.827(9)	P2	C31	1.846(8)
O1	C37	1.14(1)	O2	C38	1.15(1)
O3	C39	1.15(1)	O4	C40	1.16(1)
C1	C2	1.69(1)			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

dicated that the starting material had been completely consumed and that metal acyl complexes were the sole product. The reaction was fast only requiring few hours at room temperature to reach completion. Subsequent methylation gave the neutral bis-diphenylphosphino-o-carboranyl metal-carbene complexes **3**. Concentration followed by flash column chromatographic separation of the resulting reaction mixture gave pure form of complexes **3**. Exact mass measurement supports the proposed composition of  $^{11}\text{B}_{10}^{12}\text{C}_{30}^{1}\text{H}_{30}^{31}\text{P}_2^{16}\text{O}_4$ .

**Table 4.** Selected Bond Angles ( $^\circ$ ) in Compound 2a

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
P1	CR1	P2	88.26(9)	C25	P2	C31	100.6(4)
P1	CR1	C37	172.5(3)	P1	C1	C2	113.8(5)
P1	CR1	C38	92.6(3)	P1	C1	B3	110.8(6)
P1	CR1	C39	99.2(3)	P1	C1	B4	121.7(6)
P1	CR1	C40	87.1(3)	P1	C1	B5	127.4(6)
P2	CR1	C37	89.4(3)	P1	C1	B6	118.7(6)
P2	CR1	C38	172.8(3)	C2	C1	B3	61.5(5)
P2	CR1	C39	87.4(3)	C2	C1	B4	110.1(6)
P2	CR1	C40	102.2(3)	C2	C1	B5	111.4(6)
C37	CR1	C38	90.6(4)	C2	C1	B6	60.6(5)
C37	CR1	C39	87.8(4)	B3	C1	B4	61.5(5)
C37	CR1	C40	86.4(4)	B3	C1	B5	113.6(7)
C38	CR1	C39	85.4(4)	B3	C1	B6	114.4(7)
C38	CR1	C40	85.0(4)	B4	C1	B5	62.3(6)
C39	CR1	C40	168.7(4)	B4	C1	B6	115.5(7)
CR1	P1	C1	111.5(2)	B5	C1	B6	64.6(6)
CR1	P1	C13	110.7(3)	P2	C2	C1	115.0(5)
CR1	P1	C19	123.7(3)	P2	C2	B3	116.5(6)
C1	P1	C13	109.2(4)	P2	C2	B6	114.4(6)
C1	P1	C19	100.9(4)	P2	C2	B7	126.2(5)
C13	P1	C19	99.7(4)	P2	C2	B11	125.2(6)
CR1	P2	C2	110.8(2)	C1	C2	B3	60.3(5)
CR1	P2	C25	123.6(3)	C1	C2	B6	59.7(5)
C2	P2	C25	100.7(4)	C1	C2	B11	109.4(6)
C2	P2	C31	106.8(4)	B3	C2	B6	112.5(6)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

$^{52}\text{Cr}$  for complex **3a**. The  $^{11}\text{B}$  spectra of **3a** are also consistent with the proposed cage skeleton, showing four overlapping doublets of relative intensities 2:2:4:2. The assignment of these resonances to the B(9, 12), B(8), B(10), B(4, 7), B(5, 11), B(3), and B(6) borons, respectively, is consistent with the assignments previously made by Todd for the spectrum of *closo*-3-Ph-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ .<sup>21</sup> The  $^1\text{H}$  NMR data are likewise in agreement with the proposed structure, confirming the presence of phenyl group (6.9-7.8 ppm) of  $\text{PPh}_2$  and one methyl (1.6 ppm) and one  $\text{OCH}_3$  (3.3 ppm) resonances for carbene substituents of **3a**. The  $^{13}\text{C}$  NMR spectrum contains carbene carbon resonance at 345 ppm. Similarly, the composition of **3b** and **3c** were established by both elemental analysis and mass spectral analysis. The 64.2 MHz  $^{11}\text{B}$  NMR spectra of **3b** and **3c** have similar features and support the structures proposed in reaction 2.  $^{11}\text{B}$  NMR spectra of **3b** and **3c** consist of a set of overlapping doublets of relative intensities 2:2:4:2. This compares favorably with the 2:1:1:2:2:1:1 pattern expected for complexes **3** possessing a single symmetry plane. The  $^1\text{H}$  NMR data are likewise in agreement with the proposed cage structure, confirming the presence of a phenyl of  $\text{PPh}_2$  group (6.9-7.8 ppm) at the cage 1,2-position. The  $^1\text{H}$  NMR spectra also confirm the presence of a methyl group showing a singlet at about 1.6 ppm and one methoxy resonances at about 3.3 ppm for a carbene group either at the molybdenum or tungsten metal of complex **3b** and **3c**. The  $^{13}\text{C}$  NMR spectra contain carbene carbon resonances for **3b** and **3c** at 336 and 349 ppm, respectively. The infrared spectra of **3** exhibited a B-H stretching absorption at about  $2570\text{ cm}^{-1}$  and three sharp strong C=O stretching absorption between 2020 and  $1900\text{ cm}^{-1}$ , indicative of a  $\text{M}(\text{CO})_3$  (M=Cr, Mo, W) derivatives possessing local  $\text{C}_s$  symmetry. The spectra are similar to those reported for  $\text{Et}_4\text{N}[\text{fac-Cl}(\text{isonitrile})_2\text{W}(\text{CO})_3]$ ,<sup>22</sup> confirming the structures and affirming that the complexes **3** have the *fac*-configuration.

From this analytical, NMR, and infrared data we propose the structure in reaction 2 for these complexes **3a-c**, where the carbene moiety and chelate *bis*-diphenylphosphino-*o*-carboranyl ligand occupying the equatorial plane are located *cis*-orientation to each other. The presence of a *o*-carborane group adjacent to the carbene carbon atom does not lead to significant change in the physical properties of the metal carbene complexes when these are compared with those of carbene complexes containing alkyl substituent. However, IR spectra show the effect of the *o*-carborane group in the complexes **3**. The substitution of chelate *bis*-diphenylphosphino-*o*-carboranyl ligand produces a small increase in carbonyl stretching frequencies from their values in other alkyl-substituted systems,<sup>13</sup> suggesting that ( $\text{d}\rightarrow\text{p}$ ) $\pi$  donation in the  $\text{M-C}(\text{sp}^2)$  bond increases in the same manner as ( $\text{d}\rightarrow\pi^*$ ) $\pi$  donation in the *M-trans*(CO) bond decreases.

In summary, we provide a synthetic route to the Group VI metal carbonyl complexes containing *bis*-diphenylphosphino-*o*-carborane **2** and the corresponding Fischer-type metal carbene complexes **3**. Further application of these, and related, chelate *bis*-diphenylphosphino-*o*-carboranyl ligand **1** to organometallic chemistry is being actively pursued.

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**Supplementary Material Available.** Tables of bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atoms; listings of observed and calculated structure factors. Supplementary materials are available from one of the authors (S. O. Kang) upon request.

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