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**Synthesis and Characterization of Air Stable  $\sigma$ -Bonded *ortho*-carborane Manganese Metal Complexes 1-[Mn(CO)<sub>5</sub>]-2-R-1,2-closo-( $\sigma$ -C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) and Their Conversion to the Stable *ortho*-carborane Substituted Fischer-type Carbene Complexes 1-[(CO)<sub>4</sub>Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-R-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (R=CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>)**

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The metal-carbon  $\sigma$ -bond cluster complexes 1-Mn(CO)<sub>5</sub>-2-R-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (R=CH<sub>3</sub> **Ia**, C<sub>6</sub>H<sub>5</sub> **Ib**) have been prepared in good yields from readily available carboranyl lithium complexes, 1-Li<sup>+</sup>-2-R-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub><sup>-</sup> (R=CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>), by direct reaction with (CO)<sub>5</sub>MnBr. These manganese metal complexes are rapidly converted to the corresponding manganese metal carbene complexes, 1-[(CO)<sub>4</sub>Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-R-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (R=CH<sub>3</sub> **IIIa**, C<sub>6</sub>H<sub>5</sub> **IIIb**), via alkylation with methyllithium followed by O-methylation with CF<sub>3</sub>SO<sub>3</sub>CH<sub>3</sub>. The crystal structure of **IIIb** was determined by X-ray diffraction. Thus, complex **IIIb** crystallizes in the orthorhombic space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with cell parameters a=15.5537(5), b=19.0697(5), c=7.4286(3) Å, V=2203.4(1) Å<sup>3</sup>, and Z=4. Of the reflections measured a total of 3805 unique reflections with F<sup>2</sup>>3 $\sigma$ (F<sup>2</sup>) was used during subsequent structure refinement. Refinement converged to R<sub>1</sub>=0.053 and R<sub>2</sub>=0.091. Structural studies showed that the manganese atom had a slightly distorted pseudo-octahedral configuration about the metal center with the carbene and *ortho*-carborane occupying the equatorial plane *cis*-orientation to each other.

## Introduction

A series of extremely stable anionic chelated *ortho*-carborane-transition metal complexes containing unusually stable carbon-metal  $\sigma$ -bonds has been reported.<sup>1-5</sup> Previous study<sup>5</sup> indicated that an extensive series of stable neutral manganese(I) carborane complexes incorporating the 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub><sup>-</sup>, 1,10-C<sub>2</sub>B<sub>8</sub>H<sub>9</sub><sup>-</sup>, and 1,10-C<sub>2</sub>B<sub>8</sub>H<sub>8</sub><sup>2-</sup> ligands through metal-carbon  $\sigma$ -bonds could be prepared. We now wish to report a compilation of results obtained on carborane 1-R-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> containing manganese(I)-carbon  $\sigma$  bonds and further conversion to a corresponding metal carbene species.

Thus, metal carbene complexes in which a carboranyl group is directly attached to the manganese metal in a  $\sigma$ -bonded fashion adjacent to the metal carbene moiety 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>6</sup> of carboranyl metal carbene system in which metal and carborane are separated by one atom, have shown that some metal-carborane interaction occurs in such compounds.

In this paper we wish to report on progress made towards the syntheses of  $\sigma$ -bonded *ortho*-carborane manganese metal complexes and the formation of new manganese carbene complexes is discussed. Due to our interest in the structural features of manganese carbene complexes a single crystal X-ray diffraction determination of 1-[(CO)<sub>4</sub>Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIIb** was carried out.

## Experimental Section

**Methods and Materials.** The majority of solvents were of reagent grade and were used without further purification.

Ethyl ether and THF were purified by distillation from lithium aluminum hydride, while 1,2-dimethoxyethane was further purified by distillation from sodium-benzophenone.  $1\text{-Li}^+-2\text{-CH}_3\text{-1,2-C}_2\text{B}_{10}\text{H}_{10}^-$ ,  $1\text{-Li}^+-2\text{-C}_6\text{H}_5\text{-1,2-C}_2\text{B}_{10}\text{H}_{10}^-$ ,<sup>7,8</sup> and  $\text{Mn}(\text{CO})_5\text{Br}$ <sup>9</sup> were prepared by literature methods. All reactions involving lithiocarboranes were carried out under nitrogen atmosphere. Silica gel was obtained from J.T. Baker Co. and was dried before use.

**Physical Measurements.**  $^1\text{H}$  NMR spectra at 200 MHz and  $^{11}\text{B}$  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  $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$  (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%  $\text{C}_6\text{D}_6$ ) and then referenced to  $\text{Me}_4\text{Si}$  (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 Schwazkopf Laboratories, Woodside, NY.

**Crystallographic Data for  $1\text{-}[(\text{CO})_4\text{Mn}=\text{C}(\text{OCH}_3)(\text{CH}_3)]\text{-2-C}_6\text{H}_5\text{-1,2-C}_2\text{B}_{10}\text{H}_{10}$  IIIb.** Single crystals of IIIb were grown by slow evaporation inside a tube. A suitably sized crystal was placed inside a capillary tube, which was then sealed with glue. This tube 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  $\text{Mo-K}\alpha$  radiation ( $\lambda=0.7107 \text{ \AA}$ ). X-ray data were processed, and the structure was solved and refined using the Molecular Structure Coporation teXan<sup>10</sup> package on a Silicon Graphics Indigo R4000 computer. A total of 16251 reflections was measured over the range:  $4 < 2\theta < 54^\circ$ ,  $-19 < h < 19$ ,  $-24 < k < 24$ ,  $-9 < l < 9$ .

The intensity data were corrected for Lorentz and polarization effects but not for absorption. Of the reflections measured a total of 3805 unique reflections with  $F^2 > 3\sigma(F^2)$  was used during subsequent structure refinement.

The structure was solved by direct method (SIR88<sup>11</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 and hydrogen atoms were included as constant contributions to the structure factors and were not refined. Refinement converged to  $R_1 = 0.053$  and  $R_2 = 0.091$ . Figure 1 is an ORTEP<sup>12</sup> representation of the molecule with 30% probability thermal ellipsoids displayed.

#### General Methods for Obtaining $\sigma$ -Bonded Manganese(I)-Carborane Metal-Carbene Complexes $1\text{-}[(\text{CO})_5\text{Mn-2-R-1,2-closo-C}_2\text{B}_{10}\text{H}_{10}]$ I

**$1\text{-}[(\text{CO})_5\text{Mn}]\text{-2-CH}_3\text{-1,2-closo-}(\sigma\text{-C}_2\text{B}_{10}\text{H}_{10})$  Ia.** Under nitrogen, 6 mmol of solution of  $1\text{-Li}^+-2\text{-R-1,2-C}_2\text{B}_{10}\text{H}_{10}^-$  in 100 mL of anhydrous ethyl ether was slowly added to a

stirred suspension of 1.65 g (6 mmol) of  $\text{Mn}(\text{CO})_5\text{Br}$  in 150 mL of anhydrous ethyl ether. After stirring for 2 day at room temperature, the reaction mixture was rotary evaporated to give a brown oil. The oil was mixed with 50 mL of dry hexane and the resulting mixture was placed atop a 1 in.  $\times$  12 in. column in hexane and was flash-chromatographed with 1 : 9 ethyl 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 1.58 g (4.5 mmol, 75%) of bright yellow complex Ia.  $^{11}\text{B}$  NMR (64.2 MHz, ppm,  $\text{C}_6\text{D}_6$ );  $-1.0$  (d,  $\text{B}_9$ ,  $J_{\text{BH}} = 140 \text{ Hz}$ ),  $-4.3$  (d,  $\text{B}_{12}$ ,  $J_{\text{BH}} = 130 \text{ Hz}$ ),  $-6.3$  (d,  $\text{B}_{8,10}$ ,  $\text{B}_{4,5}$ ,  $J_{\text{BH}} = 105 \text{ Hz}$ ),  $-7.8$  (d,  $\text{B}_{7,11}$ ,  $\text{B}_{3,6}$ ,  $J_{\text{BH}} = 135 \text{ Hz}$ );  $^1\text{H}$  NMR (200.13 MHz, ppm,  $\text{C}_6\text{D}_6$ ) 1.53 (s,  $\text{CH}_3$ ); exact mass calcd for  $^{11}\text{B}_{10}^{12}\text{C}_8^{13}\text{H}_{13}^{55}\text{Mn}_1^{16}\text{O}_5$  354.1069, found 354.1288; Anal. Calcd: C, 27.28; H, 3.72. Found: C, 28.05; H, 4.67. Rf = 0.88 in Hexane; Mp = 85-87  $^\circ\text{C}$  (dec); IR spectrum (KBr pallet,  $\text{cm}^{-1}$ ) 2990w, 2600s, 2570s, 2550s, 2140s, 2050s, 2020s, 1455m, 1390w, 1200w, 1100m, 1045m, 1030w, 945w, 810w, 750m, 660s, 640s, 615m sh, 550w, 430m.

**$1\text{-}[(\text{CO})_5]\text{-2-C}_6\text{H}_5\text{-1,2-closo-}(\sigma\text{-C}_2\text{B}_{10}\text{H}_{10})$  Ib.** A solution of 6.45 mmol of  $1\text{-Li}^+-2\text{-C}_6\text{H}_5\text{-1,2-C}_2\text{B}_{10}\text{H}_{10}^-$  in 80 mL of anhydrous ethyl ether was slowly added in a nitrogen atmosphere to a rapidly stirred suspension of 1.76 g (6.4 mmol) of  $\text{Mn}(\text{CO})_5\text{Br}$  in 150 mL of anhydrous ethyl ether. After stirring for 2 day at room 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 hexane. An additional 100 mL of eluent was collected. Rotary evaporation of the eluent to 50 mL gave white crystalline needles of complex Ib. A total of 1.50 g (3.62 mmol, 57%) was collected. Rotary evaporation to dryness gave 0.30 g of a mixture of the product and  $\text{Mn}_2(\text{CO})_{10}$ . The white crystals were sublimed and recrystallized from hexane.  $^{11}\text{B}$  NMR (64.2 MHz, ppm,  $\text{C}_6\text{D}_6$ ); 0.5 (d,  $\text{B}_9$ ,  $J_{\text{BH}} = 130 \text{ Hz}$ ),  $-1.2$  (d,  $\text{B}_{12}$ ,  $J_{\text{BH}} = 160 \text{ Hz}$ ),  $-4.2$  (d,  $\text{B}_{8,10}$ ,  $J_{\text{BH}} = 100 \text{ Hz}$ ),  $-5.3$  (d,  $\text{B}_{4,5}$ ,  $J_{\text{BH}} = 140 \text{ Hz}$ ),  $-7.8$  (d,  $\text{B}_{7,11}$ ,  $J_{\text{BH}} = 145 \text{ Hz}$ ),  $-9.4$  (d,  $\text{B}_{3,6}$ ,  $J_{\text{BH}} = 140 \text{ Hz}$ );  $^1\text{H}$  NMR (200.13 MHz, ppm,  $\text{C}_6\text{D}_6$ ) 7.7 (d,  $\text{C}_6\text{H}_5$ ), 7.4 (m,  $\text{C}_6\text{H}_5$ ); exact mass calcd for  $^{11}\text{B}_{10}^{12}\text{C}_{13}^{55}\text{Mn}_1^{1}\text{H}_{15}^{16}\text{O}_5$  416.1225, found 412.2099; Anal. Calcd: C, 37.69; H, 3.65. Found: C, 39.18; H, 4.49. Rf = 0.70 in Benzene : Hexane (1 : 2); Mp = 88-90  $^\circ\text{C}$  (dec); IR spectrum (KBr pallet,  $\text{cm}^{-1}$ ) 3090w, 3060w, 3040w, 2580s, 2130s, 2030s, 2000s, 1495m, 1445m, 1075m, 1010w, 930w, 890w, 820w, 760w, 730w, 690m, 640s, 560w, 490w, 430w.

#### General Methods for Obtaining $\sigma$ -Bonded Manganese(I)-Carborane Metal-Carbene Complexes $1\text{-}[(\text{CO})_4\text{Mn}=\text{C}(\text{OCH}_3)(\text{CH}_3)]\text{-2-R-1,2-closo-C}_2\text{B}_{10}\text{H}_{10}$ III

**$1\text{-}[(\text{CO})_4\text{Mn}=\text{C}(\text{OCH}_3)(\text{CH}_3)]\text{-2-CH}_3\text{-1,2-closo-C}_2\text{B}_{10}\text{H}_{10}$  IIIa.**  $1\text{-}[(\text{CO})_4\text{Mn}(\text{O}^-\text{Li}^+)(\text{CH}_3)]\text{-2-CH}_3\text{-1,2-C}_2\text{B}_{10}\text{H}_{10}$  IIIa 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 Ia (0.352 g, 1 mmol) in tetrahydrofuran ( $\sim 25 \text{ mL}$ ) at  $\sim -78 \text{ }^\circ\text{C}$ . The reaction mixture was then allowed to react at  $0 \text{ }^\circ\text{C}$  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

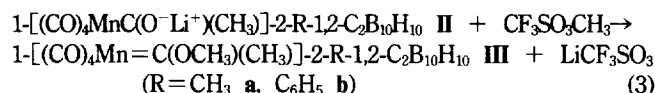
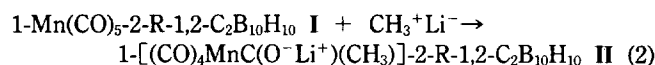
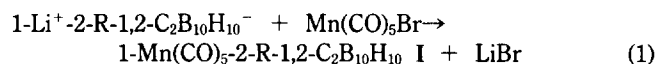
point confirmed the exclusive formation of the complex **IIa**. Methylation with  $\text{CF}_3\text{SO}_3\text{CH}_3$  followed by extraction with hexane gave slightly air-sensitive yellow solid. Subsequent separation was performed on the flash column with hexane to give 0.18 g (0.471 mmol) of  $1-[(\text{CO})_4\text{Mn}=\text{C}(\text{OCH}_3)(\text{CH}_3)]-2-\text{CH}_3-1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10}$  **IIIa**. This corresponds to a 47% yield based on consumed complex **Ia**.  $^{11}\text{B}$  NMR (64.2 MHz, ppm,  $\text{C}_6\text{D}_6$ );  $-1.8$  (d,  $\text{B}_9$ ,  $J_{\text{BH}}=140$  Hz),  $-5.0$  (d,  $\text{B}_{12}$ ,  $J_{\text{BH}}=145$  Hz),  $-6.8$  (d,  $\text{B}_{8,10}$ ,  $\text{B}_{4,5}$ ,  $J_{\text{BH}}=135$  Hz),  $-7.4$  (d,  $\text{B}_{7,11}$ ,  $\text{B}_{3,6}$ ,  $J_{\text{BH}}=100$  Hz);  $^1\text{H}$  NMR (200.13 MHz, ppm,  $\text{C}_6\text{D}_6$ ) 2.90 (s, 3,  $\text{OCH}_3$ ), 2.00 (s, 3,  $\text{CH}_3$ ), 1.88 (s, 3,  $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.3 MHz, ppm,  $\text{C}_6\text{D}_6$ ) 345 (s,  $\text{Mn}=\text{C}$ ), 211 (s, CO), 64.5 (s,  $\text{OCH}_3$ ), 40 (s,  $\text{CH}_3$ ), 28 (s,  $\text{CH}_3$ ); exact mass calcd for  $^{11}\text{B}_{10}^{12}\text{C}_{10}^{13}\text{H}_{19}^{55}\text{Mn}_1^{16}\text{O}_5$  384.1537, found 384.3001; Anal. Calcd: C, 31.42; H, 5.01. Found: C, 32.05; H, 6.62. Rf=0.70 in Benzene; Mp=74-76 °C (dec); IR spectrum (KBr pallet,  $\text{cm}^{-1}$ ) 2960w, 2610s, 2580s, 2550s, 2530s, 2520s, 2080s, 2010s, 1980s, 1460m, 1440w, 1390w, 1300s, 1180m, 1120m, 1090w, 1050w, 1030w, 1000m, 950w, 810w, 740w, 660s, 650s, 470m, 430w.

**1-[(CO)<sub>4</sub>Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIIb**.**  $1-[(\text{CO})_4\text{Mn}(\text{O}^-\text{Li}^+)(\text{CH}_3)]-2-\text{C}_6\text{H}_5-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}$  **IIb** 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 **Ib** (0.414 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 **IIb**. 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 0.25 g (0.56 mmol) of  $1-[(\text{CO})_4\text{Mn}=\text{C}(\text{OCH}_3)(\text{CH}_3)]-2-\text{C}_6\text{H}_5-1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10}$  **IIIb**. This corresponds to a 56% yield based on consumed complex **Ib**.  $^{11}\text{B}$  NMR (64.2 MHz, ppm,  $\text{C}_6\text{D}_6$ );  $-2.1$  (d,  $\text{B}_9$ ,  $J_{\text{BH}}=100$  Hz),  $-3.4$  (d,  $\text{B}_{12}$ ,  $J_{\text{BH}}=150$  Hz),  $-6.2$  (d,  $\text{B}_{8,10}$ ,  $J_{\text{BH}}=100$  Hz),  $-7.4$  (d,  $\text{B}_{4,5}$ ,  $\text{B}_{7,11}$ ,  $J_{\text{BH}}=140$  Hz),  $-9.6$  (d,  $\text{B}_{3,6}$ ,  $J_{\text{BH}}=160$  Hz);  $^1\text{H}$  NMR (200.13 MHz, ppm,  $\text{C}_6\text{D}_6$ ) 7.69 (d, 2,  $\text{C}_6\text{H}_5$ ), 7.35 (m, 3,  $\text{C}_6\text{H}_5$ ), 4.42 (s, 3,  $\text{OCH}_3$ ), 2.94 (s, 3,  $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.3 MHz, ppm,  $\text{C}_6\text{D}_6$ ) 349 (s,  $\text{Mn}=\text{C}$ ), 212 (s, CO), 132, 130, 120 (s,  $\text{C}_6\text{H}_5$ ), 65.8 (s,  $\text{OCH}_3$ ), 40 (s,  $\text{CH}_3$ ); exact mass calcd for  $^{11}\text{B}_{10}^{12}\text{C}_{15}^{13}\text{H}_{21}^{55}\text{Mn}_1^{16}\text{O}_5$  446.1693, found 446.1727; Anal. Calcd: C, 40.54; H, 4.76. Found: C, 40.05; H, 4.62. Rf=0.76 in Benzene; Mp=127-128 °C (dec); IR spectrum (KBr pallet,  $\text{cm}^{-1}$ ) 3070w, 3040w, 2960w, 2930w, 2600s, 2570s, 2550s, 2080s, 2010s, 1980s, 1500w, 1450m, 1350w, 1300s, 1180m, 1100m, 1070m, 1050w, 1000w, 990m, 950w, 890w, 820w, 770w, 750w, 700m, 650s, 640s, 630s, 470m, 450w, 420w.

## Results and Discussion

We have found that the addition of *ortho*-carborane lithium reagent  $1\text{-Li}^+-2\text{-R-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}^-$  to  $\text{Mn}(\text{CO})_5\text{Br}$  proceeds in good yield to give a stable neutral derivative  $1\text{-Mn}(\text{CO})_5\text{-}2\text{-R-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$  **I** containing a metal-carbon  $\sigma$ -bond. Subsequent reaction of complex **I** with 1 mol equivalent of methyl lithium gives rise to a corresponding metal acyl complex  $1-[(\text{CO})_4\text{Mn}(\text{O}^-\text{Li}^+)(\text{CH}_3)]-2\text{-R-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$  **II**. Further methylation of complex **II** with  $\text{CF}_3\text{SO}_3\text{CH}_3$  produces com-

pound  $1-[(\text{CO})_4\text{Mn}=\text{C}(\text{OCH}_3)(\text{CH}_3)]-2\text{-R-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$  **III** as shown in equation 1, 2, and 3.

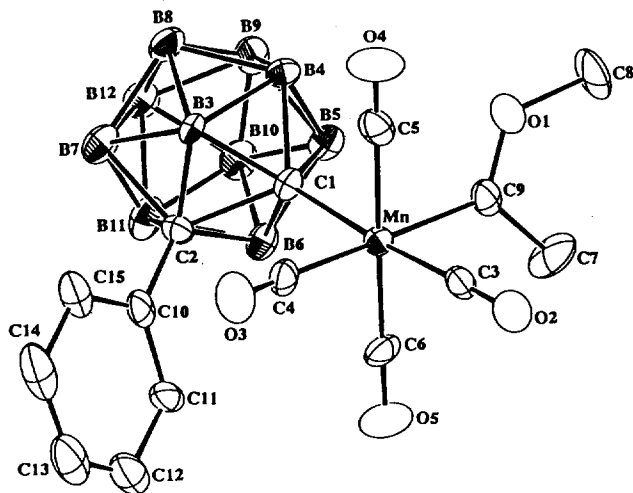


Each of the metal carbene complexes was prepared by adaptations of the general methods<sup>13</sup> currently available. The *ortho*-carboranyl carbene complexes of manganese are all moderately air stable crystalline solids which are readily soluble in all non-polar solvents (hexane, benzene) and sparingly soluble in polar solvents (ether, acetone). All of these complexes are photo-sensitive but are thermally stable above its melting point.

### $\sigma$ -Bonded Manganese(I)-Carborane Complexes 1-(CO)<sub>5</sub>Mn-2-R-1,2-closo-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (R=CH<sub>3</sub> **Ia**, C<sub>6</sub>H<sub>5</sub> **Ib**).

When a solution of  $1\text{-Li}^+-2\text{-R-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}^-$  in diethyl ether was treated with a suspension of  $\text{Mn}(\text{CO})_5\text{Br}$  in diethyl ether for 2 day, a dark solution formed. Elution of the product from a column with hexane/ethyl ether afforded white diamagnetic  $1\text{-[Mn}(\text{CO})_5\text{]-}2\text{-CH}_3\text{-}1,2\text{-closo-(}\sigma\text{-C}_2\text{B}_{10}\text{H}_{10}\text{)}$  **Ia** in ~75% yield. Compound **Ia** was first prepared *via* the same synthetic method outlined in equation 1 in 57% yields by Hawthorne *et al.*<sup>3</sup> Here, we found that **Ia** can be obtained in better yield by prolonged reaction time (2 day). The mass spectral parent ion peak was observed at  $m/e$  354.1288, corresponding to  $^{11}\text{B}_{10}^{12}\text{C}_8^{13}\text{H}_{13}^{55}\text{Mn}_1^{16}\text{O}_5^+$ . Elemental analysis also supported this formula. The infrared spectrum exhibited a strong B-H stretching absorption at  $2550\text{ cm}^{-1}$  and three sharp strong C=O stretching absorption at 2140, 2050, and  $2020\text{ cm}^{-1}$ , indicative of a  $\text{Mn}(\text{CO})_5$  derivatives possessing local  $\text{C}_{4v}$  symmetry.<sup>14</sup> No sharp carborane C-H stretching absorption around  $3060\text{ cm}^{-1}$  was observed, indicating the product to be a C(1)-substituted derivative. The 200 MHz  $^1\text{H}$  NMR spectrum consisted of a sharp resonance at 1.53 ppm, which was assigned to the methyl protons of a  $2\text{-CH}_3\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$  group by comparison with other 2-methylated-1,2-carborane derivatives.<sup>15</sup> The 64.2 MHz  $^{11}\text{B}$  NMR spectrum (Table 1) consisted of a set of overlapping doublets of relative intensities 1 : 1 : 4 : 4. This compares favorably with the 1 : 1 : 2 : 2 : 2 : 2 pattern expected for a  $1\text{-R-}2\text{-R}'\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$  derivative possessing a single symmetry plane. From this analytical, infrared, and nmr data we proposed the structure in Scheme 1 for this complex, where the metal ion is joined to the icosahedron through a Mn-C(1)  $\sigma$  bond.

Similarly, when a solution of  $1\text{-Li}^+-2\text{-C}_6\text{H}_5\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}^-$  in ethyl ether was treated with a suspension of  $\text{Mn}(\text{CO})_5\text{Br}$  in ethyl ether for 2 days, a dark solution formed. Elution of the product from a column with hexane afforded white diamagnetic  $1\text{-[Mn}(\text{CO})_5\text{]-}2\text{-C}_6\text{H}_5\text{-}1,2\text{-closo-(}\sigma\text{-C}_2\text{B}_{10}\text{H}_{10}\text{)}$  **Ib** in ~57% yield. The mass spectral parent ion peak was observed at  $m/e$  412.2099, corresponding to  $^{11}\text{B}_{10}^{12}\text{C}_{13}^{55}\text{Mn}_1^{16}\text{H}_{15}^{16}\text{O}_5^+$ . Elemental analysis also supported this formula. The infrared spectrum exhibited a strong B-H stretching absorption at  $2580\text{ cm}^{-1}$  and three sharp strong C=O stretching absorp-



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

tion at 2130, 2030, and 2000  $\text{cm}^{-1}$ , indicative of a  $\text{Mn}(\text{CO})_5$  derivatives possessing local  $C_{4v}$  symmetry. No sharp carborane C-H stretching absorption around 3060  $\text{cm}^{-1}$  was observed, indicating the product to be a C(1)-substituted derivative. The 200 MHz  $^1\text{H}$  NMR spectrum consisted of two sets of resonances at 7.7 and 7.4 ppm, which were assigned to the phenyl protons of a 2- $\text{C}_6\text{H}_5$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  group. The 64.2 MHz  $^{11}\text{B}$  NMR spectrum consisted of a set of overlapping doublets of relative intensities 1:1:2:2:2:2. This compares favorably with the 1:1:2:2:2:2 pattern expected for a 1-R-2-R'-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  derivative possessing a single symmetry plane. From this analytical, infrared, and nmr data we proposed the structure in Figure 1 for this complex, where the metal ion is joined to the icosahedron through a Mn-C(1)  $\sigma$  bond.

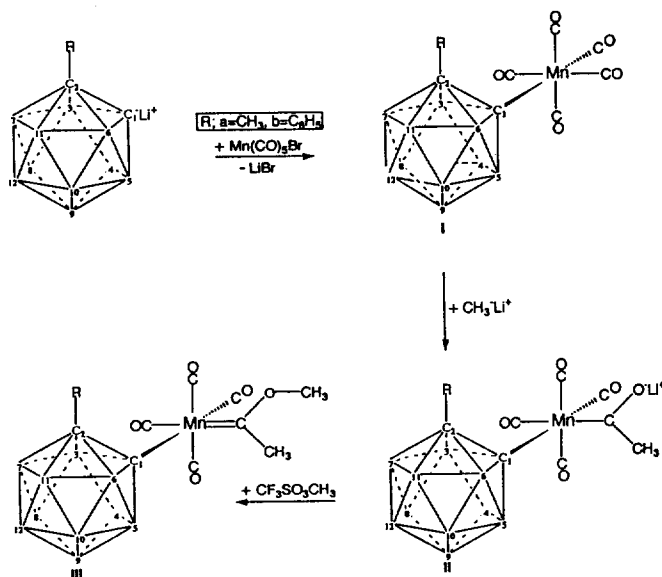
**$\sigma$ -Bonded Manganese(III)-Carborane Metal-Carbene Complexes 1-[(CO) $_4$ Mn=C(OCH $_3$ )(CH $_3$ )]-2-R-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (R=CH $_3$  **IIIa**,  $\text{C}_6\text{H}_5$  **IIIb**).** The complex 1-[(CO) $_4$ Mn=C(OCH $_3$ )(CH $_3$ )]-2-CH $_3$ -1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$  **IIIa** was prepared according to the equations 2 and 3. Thus, 1-[(CO) $_4$ Mn(CO $^-$ Li $^+$ )(CH $_3$ )]-2-CH $_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  **IIa** was prepared by the reaction of excess  $\text{CH}_3\text{Li}$  with 1-[Mn(CO) $_5$ ]-2-CH $_3$ -1,2-closo-( $\sigma$ - $\text{C}_2\text{B}_{10}\text{H}_{10}$ ) **Ia** at  $\sim -78^\circ\text{C}$ . Further reaction at room temperature produced the exclusive formation of compound **IIa**.  $^{11}\text{B}$  NMR spectra taken at this point indicated that the starting material had been completely consumed and that 1-[(CO) $_4$ Mn(CO $^-$ Li $^+$ )(CH $_3$ )]-2-CH $_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  **IIa** was the sole product. The reaction was fast only requiring few hours at room temperature to reach completion. Subsequent methylation gave the neutral carborane metal-carbene complexes, 1-[(CO) $_4$ Mn=C(OCH $_3$ )(CH $_3$ )]-2-CH $_3$ -closo-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  **IIIa** in good yield. Concentration followed by flash column chromatographic separation of the resulting reaction mixture gave 1-[(CO) $_4$ Mn=C(OCH $_3$ )(CH $_3$ )]-2-CH $_3$ -1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$  **IIIa**.

Exact mass measurement supports the proposed composition of 1-[(CO) $_4$ Mn=C(OCH $_3$ )(CH $_3$ )]-2-CH $_3$ -1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$  **IIIa**. The  $^{11}\text{B}$  spectra of **IIIa** (Table 1) are also consistent with the proposed cage skeleton, showing four overlapping doublets of relative intensities 1:1:4:4. The assignment

**Table 1.**  $^{11}\text{B}$  NMR Data

Compd	$\delta$ , ppm (J, assignment)
1-Mn(CO) $_5$ -2-CH $_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ <b>Ia</b> <sup>a,b,c</sup>	-1.0 (d, B $_9$ , $J_{\text{BH}}=140$ Hz), -4.3 (d, B $_{12}$ , $J_{\text{BH}}=130$ Hz), -6.3 (d, B $_{8,10}$ , B $_{4,5}$ , $J_{\text{BH}}=105$ Hz), -7.8 (d, B $_{7,11}$ , B $_{3,6}$ , $J_{\text{BH}}=135$ Hz)
1-Mn(CO) $_5$ -2- $\text{C}_6\text{H}_5$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ <b>Ib</b> <sup>a,b,c</sup>	0.5 (d, B $_9$ , $J_{\text{BH}}=130$ Hz), -1.2 (d, B $_{12}$ , $J_{\text{BH}}=160$ Hz), -4.2 (d, B $_{8,10}$ , $J_{\text{BH}}=100$ Hz), -5.3 (d, B $_{4,5}$ , $J_{\text{BH}}=140$ Hz), -7.8 (d, B $_{7,11}$ , $J_{\text{BH}}=145$ Hz), -9.4 (d, B $_{3,6}$ , $J_{\text{BH}}=140$ Hz)
1-[(CO) $_4$ Mn=C(OCH $_3$ )(CH $_3$ )]-2-CH $_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ <b>IIIa</b> <sup>a,b,c</sup>	-1.8 (d, B $_9$ , $J_{\text{BH}}=140$ Hz), -5.0 (d, B $_{12}$ , $J_{\text{BH}}=145$ Hz), -6.8 (d, B $_{8,10}$ , B $_{4,5}$ , $J_{\text{BH}}=135$ Hz), -7.4 (d, B $_{7,11}$ , B $_{3,6}$ , $J_{\text{BH}}=100$ Hz)
1-[(CO) $_4$ Mn=C(OCH $_3$ )(CH $_3$ )]-2- $\text{C}_6\text{H}_5$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ <b>IIIb</b> <sup>a,b,c</sup>	-2.1 (d, B $_9$ , $J_{\text{BH}}=100$ Hz), -3.4 (d, B $_{12}$ , $J_{\text{BH}}=150$ Hz), -6.2 (d, B $_{8,10}$ , $J_{\text{BH}}=100$ Hz), -7.4 (d, B $_{4,5}$ , B $_{7,11}$ , $J_{\text{BH}}=140$ Hz), -9.6 (d, B $_{3,6}$ , $J_{\text{BH}}=160$ Hz)

<sup>a</sup>All complexes were run in  $\text{C}_6\text{D}_6$ . <sup>b</sup>Chemical shifts are relative to external  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)=0.00$  ppm. Positive sign indicates a downfield shifts. <sup>c</sup>All chemical shifts are measured from the proton-decoupled spectra; because of the heavy overlapping of peaks coupling constants are given only when a doublet is clearly defined.



**Scheme 1.** Proposed pathway for the formation of **III**.

of these resonances to the B $_9$ , B $_{12}$ , B $_8$ , 10, 4, 5, and B $_7$ , 11, 3, 6 borons, respectively, (as shown in Scheme 1) is consistent with the assignments previously made by Hawthorne<sup>3</sup>

**Table 1.** Summary of Structure Determination of Compound **IIIb**

Formula:	MnB <sub>10</sub> C <sub>15</sub> H <sub>21</sub> O <sub>5</sub>
Formula Weight:	444.37
Crystal Class:	orthorhombic
Space group:	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (# 19)
Z:	4
Cell constants:	
a	15.5537(5) Å
b	19.0697(5) Å
c	7.4286(3) Å
V	2203.4(1) Å <sup>3</sup>
μ	6.23 cm <sup>-1</sup>
crystal size, mm	0.45 × 0.15 × 0.10
D <sub>calc</sub>	1.339 g/cm <sup>3</sup>
F(000)	904.00
Radiation:	Mo-Kα (λ = 0.7170 Å)
Θ range	2.0–27.0°
h, k, l collected	+19, +24, +9
No. reflections measured:	16251
No. unique reflections:	4554
No. reflections used in refinement	3805 [F <sub>o</sub> <sup>2</sup> > 3.0 σ(F <sub>o</sub> <sup>2</sup> )]
No. parameters	280
Data/Parameter Ratio	13.59
°R <sub>1</sub> :	0.053
°R <sub>2</sub> :	0.091
GOF:	7.83

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

for the spectrum of **Ia**.

The <sup>1</sup>H NMR data are likewise in agreement with the proposed cage structure, confirming the presence of a methyl group (1.88 ppm) at the cage 2-position and one methyl (2.00 ppm) and one OCH<sub>3</sub> (2.90 ppm) resonances for carbene substituents of **IIIa**. The <sup>13</sup>C NMR spectrum contains carbene carbon resonance at 345 ppm.

Similarly, the complex 1-[(CO)<sub>4</sub>Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIIb** was prepared according to the equation 2 and 3. Complex 1-[(CO)<sub>4</sub>MnC(O<sup>-</sup>Li<sup>+</sup>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIb** was prepared by the reaction of excess CH<sub>3</sub>Li with 1-[Mn(CO)<sub>5</sub>]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-(σ-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) **Ib** at ~ -78 °C. Further reaction at room temperature produced the exclusive formation of compound **IIb**. <sup>11</sup>B NMR spectra taken at this point indicated that the starting material had been completely consumed and that complex **IIb** was the sole product. The reaction was fast only requiring few hours at room temperature to reach completion. Subsequent methylation gave the neutral carborane metal-carbene complexes, 1-[Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)(CO)<sub>4</sub>]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIIb** in good yield. Concentration followed by flash column chromatographic separation of the resulting reaction mixture gave 1-[(CO)<sub>4</sub>Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIIb**.

Exact mass measurement support the proposed composition of 1-[(CO)<sub>4</sub>Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIIb**. The <sup>11</sup>B spectrum of **IIIb** (Table 1) shows five resonances of relative intensity 1 : 1 : 2 : 4 : 2 with the intensity four appearing to result from the overlap of 2 resonances of inten-

**Table 2.** Refined Positional Parameters for Compound **IIIb**

Atom	x	y	z	Beq, Å <sup>2</sup>
Mn	0.14202(8)	0.12752(7)	0.0537(2)	2.73(5)
O1	0.1444(4)	0.2615(3)	0.2185(9)	4.2(3)
O2	0.3278(4)	0.1390(3)	-0.030(1)	5.3(4)
O3	0.1297(5)	0.0371(4)	-0.273(1)	6.1(5)
O4	0.1080(5)	0.2466(4)	-0.201(1)	6.2(5)
O5	0.1878(5)	0.0094(4)	0.295(1)	6.8(5)
C1	0.0077(5)	0.1241(5)	0.132(1)	2.8(4)
C2	-0.0592(5)	0.0508(4)	0.089(1)	3.0(4)
C3	0.2559(6)	0.1354(5)	-0.000(1)	3.4(4)
C4	0.1291(6)	0.0687(5)	-0.143(1)	3.8(5)
C5	0.1170(6)	0.2028(5)	-0.100(1)	3.6(5)
C6	0.1675(6)	0.0546(5)	0.205(2)	4.1(5)
C7	0.2128(8)	0.1836(7)	0.413(2)	6.9(8)
C8	0.1650(7)	0.3201(5)	0.339(2)	6.7(7)
C9	0.1653(6)	0.1979(5)	0.244(1)	3.4(5)
C10	-0.0248(6)	-0.0149(4)	0.006(1)	3.7(5)
C11	-0.0430(7)	-0.0299(5)	-0.171(2)	5.0(6)
C12	-0.0154(8)	-0.0918(7)	-0.252(2)	6.7(8)
C13	0.0326(8)	-0.1384(7)	-0.150(2)	7.7(9)
C14	0.0503(7)	-0.1256(6)	0.026(2)	6.5(7)
C15	0.0214(6)	-0.0638(5)	0.106(1)	4.4(5)
B3	-0.0317(7)	0.0727(6)	0.308(2)	3.5(2)
B4	-0.0325(7)	0.1642(6)	0.319(2)	3.4(5)
B5	-0.0554(7)	0.1958(5)	0.109(2)	3.4(5)
B6	-0.0682(6)	0.1242(5)	-0.038(2)	3.4(4)
B7	-0.1369(8)	0.0434(6)	0.250(2)	4.3(6)
B8	-0.1227(7)	0.1140(7)	0.395(2)	4.4(6)
B9	-0.1376(8)	0.1912(6)	0.272(2)	4.0(6)
B10	-0.1612(7)	0.1673(6)	0.046(2)	4.2(6)
B11	-0.1605(7)	0.0761(6)	0.034(2)	4.3(6)
B12	-0.2010(7)	0.1174(7)	0.228(2)	4.6(6)

Hydrogen atoms were not refined.  $B_{eq} = 8/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$ .

sity 2. The plane of symmetry indicated by the NMR data can only be consistent with substitution of the carborane at C1 and C2.

The <sup>1</sup>H and <sup>13</sup>C NMR data are likewise in agreement with the proposed cage structure and confirm the presence of a carbene C(OCH<sub>3</sub>)CH<sub>3</sub> group at the manganese metal. The <sup>1</sup>H NMR spectrum confirms the presence of a phenyl group showing a multiplets of intensity five at 7.69 ppm and one methoxy resonance at 4.42 ppm and one cage methyl resonance at 2.94 ppm. The room temperature proton-spin decoupled <sup>13</sup>C NMR spectrum shows five carbon resonances, corresponding to one carbene carbon (349 ppm), five carbonyl carbon (210 ppm), three phenyl carbon (130 ppm), one methoxy carbon (65 ppm), and one methyl carbon (40 ppm).

The spectroscopic data discussed above are similar to those of other *ortho*-carborane containing Fischer-type carbene complexes<sup>6</sup> recently synthesized in our group; 1-[(CO)<sub>5</sub>Cr=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-CH<sub>3</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, 1-[(CO)<sub>5</sub>Cr=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, 1-[(CO)<sub>5</sub>W=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, 1-[(CO)<sub>5</sub>W=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-CH<sub>3</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, and 1-[(CO)<sub>5</sub>W=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-CH<sub>3</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>.

**Table 1.** Summary of Structure Determination of Compound **IIIb**

Formula:	MnB <sub>10</sub> C <sub>15</sub> H <sub>21</sub> O <sub>5</sub>
Formula Weight:	444.37
Crystal Class:	orthorhombic
Space group:	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (# 19)
Z:	4
Cell constants:	
a	15.5537(5) Å
b	19.0697(5) Å
c	7.4286(3) Å
V	2203.4(1) Å <sup>3</sup>
μ	6.23 cm <sup>-1</sup>
crystal size, mm	0.45 × 0.15 × 0.10
D <sub>calc</sub>	1.339 g/cm <sup>3</sup>
F(000)	904.00
Radiation:	Mo-Kα (λ = 0.7170 Å)
Θ range	2.0–27.0°
h, k, l collected	+19, +24, +9
No. reflections measured:	16251
No. unique reflections:	4554
No. reflections used in refinement	3805 [F <sub>o</sub> <sup>2</sup> > 3.0 σ(F <sub>o</sub> <sup>2</sup> )]
No. parameters	280
Data/Parameter Ratio	13.59
°R <sub>1</sub> :	0.053
°R <sub>2</sub> :	0.091
GOF:	7.83

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

for the spectrum of **Ia**.

The <sup>1</sup>H NMR data are likewise in agreement with the proposed cage structure, confirming the presence of a methyl group (1.88 ppm) at the cage 2-position and one methyl (2.00 ppm) and one OCH<sub>3</sub> (2.90 ppm) resonances for carbene substituents of **IIIa**. The <sup>13</sup>C NMR spectrum contains carbene carbon resonance at 345 ppm.

Similarly, the complex 1-[(CO)<sub>4</sub>Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIIb** was prepared according to the equation 2 and 3. Complex 1-[(CO)<sub>4</sub>MnC(O<sup>-</sup>Li<sup>+</sup>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIb** was prepared by the reaction of excess CH<sub>3</sub>Li with 1-[Mn(CO)<sub>5</sub>]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-(σ-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) **Ib** at ~ -78 °C. Further reaction at room temperature produced the exclusive formation of compound **IIb**. <sup>11</sup>B NMR spectra taken at this point indicated that the starting material had been completely consumed and that complex **IIb** was the sole product. The reaction was fast only requiring few hours at room temperature to reach completion. Subsequent methylation gave the neutral carborane metal-carbene complexes, 1-[Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)(CO)<sub>4</sub>]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIIb** in good yield. Concentration followed by flash column chromatographic separation of the resulting reaction mixture gave 1-[(CO)<sub>4</sub>Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIIb**.

Exact mass measurement support the proposed composition of 1-[(CO)<sub>4</sub>Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIIb**. The <sup>11</sup>B spectrum of **IIIb** (Table 1) shows five resonances of relative intensity 1 : 1 : 2 : 4 : 2 with the intensity four appearing to result from the overlap of 2 resonances of inten-

**Table 2.** Refined Positional Parameters for Compound **IIIb**

Atom	x	y	z	Beq, Å <sup>2</sup>
Mn	0.14202(8)	0.12752(7)	0.0537(2)	2.73(5)
O1	0.1444(4)	0.2615(3)	0.2185(9)	4.2(3)
O2	0.3278(4)	0.1390(3)	-0.030(1)	5.3(4)
O3	0.1297(5)	0.0371(4)	-0.273(1)	6.1(5)
O4	0.1080(5)	0.2466(4)	-0.201(1)	6.2(5)
O5	0.1878(5)	0.0094(4)	0.295(1)	6.8(5)
C1	0.0077(5)	0.1241(5)	0.132(1)	2.8(4)
C2	-0.0592(5)	0.0508(4)	0.089(1)	3.0(4)
C3	0.2559(6)	0.1354(5)	-0.000(1)	3.4(4)
C4	0.1291(6)	0.0687(5)	-0.143(1)	3.8(5)
C5	0.1170(6)	0.2028(5)	-0.100(1)	3.6(5)
C6	0.1675(6)	0.0546(5)	0.205(2)	4.1(5)
C7	0.2128(8)	0.1836(7)	0.413(2)	6.9(8)
C8	0.1650(7)	0.3201(5)	0.339(2)	6.7(7)
C9	0.1653(6)	0.1979(5)	0.244(1)	3.4(5)
C10	-0.0248(6)	-0.0149(4)	0.006(1)	3.7(5)
C11	-0.0430(7)	-0.0299(5)	-0.171(2)	5.0(6)
C12	-0.0154(8)	-0.0918(7)	-0.252(2)	6.7(8)
C13	0.0326(8)	-0.1384(7)	-0.150(2)	7.7(9)
C14	0.0503(7)	-0.1256(6)	0.026(2)	6.5(7)
C15	0.0214(6)	-0.0638(5)	0.106(1)	4.4(5)
B3	-0.0317(7)	0.0727(6)	0.308(2)	3.5(2)
B4	-0.0325(7)	0.1642(6)	0.319(2)	3.4(5)
B5	-0.0554(7)	0.1958(5)	0.109(2)	3.4(5)
B6	-0.0682(6)	0.1242(5)	-0.038(2)	3.4(4)
B7	-0.1369(8)	0.0434(6)	0.250(2)	4.3(6)
B8	-0.1227(7)	0.1140(7)	0.395(2)	4.4(6)
B9	-0.1376(8)	0.1912(6)	0.272(2)	4.0(6)
B10	-0.1612(7)	0.1673(6)	0.046(2)	4.2(6)
B11	-0.1605(7)	0.0761(6)	0.034(2)	4.3(6)
B12	-0.2010(7)	0.1174(7)	0.228(2)	4.6(6)

Hydrogen atoms were not refined.  $B_{eq} = 8/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$ .

sity 2. The plane of symmetry indicated by the NMR data can only be consistent with substitution of the carborane at C1 and C2.

The <sup>1</sup>H and <sup>13</sup>C NMR data are likewise in agreement with the proposed cage structure and confirm the presence of a carbene C(OCH<sub>3</sub>)CH<sub>3</sub> group at the manganese metal. The <sup>1</sup>H NMR spectrum confirms the presence of a phenyl group showing a multiplets of intensity five at 7.69 ppm and one methoxy resonance at 4.42 ppm and one cage methyl resonance at 2.94 ppm. The room temperature proton-spin decoupled <sup>13</sup>C NMR spectrum shows five carbon resonances, corresponding to one carbene carbon (349 ppm), five carbonyl carbon (210 ppm), three phenyl carbon (130 ppm), one methoxy carbon (65 ppm), and one methyl carbon (40 ppm).

The spectroscopic data discussed above are similar to those of other *ortho*-carborane containing Fischer-type carbene complexes<sup>6</sup> recently synthesized in our group; 1-[(CO)<sub>5</sub>Cr=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-CH<sub>3</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, 1-[(CO)<sub>5</sub>Cr=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, 1-[(CO)<sub>5</sub>W=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-CH<sub>3</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, and 1-[(CO)<sub>5</sub>W=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-CH<sub>3</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>.

**Table 3.** Selected Bond Distances (Å) and Bond Angles (°) in Compound **IIIb**

Bond Distances			
Mn-C1	2.169(7)	Mn-C9	1.983(10)
Mn-C3	1.822(9)	Mn-C4	1.853(10)
Mn-C5	1.867(10)	Mn-C6	1.831(11)
O1-C9	1.270(10)	O1-C8	1.467(11)
O2-C3	1.142(9)	O3-C4	1.139(10)
O4-C5	1.128(11)	O5-C6	1.136(11)
C1-C2	1.771(11)	C9-C7	1.479(14)
C2-C10	1.496(12)		
Bond Angles			
C1-Mn-C9	90.4(3)	C1-Mn-C3	175.9(4)
C1-Mn-C4	95.0(4)	C1-Mn-C5	89.2(4)
C1-Mn-C6	91.3(4)	C9-Mn-C3	85.9(4)
C9-Mn-C4	172.7(4)	C9-Mn-C5	87.4(4)
C9-Mn-C6	92.1(4)	C3-Mn-C4	89.0(4)
C3-Mn-C5	90.3(4)	C3-Mn-C6	89.3(4)
C4-Mn-C5	87.7(4)	C4-Mn-C6	92.7(5)
C5-Mn-C6	179.3(5)	C9-O1-C8	125.4(9)
Mn-C1-C2	122.8(5)	Mn-C9-O1	119.5(8)
Mn-C9-C7	124.8(8)	O1-C9-C7	115.5(9)
Mn-C3-O2	178.0(9)	Mn-C4-O3	171.3(9)
Mn-C5-O4	174.2(9)	Mn-C6-O5	176.1(9)

(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>. Thus, they support the formation of **III** as a 12-vertex *ortho*-carborane containing Fischer-type carbene complexes.

**Description of X-ray Structure of 1-[(CO)<sub>4</sub>Mn=C(OCH<sub>3</sub>)(CH<sub>3</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> **IIIb**.** The conformation and atomic numbering scheme for **IIIb** are shown in Figure 1; selected bond lengths (Å) and angles (°) are listed in Table 3. The manganese atom has a slightly distorted pseudo octahedral configuration with the carbene and *ortho*-carborane occupying the equatorial sites. In this complex the carbene moiety is located in a *cis* arrangement about the Mn-C1 bond with respect to the two equatorial carbonyl and two axial carbonyl groups with C<sub>1</sub> symmetry. The phenyl group substituted to *ortho*-carborane is stretched further away from the carbene ligand. Thus, **IIIb** is (η<sup>1</sup>-*ortho*-carbonyl)(η<sup>1</sup>-methoxy methyl methylene)manganese tetracarbonyl.

Notable is the distortion caused by the metal, *ortho*-carborane and the substituents on the carbene carbon leading to deviations from ideal values for the sp<sup>2</sup>-hybridized carbene carbon atom. Therefore, angles around the carbene carbon decrease in the order Mn-C9-C7 > Mn-C9-O1 > O1-C9-C7 (values for **IIIb** are 124.8°, 119.5°, and 115.5° respectively). The carbene ligand is nearly planar (excluding the methyl substituents) with the metal atom deviating 0.034(1) Å from the mean plane.

The Mn-C9 bond (1.983 Å) could also be considered a double bond since it is shorter than a Mn-C σ-bond (2.16 Å)<sup>16</sup> and slightly longer than the Mn=C(carbene) bond (1.88 Å) in [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Mn(CO)]<sub>2</sub>[C(Ph)COPh].<sup>17</sup> We have found that in (CO)<sub>5</sub>CrC(OMe)Ph<sup>18</sup> complex the Cr-C(carbene) bond order is lower, because of the poor π-donation from (CO)<sub>5</sub>Cr. By

the same argument, the Mn-C(carbene) bond order also should be low in (C<sub>6</sub>H<sub>5</sub>-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)(CO)<sub>4</sub>Mn-carbene complexes. Both types of carbene complexes should exhibit similar chemical behavior. By means of its poor back-bonding ability, (C<sub>6</sub>H<sub>5</sub>-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)(CO)<sub>4</sub>Mn supplies insufficient electron density to the carbene carbon, and thus π-donating organic substituents at the carbene carbon are necessary for the stability of such complexes.

One structural consequence of the poor π-donating ability of the (C<sub>6</sub>H<sub>5</sub>-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)(CO)<sub>4</sub>Mn fragment is that in complex **IIIb** the C9-O1 distance (1.270(10) Å) is similar to that in alkoxycarbene complexes in which alkoxy groups serve as π-donating substituents. One can conclude from the C(carbene)-O bond length that in **IIIb** the methoxy group poorly, if at all, compete with the (C<sub>6</sub>H<sub>5</sub>-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)(CO)<sub>4</sub>Mn moiety for π-bonding with the carbene carbon. Thus, only if the π-donating ability of one organic substituent considerably exceeds that of the (C<sub>6</sub>H<sub>5</sub>-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)(CO)<sub>4</sub>Mn fragment is lengthening of the Mn-C(carbene) bond (*i.e.*, decrease in the Mn-C(carbene) bond order) observed (as in [Cp(CO)<sub>2</sub>Mn(C(O)Ph)]<sup>-</sup>,<sup>19</sup> 1.96(2) Å or in MeCp(CO)<sub>2</sub>Mn(C(OMe)C(Me)PMe<sub>3</sub>),<sup>20</sup> 1.99(1) Å). The contrary would be expected in Cp(CO)<sub>2</sub>Mn(C(X)Ph) complexes where X is OEt, Ph, C(O)Ph, or F. A structural consequence of the high π-bonding ability of the Cp(CO)<sub>2</sub>Mn fragment is the fact that the Mn-C bond length (1.865(14) Å for OEt,<sup>21</sup> 1.880(20) for C(O)Ph,<sup>17</sup> and 1.830(50) Å<sup>o</sup> for F<sup>22</sup>) is shorter than that in complex **IIIb** and is not significantly influenced by the nature of the organic substituents. Therefore, the Mn-C(carbene) distance in complex **IIIb** is in the upper part of the range of values generally observed and it is close to those found in other manganese carbene complexes.<sup>23</sup>

The *ortho*-carborane ligand contains two carbon framework atoms each of which are located on the edge at the C1 and C2 cage positions, respectively. The inter cage boron-boron (1.71-1.79 Å) and boron-carbon (1.69-1.73 Å) distances are normal, and the carbon-carbon distance between the only adjacent carbons, C1-C2 1.771(11) Å, is also in the range previously observed in other *ortho*-carborane cage systems. There is one exo-polyhedral phenyl group substituted on carbon C2. Consistent with this observation the C2-C10 bond distance is found to be 1.496(12) Å. The remaining carbon-carbon distances (1.36-1.39 Å) on the phenyl appears normal. In addition to being bound to the *ortho*-carborane cage the manganese is also bonded in a η<sup>1</sup>-fashion to four carbonyl groups, which show average bond distance of 1.845 Å.

One of the most significant aspects of the structure of **IIIb** concerns the disposition of the phenyl group substituted to the cage. In compound **IIIb** the cage carbon is phenyl substituted and as a result would be expected to have increased steric repulsions around the metal. However, this complex adopts a distorted pseudo-octahedral geometry, leading to the conclusion that although the steric repulsions between the various ligands may be present, the octahedral geometry is generally favored for the metal carbonyl carbene complexes. The presence of an *ortho*-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 organic moiety.

In summary, the result described above illustrates the po-

tential utility of *ortho*-carborane ligand for the synthesis of metal carbonyl carbene complexes. Further work concerned with the application of *ortho*-carborane ligand to the synthesis of other new types of metal carbonyl carbene complexes is currently underway in this laboratory.

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**Supplementary Material Available.** Tables of bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atom; 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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## On-Line Determination of $dn/dc$ for Size Exclusion Chromatography Coupled with a Light Scattering Detector

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The internal standard method, which is widely used in chromatographic techniques, is applied to the size exclusion chromatography for the on-line determination of  $dn/dc$  value of the sample. This method is found to provide the  $dn/dc$  value with suitable accuracy in determining the absolute molecular weight and the molecular weight distribution of the polymers when a light scattering detector is used.

### Introduction

Size exclusion chromatography (SEC) is perhaps the most frequently employed technique for the molecular weight de-

termination of macromolecules.<sup>1</sup> It utilizes the exclusion phenomenon of macromolecules from small pores when they pass through a series of columns packed with porous materials. Therefore the technique separates the macromolecules