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New Class of Fischer-Type Carbene Complexes Containing an *o*-Carboranyl Substituent. Synthesis and Crystal Structure of $(CO)_5W[C(OMe)(PhC_2B_{10}H_{10})]$ and $(CO)_4(PhC_2B_{10}H_{10})Mn[C(OCH_3)(CH_3)]$

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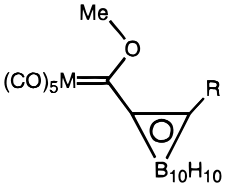
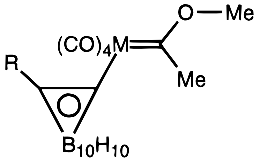
Treating lithio-*o*-carborane $RC_2B_{10}H_{10}Li$ (**3a**,**b** R = CH_3, C_6H_5) with metal carbonyl complexes $M(CO)_6$ (M = Cr, W) followed by quenching the reaction with the electrophilic reagent $[Me_3O]^+[BF_4]^-$ afforded the [(*o*-carboranyl)methoxycarbene]metal complexes $(CO)_5M[C(OMe)(RC_2B_{10}H_{10})]$ (**1a**−**d**) in yields ranging from 37 to 43%. Complexes **1a**−**d** were also formed on reaction of alkynylcarbene complexes $(CO)_5M[C(OCH_3)(C{\equiv}CR)]$ (**4a**−**d**: M = Cr, W; R = CH_3, C_6H_5) with $B_{10}H_{12}L_2$ (**5**; L = CH_3CN) in benzene in 47−63% isolated yield. The X-ray structure of complex **1d** indicates that the tungsten atom is octahedrally coordinated by (*o*-carboranyl)methoxycarbene and by five carbonyl groups. Also, the synthesis of carbene complexes of manganese, bearing an *o*-carboranyl ligand, has been studied. Complexes $(CO)_5Mn(RC_2B_{10}H_{10})$ (**6a**,**b**: R = CH_3, C_6H_5) easily react with CH_3Li to give, after methylation of the acyl anion, new (*o*-carboranyl)metal carbene complexes $(CO)_4(RC_2B_{10}H_{10})Mn[C(OCH_3)(CH_3)]$ (**2a**,**b**: R = CH_3, C_6H_5) in which the two functions are cis. X-ray analysis of this complex **2b** provides support for the assignment of the metal carbene structure to the *o*-carborane derivatives.

Introduction

Although "Fischer-type" carbene complexes have been extensively studied over the past 30 years,[1] many subclasses of these interesting compounds remain virtually unexplored. One such subclass, namely [(*o*-carboranyl)methoxycarbene]metal complexes, has received little attention. *o*-Carborane has attracted some interest due to its ease of preparation and derivatization, thermal stability, and steric bulk.[2] It was therefore of interest to investigate the possibility of synthesizing such Fischer carbene complexes using the $RC_2B_{10}H_{10}$ system ($RC_2B_{10}H_{10}$ = *o*-carborane). In this respect, we have started investigating the synthesis of Fischer carbene complexes bearing a bulky *o*-carborane unit that might potentially stabilize the desired metal carbene moiety. Thus, we now report the detailed synthesis and complete characterization of the [(*o*-carboranyl)methoxycarbene]metal complexes **1a**−**d**. Methods for preparing this type of compound **1** are generally based on (1) addition of a lithio-*o*-carborane to a metal carbonyl and (2) two-carbon insertion of an adequate (alkynylcarbene)metal fragment into a $B_{10}H_{12}L_2$ system (L = acetonitrile). This paper also reports the preparation of new (*o*-carboranyl)manganese carbene complexes **2a**,**b** by the nucleophilic reaction of methyllithium with the corresponding (*o*-carboranyl)manganese carbonyl complexes **6a**,**b**.



1



2

1a: M = Cr, R = CH_3
1b: M = Cr, R = C_6H_5
1c: M = W, R = CH_3
1d: M = W, R = C_6H_5

2a: M = Mn, R = CH_3
2b: M = Mn, R = C_6H_5

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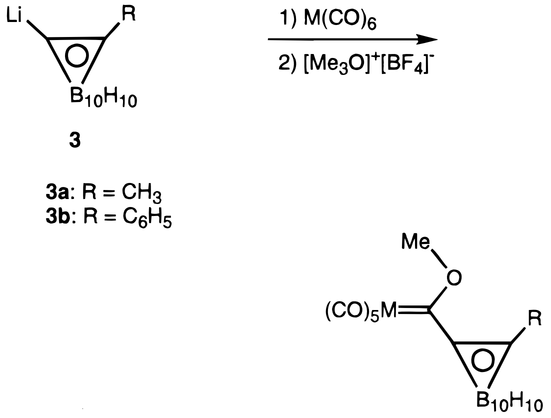
The synthesis, properties, and the structural studies of four novel [(*o*-carboranyl)methoxycarbene]metal complexes **1a**−**d** and new (*o*-carboranyl)manganese carbene complexes **2a**,**b** are reported in this paper.

Results and Discussion

$(CO)_5M[C(OMe)(RC_2B_{10}H_{10})]$ (1: M = Cr, W; R = CH_3, C_6H_6). Each of the [(*o*-carboranyl)methoxycarbene]metal complexes of type **1** (see reaction 1) was prepared by adaptation of the general methods currently available (see Experimental Section).



3

3a: R = CH_3
3b: R = C_6H_5

(1)

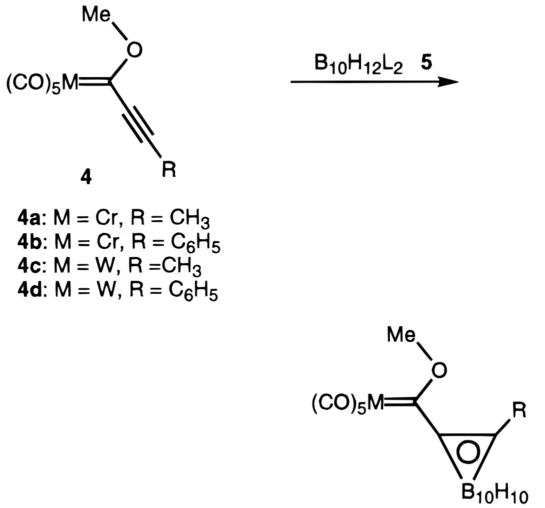
1

1a: M = Cr, R = CH_3
1b: M = Cr, R = C_6H_5
1c: M = W, R = CH_3
1d: M = W, R = C_6H_5

This one-pot procedure allows the preparation of a range of functionalized carbene complexes **1a**−**d** in satisfactory overall yields (37−43%) based on *o*-carborane complexes $RC_2B_{10}H_{11}$ (R = CH_3,[3] C_6H_5[4]). Although the process outlined in reaction 1 proved to be quite general, there were, however, structural limitations (i.e., substituents R = H) observed for the carbene complexes **1**. For example, several attempts to synthesize the parent [(*o*-carboranyl)methoxycarbene]metal complex from the respective anion $C_2B_{10}H_{11}^-$ were unsuccessful, yielding only the starting material. The recovery of reagents and thus the lack of reaction were considered the consequence of the disproportionation of monolithio-*o*-carborane, which leads to the undesired di-C-substituted product.[5] This problem was solved by blocking one of the C-positions in *o*-carborane with alkyl groups, effecting the desired reaction at another C site.[3]

Chromium and tungsten carbene complexes **1a**−**d** are all moderately air-stable crystalline solids. They are readily soluble in nonpolar solvents (hexane, benzene) and sparingly soluble in polar solvents (ether, acetone). All of these complexes are photosensitive, but they show significant thermal stability in the temperature range 25−80 °C. It was also observed that the complexes **1a**−**d** exhibited the following thermal stability trends: M = W, R = C_6H_5 (**1d**) > M = W, R = CH_3 (**1c**) > M = Cr, R = C_6H_5 (**1b**) > M = Cr, R = CH_3 (**1a**). This observation is consistent with similar findings for general Fischer carbene complexes.[6] Moreover, all the [(*o*-carboranyl)methoxycarbene]metal complexes **1a**−**d** exhibited greater thermal stability than their alkyl counterparts (i.e. R = CH_3, C_6H_5). To the best of our knowledge, this is the first example in which *o*-carborane is coordinated with a group VI metal carbonyl carbene unit, thus improving the stability of the carbene bond. Prior to our synthesis of complexes **1a**−**d**, the only report of related [(*o*-carboranyl)carbene]metal complexes was $(\eta^5\text{-}C_5H_5)(CO)_2Re[C(C_2B_{10}H_{11})(C_6H_5)]$, synthesized by the reaction of a cationic carbyne complex of rhenium, $[(\eta^5\text{-}C_5H_5)(CO)_2Re{\equiv}C(C_6H_5)]BBr_4$, with lithio-*o*-carborane.[7]

In an effort to develop a more efficient method for the preparation of [(*o*-carboranyl)methoxycarbene]metal complexes of type **1**, we have studied the transformation of the carbon−carbon triple bond in alkynylcarbene molecules into the *o*-carborane framework. In alkynylcarbene complexes **4**,[8] the carbene moiety is known to be a stronger electron-withdrawing functional group because of the higher electronegativity of the oxygen. Conversion of the acetylenic compound to the corresponding *o*-carborane is generally favored by electron-deficient alkynes; therefore, we decided to investigate the reactivity of alkynylcarbene complexes as electron-deficient triple-bond systems toward $B_{10}H_{12}L_2$ (**5**: L = CH_3CN)[9] (see reaction 2).



4

4a: M = Cr, R = CH_3
4b: M = Cr, R = C_6H_5
4c: M = W, R = CH_3
4d: M = W, R = C_6H_5

(2)

1

1a: M = Cr, R = CH_3
1b: M = Cr, R = C_6H_5
1c: M = W, R = CH_3
1d: M = W, R = C_6H_5

Indeed, compounds **1a**−**d** were produced in high yields (47−63%) from the direct two-carbon insertion reaction of alkynylcarbene complexes **4** with **5**. Although this reaction requires overnight reflux in benzene, its simple reaction path and facile product isolation make this route attractive.

$(CO)_4(RC_2B_{10}H_{10})Mn[C(OCH_3)(CH_3)]$ (R = CH_3, C_6H_5) (2). Compound **6a** was first prepared by Hawthorne et al.[10] Subsequent reaction of complexes **6a**,**b** with 1.2 mol equiv of methyllithium gave rise to the corresponding metal acyl complexes. Further methylation of the acyl anions with $CF_3SO_3CH_3$ produced new (*o*-carboranyl)metal carbene complexes **2a**,**b**, as shown in reaction 3. The (*o*-carboranyl)manganese carbene complexes **2a**,**b** are all moderately air-stable crystalline solids. They are readily soluble in nonpolar solvents

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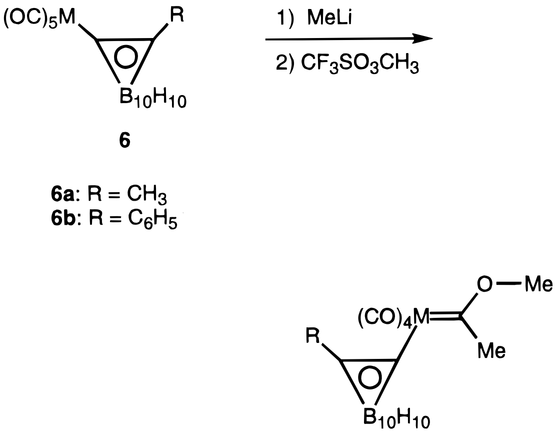

6

6a: R = CH_3
6b: R = C_6H_5

(3)

2

2a: M = Mn, R = CH_3
2b: M = Mn, R = C_6H_5

(hexane, benzene) and sparingly soluble in polar solvents (ether, acetone).

Spectroscopy. $(CO)_5M[C(OMe)(RC_2B_{10}H_{10})]$ (1: M = Cr, W; R = CH_3, C_6H_6). The compositions of **1a**−**d** were established by both elemental analysis and high-resolution mass spectral analysis. Furthermore, the spectroscopic data (^1H, ^{13}C, and ^{11}B NMR) associated with the [(*o*-carboranyl)-methoxycarbene]metal complexes of **1a**−**d** are also consistent with their assigned structures. The ^1H NMR data are likewise in agreement with the proposed cage structure, confirming the presence of a methyl resonance (0.74−0.79 ppm) at the cage 2-position and one methoxy resonance (3.87−3.97 ppm) for the carbene substituent of **1a**,**c**. The ^{13}C NMR spectra contain carbene carbon resonances at 363.3 and 337.2 ppm, respectively, for **1a**,**c**. The ^1H NMR spectra confirm the presence of a phenyl group showing a cage phenyl multiplet at about 7.5 ppm and one methoxy resonance at about 4.0 ppm for a carbene group either at the chromium or tungsten metal center of complexes **1b**,**d**. The ^{13}C NMR spectra contain carbene carbon resonances at 344.3 and 321.5 ppm, respectively, for **1b**,**d**.

$(CO)_4(RC_2B_{10}H_{10})Mn[C(OCH_3)(CH_3)]$ (2: R = CH_3, C_6H_5). The structures of **2a**,**b** were easily established through spectroscopic (^1H, ^{13}C, and ^{11}B NMR) as well as analytical methods. The ^1H and ^{13}C NMR data are likewise in agreement with the proposed cage structure and confirm the presence of a carbene $C(OCH_3)CH_3$ group at the manganese metal center. The ^1H NMR data contain a methyl resonance (2.04 ppm) for the cage 2-position, a methyl resonance (3.02 ppm), and a methoxy resonance (4.45 ppm) for the carbene substituents of **2a**. The ^{13}C NMR spectrum of **2a** contains the carbene carbon resonance at 344.8 ppm. The ^1H NMR spectrum of **2b** confirms the presence of a cage phenyl group showing a multiplet of intensity 5 at about 7.5 ppm, one methoxy resonance at 4.42 ppm, and one methyl resonance at 2.95 ppm. The ^{13}C NMR spectrum of **2b** shows a carbene carbon resonance at 349.2 ppm.

Description of the Molecular Structure of $(CO)_5W[C(OMe)(PhC_2B_{10}H_{10})]$ (1d). The molecular structure and atom-labeling scheme for complex **1d** are shown in Figure 1; selected bond distances (Å) and angles (deg) are presented in Table 2. The overall structure of **1d** contains an octahedrally disposed (methoxycarbene)tungsten pentacarbonyl fragment connected to an *o*-carboranyl group. The drawing in Figure 1 illustrates how the large *o*-carborane substituent effectively shields the carbene ligand from the side. The carbene carbon atom is coplanar, with a standard deviation of 0.0071 Å, with the three atoms W, O(26), C(1), and C(13) which surround it, as expected for such a carbene adduct. The normal to this plane almost bisects the directions of the equatorial carbonyl groups of the tungsten octahedron. Usually, in Fischer-type carbene complexes, the carbene plane is staggered with repect to the trans CO−W−CO bonds.[11]

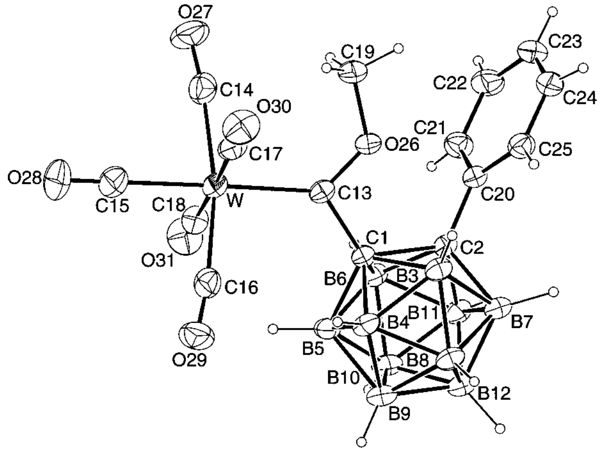

Figure 1. Molecular structure of $(CO)_5W[C(OMe)(PhC_2B_{10}H_{10})]$ (**1d**). The thermal ellipsoids are drawn at the 30% probability level.

Table 1. Crystallographic Data for Structural Studies of Compounds 1d and 2b

formula	$WB_{10}C_{15}H_{18}O_6$	$MnB_{10}C_{15}H_{21}O_5$
fw	586.25	444.37
cryst class	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)
Z	2	4
cell constants		
a, Å	9.8455(4)	15.5537(5)
b, Å	17.6610(7)	19.0697(5)
c, Å	6.7682(2)	7.4286(3)
V, Å^3	1114.69(7)	2203.4(1)
α, deg	90.506(3)	
β, deg	107.580(2)	
γ, deg	96.023(2)	
μ, cm^{-1}	5.2	6.23
cryst size, mm	0.40 × 0.20 × 0.15	0.45 × 0.15 × 0.10
D_{calcd}, g/cm^3	1.747	1.339
F(000)	560.00	904.00
radiation	Mo Kα (λ = 0.7170 Å)	Mo Kα (λ = 0.7170 Å)
θ range, deg	2.0−27.0	2.0−27.0
h, *k*, *l* collected	+11, ±21, ±8	+19, +24, +9
no. of rflns measd	14 391	16 251
no. of unique rflns	4044	4554
no. of rflns used in refinement	3591 ($F_o^2 > 3.0\sigma(F_o^2)$)	3805 ($F_o^2 > 3.0\sigma(F_o^2)$)
no. of params	362	280
data/param ratio	9.9	13.59
R1[a]	0.029	0.039
wR2[b]	0.035	0.045
GOF	1.308	1.702

[a] $R1 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [b] $wR2 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

The W−C(alkoxycarbene) distance (W−C(13), 2.142 (4) Å) is in the lower range of values generally observed in other (alkoxycarbene)tungsten structures.[12] In this complex, the carbene carbon atom carries a bulky substituent, which probably forces the carbene plane to orient in a less favorable way with respect to the $(CO)_5M$ fragment. Notable is the distortion caused by the metal carbonyl, *o*-carborane, and methoxy substituents on the carbene carbon, leading to deviations from ideal values for the sp^2-hybridized carbene carbon atom. Therefore, the angles around the carbene carbon decrease in the order W−C(13)−O(26) > W−C(13)−C(1) > O(26)−C(13)-C(1) (values for **1d** are 129.5(3), 126.8(3), and

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 1d

Bond Distances			
W−C(13)	2.142(4)	W−C(14)	2.042(6)
W−C(15)	2.045(6)	W−C(16)	2.053(6)
W−C(17)	2.033(6)	W−C(18)	2.067(7)
O(26)−C(13)	1.306(5)	O(26)−C(19)	1.447(6)
O(27)−C(14)	1.141(7)	O(28)−C(15)	1.135(7)
O(29)−C(16)	1.136(7)	O(30)−C(17)	1.147(7)
O(31)−C(18)	1.135(7)	C(1)−C(2)	1.802(6)
C(1)−C(13)	1.545(6)	C(1)−B(3)	1.738(6)
C(1)−B(4)	1.690(6)	C(1)−B(5)	1.688(6)
C(1)−B(6)	1.711(7)	C(2)−C(20)	1.503(6)
C(2)−B(3)	1.729(6)	C(2)−B(6)	1.737(6)
C(2)−B(7)	1.692(6)	C(2)−B(11)	1.686(6)
C(20)−C(21)	1.379(6)	C(20)−C(25)	1.372(6)
C(21)−C(22)	1.389(7)	C(22)−C(23)	1.362(8)
C(23)−C(24)	1.369(8)	C(24)−C(25)	1.377(7)
Bond Angles			
C(13)−W−C(14)	96.5(2)	C(13)−W−C(15)	177.1(2)
C(13)−W−C(16)	94.4(2)	C(13)−W−C(17)	90.0(2)
C(13)−W−C(18)	91.2(2)	C(14)−W−C(15)	85.4(2)
C(14)−W−C(16)	169.0(2)	C(14)−W−C(17)	89.5(2)
C(14)−W−C(18)	88.1(2)	C(15)−W−C(16)	83.7(2)
C(15)−W−C(17)	87.8(2)	C(15)−W−C(18)	91.0(2)
C(16)−W−C(17)	91.3(2)	C(16)−W−C(18)	90.8(2)
C(17)−W−C(18)	177.5(2)	C(13)−O(26)−C(19)	123.8(4)
C(2)−C(1)−C(13)	118.0(3)	C(1)−C(2)−C(20)	123.1(3)
W−C(13)−O(26)	129.5(3)	W−C(13)−C(1)	126.8(3)
O(26)−C(13−C(1)	103.6(3)	W−C(14)−O(27)	173.8(5)
W−C(15)−O(28)	177.8(6)	W−C(16)−O(29)	173.3(5)
W−C(17)−O(30)	178.7(5)	W−C(18)−O(31)	177.3(5)
C(2)−C2(0)−C(21)	120.4(4)	C(2)−C(20)−C(25)	121.1(4)
C(21)−C(20)−C(25)	118.4(4)	C(20)−C(21)−C(22)	119.8(5)
C(21)−C(22)−C(23)	121.0(5)	C(22)−C(23)−C(24)	119.2(5)
C(23)−C(24)−C(25)	120.1(5)	C(20)−C(25)−C(24)	121.4(5

103.6(3)°, respectively). The methoxy methyl group forms an angle of 123.8(4)° with the C(13)−O(26) vector and, of the two possible positions whereby it remains coplanar with the carbene group, it occupies that cis to the metal. Also, the angle between the carbene substituents is 103.6(3)°, which is comparable with that of 103° for the singlet state of methylene determined spectroscopically.[13] The bond distances and angles associated with the *o*-carboranyl group are unexceptional and are similar to those reported for other structures.[14]

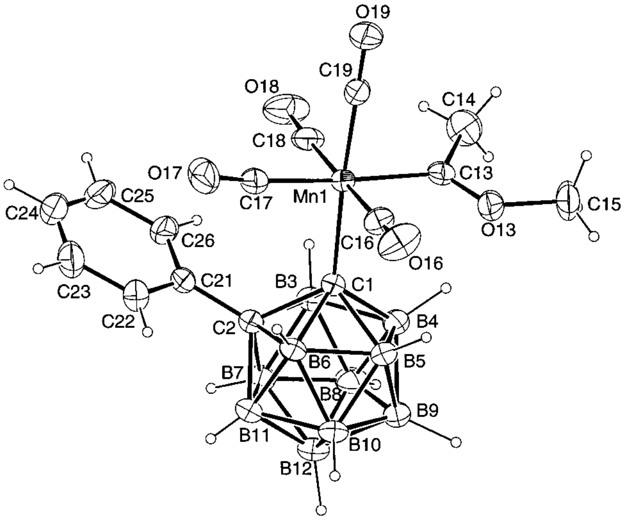

Figure 2. Molecular structure of $(CO)_4(PhC_2B_{10}H_{10})Mn$-$[C(OCH_3)(CH_3)]$ (**2b**). The thermal ellipsoids are drawn at the 30% probability level.

Table 3. Selected Bond Distances (Å) and Angles deg) for Compound 2b

Bond Distances			
Mn(1)−C(1)	2.155(3)	Mn(1)−C(13)	1.969(3)
Mn(1)−C(16)	1.854(4)	Mn(1)−C(17)	1.853(3)
Mn(1)−C(18)	1.837(4)	Mn(1)−C(19)	1.817(3)
O(13)−C(13)	1.280(4)	O(13)−C(15)	1.471(4)
O(16)−C(16)	1.148(4)	O(17)−C(17)	1.144(4)
O(18)−C(18)	1.145(4)	O(19)−C(19)	1.143(3)
C(1)−C(2)	1.758(4)	C(2)−C(21)	1.508(4)
C(13)−C(14)	1.492(5)	C(21)−C(22)	1.386(5)
C(21)−C(26)	1.381(5)	C(22)−C(23)	1.402(5)
C(23)−C(24)	1.375(7)	C(24)−C(25)	1.351(8)
C(25)−C(26)	1.396(5)		
Bond Angles			
C(1)−Mn(1)−C(13)	90.3(1)	C(1)−Mn(1)−C(16)	89.4(1)
C(1)−Mn(1)−C(17)	95.2(1)	C(1)−Mn(1)−C(18)	91.3(1)
C(1)−Mn(1)−C(19)	176.2(1)	C(13)−Mn(1)−C(16)	88.4(1)
C(13)−Mn(1)−C(17)	173.4(1)	C(13)−Mn(1)−C(18)	91.4(1)
C(13)−Mn(1)−C(19)	85.9(1)	C(16)−Mn(1)−C(17)	88.1(1)
C(16)−Mn(1)−C(18)	179.3(1)	C(16)−Mn(1)−C(19)	90.6(1)
C(17)−Mn(1)−C(18)	92.1(2)	C(17)−Mn(1)−C(19)	88.6(1)
C(18)−Mn(1)−C(19)	88.7(1)	C(13)−O(13)−C(15)	125.0(3)
Mn(1)−C(1)−C(2)	122.9(2)	C(1)−C(2)−C(21)	121.5(2)
Mn(1)−C(13)−O(13)	118.5(2)	Mn(1)−C(13)−C(14)	125.0(3)
O(13)−C(13)−C(14)	116.3(3)	Mn(1)−C(16)−O(16)	174.8(3)
Mn(1)−C(17)−O(17)	170.5(3)	Mn(1)−C(18)−O(18)	176.2(3)
Mn(1)−C(19)−O(19)	179.0(3)	C(2)−C(21)−C(22)	119.6(3)
C(2)−C(21)−C(26)	121.0(3)	C(22)−C(21)−C(26)	119.3(3)
C(21)−C(22)−C(23)	119.8(4)	C(22)−C(23)−C(24)	119.9(5)
C(23)−C(24)−C(25)	120.3(4)	C(24)−C(25)−C(26)	120.7(5)
C(21)−C(26)−C(25)	120.0(4)		

Description of the Molecular Structure of $(CO)_4$-$(PhC_2B_{10}H_{10})Mn[C(OCH_3)(CH_3)]$ (2b). The conformation and atomic numbering scheme for **2b** are shown in Figure 2; selected bond distances (Å) and angles (deg) are listed in Table 3. As shown in Figure 2, the structure of complex **2b** consists of a $(CO)_4(C_6H_5C_2B_{10}H_{10})Mn$ unit bonded to a methylmethoxycarbene fragment. In this complex, the carbene moiety is located in a cis arrangement about the Mn(1)−C(1) bond with respect to the two equatorial carbonyl and two axial carbonyl groups with C_1 symmetry. One of the most significant aspects of the structure of **2b** concerns the disposition of the phenyl group substituted on the cage. In compound **2b**, the cage carbon is phenyl-substituted and as a result would be expected to have increased steric repulsion around the metal. Indeed, the phenyl group substituted on *o*-carborane is stretched further away from the carbene ligand in the solid state. Thus, the steric argument alone would predict the orientation in Figure 2, with the carbene located away from the phenyl substituent of the *o*-carborane ligand. The manganese octahedron is slightly distorted, the principal axes deviating from linearity as follows: C(13)−Mn(1)−C(17), 173.4(1)°; C(1)−Mn-

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(1)−C(19), 176.2(1)°; C(16)−Mn(1)−C(18), 179.3(1)°. The manganese atom, the atoms of the carbene moiety (C(13), C(14), O(13)), and the carbon atoms of the three equatorial carbonyls are essentially coplanar (average deviation from the mean plane of 0.113 Å with a maximum deviation of 0.380 Å associated with C(14)). This plane is perpendicular to the Mn(1)−C(1) bond (torsional angle{C(1)−Mn(1)−C(13)}−{C(14)−O(13)−C(13)} = 103.44°). It has been noted that, due to the poor π-donation from the $(CO)_4Mn$ fragment[15] in compound **2b**, the Mn(1)−C(13) bond length of 1.969(3) Å is significantly longer than that found in other manganese−carbene complexes ($Cp(CO)(PPh_3)Mn{=}C(OMe)Et$, 1.743(7) (molecule 1) and 1.737(6) Å (molecule 2);[16a] $Cp(CO)_2Mn{=}C(OEt)Ph$, 1.865(14) Å;[16b] $Cp(CO)_2Mn{=}CPh_2$, 1.885(2) Å;[16c] $Cp(CO)_2Mn{=}C(C\{O\}\text{-}Ph)Ph$, 1.88(2) Å;[16d] $Cp(CO)_2Mn{=}CMe_2$, 1.872(10) (molecule 1) and 1.864(10) Å (molecule 2)[16e]).

Noticeably, the Mn−C(carbene) distance is even longer than that found for the analogous bond in the binuclear compound *cis*-$Mn_2(CO)_9[C(OCH_3)(C_6H_5)]$ (1.950 Å).[17] The carbene carbon−oxygen C(13)−O(13) bond length in **2b** is 1.280(4) Å and is shorter than that in the binuclear compound (1.315 Å), whereas the Mn(1)−C(13)−O(13) angle in the carbene unit of **2b** is 118.5(2)°, compared to only 119.4° in the binuclear compound. The significant shortening of the carbene C(13)−O(13) bond in compound **2b** compared to the analogous bond in the binuclear compound can be taken as evidence of the increased π-donating character of the heteroatom (O(13)) in **2b**. Therefore, the Mn−C(carbene) distance in complex **6b** is in the upper part of the range of values generally observed in other manganese carbene complexes. The compound has adopted the anti conformation about the C(13)−O(13) bond. The binuclear compound also exhibits a trans geometry about the carbon−oxygen bond. In addition to being bound to the *o*-carborane cage, the manganese is also bonded in an η^1-fashion to four carbonyl groups, which show an average bond distance of 1.840 Å. Likewise, the bond distances and angles associated with the *o*-carboranyl group in **2b** are similar to the structural parameters reported for other organometallic molecules containing this group.[14]

Conclusions

This report provides the first detailed report of the new Fischer-type carbene complexes bearing an *o*-carborane substituent. A combination of X-ray crystallographic and spectroscopic studies confirms the nature of these compounds. The X-ray crystallographic study of complex **1d**, described above, provides the first structural data for the (*o*-carboranyl)methoxycarbene group VI metal complexes. Moreover, all the complexes **1a**−**d** exhibited greater thermal stability than their alkyl counterparts due to the introduction of an *o*-carboranyl group onto the metal carbene unit. Additionally, we describe the efficient and selective synthesis of complexes **1** by the following approaches: (1) using the lithio-*o*-carborane as a nucleophile and (2) reacting a carbene complex containing an alkynyl group with the $B_{10}H_{10}(CH_3CN)_2$ system. The *o*-carborane system is valuable for the synthesis of a new class of Fischer-type carbene complexes with different coordination environments. On the basis of this finding, we transformed (*o*-carboranyl)manganese complexes to carbene complexes by nucleophilic addition reactions with methyllithium reagent.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. THF was freshly distilled over potassium benzophenone. Ether was dried and distilled from sodium benzophenone. Dichloromethane and hexane were dried and distilled over CaH_2. ^1H, ^{11}B, and ^{13}C NMR spectra were recorded on a Bruker AM-200 instrument operating at 200.1, 64.2, and 50.3 MHz, respectively. All boron-11 chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2$ (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% C_6D_6) and then referenced to Me_4Si (0.00 ppm). IR spectra were recorded on a Shimadzu FT-IR-8501 spectrometer. 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. The following starting materials were prepared according to literature procedures: $MeC_2B_{10}H_{11}$,[3] $PhC_2B_{10}H_{11}$,[4] and $Mn(CO)_5Br$.[18] $[Me_3O]^+[BF_4]^-$ and $CF_3SO_3CH_3$ were purchased from Aldrich. Merck silica gel 60 (240−400 mesh) was used for flash chromatography.

General Synthesis of $(CO)_5M[C(OMe)(RC_2B_{10}H_{10})]$ (1: M = Cr, W; R = CH_3, C_6H_6). Method A. To a stirred solution of $RC_2B_{10}H_{11}$ (R = CH_3,[3] C_6H_5[4]) (3.0 mmol) in 30 mL of diethyl ether, which was cooled to −20 °C, was added 1.6 M *n*-BuLi (2 mL, 3.2 mmol) via a syringe. The resulting white suspension was stirred at −20 °C for 2 h and then transferred through a cannula to a suspension of $M(CO)_6$ (M = Cr, W) (3.2 mmol) in 80 mL of diethyl ether at 25 °C. After the reaction mixture was stirred, the solution gradually turned dark brown, suggesting the formation of a metal acyl complex. The completion of the reaction was monitored by IR spectroscopy. The resulting dark brown reaction mixture was stirred at 25 °C for 3 h, and then the solvent was removed under vacuum. The resulting residue was then taken up in 5 mL of nitrogen-saturated water. This aqueous solution was cooled to 0 °C, the electrophilic reagent $[Me_3O]^+[BF_4]^-$ (0.85 g, 6.0 mmol, 2 equiv) was added in small portions, and the solution was stirred for 1 h. The resulting carbene complex was extracted into methylene chloride, and the combined organic extracts were washed twice with 25 mL of water and then dried over anhydrous magnesium sulfate. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of methylene chloride and then transferred to a column of silica gel. The crude residue was purified by column chromatography affording >95% pure metal carbene complex as crystals.

Analytical Data for the Chromium and Tungsten Carbene Complexes 1a−d. $(CO)_5Cr[C(OMe)(MeC_2B_{10}H_{10})]$ (1a). 1a was prepared from 3.0 mmol of the methyl-*o*-carborane $MeC_2B_{10}H_{11}$. After chromatography on silica gel with hexane, **1a** (0.44 g, 1.1 mmol, 37% yield) was isolated as a yellow solid. ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 1.3 (d, B_9, J_{BH} = 150 Hz), −4.6 (d, B_{12}, J_{BH} = 200 Hz), −7.9 (d, $B_{8,10}$, $B_{4,5}$, J_{BH} = 140 Hz), −9.9 (d, $B_{7,11}$, $B_{3,6}$, J_{BH} = 180 Hz). ^1H NMR (200.13 MHz, ppm, C_6D_6): 3.97 (s, 3H, OCH_3), 0.74 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, C_6D_6): 363.3 (s, Cr=*C*), 223.1 (s, *C*O), 216.9 (s, *C*O), 67.1 (s, O*C*H$_3$), 28.4 (s, *C*H$_3$). Exact mass: calcd for $^{11}B_{10}{}^{12}C_{10}{}^{52}Cr^1H_{16}{}^{16}O_6$ 394.1283, found

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394.1296. Anal. Calcd: C, 30.61; H, 4.11. Found: C, 30.75; H, 4.14. $R_f = 0.88$ by silica gel TLC analysis (hexane). Mp = 78 °C. IR spectrum (KBr pellet, cm^{-1}): 2970 (w), 2940 (w), 2880 (w), 2600 (s), 2070 (s), 1985 (s), 1940 (vs), 1460 (w), 1260 (m), 1115 (w), 1040 (w), 950 (w), 920 (w), 870 (w), 850 (w), 830 (w), 800 (w), 730 (w), 690 (w), 670 (m), 660 (m), 630 (w).

$(CO)_5Cr[C(OMe)(PhC_2B_{10}H_{10})]$ (1b). **1b** was prepared from 3.0 mmol of the phenyl-*o*-carborane $PhC_2B_{10}H_{11}$. After chromatography on silica gel with hexane, **1b** (0.48 g, 1.1 mmol, 37% yield) was isolated as a yellow solid. ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 1.7 (d, B_9, $J_{BH} = 150$ Hz), −4.5 (d, B_{12}, $J_{BH} = 200$ Hz), −7.5 (d, $B_{8,10}$, $B_{4,5}$, $J_{BH} = 140$ Hz), −9.4 (d, $B_{7,11}$, $B_{3,6}$, $J_{BH} = 180$ Hz). ^1H NMR (200.13 MHz, ppm, C_6D_6): 7.56 (m, 2H, C_6H_5), 7.39 (m, 3H, C_6H_5), 3.99 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, C_6D_6): 344.3 (s, Cr=*C*), 205.3 (s, *C*O), 198.2 (s, *C*O), 136.6, 134.2, 130.1 (s, C_6H_5), 58.6 (s, OCH_3). Exact mass: calcd for $^{11}B_{10}{}^{12}C_{15}{}^{52}Cr^1H_{18}{}^{16}O_6$ 456.1439, found 456.1428. Anal. Calcd: C, 39.65; H, 3.99. Found: C, 39.58; H, 3.95. $R_f = 0.66$ by silica gel TLC analysis (benzene/hexane, 50/50). Mp = 84 °C. IR spectrum (KBr pellet, cm^{-1}): 3070 (w), 2970 (w), 2940 (w), 2600 (s), 2080 (s), 1990 (s), 1930 (vs), 1490 (w), 1445 (w), 1385 (w), 1330 (m), 1260 (w), 1220 (w), 1170 (w), 995 (w), 920 (w), 875 (w), 810 (w), 760 (w), 700 (w), 665 (w), 620 (w), 590 (w), 565 (w), 490 (w), 370 (m).

$(CO)_5W[C(OMe)(MeC_2B_{10}H_{10})]$ (1c). **1c** was prepared from 3.0 mmol of the methyl-*o*-carborane $MeC_2B_{10}H_{11}$. After chromatography on silica gel with hexane, **1c** (0.63 g, 1.2 mmol, 40% yield) was isolated as a yellow solid. ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 1.4 (d, B_9, $J_{BH} = 150$ Hz), −4.6 (d, B_{12}, $J_{BH} = 200$ Hz), −7.8 (d, $B_{8,10}$, $B_{4,5}$, $J_{BH} = 140$ Hz), −9.9 (d, $B_{7,11}$, $B_{3,6}$, $J_{BH} = 180$ Hz). ^1H NMR (200.13 MHz, ppm, C_6D_6): 3.87 (s, 3H, OCH_3), 0.79 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, C_6D_6): 337.2 (s, W=*C*), 204.1 (s, *C*O), 197.6 (s, *C*O), 64.9 (s, OCH_3), 27.4 (s, CH_3). Exact mass: calcd for $^{11}B_{10}{}^{12}C_{10}{}^{184}W^1H_{16}{}^{16}O_6$ 526.1387, found 526.1398. Anal. Calcd: C, 22.91; H, 3.08. Found: C, 22.88; H, 3.04. $R_f = 0.82$ by silica gel TLC analysis (hexane). Mp = 88 °C. IR spectrum (KBr pellet, cm^{-1}): 2960 (m), 2870 (m), 2600 (s), 2080 (s), 1980 (s), 1940 (vs), 1470 (m), 1450 (m), 1400 (w), 1370 (w), 1260 (s), 1110 (w), 1055 (w), 1035 (w), 940 (w), 910 (w), 860 (m), 840 (m), 820 (s), 800 (w), 735 (w), 700 (w), 680 (w), 660 (w), 630 (w), 600 (w), 575 (w), 410 (w), 385 (s), 340 (w).

$(CO)_5W[C(OMe)(PhC_2B_{10}H_{10})]$ (1d). **1d** was prepared from 3.0 mmol of the phenyl-*o*-carborane $PhC_2B_{10}H_{11}$. After chromatography on silica gel with hexane, **1d** (0.76 g, 1.3 mmol, 43% yield) was isolated as a yellow solid. ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 1.6 (d, B_9, $J_{BH} = 150$ Hz), −4.4 (d, B_{12}, $J_{BH} = 200$ Hz), −7.3 (d, $B_{8,10}$, $B_{4,5}$, $J_{BH} = 140$ Hz), −10.2 (d, $B_{7,11}$, $B_{3,6}$, $J_{BH} = 180$ Hz). ^1H NMR (200.13 MHz, ppm, C_6D_6): 7.54 (m, 2H, C_6H_5), 7.40 (m, 3H, C_6H_5), 3.88 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, C_6D_6): 321.5 (s, W=*C*), 202.5 (s, *C*O), 196.1 (s, *C*O), 133.2, 130.1, 128.6 (s, C_6H_5), 53.4 (s, OCH_3). Exact mass: calcd for $^{11}B_{10}{}^{12}C_{15}{}^1H_{18}{}^{16}O_6{}^{184}W$ 588.1543, found 588.1539. Anal. Calcd: C, 30.73; H, 3.09. Found: C, 30.69; H, 3.07. $R_f = 0.79$ by silica gel TLC analysis (benzene/hexane, 50/50). Mp = 92 °C. IR spectrum (KBr pellet, cm^{-1}): 3070 (w), 2970 (w), 2940 (w), 2600 (s), 2080 (s), 1990 (s), 1930 (vs), 1445 (w), 1385 (w), 1330 (m), 1260 (w), 1220 (w), 1170 (w), 995 (w), 920 (w), 810 (w), 760 (w), 700 (w), 590 (w), 565 (w), 490 (w), 370 (m).

Method B. In a typical reaction, 3.0 mmol of $B_{10}H_{12}(CH_3CN)_2$[9] (**5**) and 3.2 mmol of alkynylcarbene complexes[7] **4a**−**d** were mixed in 30 mL of benzene. The mixture was then allowed to react at 25 °C for 1 h. The solution was stirred for another 10−12 h at reflux temperature, resulting in the formation of a dark brown solution. ^{11}B NMR spectra taken at this point indicated that the starting material had been completely consumed and that complex **1** was the sole product. Concentration followed by flash column chromatographic separation of the resulting reaction mixture gave complex **1**. The same procedure was applied for the rest of the [(*o*-carboranyl)methoxycarbene]metal complexes **1a**−**d**, with the following variations in the procedure of purification. In each case, the mother liquors were evaporated to dryness, and the ^{11}B and ^1H NMR spectra were studied.

$(CO)_5Cr[C(OMe)(MeC_2B_{10}H_{10})]$ (1a). Reaction time: 10 h. Procedure variation: Evaporation of the benzene solution to dryness and flash chromatography (hexane/$CHCl_3$, 98/2) on silica; 47% yield (0.53 g, 1.4 mmol).

$(CO)_5Cr[C(OMe)(PhC_2B_{10}H_{10})]$ (1b): reaction time, 10 h; procedure variation, evaporation of the benzene solution to dryness and flash chromatography (hexane/benzene, 95/5) on silica; 53% yield (0.71 g, 1.6 mmol).

$(CO)_5W[C(OMe)(MeC_2B_{10}H_{10})]$ (1c): reaction time, 12 h; procedure variation, evaporation of the benzene solution to dryness and flash chromatography (hexane/$CHCl_3$, 98/2) on silica; 47% yield (0.75 g, 1.4 mmol).

$(CO)_5W[C(OMe)(PhC_2B_{10}H_{10})]$ (1d): reaction time, 12 h; procedure variation, evaporation of the benzene solution to dryness and flash chromatography (hexane/benzene, 95/5) on silica; 63% yield (1.13 g, 1.9 mmol).

Preparation of $(CO)_5Mn(PhC_2B_{10}H_{10})$ (6b). A solution of 6.5 mmol of $PhC_2B_{10}H_{10}Li$ (**3b**) in 80 mL of anhydrous ethyl ether was slowly added under a nitrogen atmosphere to a rapidly stirred suspension of 1.76 g (6.4 mmol) of $Mn(CO)_5Br$ in 150 mL of anhydrous ethyl ether. After it was stirred for 2 days 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. × 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 **6b**. A total of 1.50 g (3.6 mmol, 55%) was collected. Rotary evaporation to dryness gave 0.30 g of a mixture of the product and $Mn_2(CO)_{10}$. The white crystals were sublimed and recrystallized from hexane. ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 0.5 (d, B_9, $J_{BH} = 130$ Hz), −1.2 (d, B_{12}, $J_{BH} = 160$ Hz), −4.2 (d, $B_{8,10}$, $J_{BH} = 100$ Hz), −5.3 (d, $B_{4,5}$, $J_{BH} = 140$ Hz), −7.8 (d, $B_{3,6}$, $J_{BH} = 145$ Hz), −9.4 (d, B_7, $J_{BH} = 140$ Hz), −11.3 (d, B_{11}, $J_{BH} = 145$ Hz). ^1H NMR (200.13 MHz, ppm, C_6D_6): 7.74 (d, 2H, C_6H_5), 7.46 (m, 3H, C_6H_5). Exact mass: calcd for $^{11}B_{10}{}^{12}C_{13}{}^{55}Mn^1H_{15}{}^{16}O_5$ 416.1230, found 416.1239. Anal. Calcd: C, 37.69; H, 3.65. Found: C, 37.88; H, 3.59. $R_f = 0.70$ by silica gel TLC analysis (benzene/hexane, 33/67). Mp = 88−90 °C. IR spectrum (KBr pellet, cm^{-1}): 3090 (w), 3060 (w), 3040 (w), 2580 (s), 2130 (s), 2030 (s), 2000 (s), 1495 (m), 1445 (m), 1075 (m), 1010 (w), 930 (w), 890 (w), 820 (w), 760 (w), 730 (w), 690 (m), 640 (s), 560 (w), 490 (w), 430 (w).

General Procedure for the Preparation of $(CO)_4(RC_2B_{10}H_{10})Mn[C(OCH_3)(CH_3)]$ (2: R = CH_3, C_6H_5). In a typical experiment, 1.0 mmol of **6** was dissolved in 25 mL of THF and the solution cooled to −78 °C. CH_3Li (1.0 M, 1.2 mL, 1.2 mmol) was added to the reaction mixture, and the mixture was stirred for 1 h at −78 °C. The 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. IR spectra taken at this point confirmed the exclusive formation of the corresponding metal acyl complexes. Methylation with $CF_3SO_3CH_3$ (3.0 mmol, 3 equiv) followed by extraction with hexane gave a yellow solid. Subsequent separation was performed on the flash column with hexane to give >95% pure metal carbene complexes **2a**,**b** as crystals.

$(CO)_4(MeC_2B_{10}H_{10})Mn[C(OCH_3)(CH_3)]$ (2a). **2a** was prepared from 1.0 mmol of **6a**. After chromatography on silica gel with hexane, 0.18 g (0.47 mmol) of **2a** was isolated as a yellow solid. This corresponds to a 47% yield based on the consumed complex **6a**. ^{11}B NMR (64.2 MHz, ppm, C_6D_6): −1.8 (d, B_9, $J_{BH} = 140$ Hz), −5.0 (d, B_{12}, $J_{BH} = 145$ Hz), −6.8 (d, $B_{8,10}$, $B_{4,5}$, $J_{BH} = 135$ Hz), −7.4 (d, $B_{7,11}$, $B_{3,6}$, $J_{BH} = 100$ Hz).

^{1}H NMR (200.13 MHz, ppm, C_6D_6): 4.45 (s, 3H, $\mathrm{OC}\mathit{H}_3$), 3.02 (s, 3H, $\mathrm{C}\mathit{H}_3$), 2.04 (s, 3, $\mathrm{C}\mathit{H}_3$). ^{13}C{^{1}H} NMR (50.3 MHz, ppm, C_6D_6): 344.8 (s, $\mathrm{Mn}{=}\mathit{C}$), 211.8 (s, *C*O), 64.5 (s, $\mathrm{O}\mathit{C}\mathrm{H}_3$), 40.3 (s, $\mathit{C}\mathrm{H}_3$), 28.5 (s, $\mathit{C}\mathrm{H}_3$). Exact mass: calcd for $^{11}B_{10}{}^{12}C_{10}{}^{1}H_{19}{}^{55}Mn^{16}O_5$ 384.1543, found 384.1551. Anal. Calcd: C, 31.42; H, 5.01. Found: C, 31.51; H, 5.10. $R_f = 0.70$ by silica gel TLC analysis (benzene). Mp = 74−76 °C. IR spectrum (KBr pellet, cm^{-1}): 2960 (w), 2610 (s), 2580 (s), 2550 (s), 2530 (s), 2520 (s), 2080 (s), 2010 (s), 1980 (s), 1460 (m), 1440 (w), 1390 (w), 1300 (s), 1180 (m), 1120 (m), 1090 (w), 1050 (w), 1030 (w), 1000 (m), 950 (w), 810 (w), 740 (w), 660 (s), 650 (s), 470 (m), 430 (w).

$(CO)_4(PhC_2B_{10}H_{10})Mn[C(OCH_3)(CH_3)]$ (2b). **2b** was prepared from 1.0 mmol of **6b**. After chromatography on silica gel with hexane, 0.25 g (0.56 mmol) of **2b** was isolated as a yellow solid. This corresponds to a 56% yield based on the consumed complex **6b**. ^{11}B NMR (64.2 MHz, ppm, C_6D_6): −2.1 (d, B_9, $J_{BH} = 100$ Hz), −3.4 (d, B_{12}, $J_{BH} = 150$ Hz), −6.2 (d, $B_{8,10}$, $J_{BH} = 100$ Hz), −7.4 (d, $B_{4,5}$, $B_{7,11}$, $J_{BH} = 140$ Hz), −9.6 (d, $B_{3,6}$, $J_{BH} = 160$ Hz). ^{1}H NMR (200.13 MHz, ppm, C_6D_6): 7.70 (d, 2H, $\mathrm{C}_6\mathit{H}_5$), 7.36 (m, 3H, $\mathrm{C}_6\mathit{H}_5$), 4.41 (s, 3H, $\mathrm{OC}\mathit{H}_3$), 2.95 (s, 3H, $\mathrm{C}\mathit{H}_3$). ^{13}C{^{1}H} NMR (50.3 MHz, ppm, C_6D_6): 349.2 (s, $\mathrm{Mn}{=}\mathit{C}$), 212.5 (s, *C*O), 132.4, 130.4, 128.7 (s, $\mathit{C}_6\mathrm{H}_5$), 65.9 (s, $\mathrm{O}\mathit{C}\mathrm{H}_3$), 42.3 (s, $\mathit{C}\mathrm{H}_3$). Exact mass: calcd for $^{11}B_{10}{}^{12}C_{15}{}^{1}H_{21}{}^{55}Mn^{16}O_5$ 446.1700, found 446.1727. Anal. Calcd: C, 40.54; H, 4.76. Found: C, 40.65; H, 4.72. $R_f = 0.76$ by silica gel TLC analysis (benzene). Mp = 127−128 °C dec. IR spectrum (KBr pellet, cm^{-1}): 3070 (w), 3040 (w), 2960 (w), 2930 (w), 2600 (s), 2570 (s), 2550 (s), 2080 (s), 2010 (s), 1980 (s), 1500 (w), 1450 (m), 1350 (w), 1300 (s), 1180 (m), 1100 (m), 1070 (m), 1050 (w), 1000 (w), 990 (m), 950 (w), 890 (w), 820 (w), 770 (w), 750 (w), 700 (m), 650 (s), 640 (s), 630 (s), 470 (m), 450 (w), 420 (w).

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **1d** and **2b** are given in Table 1. The crystals of **1d** and **2b** were grown from a hexane solution at −5 °C and were mounted in thin-walled glass capillaries and sealed under argon. The data sets of **1d** and **2b** were collected on a Rigaku diffractometer with an area detector employing graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) at a temperature of 253 K. X-ray data for **1d** and **2b** were processed, and the structure was solved and refined using the Molecular Structure Corp.'s Texsan[19] package on a Silicon Graphics Indigo R4000 computer. The intensity data were corrected for Lorentz and polarization effects. Intensities for **1d** were corrected for absorption by applying the program REQAB.[20] The structure was solved by a direct method (SIR88[21]). 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 of **1d** and **2b** were anisotropically refined, and hydrogen atoms were isotropically refined. The absolute configuration of **2b** was confirmed by the refinement of the Flack parameter. The refinement of **1d** converged to R1 = 0.029 and wR2 = 0.035, and that of **2b** converged to R1 = 0.039 and wR2 = 0.045. Selected bond distances and angles for **1d** and **2b** are given in Tables 2 and 3, respectively. The molecular structures of compounds **1d** and **2b** are given in Figures 1 and 2, respectively.

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Supporting Information Available: Tables of bond distances and angles, atomic coordinates, and thermal parameters and ORTEP diagrams for compounds **1d** and **2b** (18 pages). Ordering information is given on any current masthead page.

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