Synthesis and Reactivity of Monocarbollide Carbonyl Complexes of Iron and Molybdenum with Icosahedral Frameworks[†]

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The $[NEt_4]^+$ (**1a**), $[NHMe_3]^+$ (**1b**), and $[N(PPh_3)_2]^+$ (**1c**) salts of the monoanion $[Fe(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ have been prepared via the reaction between $[Fe_3(CO)_{12}]$ and $[NHMe_3]$[*nido*-7-$CB_{10}H_{13}$] in THF (tetrahydrofuran). The complexes $[N(PPh_3)_2][Fe(CO)_2(L)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (L = PPh_3 (**2**), $CNBu^t$ (**3**)) were obtained by treating **1c** in THF with PPh_3 and $CNBu^t$, respectively, in the presence of Me_3NO. The compound $[N(PPh_3)_2][Mo(CO)_4(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**4**) has been synthesized from $[Na]_3$[*nido*-7-$CB_{10}H_{11}$] and $[Mo(CO)_3(NCMe)_3]$ in the presence of CO and with addition of $HBF_4{\cdot}Et_2O$ and $[N(PPh_3)_2]Cl$. An X-ray diffraction study established that in the anion of **4** the Mo atom is coordinated on one side by the four CO molecules and on the other by a *nido*-7-$CB_{10}H_{11}$ carborane in a η^5 manner. In reactions with PPh_3 and $CNBu^t$, the salt **4** gives the species $[N(PPh_3)_2][Mo(CO)_3(L)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (L = PPh_3 (**5a**), $CNBu^t$ (**6**)). Salts of the anions $[Fe(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ and $[Mo(CO)_3(PPh_3)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ react with donor molecules (THF, OEt_2, SMe_2) in the presence of acids and other hydride abstracting reagents to give zwitterionic complexes: $[Fe(CO)_3(\eta^5\text{-}9\text{-}L\text{-}7\text{-}CB_{10}H_{10})]$ (L = $O(CH_2)_4$ (**7**), OEt_2 (**8**), SMe_2 (**9**)) and $[Mo(CO)_3(PPh_3)(\eta^5\text{-}9\text{-}L\text{-}7\text{-}CB_{10}H_{10})]$ (L = $O(CH_2)_4$ (**10**), OEt_2 (**11**)), formed as single isomers. That the donor molecules L are bonded to a boron atom which lies in a β-site with respect to the carbon in the $\overline{\text{CB}\mathit{B}\text{BB}}$ ring ligating the metal was established by X-ray diffraction studies on **7** and **10**. In the latter the PPh_3 molecule is transoid to the $BO(CH_2)_4$ group, presumably for steric reasons. Alkyne−molybdenum complexes $[N(PPh_3)_2][Mo(CO)_2(Bu^tC{\equiv}CH)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**13**) and $[N(PPh_3)_2][Mo(CO)_2(PhC{\equiv}CR)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (R = H (**14**), Ph (**15**)) have also been prepared.

Introduction

Cyclopentadienide metal carbonyl complexes continue to be of great importance in the development of organotransition-metal chemistry. The isolobal mapping of the $[C_5H_5]^-$ ligand with the icosahedral cage fragments [*nido*-7,8-$C_2B_9H_{11}]^{2-}$ and [*nido*-7-$CB_{10}H_{11}]^{3-}$ suggests that studies on the reactions of carbonyl metallacarboranes should also contribute to the development of organometallic chemistry. However, differences between the donor and steric requirements of the two classes of ligands are likely to result in different patterns of behavior in their complexes.[1] Moreover, the tendency of carbollide groups to adopt nonspectator roles, a property associated with activation of BH vertexes in the *closo*-3,1,2-$MC_2B_9H_{11}$[2a,b] and *closo*-2,1-$MCB_{10}H_{11}$[2c,d] frameworks, also leads to many species with unusual molecular structures. Studies with the reagents $[Pt(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$,[3] $[Co_2(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$,[4] $[Ru(CO)_3(\eta^5\text{-}7,8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_9)]$ (R = H, Me),[5] and $[Cs][Re(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$[6] amply support these considerations. Indeed, the ruthenium complex $[Ru(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$, isolobal with $[Ru(CO)_3(\eta^5\text{-}C_5H_5)]^+$ or $[M(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mn, Re), is the precursor to numerous mono- and polynuclear metal compounds very different from those found in cyclopentadienide metal chemistry.[7]

Reports of compounds in which the monocarbon [*nido*-7-$CB_{10}H_{11}]^{3-}$ group, or a derivative thereof, and CO ligands simultaneously ligate a metal center have as yet been very limited. Several years ago the anionic molybdenum complex $[Mo(CO)_4(\eta^5\text{-}7\text{-}OH\text{-}7\text{-}CB_{10}H_{10})]^-$ was the unexpected product of the reaction between

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[†] The compounds described in this paper have iron or molybdenum atoms incorporated into *closo*-1-carba-2-metalladodecaborane frameworks. However, to avoid a complicated nomenclature for the complexes reported, and to relate them to the many known iron and molybdenum species with η^5-coordinated cyclopentadienyl ligands, we treat the cages as *nido*-11-vertex ligands with numbering as for an icosahedron from which the 12th vertex has been removed.

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Table 1. Analytical and Physical Data

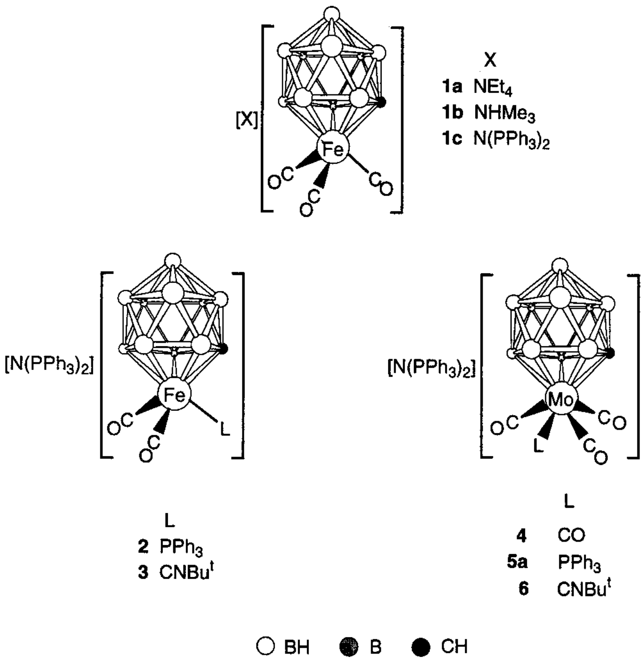
compd	color	yield/%	$\nu_{max}(CO)^a/cm^{-1}$	anal./%[b] C	H	N
$[NEt_4][Fe(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**1a**)	colorless	80	2065 s, 1999 s	35.9 (35.6)	7.7 (7.8)	
$[N(PPh_3)_2][Fe(CO)_2(PPh_3)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**2**)	yellow	41	1993 s,1940 s	65.4 (65.6)	5.4 (5.4)	
$[N(PPh_3)_2][Fe(CO)_2(CNBu^t)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**3**)	yellow	35	2005 s,[c] 1964 s	61.2 (61.1)	5.9 (5.8)	
$[N(PPh_3)_2][Mo(CO)_4(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**4**)	yellow	40	2070 s, 1994 s, 1956 s	56.4 (56.1)	4.7 (4.7)	1.6 (1.6)
$[NEt_3(CH_2Ph)][Mo(CO)_3(PPh_3)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**5b**)[d]	yellow	93	2009 s, 1932 s, 1908 s	54.8 (54.9)	6.4 (6.3)	1.9 (1.8)
$[N(PPh_3)_2][Mo(CO)_3(CNBu^t)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**6**)	yellow	70	2020 s,[e] 1950 s, 1926 s	58.8 (57.9)	5.5 (5.4)	2.6 (3.0)
$[Fe(CO)_3\{\eta^5\text{-}9\text{-}O(CH_2)_4\text{-}7\text{-}CB_{10}H_{10}\}]$ (**7**)	colorless	40	2076 s, 2029 m, 2011 m	27.9 (28.1)	5.4 (5.3)	
$[Fe(CO)_3(\eta^5\text{-}9\text{-}OEt_2\text{-}7\text{-}CB_{10}H_{10})]$ (**8**)	colorless	36	2076 s, 2029 m, 2011 m	27.9 (27.9)	5.9 (5.9)	
$[Fe(CO)_3(\eta^5\text{-}9\text{-}SMe_2\text{-}7\text{-}CB_{10}H_{10})]$ (**9**)	yellow	53	2082 s, 2029 m, 2017 m	21.9 (21.7)	4.9 (4.9)	
$[Mo(CO)_3(PPh_3)\{\eta^5\text{-}9\text{-}O(CH_2)_4\text{-}7\text{-}CB_{10}H_{10}\}]$ (**10**)	yellow	45	2024 s, 1954 s, 1922 s	48.3 (48.4)	5.1 (5.1)	
$[Mo(CO)_3(PPh_3)(\eta^5\text{-}9\text{-}OEt_2\text{-}7\text{-}CB_{10}H_{10})]$ (**11**)	yellow	82	2024 s, 1954 s, 1924 s	48.3 (48.3)	5.5 (5.4)	
$[Mo(CO)_3(CNBu^t)(\eta^5\text{-}9\text{-}OEt_2\text{-}7\text{-}CB_{10}H_{10})]$ (**12**)	yellow	50	2037 s,[f] 1977 s, 1937 s	32.2[g] (31.8)	5.9 (5.9)	2.8 (2.8)
$[N(PPh_3)_2][Mo(CO)_2(Bu^tC{\equiv}CH)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**13**)	purple	60	2018 s, 1952 s	58.9 (59.8)	5.7 (5.7)	1.6 (1.6)
$[N(PPh_3)_2][Mo(CO)_2(PhC{\equiv}CH)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**14**)	purple	50	2023 s, 1958 s	60.3 (61.1)	5.3 (5.1)	1.7 (1.5)
$[N(PPh_3)_2][Mo(CO)_2(PhC{\equiv}CPh)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**15**)	purple	53	2020 s, 1960 s	64.0 (63.7)	5.2 (5.1)	1.5 (1.4)
$[PPh_4][Mo(CO)_2(PPh_3)_2(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**16**)	yellow	50	1918 m, 1826 s	63.1[g] (64.1)	5.2 (5.2)	

[a] Measured in CH_2Cl_2; broad medium-intensity bands observed at ca. 2550 cm^{-1} in the spectra of all compounds are due to B−H adsorptions. [b] Calculated values are given in parentheses. [c] $\nu_{max}(NC)$ 2154 m cm^{-1}. [d] Complex prepared and used as its $[N(PPh_3)_2]^+$ salt **5a**; see Experimental Section. [e] $\nu_{max}(NC)$ 2158 m cm^{-1}. [f] $\nu_{max}(NC)$ 2169 m cm^{-1}. [g] Crystallizes with 0.5 mol equiv of CH_2Cl_2.

$[Mo(CO)_6]$ and $[Na][nido\text{-}B_{10}H_{13}]$.[8a] Its triphenylphosphine derivative $[Mo(CO)_3(PPh_3)(\eta^5\text{-}7\text{-}OH\text{-}7\text{-}CB_{10}H_{10})]^-$ was subsequently obtained by treating $[Mo(CO)_3(NCMe)_2(PPh_3)]$ with $[NEt_4]_2[arachno\text{-}B_{10}H_{14}]$.[8b] Formation of these complexes is interesting, since it involved incorporation of a carbon atom from a CO group into the cage framework. Clearly neither reaction was designed to prepare a monocarbollide carbonyl molybdenum species. However, by using the rational process of treating $[ReBr(CO)_3(THF)_2]$ with $[Na]_3[nido\text{-}7\text{-}CB_{10}H_{11}]$ followed by addition of $[N(PPh_3)_2]Cl$, we recently obtained the complex $[N(PPh_3)_2]_2[Re(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$.[2c] The anion $[Re(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^{2-}$ reacts readily with electrophilic metal−ligand fragments containing Pd, Pt, Rh, or Ir to afford binuclear metal compounds in which these metals and their associated ligands are attached to the *closo*-2,1-$ReCB_{10}H_{11}$ cage system by a metal−metal bond and by at least one exopolyhedral B−H⇀ML_n three-center−two-electron linkage.[2c,d] In another study[9] the reaction between $[Ru_3(CO)_{12}]$ and $[NHMe_3][nido\text{-}7\text{-}CB_{10}H_{13}]$ afforded the triruthenium compound $[NHMe_3][Ru_3(CO)_8(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$, and the latter was then used as a precursor to mixed-metal clusters containing ruthenium bonded to copper, silver, and gold.

These results strongly suggest that monocarbollide metal carbonyls are likely to be sources of much new chemistry, and to exploit this area we report herein the synthesis of salts of the anionic complexes $[M(CO)_n(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ (M = Fe, n = 3; M = Mo, n = 4) and describe some reactions of these compounds.

Chart 1



Results and Discussion

When $[Fe_3(CO)_{12}]$ and $[NHMe_3][nido\text{-}7\text{-}CB_{10}H_{13}]$ are refluxed in THF, the anionic complex $[Fe(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ is formed and may be isolated pure as its $[NEt_4]^+$ salt **1a** (Chart 1). The $[NHMe_3]^+$ (**1b**) and $[N(PPh_3)_2]^+$ (**1c**) salts may be prepared in essentially quantitative yields and used in situ since when formed they are sufficiently pure for further reactions. In the IR spectrum of the anion strong CO stretching bands are observed at 2065 and 1999 cm^{-1} (Table 1). In the spectra of the neutral isolobal species $[Fe(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ the CO absorptions occur, as expected, at higher frequency (2103 and 2042 cm^{-1}).[10] In the IR spectrum of the isoelectronic cation $[Fe(CO)_3(\eta^5\text{-}C_5H_5)]^+$ the corresponding bands are seen at 2121 and 2074

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Table 2. ^{1}H, ^{13}C, and ^{11}B NMR Data[a]

	^{1}H/δ[b]	^{13}C/δ[c]	^{11}B{^{1}H}/δ[d]
1b	6.90 (br s, 1 H, NH), 3.00 (s, 9 H, Me), 1.80 (s, 1 H, cage CH)	208.5 (CO), 49.8 (cage C), 46.8 (Me)	9.9 (1 B), −2.5 (2 B), −5.7 (2 B), −8.6 (1 B), −11.1 (2 B), −16.0 (2 B)
2	7.65−7.37 (m, 45 H, Ph), 1.54 (s, 1 H, cage CH)	215.8 (d, CO, *J*(PC) = 23), 134.0−126.7 (Ph), 48.9 (cage C)	7.1 (1 B), −2.8 (2 B), −5.7 (2 B), −8.2 (1 B), −12.5 (2 B), −17.6 (2 B)
3	7.66−7.46 (m, 30 H, Ph), 1.61 (s, 1 H, cage CH), 1.45 (s, 9 H, Bu^t)	213.7 (CO), 158.5 (CN), 134.0−126.7 (Ph), 57.6 (*C*Me$_3$), 48.2 (cage C), 30.5 (C*Me*$_3$)	6.9 (1 B), −3.3 (2 B), −6.7 (2 B), −8.1 (1 B), −12.2 (2 B), −17.3 (2 B)
4	7.69−7.46 (m, 30 H, Ph), 1.81 (s, 1 H, cage CH)	227.8 (CO), 134.0−126.7 (Ph), 51.2 (cage CH)	6.7 (1 B), −3.0 (2 B), −5.5 (1 B), −8.8 (2 B), −11.0 (2 B), −15.8 (2 B)
5a	7.66−7.37 (m, 45 H, Ph), 1.52 (s, 1 H, cage CH)	239.6 (d, CO, *J*(PC) = 7), 236.4 (d, CO × 2, *J*(PC) = 28), 134.0−126.7 (Ph), 54.1 (cage CH)	3.0 (1 B), −3.1 (2 B), −5.3 (1 B), −10.3 (4 B), −16.7 (2 B)
6	7.68−7.47 (m, 30 H, Ph), 1.60 (s, 1 H, cage CH), 1.50 (s, 9 H, Bu^t)	238.6 (CO), 233.9 (CO × 2), 159.0 (br, CN), 134.0−126.7 (Ph), 58.9 (*C*Me$_3$), 50.6 (cage CH), 30.3 (C*Me*$_3$)	2.8 (1 B), −3.7 (2 B), −6.4 (1 B), −11.7 (4 B), −16.7 (2 B)
7	4.36 (br m, 4 H, OCH$_2$), 2.19 (br m, 4 H, CH$_2$), 1.83 (s, 1 H, cage CH)	207.0 (CO), 81.8 (OCH$_2$), 46.0 (cage C), 25.3 (CH$_2$)	20.4* (1 B), 9.6 (1 B), −2.9 (1 B), −6.6 (1 B), −8.3 (2 B), −11.3 (2 B), −17.2 (1 B), −19.1 (1 B)
8	4.46 (br m, 4 H, OCH$_2$), 1.69 (s, 1 H, cage CH), 1.47 (t, 6 H, Me, *J*(HH) = 7)	207.0 (CO), 78.0 (OCH$_2$), 45.7 (cage C), 12.8 (Me)	22.8* (1 B), 9.8 (1 B), −2.8 (1 B), −6.6 (1 B), −8.2 (2 B), −11.1 (2 B), −17.3 (1 B), −19.0 (1 B)
9	2.53, 2.42 (s × 2, 6H, Me), 1.92 (s, 1 H, cage CH)	206.3 (CO), 50.0 (cage C), 26.2, 25.8 (Me × 2)	11.9 (1 B), 1.7* (1 B), 0.4 (1 B), −5.2 (1 B), −5.9 (1 B), −9.1 (2 B), −12.6 (1 B), −14.4 (1 B), −16.1 (1 B)
10	7.52−7.28 (m, 15 H, Ph), 4.21 (br m, 4 H, OCH$_2$), 2.07 (br m, 4 H, CH$_2$), 1.33 (s, 1 H, cage CH)	238.3 (d, CO, *J*(PC) = 6), 233.9 (d, CO, *J*(PC) = 30), 231.3 (d, CO, *J*(PC) = 28), 133.7−129.0 (Ph), 79.8 (OCH$_2$), 52.6 (cage CH), 24.9 (CH$_2$)	22.9* (1 B), −0.9 (1 B), −6.4 (2 B), −10.2 (1 B), −11.3 (1 B), −12.7 (1 B), −14.6 (1 B), −17.4 (1 B), −21.0 (1 B)
11	7.52−7.27 (m, 15 H, Ph), 4.23 (AB q, 4 H, OCH$_2$, *J*(AB) = 16, *J*(HH) = 7), 1.56 (s, 1 H, cage CH), 1.34 (t, 6 H, Me, *J*(HH) = 7)	238.0 (d, CO, *J*(PC) = 6), 233.7 (d, CO, *J*(PC) = 30), 231.2 (d, CO, *J*(PC) = 29), 133.7−129.0 (Ph), 74.2 (OCH$_2$), 52.5 (cage CH), 12.2 (Me)	25.9* (1 B), −0.6 (1 B), −6.2 (2 B), −10.1 (1 B), −11.1 (1 B), −12.9 (1 B), −14.9 (1 B), −17.5 (1 B), −20.8 (1 B)
12	4.21 (br m, 4 H, OCH$_2$), 1.72 (s, 1 H, cage CH), 1.55 (s, 9 H, Bu^t), 1.36 (t, 6 H, Me, *J*(HH) = 7)	234.8,[e] 229.3, 228.3 (CO × 3), 75.0 (OCH$_2$), 60.0 (*C*Me$_3$), 48.4 (cage CH), 30.2 (C*Me*$_3$), 12.6 (CH$_2$*Me*)	24.8* (1 B), −0.5 (1 B), −7.2 (2 B), −10.8 (1 B), −12.0 (1 B), −13.0 (1 B), −15.0 (1 B), −17.0 (1 B), −21.3 (1 B)
13	9.86 (s, 1 H, CCH), 7.69−7.47 (m, 30 H, Ph), 4.02 (s, 1 H, cage CH), 1.45 (s, 9 H, Bu^t)	230.8 (CO), 196.4 (C*C*H), 164.4 (C*C*Bu^t), 134.0−126.0 (Ph), 47.9 (cage CH), 39.8 (*C*Me$_3$), 31.3 (C*Me*$_3$)	1.6 (1 B), −2.0 (4 B), −12.7 (2 B), −14.7 (2 B), −15.2 (1 B)
14	10.66 (s, 1 H, CCH), 7.66−7.44 (m, 35 H, Ph), 3.75 (s, 1 H, cage CH)	229.2 (CO), 185.5 (C*C*Ph), 170.3 (C*C*H), 134.0−126.7 (Ph), 51.3 (cage CH)	1.8 (1 B), −0.6 (2 B), −2.2 (2 B), −12.4 (2 B), −14.6 (2 B), −15.2 (1 B)
15	7.65−7.45 (m, 40 H, Ph), 3.49 (s, 1 H, cage CH)	229.4 (CO), 181.5 (CPh), 137.9−126.7 (Ph), 54.1 (CH)	2.0 (1 B), −0.7 (2 B), −1.9 (2 B), −11.9 (3 B), −14.4 (2 B)
16	7.74−7.71 (m, 50 H, Ph), 0.96 (s, 1 H, cage CH)	245.8 (t, CO, *J*(PC) = 30), 136.0−117.2 (Ph), 56.0 (cage CH)	0.9 (1 B), −2.8 (2 B), −9.5 (3 B), −12.5 (2 B), −17.6 (2 B)

[a] Chemical shifts (δ) in ppm, coupling constants (*J*) in hertz, measurements at ambient temperatures in CD$_2$Cl$_2$. [b] Resonances for terminal BH protons occur as broad unresolved signals in the range δ ca. −1 to +3. [c] ^{1}H-decoupled chemical shifts are positive to high frequency of SiMe$_4$. [d] Chemical shifts (δ) are positive to high frequency of BF$_3$·Et$_2$O (external). Signals ascribed to more than one boron nucleus may result from overlapping peaks and do not necessarily indicate symmetry equivalence. Peaks marked with an asterisk are assigned to cage-boron nuclei carrying L substituents (see text), since they occur as singlets in fully coupled ^{11}B spectra. [e] Peak due to *C*NBu^t nucleus not observed.

cm^{-1}.[11] That the absorptions for these neutral and cationic species are at significantly higher frequencies than those observed for the anionic monocarbollide iron complex **1** is in accordance with its anionic nature, leading to a more electron rich metal center.

It was difficult to replace the CO groups in **1** with other donor molecules. Thus, no reactions occurred on heating **1c** with PPh$_3$ or CNBu^t in THF, but upon addition of Me$_3$NO to the reaction mixtures, the complexes [N(PPh$_3$)$_2$][Fe(CO)$_2$(L)(η^5-7-CB$_{10}$H$_{11}$)] (L = PPh$_3$ (**2**), CNBu^t (**3**)) were formed at room temperature. Data characterizing these compounds are given in Tables 1 and 2.

In an attempt to form a molybdenum species related to compound **1**, [Mo(CO)$_3$(NCMe)$_3$] was treated with [NHMe$_3$][*nido*-7-CB$_{10}$H$_{13}$] and, albeit in very poor yield, this did give the complex anion [Mo(CO)$_4$(η^5-7-CB$_{10}$H$_{11}$)]$^-$. This complex was also obtained from the reaction between [Na]$_3$[*nido*-7-CB$_{10}$H$_{11}$] and [Mo(CO)$_3$(NCMe)$_3$], presumably via the intermediate species [Mo(CO)$_3$(η^5-7-CB$_{10}$H$_{11}$)]$^{3-}$, which is isolobal with the long-known[12] dianion [Mo(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_{11}$)]$^{2-}$. Evidently any salt of [Mo(CO)$_3$(η^5-7-CB$_{10}$H$_{11}$)]$^{3-}$ is readily oxidized, abstracting a CO molecule to afford the final product. We were, however, able to prepare the salt [N(PPh$_3$)$_2$]-[Mo(CO)$_4$(η^5-7-CB$_{10}$H$_{11}$)] (**4**) in moderate yield by bubbling CO through a mixture containing [Na]$_3$[*nido*-7-CB$_{10}$H$_{11}$], suspended in THF, and [Mo(CO)$_3$(NCMe)$_3$] in MeCN followed by successive addition of HBF$_4$·Et$_2$O and [N(PPh$_3$)$_2$]Cl at −78 °C. We propose that **4** is formed via a pathway involving the intermediacy of unstable hydrido species [MoH(CO)$_3$(η^5-7-CB$_{10}$H$_{11}$)]$^{2-}$ and [Mo-

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Table 3. Selected Internuclear Distances (Å) and Angles (deg) for the Anion of $[N(PPh_3)_2][Mo(CO)_4(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (4) with Estimated Standard Deviations in Parentheses

Mo−C(2)	1.998(9)	Mo−C(5)	1.998(9)	Mo−C(3)	2.015(9)	Mo−C(4)	2.019(11)
Mo−B(2)	2.368(7)	Mo−B(4)	2.374(7)	Mo−B(3)	2.381(6)	Mo−B(5)	2.386(7)
Mo−C(1)	2.388(6)	C(2)−O(2)	1.116(9)	C(3)−O(3)	1.113(9)	C(4)−O(4)	1.172(10)
C(5)−O(5)	1.202(10)						
C(2)−Mo−C(5)	78.7(6)	O(5)−C(5)−Mo	174.1(13)	O(3)−C(3)−Mo	176.0(11)	C(3)−Mo−C(4)	75.5(5)
C(2)−Mo−C(4)	114.0(6)	C(2)−Mo−C(3)	82.6(7)	C(5)−Mo−C(3)	130.8(4)	O(4)−C(4)−Mo	176.8(11)
O(2)−C(2)−Mo	178(2)	C(5)−Mo−C(4)	71.6(6)				

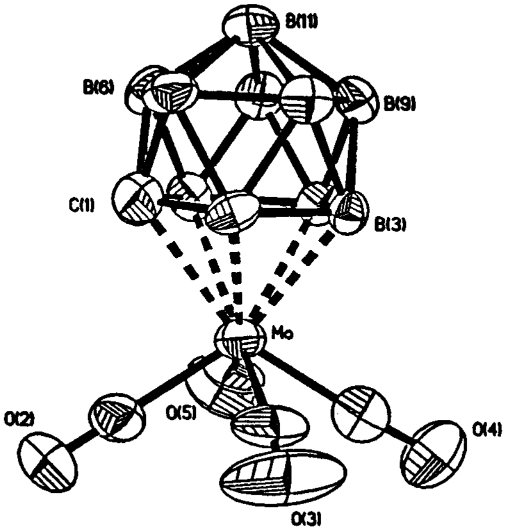


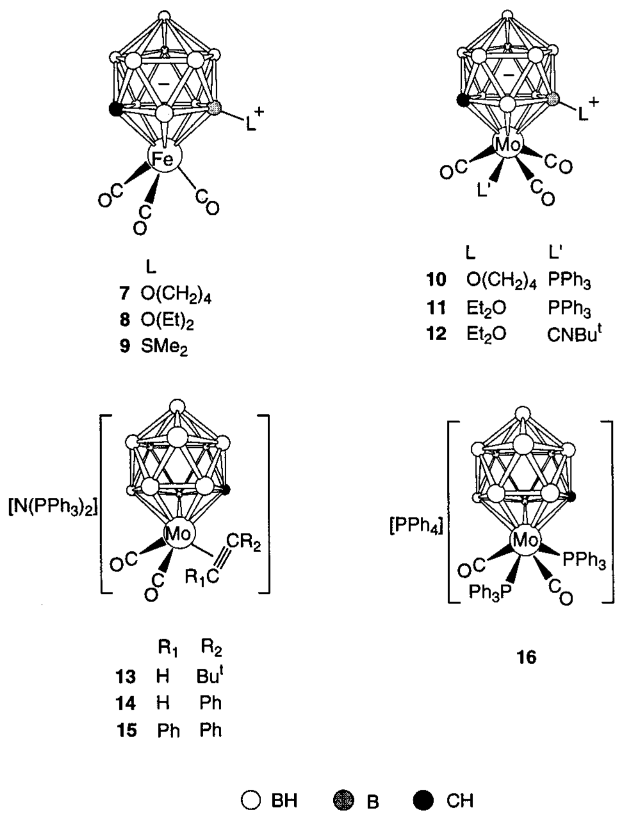
Figure 1. Structure of the anion $[Mo(CO)_4(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ of **4**, showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are shown at the 40% probability level.

$(H)_2(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$, with the latter releasing hydrogen in the presence of CO to produce the anion of **4**. In the IR spectrum of **4** there are three CO bands at 2070, 1994, and 1956 cm^{-1}. These frequencies may usefully be compared with those in the spectra of the isoelectronic cation $[Mo(CO)_4(\eta^5\text{-}C_5H_5)]^+$ (2128, 2041, and 1980 cm^{-1})[13] and the neutral species $[Mo(CO)_4(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (2097, 2034, and 2013 cm^{-1}).[14]

Because the salts **1** and **4** are precursors to other compounds, an X-ray structural study on one species seemed merited to place the work on a firm structural basis. The anion $[Mo(CO)_4(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ of **4** is shown in Figure 1, and selected structural parameters are listed in Table 3. As anticipated, the molybdenum atom is ligated on one side by the *nido*-7-$CB_{10}H_{11}$ group in an η^5 manner and on the other by the four CO molecules adopting essentially linear bonding modes. If the cage ligand is formally regarded as a three-orbital ligand, the Mo^{II} center adopts a “3:4 piano-stool configuration”. The cage−metal distances are Mo−C(1) = 2.388(6) Å, Mo−B(2) = 2.368(7) Å, Mo−B(3) = 2.381(6) Å, Mo−B(4) = 2.374(7) Å, and Mo−B(5) = 2.386(7) Å. An X-ray diffraction study on the closely related monoanion $[Mo(CO)_3(PPh_3)(\eta^5\text{-}7\text{-}OH\text{-}7\text{-}CB_{10}H_{10})]^-$ revealed a similar structure with cage−metal distances of Mo−C = 2.409(7) Å and Mo−B = 2.354(9), 2.353(8), 2.403(8), and 2.401(8) Å.[8b]

Since compound **4** has four ligated CO molecules rather than three, it reacts much more readily with Lewis bases than does **1**. Thus, the complexes $[N(PPh_3)_2]$-$[Mo(CO)_3(L)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (L = PPh_3 (**5a**), or $CNBu^t$ (**6**)), data for which are given in Tables 1 and 2, are readily formed by heating solutions of **4** in THF with PPh_3 and $CNBu^t$, respectively.

Chart 2



We have recently reported the synthesis of $[Re(CO)_2$-$(NO)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ by treating the anion $[Re(CO)_3$-$(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]^-$ with $[NO][BF_4]$.[15] In the expectation that a similar reaction between $[NO][BF_4]$ and one or other of the salts **1** would yield $[Fe(CO)_2(NO)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$, complex **1b** was treated in THF with the nitrosyl reagent. Surprisingly the product was the charge-compensated complex $[Fe(CO)_3\{\eta^5\text{-}9\text{-}O(CH_2)_4\text{-}7\text{-}CB_{10}H_{10}\}]$ (**7**; Chart 2), the structure of which was only established after an X-ray crystallographic study. The complex crystallizes with three independent molecules in the asymmetric unit, selected structural parameters for which are listed in Table 4. It was immediately apparent (Figure 2) that the THF molecule is bonded to a boron atom which is in a *β*-site with respect to the carbon in the $\overline{\mathrm{CB}\mathit{B}\mathrm{BB}}$ ring ligating the iron atom. All three molecules are structurally akin with B(3)−O(5)

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Table 4. Selected Internuclear Distances (Å) and Angles (deg) for [Fe(CO)$_3${η^5-9-O(CH$_2$)$_4$-7-CB$_{10}$H$_{10}$}] (7) with Estimated Standard Deviations in Parentheses

Molecule 1							
Fe(1)−C(4)	1.782(4)	Fe(1)−C(3)	1.803(3)	Fe(1)−C(2)	1.813(4)	Fe(1)−C(1)	2.129(3)
Fe(1)−B(5)	2.148(3)	Fe(1)−B(2)	2.157(3)	Fe(1)−B(3)	2.161(3)	Fe(1)−B(4)	2.190(4)
C(2)−O(2)	1.132(4)	C(3)−O(3)	1.138(4)	C(4)−O(4)	1.139(4)	B(3)−O(5)	1.519(4)
C(4)−Fe(1)−C(3)	93.60(14)	C(4)−Fe(1)−C(2)	94.9(2)	C(3)−Fe(1)−C(2)	91.61(14)	O(4)−C(4)−Fe(1)	176.6(3)
O(2)−C(2)−Fe(1)	180.0(4)	O(3)−C(3)−Fe(1)	178.7(3)				
Molecule 2							
Fe(2)−C(23)	1.778(4)	Fe(2)−C(24)	1.804(3)	Fe(2)−C(22)	1.812(4)	Fe(2)−C(21)	2.124(3)
Fe(2)−B(25)	2.137(4)	Fe(2)−B(22)	2.150(4)	Fe(2)−B(23)	2.164(3)	Fe(2)−B(24)	2.191(3)
C(22)−O(22)	1.134(4)	C(23)−O(23)	1.142(4)	C(24)−O(24)	1.141(3)	B(23)−O(25)	1.520(4)
C(23)−Fe(2)−C(24)	94.99(14)	C(23)−Fe(2)−C(22)	93.2(2)	C(24)−Fe(2)−C(22)	89.98(13)	O(24)−C(24)−Fe(2)	178.6(3)
O(22)−C(22)−Fe(2)	177.3(3)	O(23)−C(23)−Fe(2)	178.1(3)				
Molecule 3							
Fe(3)−C(43)	1.777(4)	Fe(3)−C(44)	1.804(4)	Fe(3)−C(42)	1.810(4)	Fe(3)−C(41)	2.123(3)
Fe(3)−B(45)	2.138(4)	Fe(3)−B(42)	2.157(4)	Fe(3)−B(43)	2.176(3)	Fe(3)−B(44)	2.186(3)
C(42)−O(42)	1.132(4)	C(43)−O(43)	1.143(4)	C(44)−O(44)	1.136(4)	B(43)−O(45)	1.509(4)
C(43)−Fe(3)−C(44)	95.21(14)	C(43)−Fe(3)−C(42)	92.6(2)	C(44)−Fe(3)−C(42)	91.18(14)	O(44)−C(44)−Fe(3)	178.6(3)
O(42)−C(42)−Fe(3)	178.2(3)	O(43)−C(43)−Fe(3)	177.9(3)				

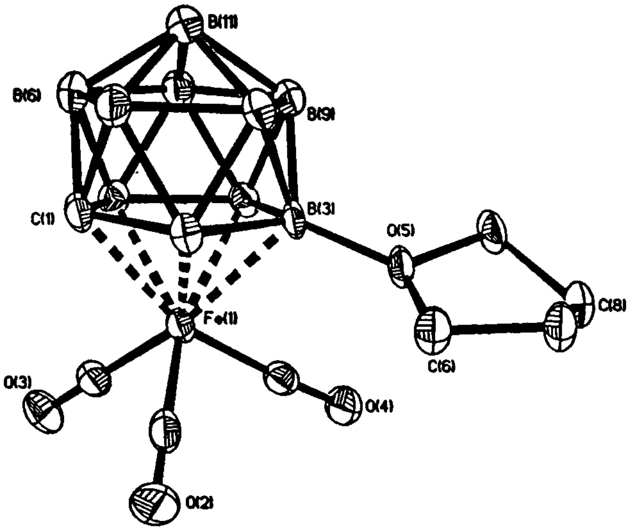

Figure 2. Structure of [Fe(CO)$_3${η^5-9-O(CH$_2$)$_4$-7-CB$_{10}$H$_{10}$}] (**7**), showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are shown at the 40% probability level.

= 1.519(4) Å, B(23)−O(25) = 1.520(4) Å, and B(43)−O(45) = 1.509(4) Å.

The NMR data (Table 2) for **7** are in accord with the X-ray diffraction results. The presence of the boron-bound exopolyhedral THF group is apparent from the ^{1}H and ^{13}C{^{1}H} NMR spectra. The ^{11}B{^{1}H} NMR data are especially informative. There are seven peaks in the range δ +9.6 to −19.1 corresponding in intensity to nine boron nuclei, with an eighth resonance due to one boron at δ 20.4. The latter peak remained a singlet in a fully coupled ^{11}B spectrum, while the others became doublets (J(BH) = ca. 130 Hz). This pattern and the chemical shift are diagnostic for a BH cage substitution of the type observed,[16] although only from the result of the X-ray structure determination could a confident discrimination be made between the α- and β-isomers, both of which would give rise to asymmetrical structures. In Et$_2$O solutions **1b** also reacts with [NO][BF$_4$], yielding the cage-substitution product [Fe(CO)$_3$(η^5-9-OEt$_2$-7-CB$_{10}$H$_{10}$)] (**8**) (Tables 2 and 3). The NMR data leave no doubt about the nature of this product. The resonance observed in the ^{11}B{^{1}H} NMR spectrum at δ 22.8 is diagnostic of the BOEt$_2$ nucleus.[16a] Again, only one isomer is formed, and that is most likely to be the β-system as observed for **7**.

During the course of the study it was observed that **7** also formed, but in low yield, when HBF$_4$·OEt$_2$ was added to THF solutions of the salts **1** in the absence of [NO][BF$_4$]. There was no evidence for the existence of the hydrido species [FeH(CO)$_3$(η^5-7-CB$_{10}$H$_{11}$)], reflecting an absence of nucleophilicity at the iron center in the monoanion. The salts **1** are thus similar to those of [Re(CO)$_3$(η^5-7-CB$_{10}$H$_{11}$)]$^{2-}$ and [Re(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_{11}$)]$^-$ in this respect.[2c,6]

Charge-compensated metallacarborane complexes with 12-vertex *closo*-3,1,2-MC$_2$B$_9$ core structures are well-established.[17] More recently several zwitterionic metallacarboranes based on *closo*-2,1-MCB$_{10}$ (M = Rh,[18,19] Ru,[20a] Os[20b]) icosahedral frameworks have also been reported. These monocarbon metallacarboranes were prepared from reactions between metal complexes and a carborane precursor which carried a substituent other than H on a cage-carbon vertex. In contrast, compounds **7** and **8** are formed by formal hydride removal from a boron vertex on a preformed metallacarborane in the presence of a donor molecule, leading to nucleophilic substitution on boron by the latter. Hawthorne and coworkers[17a] were the first to use this methodology to form B-substituted derivatives of carbollide ligands. Species

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(16) (a) Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A.; Woollam, S. F. *Organometallics* **1994**, *13*, 157. (b) Gómez-Saso, M,; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Polyhedron* **1996**, *15*, 793.

(17) (a) Hawthorne, M. F.; Warren, L. F.; Callahan, K. P.; Travers, N. F. *J. Am. Chem. Soc.* **1971**, *93*, 2407. (b) King, R. E.; Miller, S. B.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1983**, *22*, 3548. (c) Kang, H. C.; Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2024.

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(19) Chizhevsky, I. T.; Pisareva, I. V.; Petrovskii, P. V.; Bregadze, V. I.; Yanovsky, A. I.; Struchkov, Y. T.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1993**, *32*, 3393.

(20) (a) Lebedev, V. N.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1996**, *15*, 1669. (b) Lebedev, V. N.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *J. Organomet. Chem.* **1997**, *536*–*537*, 537.

Table 5. Selected Internuclear Distances (Å) and Angles (deg) for [Mo(CO)$_3$(PPh$_3$){η^5-9-O(CH$_2$)$_4$-7-CB$_{10}$H$_{10}$}] (10) with Estimated Standard Deviations in Parentheses

Mo−C(4)	1.981(2)	Mo−C(5)	2.020(2)	Mo−C(3)	2.023(2)	Mo−B(3)	2.370(2)
Mo−B(5)	2.378(2)	Mo−B(4)	2.381(2)	Mo−B(2)	2.394(2)	Mo−C(1)	2.396(2)
Mo−P	2.5542(7)	C(3)−O(3)	1.149(2)	C(4)−O(4)	1.148(2)	C(5)−O(5)	1.145(2)
B(3)−O(6)	1.532(2)						
C(4)−Mo−C(5)	73.95(7)	O(4)−C(4)−Mo	176.44(14)	B(5)−Mo−P	100.66(5)	C(3)−Mo−P	74.93(5)
C(4)−Mo−P	120.45(5)	C(4)−Mo−C(3)	78.50(7)	O(5)−C(5)−Mo	173.9(2)	B(3)−Mo−P	151.49(5)
C(1)−Mo−P	85.90(4)	C(5)−Mo−P	79.01(5)	C(5)−Mo−C(3)	124.40(7)	O(3)−C(3)−Mo	177.96(14)
B(4)−Mo−P	144.34(4)	B(2)−Mo−P	107.07(5)				

with Fe(η^5-7,8-C$_2$B$_9$H$_{11}$) groups were converted to those having Fe(η^5-10-SR$_2$-7,8-C$_2$B$_9$H$_{10}$) (R = Me, Et) moieties by adding alkyl sulfides to the former, employing strongly acid media for the deprotonation step.

Following on Quintana and Sneddon's[21] discovery that the monocarbon carborane anion [*nido*-7-CB$_{10}$H$_{13}$]$^-$ reacts with SMe$_2$ in the presence of concentrated sulfuric acid to give zwitterionic [*nido*-8-SMe$_2$-7-CB$_{10}$H$_{12}$], we have found that the compound [Fe(CO)$_3$(η^5-9-SMe$_2$-7-CB$_{10}$H$_{10}$)] (**9**) can be prepared by treating **1b** under the same conditions. Data characterizing **9** are listed in Tables 1 and 2. The ^{11}B{^{1}H} NMR spectrum of the compound displayed a resonance at δ 1.7 which remained a singlet in a fully coupled ^{11}B spectrum and thus may be assigned to the BSMe$_2$ nucleus.

Interestingly, the charge-compensated complexes **7**−**9** are also formed in reactions with the respective donor molecules when [CPh$_3$][BF$_4$] is used for hydride abstraction at the BH vertex. This correlates with our earlier results[16a] when the complexes [NEt$_4$][Mo(CO)$_2$(η^3-C$_3$H$_5$)(η^5-7,8-R$_2$-C$_2$B$_9$H$_9$)] (R = H, Me) underwent formal hydride abstraction with [CPh$_3$][BF$_4$] in the presence of donors generating the charge-compensated compounds [Mo(CO)$_2$(η^3-C$_3$H$_5$)(η^5-10-L-7,8-R$_2$-C$_2$B$_9$H$_8$)] (L = OEt$_2$, THF, SMe$_2$).

Following studies leading to the isolation of the iron complexes **7**−**9**, similar reactions were carried out with the molybdenum complex **5a**. This compound was chosen for study rather than the tetracarbonyl **4** because solutions of the latter in organic solvents decomposed, albeit slowly. Addition of tris(4-bromophenyl)aminium hexachloroantimonate to THF solutions of **5a** resulted in the immediate discharge of the blue color of the oxidant and formation of [Mo(CO)$_3$(PPh$_3$){η^5-9-O(CH$_2$)$_4$-7-CB$_{10}$H$_{10}$}] (**10**). There was no evidence for the conversion of **5a** into a dimolybdenum species as in the oxidation of [Mo(CO)$_3$(η^5-C$_5$H$_5$)]$^-$ to give [Mo$_2$(CO)$_6$(η^5-C$_5$H$_5$)$_2$]. Data for **10** are given in Tables 1 and 2. The resonance for the BO(CH$_2$)$_4$ nucleus is observed as a singlet at δ 22.9 in the fully coupled ^{11}B NMR spectrum. The corresponding peak in the spectrum of [Mo(CO)$_2$(η^3-C$_3$H$_5$)(η^5-7,8-Me$_2$-10-O(CH$_2$)$_4$-7,8-C$_2$B$_9$H$_8$)] is seen at δ 23.8.[16a] Complex **10** could also be prepared by reacting **5a** in THF with CF$_3$SO$_3$Me, a β-B site in the precursor undergoing hydride removal by Me$^+$ instead of the metal center in the anion being alkylated to generate a Mo−Me linkage. An X-ray diffraction study was made on **10** because the NMR data did not unambiguously establish whether the THF molecule was coordinated to an α- or a β-boron with respect to the carbon in the CBBBB ring ligating the Mo atom. The molecule is shown in Figure 3, and some structural parameters are listed in Table 5. As in compound **7** the THF molecule is attached to a boron in the β-site (B(3)−O(6) = 1.532(2) Å) in the CB*B*BB ring. The PPh$_3$ molecule lies transoid to B(3) and B(4) and cisoid to C(1) (P−Mo−B(3) = 151.49(5)°, P−Mo−B(4) = 144.34(4)°, P−Mo−C(1) = 85.90(4)°), probably in order to reduce steric interactions between this ligand and the THF group. The Mo−P bond length (2.5542(7) Å) is typical of such distances.[22] Neither with **10** nor with **7** was formation of more than one isomer observed. Hence, the reactions leading to their synthesis are remarkably regiospecific.

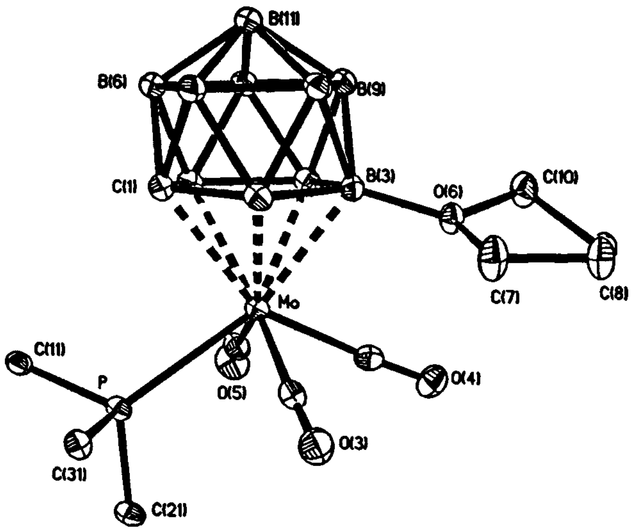

Figure 3. Structure of [Mo(CO)$_3$(PPh$_3$){η^5-9-O(CH$_2$)$_4$-7-CB$_{10}$H$_{10}$}] (**10**), showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are shown at the 40% probability level.

Addition of HBF$_4$·Et$_2$O to **5a** in a 1:1 CH$_2$Cl$_2$−Et$_2$O mixture at −78 °C afforded the complex [Mo(CO)$_3$(PPh$_3$)(η^5-9-OEt$_2$-7-CB$_{10}$H$_{10}$)] (**11**). Similarly **6** with HBF$_4$·Et$_2$O gave [Mo(CO)$_3$(CNBu^t)(η^5-9-OEt$_2$-7-CB$_{10}$H$_{10}$)] (**12**). Data characterizing these two compounds are given in Tables 1 and 2. The pattern of chemical shifts displayed in the ^{11}B{^{1}H} NMR spectra of these complexes is very similar to that in the same spectrum of **10**, leaving no doubt as to their structures. Again, there was no evidence for formation of a second isomer of either of these species having α-BOEt$_2$ groups.

During the course of our studies the alkyne−molybdenum complexes [N(PPh$_3$)$_2$][Mo(CO)$_2$(Bu^{t}C≡CH)(η^5-7-CB$_{10}$H$_{11}$)] (**13**) and [N(PPh$_3$)$_2$][Mo(CO)$_2$(PhC≡CR)(η^5-7-CB$_{10}$H$_{11}$)] (R = H (**14**), Ph (**15**)) were prepared by treating **4** in THF with the alkyne and warming to ca. 60 °C. Examination of the ^{13}C{^{1}H} NMR spectra of these compounds (Table 2) revealed that the contact carbons

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[21] Quintana, W.; Sneddon, L. G. *Inorg. Chem.* **1990**, *29*, 3242.

[22] Allen, F. H.; Brammer, L.; Kennard, O.; Orpen, A. G.; Taylor, R.; Watson, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

resonated between δ 196.4 and 164.4 in the range associated with alkynes functioning as four-electron donors.[23] It was anticipated that the complexes could be used in further syntheses, but protonation in CH_2Cl_2 at −78 °C resulted in decomposition. The alkyne was displaced with PPh_3 from the $[PPh_4]^+$ salt of **13** to yield $[PPh_4][Mo(CO)_2(PPh_3)_2(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**16**).

Conclusions

The complexes **1** and **4** are evidently useful starting reagents for preparing organoiron and -molybdenum species involving the monocarbon carbollide ligand $[\textit{nido}\text{-}7\text{-}CB_{10}H_{11}]^{3-}$ and are thus well worthy of further study. Although protonation of the monoanions did not yield neutral hydrido complexes, the charge-compensated molecules **7**−**12** are themselves potential precursors to other metallacarboranes, especially through reduction in the charge by one unit in passing from the anions $[M(CO)_n(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ (M = Fe, $n = 3$; M = Mo, $n = 4$) to the neutral species $[M(CO)_n(\eta^5\text{-}9\text{-}L\text{-}7\text{-}CB_{10}H_{10})]$ (L = donor molecule). Clearly replacement of the CO ligands in the latter by other groups will be of interest and other reactions are under investigation.

Experimental Section

General Considerations. Solvents were distilled from appropriate drying agents under nitrogen prior to use. Petroleum ether refers to that fraction of boiling point 40−60 °C. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk line techniques. Chromatography columns (ca. 15 cm in length and ca. 2 cm in diameter) were packed with silica gel (Acros, 60−200 mesh). Celite pads used for filtration were ca. 3 cm in length and 2 cm in diameter. NMR spectra were recorded at the following frequencies: ^1H, 360.1 MHz; ^{13}C, 90.6 MHz; ^{31}P, 145.7 MHz;, ^{11}B, 115.5 MHz. The $^{31}P\{^1H\}$ chemical shifts listed below are positive to high frequency of H_3PO_4 (external). Species with the cation $[N(PPh_3)_2]^+$ show a $^{31}P\{^1H\}$ resonance at δ 21.7, except for **16** (δ 23.8, $[PPh_4]^+$). The salts $[Na]_3[\textit{nido}\text{-}7\text{-}CB_{10}H_{11}]$ and $[NHMe_3][\textit{nido}\text{-}7\text{-}CB_{10}H_{13}]$ were synthesized from *nido*-7-NMe_3-7-$CB_{10}H_{12}$ according to the method of Knoth and co-workers.[24] The acid $HBF_4{\cdot}Et_2O$ as a 54% solution in Et_2O was used as purchased from Aldrich Chemical Co.

Synthesis of Salts of the Anion $[Fe(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$. The compounds $[Fe_3(CO)_{12}]$ (0.25 g, 0.50 mmol) and $[NHMe_3][\textit{nido}\text{-}7\text{-}CB_{10}H_{13}]$ (0.10 g, 0.50 mmol) were refluxed in THF (10 mL) for 24 h. The mixture containing $[NHMe_3][Fe(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ was then cooled to room temperature, and $[NEt_4]I$ (0.26 g, 1.00 mmol) was added. Solvent was removed in vacuo, and the residue was treated with CH_2Cl_2 (20 mL). After filtration through a Celite plug and addition of silica gel (ca. 2 g) to the filtrate, solvent was removed in vacuo, affording a yellow brownish powder. The latter was transferred to the top of a chromatography column. Elution with CH_2Cl_2−MeCN (4:1) gave a yellow brownish fraction. Removal of solvent in vacuo followed by crystallization from CH_2Cl_2 layered with petroleum ether yielded pale yellow microcrystals of $[NEt_4][Fe(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**1a**; 0.16 g). Reactions of the ferracarborane anion described below were studied using the $[NHMe_3]^+$ (**1b**) and $[N(PPh_3)_2]^+$ (**1c**) salts. The former was obtained by omitting addition of $[NEt_4]I$ and the latter by adding $[N(PPh_3)_2]Cl$ instead of $[NEt_4]I$.

Synthesis of $[N(PPh_3)_2][Fe(CO)_2(L)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (L = PPh_3, $CNBu^t$). (i) The compounds **1c** (0.41 g, 0.50 mmol) and PPh_3 (0.26 g, 1.00 mmol) were dissolved in THF (10 mL), and Me_3NO (0.08 g, 1.00 mmol) was added. After the mixture was stirred at room temperature for 12 h, solvent was removed in vacuo, and the residue was treated with CH_2Cl_2 (20 mL). Following filtration through a Celite plug, and addition of silica gel (ca. 2 g) to the filtrate, solvent was removed in vacuo, affording a yellow powder. The latter was transferred to the top of a chromatography column. Elution with neat CH_2Cl_2 gave a pale yellow fraction. Removal of solvent in vacuo yielded pale yellow microcrystals of $[N(PPh_3)_2][Fe(CO)_2(PPh_3)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**2**; 0.21 g). $^{31}P\{^1H\}$ NMR: δ 67.4 (s, PPh_3).

(ii) Compound **1c** (0.41 g, 0.50 mmol) was dissolved in THF (10 mL), and $CNBu^t$ (0.11 mL, 1.00 mmol) and Me_3NO (0.08 g, 1.00 mmol) were added. After the mixture was stirred at room temperature for 12 h, solvent was removed in vacuo, and the residue was treated with CH_2Cl_2 (20 mL). Following filtration through a Celite plug, and addition of silica gel (ca. 2 g), solvent was removed in vacuo, affording a yellow powder. The latter was transferred to the top of a chromatography column. Elution with neat CH_2Cl_2 gave a pale yellow fraction. Removal of solvent in vacuo yielded a pale yellow powder of $[N(PPh_3)_2][Fe(CO)_2(CNBu^t)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**3**; 0.15 g).

Synthesis of $[N(PPh_3)_2][Mo(CO)_4(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$. The reagent *nido*-7-$NMe_3$-7-$CB_{10}H_{12}$ (0.96 g, 5.00 mmol) was dissolved in dry THF (15 mL), and three small pieces of freshly cut sodium metal (ca. 0.30 g) were added. The mixture was refluxed for ca. 3 days, yielding a white precipitate of $[Na]_3[\textit{nido}\text{-}7\text{-}CB_{10}H_{11}]$. Approximately 6 h before the $[Na]_3[\textit{nido}\text{-}7\text{-}CB_{10}H_{11}]$ was required, the compound $[Mo(CO)_3(NCMe)_3]$ was prepared by heating $[Mo(CO)_6]$ (1.32 g, 5.00 mmol) in MeCN (15 mL) to reflux temperatures in a Schlenk tube fitted with a condenser. When ready, heating was simultaneously discontinued from the two refluxing reagents. Any residual sodium was carefully removed from the $[Na]_3[\textit{nido}\text{-}7\text{-}CB_{10}H_{11}]$ suspension. Then the $[Mo(CO)_3(NCMe)_3]$ solution was transferred into the $[Na]_3[\textit{nido}\text{-}7\text{-}CB_{10}H_{11}]$ suspension via a cannula. The resulting mixture was stirred at room temperature for ca. 1 h. Following this, CO was bubbled through the solution at −78 °C and $HBF_4{\cdot}Et_2O$ (1.38 mL, 10 mmol) was added. The resulting mixture was then warmed to room temperature and stirred for ca. 2 h. The salt $[N(PPh_3)_2]Cl$ (2.87 g, 5.00 mmol) was added and the mixture stirred overnight. After filtration through a Celite plug, the solvent was removed in vacuo. The residue was taken up in CH_2Cl_2 (2 mL) and the solution chromatographed. A yellow fraction was eluted with CH_2Cl_2−petroleum ether (4:1). The salt $[N(PPh_3)_2][Mo(CO)_4(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**4**; 1.76 g) was isolated after removal of solvent in vacuo.

Synthesis of $[N(PPh_3)_2][Mo(CO)_3(L)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (L = PPh_3, $CNBu^t$). (i) The reagents **4** (1.00 g, 1.15 mmol) and PPh_3 (0.32 g, 1.27 mmol) were dissolved in THF (15 mL), and the mixture was stirred for 2 h at 60 °C. Solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2 (1 mL), and this solution was chromatographed. A yellow fraction was eluted with CH_2Cl_2−petroleum ether (4:1), affording $[N(PPh_3)_2][Mo(CO)_3(PPh_3)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**5a**; 1.20 g) after removal of solvent. The product was obtained analytically pure as its $[NEt_3(CH_2Ph)]^+$ salt **5b** (Table 1). $^{31}P\{^1H\}$ NMR: **5a**, δ 53.4 (s, PPh_3).

(ii) Compound **4** (0.22 g, 0.25 mmol) was dissolved in THF (15 mL), $CNBu^t$ (29 μL, 0.28 mmol) was added, and the mixture was stirred for 2 h at 60 °C. Solvent was removed in vacuo, the residue was taken up in CH_2Cl_2 (1 mL), and this solution was chromatographed. A yellow fraction was eluted with CH_2Cl_2−petroleum ether (4:1), from which $[N(PPh_3)_2][Mo(CO)_3(CNBu^t)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**6**; 0.16 g) was obtained after removal of solvent in vacuo.

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[23] Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

[24] Knoth, W. H.; Little, J. L.; Lawrence, J. R.; Scholer, F. R.; Todd, L. J. *Inorg. Synth.* **1968**, *11*, 33.

Cage Substitution Reactions of $[NHMe_3][Fe(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$. (i) The compounds $[Fe_3(CO)_{12}]$ (0.25 g, 0.50 mmol) and $[NHMe_3][\textit{nido}\text{-}7\text{-}CB_{10}H_{13}]$ (0.10 g, 0.50 mmol) were heated at reflux in THF (10 mL) for 24 h to generate the salt **1b** in situ. The mixture was cooled to room temperature and $[NO][BF_4]$ (0.12 g, 1.00 mmol) added. After this mixture was stirred at room temperature for ca. 24 h, solvent was removed in vacuo and the dark brown residue was taken up in CH_2Cl_2 (20 mL). After filtration through a Celite plug, ca. 2 g of silica gel was added to the filtrate, and solvent was removed in vacuo, affording a yellow brownish powder which was transferred to the top of a chromatography column. Elution with neat CH_2Cl_2 gave a pale yellow fraction. Removal of solvent in vacuo followed by crystallization from CH_2Cl_2 layered with petroleum ether yielded pale yellow microcrystals of $[Fe(CO)_3\{\eta^5\text{-}9\text{-}O(CH_2)_4\text{-}7\text{-}CB_{10}H_{10}\}]$ (**7**; 0.07 g).

(ii) The salt **1b** (0.50 mmol) was formed in THF (10 mL) as described above. After the mixture was cooled to room temperature, solvent was removed in vacuo. The residue was dissolved in diethyl ether (10 mL), and $[NO][BF_4]$ (0.12 g, 1.00 mmol) was added. After this mixture was stirred at room temperature for ca. 24 h, solvent was removed in vacuo and the dark brown residue taken up in CH_2Cl_2 (20 mL). Following filtration through a Celite plug, silica gel (ca. 2 g) was added to the filtrate, the solvent was removed in vacuo, and the yellow brownish powder was transferred to the top of a chromatography column. Elution with CH_2Cl_2, removal of solvent in vacuo, and crystallization of the product from CH_2Cl_2 layered with petroleum ether yielded pale yellow microcrystals of $[Fe(CO)_3\{\eta^5\text{-}9\text{-}OEt_2\text{-}7\text{-}CB_{10}H_{10}\}]$ (**8**; 0.06 g).

(iii) After formation of the salt **1b** (0.50 mmol) as a solid as in (ii), the residue was treated with dimethyl sulfide (12 mL), followed by concentrated sulfuric acid (2 mL). The resulting two-phase solution was stirred for 24 h. The dimethyl sulfide layer was then extracted with CH_2Cl_2. After removal of solvent in vacuo, the brown residue was taken up in CH_2Cl_2 (20 mL) and this solution filtered through a Celite plug. Silica gel (ca. 2 g) was added to the filtrate, solvent was removed in vacuo, and the yellow brownish powder was transferred to the top of a chromatography column. Elution with neat CH_2Cl_2 gave a pale yellow fraction. Removal of solvent in vacuo followed by crystallization from CH_2Cl_2−petroleum ether yielded pale yellow microcrystals of $[Fe(CO)_3(\eta^5\text{-}9\text{-}SMe_2\text{-}7\text{-}CB_{10}H_{10})]$ (**9**; 0.09 g).

Cage Substitution Reactions of $[N(PPh_3)_2][Mo(CO)_3(PPh_3)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$. (i) (a) A THF solution of tris(4-bromophenyl)aminium hexachloroantimonate (0.20 g, 0.25 mmol) was added to a THF (20 mL) solution of **5a** (0.25 g, 0.23 mmol) via a cannula. The deep blue color of tris(4-bromophenyl)aminium hexachloroantimonate immediately disappeared. The mixture was stirred for 30 min, and then the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 (1 mL) and chromatographed, with CH_2Cl_2−petroleum ether (2:1) as eluent. A yellow fraction was collected, which gave $[Mo(CO)_3(PPh_3)\{\eta^5\text{-}9\text{-}O(CH_2)_4\text{-}7\text{-}CB_{10}H_{10}\}]$ (**10**; 0.02 g) after removal of solvent in vacuo. $^{31}P\{^1H\}$ NMR: δ 49.4 (s, PPh_3).

(b) Compound **5a** (0.25 g, 0.23 mmol) was dissolved in THF (20 mL), methyl trifluoromethanesulfonate (29 μL, 0.25 mmol) was added, and the mixture was stirred for 30 min. Solvent was removed in vacuo, the residue was taken up in CH_2Cl_2 (1 mL), and this solution was chromatographed. A yellow fraction was eluted with CH_2Cl_2−petroleum ether (2:1), affording $[Mo(CO)_3(PPh_3)\{\eta^5\text{-}9\text{-}O(CH_2)_4\text{-}7\text{-}CB_{10}H_{10}\}]$ (**10**; 0.07 g) after removal of solvent in vacuo.

(ii) Compound **5a** (0.25 g, 0.23 mmol) was dissolved in CH_2Cl_2−Et_2O (20 mL, 1:1) and the solution cooled to −78 °C. After addition of $HBF_4\cdot Et_2O$ (340 μL, 2.30 mmol) the mixture was gradually warmed to room temperature and stirred for 2 h. Solvent was removed in vacuo, the residue was taken up in CH_2Cl_2 (1 mL), and this solution was chromatographed. A yellow fraction was eluted with CH_2Cl_2−petroleum ether (2:1), which gave $[Mo(CO)_3(PPh_3)(\eta^5\text{-}9\text{-}OEt_2\text{-}7\text{-}CB_{10}H_{10})]$ (**11**; 0.12 g) after removal of solvent. $^{31}P\{^1H\}$ NMR: δ 49.3 (s, PPh_3).

(iii) Similarly **6** (0.21 g, 0.23 mmol) in CH_2Cl_2−Et_2O (20 mL, 1:1) at −78 °C with $HBF_4\cdot Et_2O$ (340 μL, 2.30 mmol) gave $[Mo(CO)_3(CNBu^t)(\eta^5\text{-}9\text{-}OEt_2\text{-}7\text{-}CB_{10}H_{10})]$ (**12**; 0.05 g).

Synthesis of Alkyne−Molybdenum Complexes. (i) Compound **4** (0.22 g, 0.25 mmol) was dissolved in THF (15 mL), $Bu^tC{\equiv}CH$ (34 μL, 0.28 mmol) was added, and the mixture was stirred for 2 h at 60 °C. Solvent was removed in vacuo, the residue was taken up in CH_2Cl_2 (1 mL), and this solution was chromatographed. A violet fraction was eluted with CH_2Cl_2−petroleum ether (4:1). The compound $[N(PPh_3)_2][Mo(CO)_2(Bu^tC{\equiv}CH)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**13**; 0.14 g) was obtained after removal of solvent in vacuo.

(ii) The compounds $[N(PPh_3)_2][Mo(CO)_2(PhC{\equiv}CH)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**14**; 0.12 g) and $[N(PPh_3)_2][Mo(CO)_2(PhC{\equiv}CPh)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**15**; 0.13 g) were similarly obtained from **4** (0.22 g, 0.25 mmol) using 0.28 mmol of $PhC{\equiv}CH$ (31 μL) and $PhC{\equiv}CPh$ (0.05 g), respectively.

(iii) The $[PPh_4]^+$ salt of **13** (0.18 g, 0.25 mmol) was dissolved in THF (20 mL), and PPh_3 (0.14 g, 0.55 mmol) was added. The mixture was stirred at 60 °C, affording a yellow precipitate, which was removed by filtration after 2 h. Yellow microcrystals of $[PPh_4][Mo(CO)_2(PPh_3)_2(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**16**; 0.14 g) were obtained after recrystallization from CH_2Cl_2−petroleum ether using the layering method. $^{31}P\{^1H\}$ NMR: δ 68.5 (s, PPh_3).

Crystal Structure Determinations and Refinements. Crystals of **7** were grown from CH_2Cl_2−pentane, while those of **4** and **10** were grown from CH_2Cl_2−petroleum ether. The asymmetric unit of **7** contained three crystallographically independent molecules of the complex in general positions. Diffracted intensities for **4** were collected on an Enraf-Nonius CAD-4 diffractometer operating in the ω−2θ scan mode, using graphite-monochromated Mo Kα X-radiation. The final unit cell dimensions were determined from the setting angle values of 25 accurately centered reflections. The stability of the crystal during the period of the data collection was monitored by measuring the intensities of three standard reflections every 2 h. Data were collected at a constant scan speed of 5.17° m^{-1} in ω with a scan range of $1.15° + 0.35 \tan \theta$. The data were corrected for Lorentz, polarization, and X-ray absorption effects, the last by a semiempirical method based on azimuthal scans of ψ data of several Euclerian angles (χ) near 90°.

Single crystals of **7** and **10** were mounted on glass fibers, and low-temperature data (173 K for **7** and 163 K for **10**) were collected on a Bruker SMART CCD area-detector three-circle diffractometer (Mo Kα X-radiation, graphite monochromator, $\bar{\lambda} = 0.710\ 73$ Å). For three or four settings of φ, narrow data “frames” were collected for 0.3° increments in ω. For complex **7** just over a hemisphere of data was collected, while for **10** a full sphere of data was collected. It was confirmed that crystal decay had not taken place during the course of the data collection. The substantial redundancy in data allows empirical absorption corrections (SADABS)[25] to be applied using multiple measurements of equivalent reflections. The data frames were integrated using SAINT[25] and refined by full-matrix least squares on all F^2 data using SHELXTL version 5.03[25] or SHELXL-97.[26]

The structures were solved by conventional direct methods, and the non-hydrogen atoms, except for those described below, were refined with anisotropic thermal parameters. The cage carbon atom in each complex was identified from the magnitude of its anisotropic thermal parameters and from a

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(25) SHELXTL-PC; Bruker AXS, Madison, WI, 1995.

(26) Sheldrick, G. M. University of Göttingen, Göttingen, Germany, 1997.

Table 6. Data for X-ray Crystal Structure Analyses

	4	**7**	**10**
cryst dimens (mm)	0.30 × 0.20 × 0.20	0.20 × 0.18 × 0.10	0.50 × 0.45 × 0.10
formula	$C_{41}H_{41}B_{10}NO_4P_2Mo$	$C_8H_{18}B_{10}O_4Fe$	$C_{26}H_{33}B_{10}O_4PMo$
M_r	877.73	342.17	644.53
cryst color, shape	yellow prisms	pale yellow plates	yellow blocks
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	16.577(2)	17.5961(14)	10.7962(19)
b (Å)	15.845(5)	16.6039(13)	10.943(3)
c (Å)	18.448(4)	16.8279(13)	13.959(3)
α (deg)			107.392(15)
β (deg)	113.22(2)	102.73(2)	95.60(2)
γ (deg)			100.476(19)
V (Å^3)	4452.9(18)	4795.7(7)	1527.1(6)
Z	4	12	2
d_{calcd} (g cm^{-3})	1.309	1.422	1.402
μ(Mo Kα) (cm^{-1})	4.07	9.48	5.14
F(000) (e)	1792	2088	656
T (K)	293	173	163
2θ range (deg)	4.4−45.0	3.4−50.0	3.8−55.0
no. of rflns coll (excld stds)	6025	13 199	15 477
no. of unique rflns	5789	7279	6884
no. of obsd rflns	3621	4924	5963
rfln limits: h, k, l	0−17, 0−17, −19 to +18	−20 to +19, −19 to +10, −18 to +20	−14 to +14, −13 to +14, −17 to +18
no. of params refined	566	622	379
final residuals wR2 (R1), all data[a]	0.1120 (0.0527)	0.0997 (0.0389)	0.0576 (0.0221)
weighting factors[a]	$a = 0.0340$, $b = 4.1318$	$a = 0.0554$, $b = 0.000$	$a = 0.0335$, $b = 0.000$
goodness of fit on F^2	1.051	0.948	0.962
final electron density diff features (max/min) (e Å^{-3})	0.362, −0.438	0.688, −0.399	0.409, −0.273

[a] Refinement was block full-matrix least squares on all F^2 data: $wR2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum w(F_o^2)^2]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. The value in parentheses is given for comparison with refinements based on F_o with a typical threshold of $F_o > 4\sigma(F_o)$ and $R1 = \sum||F_o^2| - |F_c||/\sum|F_o|$ and $w^{-1} = [\sigma^2(F_o) + g(F_o^2)]$.

comparison of the bond lengths to adjacent boron atoms. All the carbonyl groups of **4** were disordered across two sites (78:22): their bond distances were restrained and all the minor component atoms refined with isotropic thermal parameters. The final residuals for complex **4** were high, presumably due to the poorly diffracting crystals obtained and the disorder of the carbonyl groups. All hydrogen atoms were included in calculated positions and allowed to ride on the parent boron or carbon atoms with isotropic thermal parameters ($U_{iso} = 1.2U_{iso}$ of the parent atom). All calculations were carried out on Dell or Viglen PC computers, and the experimental data are summarized in Table 6.

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Supporting Information Available: Tables of atomic coordinates and U values, bond lengths and angles, and anisotropic thermal parameters and ORTEP diagrams for **4**, **7**, and **10** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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