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Articles

Revisiting $[Mn(CO)_3(\eta^5\text{-}nido\text{-}7,8\text{-}C_2B_9H_{11})]^-$, the Dicarbollide Analogue of $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$: Reactivity Studies Leading to Boron Atom Functionalization†

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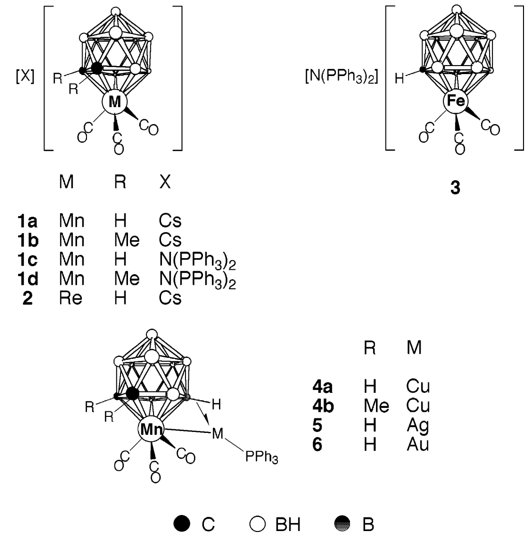
Treatment of $Na_2[7,8\text{-}R_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_9]$ (R = H, Me) with the reagent $[Mn(NCMe)_3(CO)_3][PF_6]$ affords the anions $[3,3,3\text{-}(CO)_3\text{-}1,2\text{-}R_2\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_9]^-$, typically isolated as Cs^+ or $[N(PPh_3)_2]^+$ salts. These anions interact with cationic metal fragments $\{M(PPh_3)\}^+$ (M = Cu, Ag, Au) to give the bimetallic compounds $[3,8\text{-}\{M(PPh_3)\}\text{-}8\text{-}\mu\text{-}H\text{-}3,3,3\text{-}(CO)_3\text{-}1,2\text{-}R_2\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_8]$, for which the structures of the Cu and Au species (R = H) have been confirmed by X-ray diffraction studies. In contrast, other electrophiles such as H^+ and Me^+ abstract hydride from carborane boron vertexes, which in the presence of donors (L) produces the neutral zwitterions $[8\text{-}L\text{-}3,3,3\text{-}(CO)_3\text{-}1,2\text{-}R_2\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_8]$. The halogenated derivatives $[8\text{-}X\text{-}3,3,3\text{-}(CO)_3\text{-}1,2\text{-}R_2\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_8]^-$ (X = Cl, Br, I) of the parent anions are obtained by hydride abstraction in halogenated solvents or by direct reaction with Br_2 or I_2. Moreover, further cluster functionalization is achieved by treating the 8-iodo species with the Grignard reagents R′MgBr, leading to the anions $[8\text{-}R'\text{-}3,3,3\text{-}(CO)_3\text{-}1,2\text{-}R_2\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_8]^-$. When the substitution processes are repeated, the latter series of anions yield compounds with yet more functionality. Crystallographic studies of the boron-substituted derivatives $[8\text{-}\{(E)\text{-}N(Me){=}C(H)Me\}\text{-}3,3,3\text{-}(CO)_3\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_{10}]$, $[N(PPh_3)_2][8\text{-}(p\text{-}C_6H_4Me)\text{-}3,3,3\text{-}(CO)_3\text{-}1,2\text{-}Me_2\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_8]$, and $[4\text{-}\{(Z)\text{-}N(Me){=}C(H)Me\}\text{-}3,3,3\text{-}(CO)_3\text{-}1,2,8\text{-}Me_3\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_7]$ confirmed their structures and the sites of cage substitution.

Introduction

Cyclopentadienylmanganese tricarbonyl was one of the original "piano-stool" complexes of organo-transition-metal chemistry, discovered half a century ago in the infancy of modern organometallic chemistry. It is now the basis for an extensive area of chemistry.[1] The analogous dicarbollide species $Cs[3,3,3\text{-}(CO)_3\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_{11}]$ (**1a**) (Chart 1) was first reported by Hawthorne and co-workers almost 40 years ago,[2,3] and yet its chemistry has scarcely been examined. This paucity may in part be due to the difficulty of achieving carbonyl substitution at manganese.[1] Such studies as have been reported have instead largely been limited to the preparation of cage-substituted analogues using preformed functionalized carboranes[4−7] and to theoretical analyses.[5,7,8] Compound **2**, the rhenium analogue of **1a**, has recently received renewed attention as a substrate

Chart 1



	M	R	X
1a	Mn	H	Cs
1b	Mn	Me	Cs
1c	Mn	H	$N(PPh_3)_2$
1d	Mn	Me	$N(PPh_3)_2$
2	Re	H	Cs

	R	M
4a	H	Cu
4b	Me	Cu
5	H	Ag
6	H	Au

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† Dedicated to Professor José Vicente, University of Murcia, on the occasion of his 60th birthday.

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for the formation of several remarkable bi- and polymetallic species[9−11] and as a precursor to a set of rhenacarboranes bearing nitrosyl and alkylidene ligands.[12] Contemporary studies in our laboratories upon the related iron−monocarbollide species exemplified by $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}FeCB_{10}H_{11}]$ (**3**),[13] the anion of which is formally isoelectronic with that of **1a**, have revealed a wide range of reactions with electrophiles, leading both to bimetallic compounds[14] and to cage-boron-substituted derivatives.[13,15] We now report upon an exploration of the chemistry of compound **1a** and its dimethylated analogue (**1b**), which demonstrate behavior related to that of both **2** and **3**: in particular, an extensive cage substitution chemistry.

Results and Discussion

The anions $[3,3,3\text{-}(CO)_3\text{-}closo\text{-}3,1,2\text{-}MC_2B_9H_{11}]^-$ (M = Mn, Re) were originally prepared by the reaction of $Na_2[nido\text{-}7,8\text{-}C_2B_9H_{11}]$ with $[MBr(CO)_5]$ in refluxing THF (THF = tetrahydrofuran) and isolated as the Cs^+ salts **1a** and **2** in reported yields of 55.5% and 42%, respectively.[3] Recent studies in our laboratories have shown that the yield of **2** is improved to over 95% by use of $[ReBr(CO)_3(THF)_2]$ as the rhenium source.[9] Seeking a parallel route to the manganese species, that is, one employing a source of $\{Mn(CO)_3\}$ that bears other labile ligands, we found that treatment of $Na_2[nido\text{-}7,8\text{-}C_2B_9H_{11}]$ with $[Mn(NCMe)_3(CO)_3][PF_6]$[16] in refluxing THF afforded the desired product in superior yields. This manganese reagent has recently also been used to prepare a manganese−monocarbollide species.[17] Indeed, we observed in the present work that use of $[Mn(NCMe)_3(CO)_3]Br$ (prepared in situ from $[MnBr(CO)_5]$ in refluxing NCMe)[16] gave **1a** more conveniently, ultimately in up to 68% isolated yield. The dimethyl analogue **1b** was prepared similarly to **1a**, albeit in somewhat lower yield. Metathesis of **1a** and **1b** to the corresponding $[N(PPh_3)_2]^+$ salts, **1c** and **1d**, respectively, was readily achieved by treatment with $[N(PPh_3)_2]Cl$ in THF.

The anions of compounds **1** readily react with sources of the cationic metal fragments $\{M(PPh_3)\}^+$ (M = Cu, Ag, Au), to afford the neutral bimetallic species $[3,8\text{-}\{M(PPh_3)\}\text{-}8\text{-}\mu\text{-}H\text{-}3,3,3\text{-}(CO)_3\text{-}1,2\text{-}R_2\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_8]$ (R = H, M = Cu (**4a**), Ag (**5**), Au, (**6**); R = Me, M = Cu (**4b**)). In contrast with the corresponding reactions of **2**, the isolation of the gold−manganese species **6** was somewhat surprising: it had previously been found that the rhenium anion does not aurate under conditions similar to those employed here.[9] Compounds **4** and **5** were expected to be isostructural, similar to the products obtained by reaction of **2** with copper− and silver−phosphine cations;[9] that is, having an Mn−M bond supported by a B−H⇀M agostic-type interaction. In contrast, it was thought likely that the gold−manganese species **6** would have only a direct Mn−Au bond, and no agostic B−H⇀Au contact, in keeping with the known preference of gold(I) for linear coordination.[18] The structural studies on **4a** and **6**, described below, proved these expectations to be only partly correct.

Spectral data characterizing compounds **4**−**6** are listed in Tables 1 and 2. In their ^1H NMR spectra, **4**−**6** showed no resonance attributable to the H atoms involved in the B−H⇀M agostic-type linkages. This is presumably due to dynamic processes that are rapid on the NMR time scale; the absence of such signals, even at low temperatures, is typical in compounds of this type.[9,14] Peaks for the cage C−H or C−Me units and metal-bound PPh_3 moieties are seen in typical positions in the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **4**−**6**. Likewise, the $^{11}B\{^1H\}$ NMR spectra are unremarkable, all showing resonances in a 1:2:2:1:1:2 ratio (some are coincident), consistent with the approximate molecular symmetry seen in the solid state and a time-averaged structure in solution.

The structure determined for compound **4a** by an X-ray diffraction study is shown in Figure 1a. An Mn−Cu bond is clearly present in the molecule (Mn−Cu = 2.5719(4) Å), with the bonding of the exo-polyhedral copper fragment additionally supported by a B−H⇀Cu interaction involving the unique β-boron atom (B(8)) of the manganese-bound $\overline{\mathrm{CC}B\mathrm{BB}}$ face (B(8)···Cu = 2.152(2) Å, B(8)−H(8) = 1.10(2) Å, and Cu−H(8) = 1.68(2) Å). One of the Mn-bound CO groups makes a close approach to the Cu center (Cu···C(11) = 2.4297(18) Å), resulting in a slight deviation from linearity of the Mn−C(11)−O(11) angle (173.86(17)°), but this is a minimal interaction. Apart from the presence of the Mn (rather than Re) vertex, the architecture of **4a** is essentially identical with that of the corresponding complex derived from **2** and merits little further comment.

Conversely, the structure found for the gold−manganese species **6** (Figure 1b) was somewhat surprising, in that it too is isostructural with **4a** and also with the Cu and Ag derivatives of **2**. The exo-polyhedral gold fragment is bonded to manganese with an Mn−Au distance of 2.9284(4) Å, significantly longer than in the simpler complexes $[(OC)_4(L)Mn{-}AuPPh_3]$ (L = PPh_3, Mn−Au = 2.52(3) Å; L = $P(OPh)_3$, Mn−Au = 2.573(7)

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Table 1. Analytical and Physical Data[a]

compd	yield/%	ν_{max}(CO)[b]/cm^{-1}	anal.[c]/% C	H	N
[3,8-{Cu(PPh$_3$)}-8-μ-H-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**4a**)	41	2021 vs, 1954 s, 1925 s	46.5 (46.3)	4.4 (4.4)	
[3,8-{Cu(PPh$_3$)}-8-μ-H-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**4b**)	78	2015 vs, 1946 s, 1924 s	48.3 (48.0)	5.0 (4.8)	
[3,8-{Ag(PPh$_3$)}-8-μ-H-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**5**)	87	2017 vs, 1926 br s	41.3 (41.3)	3.9 (4.0)[d]	
[3,8-{Au(PPh$_3$)}-8-μ-H-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**6**)	55	2019 vs, 1936 br s	37.4 (37.8)	3.6 (3.6)	
[8-{O(CH$_2$)$_4$}-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**7b**)	23	2010 vs, 1928 vs	35.8 (35.7)	6.1 (6.0)	
[8-SMe$_2$-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7c**)	64	2023 vs, 1947 vs	24.0 (24.0)	4.4 (4.6)[d]	
[8-{(*E*)-N(Me)═C(H)Me}-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7d**)	73	2019 vs, 1938 s, 1927 s	29.2 (29.3)	5.2 (5.2)	4.6 (4.3)
[8-{(*E*)-N(Me)═C(H)Et}-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7e**)	65	2018 vs, 1937 vs	31.4 (31.7)	5.4 (5.6)	4.1 (4.1)
[8-{NH(Me)Et}-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7f**)	53	2019 vs, 1941 s, 1925 s	29.1 (29.2)	5.6 (5.8)	4.2 (4.2)
[8-NH$_2$Me-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7g**)	57	2019 vs, 1941 s, 1923 s	23.8 (23.9)	4.9 (5.0)	4.6 (4.6)
[8-{(*Z*)-N(Me)═C(H)Me}-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7h**)	53	2018 vs, 1929 br s	29.3 (29.3)	5.2 (5.2)	4.3 (4.3)
[8-{(*Z*)-N(Me)═C(H)Et}-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7j**)	76	2014 vs, 1936 vs, 1921 vs	31.6 (31.7)	5.6 (5.6)	4.1 (4.1)
[N(PPh$_3$)$_2$][8-Cl-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**9**)	79	2009 vs, 1925 vs	58.9 (58.3)	4.8 (4.8)	1.8 (1.7)
[N(PPh$_3$)$_2$][8-Br-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**10**)	73	2011 vs, 1925 vs	55.6 (55.4)	4.6 (4.5)	1.8 (1.6)
[N(PPh$_3$)$_2$][8-I-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**11a**)	95	2011 vs, 1926 vs	52.7 (52.6)	4.4 (4.3)	1.6 (1.5)
[N(PPh$_3$)$_2$][8-I-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**11b**)	95	2007 vs, 1927 s, 1915 s	53.6 (53.6)	4.6 (4.6)	1.5 (1.4)
[3,3-(CO)$_2$-3-NO-*closo*-3,1,2-MnC$_2$B$_9$H$_{11}$] (**12b**)	22	2093 vs, 2055 s[e]	18.0 (17.6)	4.1 (4.1)	5.0 (5.1)
[N(PPh$_3$)$_2$][8-(*p*-C$_6$H$_4$Me)-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**13a**)	82	1997 vs, 1914 br s	65.0 (64.7)	5.6 (5.5)	1.4 (1.5)
[N(PPh$_3$)$_2$][8-(*p*-C$_6$H$_4$Me)-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**13b**)	30	2001 vs, 1914 br s	64.3 (64.0)	5.3 (5.3)	1.4 (1.6)
[N(PPh$_3$)$_2$][3,3,3-(CO)$_3$-1,2,8-Me$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**13c**)	78	1992 vs, 1910 br s	61.8 (62.0)	5.6 (5.6)	1.6 (1.6)
[N(PPh$_3$)$_2$][8-{CH$_2$CH═CH$_2$}-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**13d**)	76	1995 vs, 1911 br s	63.4 (62.9)	5.8 (5.6)	1.6 (1.6)
[N(PPh$_3$)$_2$][8-(*p*-C$_6$H$_4$C≡CSiMe$_3$)-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**13e**)	34	2006 vs, 1912 br s	63.3 (63.2)	5.7 (5.6)	1.4 (1.4)[f]
[N(PPh$_3$)$_2$][4-I-3,3,3-(CO)$_3$-1,2,8-Me$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_7$] (**14**)	46	2002 vs, 1925 br s	50.3 (50.8)	4.4 (4.6)	1.3 (1.3)[g]
[N(PPh$_3$)$_2$][4-(*p*-C$_6$H$_4$Me)-3,3,3-(CO)$_3$-1,2,8-Me$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_7$] (**15**)	79	1992 vs, 1924 br s	65.2 (65.0)	5.6 (5.7)	1.5 (1.5)
[4-{(*Z*)-N(Me)═C(H)Me}-3,3,3-(CO)$_3$-1,2,8-Me$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_7$] (**16**)	39	2017 vs, 1932 br s	38.6 (38.4)	7.3 (6.8)	3.6 (3.6)[h]

[a] All compounds are yellow, except **12b**, which is orange. [b] Measured in CH$_2$Cl$_2$; broad medium-intensity bands observed at ~2500–2550 cm^{-1} in the spectra of all compounds are due to B–H absorptions. [c] Calculated values are given in parentheses. [d] Cocrystallizes with 0.5 mol equiv of CH$_2$Cl$_2$. [e] ν_{max}(NO) 1812 s cm^{-1}. [f] Cocrystallizes with 0.25 mol equiv of CH$_2$Cl$_2$. [g] Cocrystallizes with 1 mol equiv of CH$_2$Cl$_2$. [h] Cocrystallizes with 0.25 mol equiv of C$_6$H$_{14}$.

Å)[19] and [{(OC)$_5$Mn–Au}$_2$-μ-(dppf)] (Mn–Au = 2.56(3), 2.58(3) Å; dppf = 1,1′-bis(diphenylphosphino)ferrocene).[20] As in the Mn–Cu compound **4a**, the Au center is rather close to B(8) (Au···B(8) = 2.3077(17) Å, B(8)–H(8) = 1.179(19) Å, and Au···H(8) = 1.796(19) Å). Moreover, the Mn–Au–P angle (132.508(13)°) is significantly distorted from linearity and indeed is more bent than the Mn–Cu–P angle (140.193(17)°) in **4a**. These features certainly are consistent with the existence of a B–H⇀Au agostic-type interaction, but in the absence of definitive ^{1}H NMR data the presence of such an interaction in solution cannot be confirmed. It may be noted in this connection, however, that a pair of bis-{M(PPh$_3$)} derivatives (M = Cu, Au) of a {ReCB$_9$} cluster have also been reported to be isostructural in the solid state. Both exo-polyhedral fragments there were also supported by B–H⇀M interactions, although full structural data for the Au species were not available.[21] To our knowledge, the only other structurally characterized species bearing an exo-polyhedral {Au(PPh$_3$)} fragment comparable with that in **6** is the digold species [9-*exo*-{Au(PPh$_3$)}-9-μ-H-10-*endo*-{Au(PPh$_3$)}-7,8-Me$_2$-*nido*-7,8-C$_2$B$_9$H$_8$].[22] For the latter compound, the geometric parameters associated with the B–H⇀Au unit, Au···B = 2.28(1) Å, B–H = 1.20(9) Å, and Au···H = 1.9(1) Å, are comparable with those of **6**. However, as with **6**, no parallel evidence for this interaction could be gleaned from ^{1}H NMR studies. A final comparison may be drawn between the structure of **6** and those of the species [(η^5-C$_5$H$_5$)M(CO)$_3${Au(PPh$_3$)}] (M = Mo, W).[23] The anions [(η^5-C$_5$H$_5$)M(CO)$_3$]$^-$ in the latter complexes may be considered isolobal with the anion of **1**, and yet their M–Au–P angle is close to linearity, in sharp contrast to the geometry in compound **6**.

Whereas the above reactions of the anions of **1** with {M(PPh$_3$)}$^+$ occur essentially at the manganese center, no similar reaction was observed with isolobal H$^+$ or Me$^+$ to form, for example, [3-R-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{11}$] (R = H, Me). As this would formally require an Mn^{III} center, which is rare, this failure is unsurprising.[1a] Instead, the electrophiles H$^+$ and Me$^+$ behave

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

compd	^{1}H/δ[b]	^{13}C/δ[c]	^{11}B/δ[d]
1b	2.03 (s, 6H, Me)	225.2 (CO), 65.6 (br, cage C), 32.2 (Me)[e]	−4.8, −6.8 (2B), −7.8, −10.6 (2B), −12.0, −14.6 (2B)
4a	7.67−7.46 (m, 15H, Ph), 2.90 (br s, 2H, cage CH)	219.3 (CO), 134.2−129.8 (Ph), 42.4 (br, cage C)	−1.3, −11.1 (2B), −13.4 (2B), −14.4, −18.8 (3B)
4b	7.56−7.45 (m, 15H, Ph), 2.13 (s, 6H, Me)	219.9 (CO), 134.2−128.5 (Ph), 70.5 (br, cage C), 31.9 (Me)	−2.2, −8.1 (3B), −13.3 (4B), −15.9
5	7.54−7.45 (m, 15H, Ph), 2.75 (br s, 2H, cage CH)	221.3 (CO), 135.1−128.8 (Ph), 40.6 (br, cage C)	−2.9, −11.0 (2B), −12.8 (2B), −14.0, −20.1 (3B)
6	7.63−7.53 (m, 15H, Ph), 2.82 (br s, 2H, cage CH)	220.4 (CO), 135.4−127.5 (Ph), 41.2 (br, cage C)	−1.1, −8.8 (2B), −11.2 (3B), −16.8, −20.3 (2B)
7b	4.30 (s, 4H, $\mathrm{OCH_2}$), 2.17 (s, 4H, $\mathrm{CH_2}$), 2.00 (s, 6H, Me)	222.7 (CO), 81.4 ($\mathrm{OCH_2}$), 62.9 (br, cage C), 31.5 ($\mathrm{CH_2}$), 25.5 (Me)	18.4 (B(8)), −7.6, −9.1 (2B), −11.3 (2B), −15.8 (3B)
7c	2.84 (br s, 6H, Me), 2.71 (br s, 2H, cage CH)	221.5 (CO), 38.1 (br, cage C), 19.3 (Me)	−0.4 (B(8)), −4.9, −11.3 (4B), −21.7 (3B)
7d	7.84 (vbr, 1H, =CH), 3.57 (s, 3H, NMe), 2.68 (br s, 2H, cage CH), 2.51 (br, 3H, =CMe)	222.3 (CO), 176.0 (C=N), 36.2 (br, cage C), 20.8 (=C*Me*)[f]	5.3 (B(8)), −6.9, −10.1 (2B), −12.7 (2B), −21.9 (2B), ca. −22.5 (sh)
7e	7.67 (vbr, 1H, =CH), 3.57 (s, 3H, NMe), 2.93 (br s, 2H, cage CH), 2.49 (br, 2H, $=\mathrm{CCH_2}$), 1.21 (br, 3H, $\mathrm{CH_2}\mathit{Me}$)	222.2 (CO), 181.2 (C=N), 53.2 (NMe), 36.1 (br, cage C), 27.2 ($\mathit{C}\mathrm{H_2}$), 10.2 ($\mathrm{CH_2}\mathit{Me}$)	5.5 (B(8)), −6.9, −10.0 (2B), −12.7 (2B), −22.0 (3B)
7f	3.86 (vbr, 1 H, NH), 3.33, 2.92 (m × 2, 1H × 2, $\mathrm{NC}\mathit{H_2}\mathrm{Me}$), 2.74 (s, 3H, NMe), 2.46 (br s, 2H, cage CH), 1.28 (vt, 3H, $\mathrm{NCH_2}\mathit{Me}$, J(HH) = 7)	222.3 (CO), 53.1 (NMe), 40.9 ($\mathrm{CH_2}$), 35.5 (br, cage C), 12.7 ($\mathrm{CH_2}\mathit{Me}$)	9.0 (B(8)), −6.4, −10.1 (2B), −12.5 (2B), −22.8 (2B), −24.1
7g	4.35 (vbr, 2H, NH), 2.71 (br, 3H, NMe), 2.48 (br s, 2H, cage CH)	222.4 (CO), 36.6 (br, cage C), 34.7 (NMe)	5.0 (B(8)), −7.0, −11.1 (2B), −13.4 (2B), −23.0 (2B), −25.4
7h	8.04 (vbr, 1H, =CH), 3.32 (s, 3H, NMe), 2.49 (br s, 2H, cage CH), 2.23 (d, 3H, CMe, J(HH) = 6)	222.6 (CO), 172.6 (C=N), 36.2 (br, cage C), 18.6 (=C*Me*)[f]	8.2 (B(8)), −6.2, −9.6 (2B), −13.2 (2B), −22.6 (2B), −24.3
7j	7.89 (vbr, 1H, =CH), 3.32 (s, 3H, NMe), 2.49 (br, 4H, cage CH and $=\mathrm{CCH_2}$), 1.26 (br, 3H, $\mathrm{CH_2}\mathit{Me}$)	222.5 (CO), 177.7 (C=N), 53.2 (NMe), 36.1 (br, cage C), 25.6 ($\mathit{C}\mathrm{H_2}$), 9.8 ($\mathrm{CH_2}\mathit{Me}$)[f]	8.2 (B(8)), −6.2, −9.5 (2B), −13.2 (2B), −22.6 (2B), −24.3
9	7.68−7.50 (m, 30H, Ph), 2.26 (br s, 2H, cage CH)	224.1 (CO), 134.9−126.7 (Ph), 34.2 (br, cage C)	8.3 (B(8)), −7.1, −7.9 (2B), −11.5 (2B), −22.9 (2B), −26.9
10	7.66−7.48 (m, 30H, Ph), 2.27 (br s, 2H, cage CH)	224.1 (CO), 135.0−126.8 (Ph), 34.9 (br, cage C)	0.5 (B(8)), −6.5, −7.8 (2B), −11.2 (2B), −22.6 (2B), −25.8
11a	7.68−7.50 (m, 30H, Ph), 2.32 (br s, 2H, cage CH)	224.0 (CO), 135.0−126.7 (Ph), 36.1 (br, cage C)	−5.2, −7.3 (2B), −10.6 (2B), −16.5 (B(8)), −22.2 (2B), −23.6
11b	7.70−7.53 (m, 30H, Ph), 1.94 (s, 6H, Me)	224.0 (CO), 135.0−126.7 (Ph), 64.1 (br, cage C), 31.6 (Me)	−4.8, −5.8 (2B), −7.4 (2B), ca. −14.8 (B(8) and 3B)
12b	3.16 (br s, 2H, cage CH)	214.5 (CO), 51.6 (br, cage C)	8.0, 3.5, −2.1 (2B), −6.1 (2B), −13.6 (2B), −16.9
13a	7.66−7.48 (m, 30H, PPh), 7.14, 6.84 (br m × 2, 2H × 2, $\mathrm{C_6H_4}$), 2.20 (s, 3H, $\mathrm{C_6H_4}\mathit{Me}$), 2.05 (s, 6H, cage CMe)	224.6 (CO), 134.1−126.8 (Ph and $\mathrm{C_6H_4}$), 115.4 (br, B−$\mathrm{C_6H_4}$(*ipso*)), 63.9 (br, cage C), 32.0 (cage C*Me*), 21.1 ($\mathrm{C_6H_4}\mathit{Me}$)	5.2 (B(8)), −4.3, −6.4 (2B), −7.6 (2B), −15.2 (3B)
13b	7.66−7.48 (m, 30H, PPh), 7.03, 6.84 (br d × 2, J(HH) = ca. 8, 2H × 2, $\mathrm{C_6H_4}$), 2.48 (br s, 2H, cage CH), 2.20 (s, 3H, $\mathrm{C_6H_4}\mathit{Me}$)	224.6 (CO), 134.2−126.8 (Ph and $\mathrm{C_6H_4}$), 115.2 (br, B−$\mathrm{C_6H_4}$(*ipso*)), 36.1 (br, cage C), 21.1 ($\mathrm{C_6H_4}\mathit{Me}$)	5.5 (B(8)), −4.7, −7.6 (2B), −11.4 (2B), −22.6 (3B)
13c	7.69−7.50 (m, 30H, Ph), 1.97 (s, 6H, cage CMe), 0.18 (s, 3H, BMe)	225.3 (CO), 134.1−126.8 (Ph), 63.9 (br, cage *C*Me), 32.0 (cage C*Me*), ca. 9.0 (vbr, BMe)	5.3 (B(8)), −4.7 (3B), −7.1 (2B), −14.8 (2B), −15.7
13d	7.66−7.31 (m, 30H, Ph), 5.90 (br, 1H, $\mathrm{C}\mathit{H}{=}\mathrm{CH_2}$), 5.16 (br, 2H, $\mathrm{CH{=}C}\mathit{H_2}$), 3.47 (br, 2H, B−$\mathrm{CH_2}$) 1.96 (br s, 6H, cage CMe)	224.9 (CO), 135.5 ($\mathit{C}\mathrm{H{=}CH_2}$), 134.1−126.7 (Ph), 117.2 ($\mathrm{CH{=}}\mathit{C}\mathrm{H_2}$), 63.8 (br, cage C), 40.2 (br, B−$\mathrm{CH_2}$), 32.0 (cage C*Me*)	5.9 (B(8)), −5.1 (3B), −8.2 (2B), −15.1 (3B)
13e	7.64−7.45 (m, 30H, PPh), 7.08, 6.79 (d × 2, J(HH) = 8, 2H × 2, $\mathrm{C_6H_4}$), 2.01 (s, 6H, cage CMe), 0.02 (s, 9H, $\mathrm{SiMe_3}$)	224.3 (CO), 134.1−126.8 (Ph and $\mathrm{C_6H_4}$), 117.5 (br, B−$\mathrm{C_6H_4}$(*ipso*)), 107.8, 91.5 (≡C × 2), 64.2 (br, cage C), 31.9 (cage C*Me*), 0.2 ($\mathrm{SiMe_3}$)	4.4 (B(8)), −4.4, −6.6 (2B), −7.9 (2B), −15.1 (3B)
14	7.64−7.32 (m, 30H, Ph), 2.38, 1.98 (s × 2, 3H × 2, cage CMe × 2), 0.34 (br s, 3H, BMe)	224.0 (CO), 134.1−126.8 (Ph), 64.3, 62.9 (br × 2, cage *C*Me × 2), 31.7, 31.1 (cage C*Me* × 2), ca. 8.5 (vbr, BMe)	5.4 (B(8)), −3.6, −4.6, −5.3, −6.6, −11.4, −14.7, ca. −15.5 (B(4)), ca. −15.7
15	7.64−7.09 (br m, 32H, Ph and $\mathrm{C_6H_4}$), 6.99 (br, 2H, $\mathrm{C_6H_4}$), 2.31, 2.27 (br s × 2, 3H × 2, cage CMe and $\mathrm{C_6H_4}\mathit{Me}$), 2.04 (br s, 3H, cage CMe), 0.27 (s, 3 H, BMe)	224.4 (CO), 134.1−126.8 (Ph and $\mathrm{C_6H_4}$), 115.3 (B−$\mathrm{C_6H_4}$(*ipso*)), 60.0 (vbr, cage *C*Me × 2), 31.9, 31.1 (cage C*Me* × 2), 21.1 ($\mathrm{C_6H_4}\mathit{Me}$), ca. 9.0 (vbr, BMe)	7.1 (B(8)),[g] 1.8 (B(4)),[g] −4.0, −5.7 (2B), ca. −6.4 (sh), −11.7, −14.8 (2B)
16	8.06 (br, 1H, =CH), 3.86 (br s, 3H, NMe), 2.63, 2.48, 1.99 (br s × 3, 3H × 3, cage CMe × 2 and =C*Me*), 0.39 (br s, 3H, BMe)	222.4 (CO), 177.7 (C=N), 62.7, 60.8 (br, cage *C*Me × 2), 32.2, 31.5 (cage C*Me* × 2), 19.2 (=C*Me*), ca. 7.5 (vbr, BMe)[f]	3.7 (2B, B(4) and B(8)), −3.2, −5.0, −6.0, −8.4, −14.5 (3B)

[a] Chemical shifts (δ) in ppm, coupling constants (J) in Hz; measurement at ambient temperatures in $\mathrm{CD_2Cl_2}$, except where indicated. [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 $\mathrm{SiMe_4}$. [d] ^{1}H-decoupled chemical shifts are positive to high frequency of $\mathrm{BF_3{\cdot}Et_2O}$ (external); resonances are of unit integral except where indicated. [e] Measured in $\mathrm{(CD_3)_2CO}$. [f] The signal for the NMe carbon is obscured by the solvent. [g] Tentative assignment.

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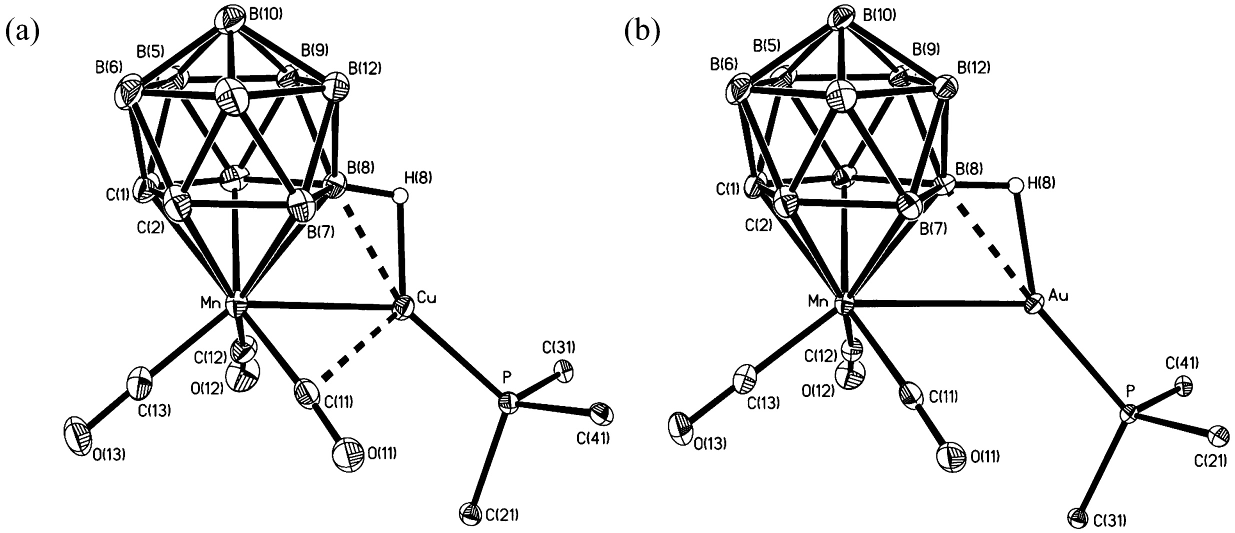
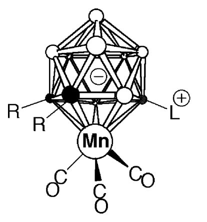


Figure 1. Molecular structures of (a) compound **4a** and (b) compound **6**, showing the crystallographic labeling schemes. Only the *ipso* carbons of phenyl rings are shown. In this and in Figures 2–4, thermal ellipsoids are drawn with 40% probability and H atoms are omitted except where chemically important. Selected interatomic distances (Å) and interbond angles (deg) are as follows. For **4a**: Mn–C(1) = 2.153(2), Mn–C(2) = 2.1536(19), Mn–B(4) = 2.227(2), Mn–B(7) = 2.240(2), Mn–B(8) = 2.264(2), Mn–C(11) = 1.814(2), Mn–C(12) = 1.8143(19), Mn–C(13) = 1.825(2), C(1)–C(2) = 1.622(3), Mn–Cu = 2.5719(4), B(8)–H(8) = 1.10(2), B(8)···Cu = 2.152(2), Cu–H(8) = 1.68(2), Cu–P = 2.2137(6), C(11)–O(11) = 1.159(2), C(11)···Cu = 2.4297(18), C(12)–O(12) = 1.150(2), C(13)–O(13) = 1.147(2); O(11)–C(11)–Mn = 173.86(17), O(12)–C(12)–Mn = 175.7(2), O(13)–C(13)–Mn = 178.8(2), O(11)–C(11)–Cu = 112.56(15), Cu–B(8)–Mn = 71.18(7), B(8)–Cu–P = 161.33(6), B(8)–Cu–Mn = 56.43(6), P–Cu–Mn = 140.193(17). For **6**: Mn–C(1) = 2.1630(16), Mn–C(2) = 2.1593(16), Mn–B(4) = 2.2318(18), Mn–B(7) = 2.2413(18), Mn–B(8) = 2.2720(18), Mn–C(11) = 1.8188(17), Mn–C(12) = 1.8199(17), Mn–C(13) = 1.8191(17), C(1)–C(2) = 1.619(2), Mn–Au = 2.9284(4), B(8)–H(8) = 1.179(19), B(8)···Au = 2.3077(17), Au–H(8) = 1.796(19), Au–P = 2.2739(4), C(11)–O(11) = 1.155(2), C(12)–O(12) = 1.149(2), C(13)–O(13) = 1.147(2); O(11)–C(11)–Mn = 174.74(16), O(12)–C(12)–Mn = 174.98(15), O(13)–C(13)–Mn = 179.41(16), Mn–B(8)–Au = 79.50(5), P–Au–B(8) = 173.78(4), B(8)–Au–Mn = 49.71(5), P–Au–Mn = 132.508(13).

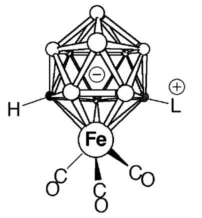
as hydride abstracting agents toward the manganacarborane anions of **1**. When this process occurs in the presence of donors L, a cluster vertex, formally $\{B-H\}^-$, may be converted to $\{B-L\}$, so that an anionic cluster such as those of compounds **1** would become neutral and zwitterionic.[13,15,24–30] Thus, treatment of **1a** or **1b** in CH_2Cl_2–THF with CF_3SO_3Me as the source of Me^+ gives the B–THF compounds [8-$\{O(CH_2)_4\}$-3,3,3-$(CO)_3$-1,2-R_2-*closo*-3,1,2-$MnC_2B_9H_8$] (R = H (**7a**), Me (**7b**)), while **1a** in SMe_2 with H_2SO_4 gives [8-SMe_2-3,3,3-$(CO)_3$-*closo*-3,1,2-$MnC_2B_9H_{10}$] (**7c**) (Chart 2). A similar reaction of **1a** with CF_3SO_3Me in CH_2Cl_2–NCMe proceeds first via nitrile N-methylation to form the nitrilium cation $[MeN\equiv CMe]^+$, which itself acts as the hydride abstracting agent to ultimately form the B–iminium species[15] [8-$\{(E)$-N(Me)=C(H)Me$\}$-3,3,3-$(CO)_3$-*closo*-3,1,2-$MnC_2B_9H_{10}$] (**7d**). An analogous compound, [8-$\{(E)$-N(Me)=C(H)Et$\}$-3,3,3-$(CO)_3$-*closo*-3,1,2-$MnC_2B_9H_{10}$] (**7e**), was obtained by using NCEt instead of NCMe.

The formation of compounds **7a–e** closely mirrors that of compounds **8**, which were similarly obtained from compound **3**.[13,15] Compound **7a** was previously isolated from the reaction between [Mn(Me)$(CO)_5$] and [*nido*-7,8-$C_2B_9H_{13}$] in refluxing THF.[31] Initial identification of **7a**[31] and **7b–e** (Tables 1 and 2) was made on the basis of their spectroscopic data. Characteristic signals due to the boron-bound ligands are seen in the ^1H and $^{13}C\{^1H\}$ NMR spectra of **7a–e**. Their $^{11}B\{^1H\}$ NMR spectra each show six resonances whose relative intensities are in the ratio 1:1:2:2:1:2 (with some

Chart 2



	R	L
7a	H	$O(CH_2)_4$
7b	Me	$O(CH_2)_4$
7c	H	SMe_2
7d	H	(*E*)-N(Me)=C(H)Me
7e	H	(*E*)-N(Me)=C(H)Et
7f	H	NH(Me)Et
7g	H	NH_2Me
7h	H	(*Z*)-N(Me)=C(H)Me
7j	H	(*Z*)-N(Me)=C(H)Et



	L
8a	$O(CH_2)_4$
8b	SMe_2
8c	(*E*)-N(Me)=C(H)Me

● C ○ BH ● B

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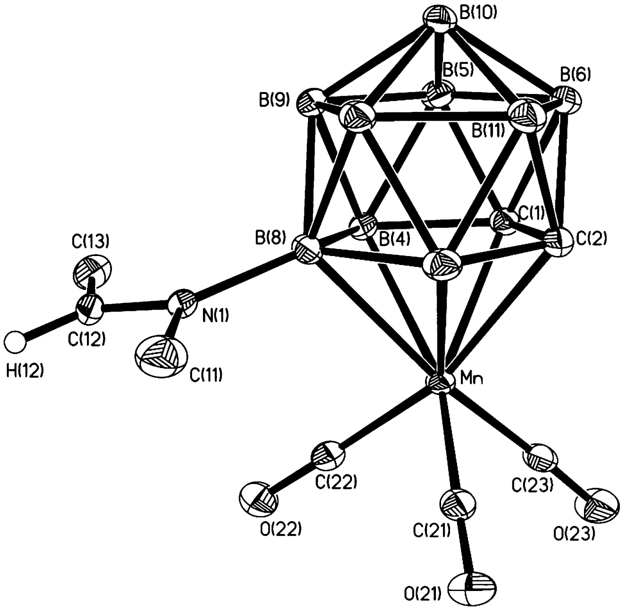

Figure 2. Molecular structure of **7d** showing the crystallographic labeling scheme, drawn as in Figure 1. Only the major component of the disordered imine moiety is shown. Selected interatomic distances (Å) and interbond angles (deg): Mn−C(1) = 2.1572(17), Mn−C(2) = 2.1493(16), Mn−B(4) = 2.2176(19), Mn−B(7) = 2.206(2), Mn−B(8) = 2.2387(19), C(1)−C(2) = 1.613(2), Mn−C(21) = 1.7959(19), Mn−C(22) = 1.7896(19), Mn−C(23) = 1.8184(19), C(21)−O(21) = 1.145(2), C(22)−O(22) = 1.147(2), C(23)−O(23) = 1.144(2), B(8)−N(1) = 1.558(3), N(1)−C(11) = 1.577(4), N(1)−C(12) = 1.277(4), C(12)−C(13) = 1.407(3); B(8)−N(1)−C(12) = 125.9(3), C(12)−N(1)−C(11) = 115.0(2), B(8)−N(1)−C(11) = 119.0(2), N(1)−C(12)−C(13) = 124.3(3), O(21)−C(21)−Mn = 178.57(16), O(22)−C(22)−Mn = 178.41(17), O(23)−C(23)−Mn = 177.72(16).

coincidences), indicating a mirror-symmetric structure. In each case the highest frequency, unit-integral resonance appears as a singlet in the corresponding ^{11}B NMR spectra (δ 17.8 (**7a**),[31] 18.4 (**7b**), −0.4 (**7c**), 5.3 (**7d**) and 5.5 (**7e**)), this being the site of attachment of the exo-polyhedral donor groups; these are at chemical shifts comparable to those of compounds **8** (δ 20.4 (**8a**), 1.7 (**8b**) and 8.3 (**8c**)).[13,15] It may be noted in passing that an isomer of **7c** has been obtained from the reaction between the salts $[Mn(NCMe)_3(CO)_3][BPh_4]$ and K[9-SMe_2-7,8-*nido*-$C_2B_9H_{10}$] in CH_2Cl_2, the isomerism of the product arising from the position of attachment of the SMe_2 group.[7] In the latter case the sulfide moiety is bonded to an α-boron atom in the $\overline{\mathrm{CC}B\mathrm{BB}}$ belt bonded to manganese, giving rise to an asymmetric molecule. Conversely, compound **7a** was earlier characterized by an X-ray diffraction experiment that confirmed the THF unit to be attached to a β-boron atom in the metal-bound $\overline{\mathrm{CCB}B\mathrm{B}}$ face.[31] Substitution at that boron atom does not disrupt the C_s symmetry of the parent anion, so that molecular mirror symmetry is retained in **7a**, consistent with its NMR data; a similar situation was assumed for **7b**−**e**.

This structural feature was further confirmed by a crystallographic study on **7d** (Figure 2). In addition, this experiment served to verify the *E* geometry of the B−{N(Me)=C(H)Me} moiety. It is notable (but perhaps unsurprising) that the similarity between compounds **7d** and **8c** includes crystallographic isomorphism and even near-identical disorder in their iminium groups. In **7d** the B(8)−N(1) distance is 1.558(3) Å and N(1)−C(12) = 1.277(4) Å, compared to 1.562(6) and 1.301(10) Å, respectively, in **8c**.[15] The two methyl groups of the pendant organic unit again have a mutually transoid disposition, with a C(11)−N(1)−C(12)−C(13) torsion angle of 179.4(2)° (cf. 175.0(8)° in **8c**). As discussed previously,[15] it is thought that a (*Z*)-imine is necessarily formed upon hydride abstraction and that this unit isomerizes to the favored *E* form prior to coordination to the boron vertex.

The introduction of substituents at boron vertexes, as in compounds **7a**−**e**, is important with respect to current interest in the derivatization of metallacarboranes.[32] In particular, the iminium moieties in **7d**,**e** offer the possibility of generating yet further boron-based functionality via simple organic transformations; such reactivity has already been demonstrated for compound **8c**.[15] Thus, reduction of the {N(Me)=C(H)Me} group in **7d** with $Na[BH_3CN]$ in dry MeOH gave [8-NH(Me)-Et-3,3,3-$(CO)_3$-*closo*-3,1,2-$MnC_2B_9H_{10}$] (**7f**), while the same reaction of **7d** in "wet" MeOH afforded [8-NH_2-Me-3,3,3-$(CO)_3$-*closo*-3,1,2-$MnC_2B_9H_{10}$] (**7g**). The latter reaction may be viewed as a simple base-catalyzed hydrolysis of the imine function. Both of these examples have parallels in the chemistry of **8c**. However, for **8c** the hydrolysis was shown also to be catalyzed by PMe_3: this was not the case for **7d**. Treatment of **7d** in THF with PMe_3 under a variety of conditions—including addition of H_2O and/or NH_4OH—did not yield **7g**. Similarly, **7e** with PMe_3 did not give a hydrolyzed product. Instead, the sole product obtained in each case was the isomer [8-{(*Z*)-N(Me)=C(H)R}-3,3,3-$(CO)_3$-*closo*-3,1,2-$MnC_2B_9H_{10}$] (R = Me (**7h**), Et (**7j**)).

All four of the compounds **7f**−**j** were readily identified by their spectroscopic properties (Tables 1 and 2). Their $^{11}B\{^1H\}$ NMR spectra confirm retention of molecular C_s symmetry, with singlet resonances at δ 9.0 (**7f**), 5.0 (**7g**), and 8.2 (**7h**,**j**) in the ^{11}B NMR spectra, these chemical shifts being typical in such systems for boron atoms with nitrogen-based functional groups attached.[15,33,34] The amine Me and Et moieties of **7f**,**g** were recognized in ^1H and $^{13}C\{^1H\}$ NMR spectra, again in characteristic positions. Likewise, {N(Me)=C(H)R} units were clearly evident in the spectra of **7h**,**j**, but it was equally clear that these species differed from their precursors **7d**,**e**, respectively: for example, their iminium N=*CH* atoms resonate at δ 7.84 (**7d**) versus 8.04 (**7h**) and δ 7.67 (**7e**) versus 7.89 (**7j**) in ^1H NMR spectra and at δ 176.0 (**7d**) versus 172.6 (**7h**) and δ 181.2 (**7e**) versus 177.7 (**7j**) in $^{13}C\{^1H\}$ NMR spectra. Hence, it was deduced that the boron-appended group had isomerized to the *Z* form: indeed, this arrangement now has the =C−(alkyl) and

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(32) Recent examples include: (a) Yao, H.; Grimes, R. N.; Corsini, M.; Zanello, P. *Organometallics* **2003**, *22*, 4381. (b) Rojo, I.; Teixidor, F.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Chem. Eur. J.* **2003**, *9*, 4311. (c) Olejniczak, A. B.; Plesek, J.; Kriz, O.; Lesnikowski, Z. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5740. See also: Grimes, R. N. *Coord. Chem. Rev.* **2000**, *200*−*202*, 773. Davidson, M. G., Hughes, A. K., Marder, T. B., Wade, K., Eds. *Contemporary Boron Chemistry*; Royal Society of Chemistry: Cambridge, U.K., 2000.

(33) Du, S.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. *Inorg. Chem.* **2002**, *41*, 3202.

(34) Du, S.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. *Dalton Trans.* **2003**, 46.

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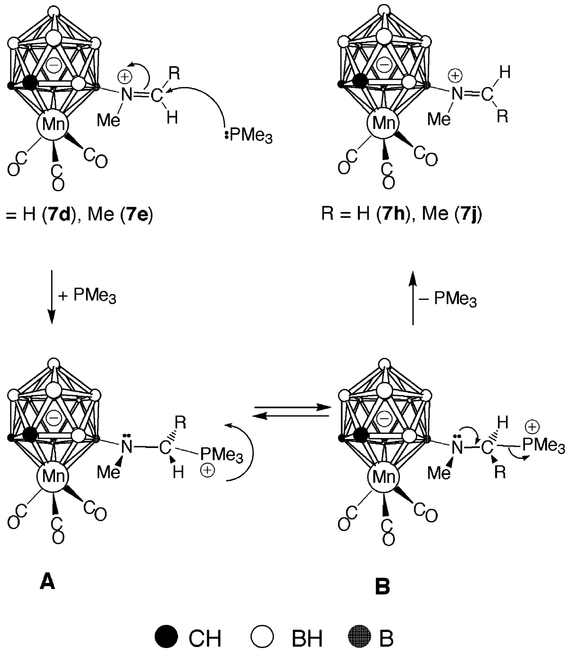
Scheme 1. Proposed Mechanism for the *E* → *Z* Isomerization of B−Iminium Substituents



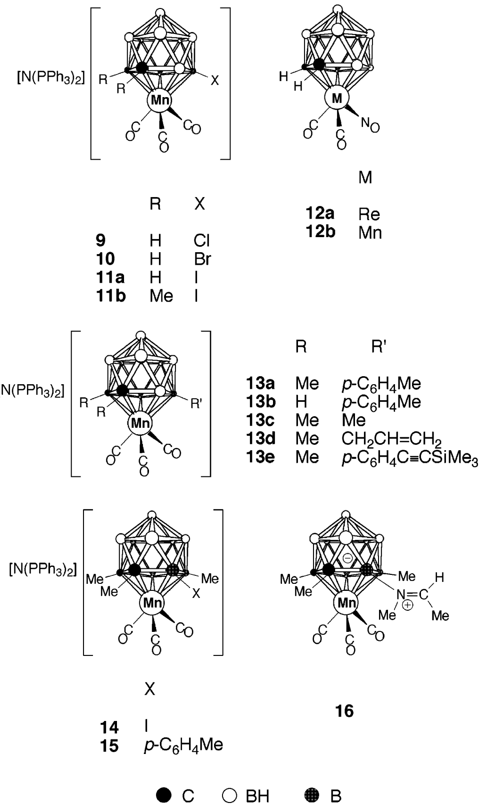
=N−(metallacarborane) substituents in a transoid disposition, arguably the thermodynamically more favorable form.

Mechanistically, this transformation may readily be understood in terms of Scheme 1. Nucleophilic attack at a site adjacent to the formally positively charged center in such zwitterions is well established.[29−31] Thus, in the present system, coordination of PMe_3 at the iminium C terminus of **7d**,**e** produces a canonical form (**A**) with a C−N single bond, allowing rotation about this vector to give form **B**. Subsequent dissociation of PMe_3 then regenerates the isomeric iminium moiety of **7h**,**j**. The reasons for this difference in behavior between **7d**/**7e** and **8c** are not clear but presumably may be related to the clearly differing electronic properties of the $\{MnC_2B_9\}$ and $\{FeCB_{10}\}$ cage systems.

In contrast to the reactions above, where hydride abstraction from the anions of **1** in the presence of donors L gives neutral B−L substituted species, treatment of compound **1c** with CF_3SO_3Me in neat CH_2Cl_2 instead gave the anionic halogen-substituted species $[N(PPh_3)_2][8\text{-Cl-}3,3,3\text{-(CO)}_3\text{-}\mathit{closo}\text{-}3,1,2\text{-MnC}_2B_9H_{10}]$ (**9**) (Chart 3) in good yield. An analogous reaction in CH_2Br_2 gave the corresponding 8-bromo-substituted species **10**, albeit only in low yield. However, compound **10** can be obtained in far superior yields by direct reaction between **1a** and elemental bromine in THF, followed by addition of $[N(PPh_3)_2]Cl$. The iodo-substituted species $[N(PPh_3)_2][8\text{-I-}3,3,3\text{-(CO)}_3\text{-}1,2\text{-R}_2\text{-}\mathit{closo}\text{-}3,1,2\text{-MnC}_2B_9H_8]$ (R = H (**11a**), Me (**11b**)) were obtained similarly from **1a**,**b**, respectively, and I_2.

Compounds **9**−**11** were characterized by the data given in Tables 1 and 2. Apart from the presence of the C(cage)−Me groups (rather than C−H) for compound **11b**, the ^1H and $^{13}C\{^1H\}$ NMR spectra of all four species are broadly similar. In their $^{11}B\{^1H\}$ NMR spectra, a 1:1:2:2:2:1 intensity ratio is seen, with one unit-integral resonance remaining a singlet upon retention of proton coupling. This peak, at δ 8.3 (**9**), 0.5 (**10**), −16.5 (**11a**), and ca. −14.8 (**11b**), progressively moves to lower frequency and is clearly due to the differing halogen-substituted boron atoms. Such halogen-induced chemical shift differences are typical in halo−heteroborane species.[35] The pattern observed in the $^{11}B\{^1H\}$ NMR is consistent with a mirror-symmetric structure and again implies that substitution took place at the β-boron atom in the Mn-bound $\overline{\mathrm{CCB}\mathit{B}\mathrm{B}}$ belt, this being the site of the more hydridic B−H unit as seen above.

Chart 3



The formation of **9** and **10** by reaction of **1c** with CF_3SO_3Me in CH_2Cl_2 and CH_2Br_2, respectively, presumably results from hydride abstraction by Me^+ and then halide abstraction from the solvent by the naked boron vertex. Alternatively, compounds **10** and **11** are envisaged as arising from oxidative removal[36] of the hydride by the dihalogen X_2 (formally giving $HX + X^-$)[37] and then immediate boron coordination of the liberated X^- to give the B−X substituent. These latter reactions appear to be rapid, as they are selective: little or none of compounds **7a**,**b** was observed, despite the proposed vacant boron site in the presence of THF molecules as solvent.

In previous studies it was reported that the anions of **2** and **3**, despite their ostensibly isoelectronic natures, reacted differently when treated with $[NO][BF_4]$ in THF. Whereas the rhenium complex gave a neutral nitrosyl complex, $[3,3\text{-(CO)}_2\text{-}3\text{-NO-}\mathit{closo}\text{-}3,1,2\text{-ReC}_2B_9H_{11}]$ (**12a**),[12] the ferracarborane gave the neutral, zwitterionic B−THF

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(35) For example: (a) Sprecher, R. F.; Aufderheide, B. E.; Luther, G. W.; Carter, J. C. *J. Am. Chem. Soc.* **1974**, *96*, 4404. (b) Bauer, C.; Gabel, D.; Dörfler, U.; McGrath, T. D. *Inorg. Chim. Acta* **2002**, *332*, 181.

(36) Young, D. C.; Howe, D. V.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1969**, *91*, 859.

(37) Du, S.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **2001**, 2791.

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species $[7\text{-}\{O(CH_2)_4\}\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}FeCB_{10}H_{10}]$.[13] The latter may be viewed as the result formally of oxidative removal of a boron-bound hydride by $[NO]^+$ in the presence of THF. In the context of these results, it was clearly of interest to investigate the reaction of compounds **1**, also isoelectronic with **2** and **3**, with $[NO][BF_4]$.

Initial investigations revealed a combination of the above observations, namely that treatment of **1a** with $[NO][BF_4]$ in THF did indeed give the nitrosyl species $[3,3\text{-}(CO)_2\text{-}3\text{-}NO\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_{11}]$ (**12b**, characterized by the data in Tables 1 and 2), but also that a significant quantity of compound **7a** (identified spectroscopically) was formed. Although **7a** was a relatively minor product (the ratio of **7a** to **12b** was ca. 1:5 by integrated $^{11}B\{^1H\}$ NMR spectroscopy) and their combined yield was good (up to ca. 60%), the formation of a mixture proved troublesome. The two neutral products proved very difficult to separate, having very similar chromatographic properties, and therefore in order to easily obtain a pure compound an alternative synthesis of **12b** was sought. Reaction of compound **1c** with $[NO][BF_4]$ (1 equiv) in CH_2Cl_2 gave a mixture of **12b** (14% yield) and chloro-substituted **9** (43%), and with excess reagent the isolated yield of **12b** improved to 17%. The best yield thus far of **12b** (22%) was obtained from **1c** with $[NO][BF_4]$ (1 equiv), using MeI as solvent, with compound **11a** (35%) also formed. The neutral nitrosyl species was now much more readily separated chromatographically from the anionic halogenated products.

The spectroscopic properties of compound **12b** (Tables 1 and 2) are somewhat different from those of the Re analogue **12a**.[12] For example, their NO stretching frequencies are 1776 cm^{-1} (**12a**) versus 1812 cm^{-1} (**12b**); and the ^{11}B chemical shift range for **12a** is δ 1.7 to -16.6 versus δ 8.0 to -16.9 for **12b**. This may be indicative of significant differences in the electronic structures of compounds **12** and has parallels in simpler cyclopentadienyl−manganese and −rhenium species. An illustration of this is the NO stretching frequencies of the isolobal analogues $[(\eta^5\text{-}C_5H_5)M(CO)_2(NO)]^+$ (M = Mn, Re) which similarly differ by around 40 cm^{-1}.[38] As mentioned earlier, compound **12a** was the starting point for the synthesis of a series of rhenium−alkylidene species, and moreover it is amenable to carbonyl substitution reactions. Any further investigation of the comparative reactivities of compounds **12**, however, awaits a more satisfactory synthesis of **12b**.

The facile syntheses, discussed earlier, of halogen-substituted compounds **9**−**11**, which still retain an anionic charge, opens up the possibility of accessing species with a second boron-bound substituent via reactions such as those described above. However, preliminary experiments indicated that, for example, treatment of **9** with CF_3SO_3Me in CH_2Cl_2−THF did not afford a B−THF compound. Similarly, the $\{Cu(PPh_3)\}^+$ fragment did not add to **9** to form a bimetallic species. These observations may be related to the nonavailability of the β-BH that is present in compounds **1**. This hydrogen in **1** is clearly far more hydridic than the adjacent α-BH, as evidenced by the formation of only one isomer in the synthesis of compounds **7a**−**e** and **9**−**11**. In the case of **9**, it may be argued that the α-BH is even less hydridic than in **1**, as a result of the adjacent electronegative halogen.

In contrast to this, the B−I group in compounds **11** is susceptible to "cross-coupling" reactions using Grignard reagents in the presence of $[PdCl_2(PPh_3)_2]$ as catalyst. This methodology has been used to form boron−carbon bonds in various cluster (hetero)boranes.[39] In the present work, the substrate of choice was **11b**, as it was formed in good yield; moreover, it was feared that the protonic C(cage)-bound hydrogens in **11a** could interfere with the Grignard reagent. Thus, treatment of **11b** with $p\text{-}MeC_6H_4MgBr$ and $[PdCl_2(PPh_3)_2]$ in THF afforded $[N(PPh_3)_2][8\text{-}(p\text{-}C_6H_4Me)\text{-}3,3,3\text{-}(CO)_3\text{-}1,2\text{-}Me_2\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_8]$ (**13a**) in 82% yield, following a standard acid workup procedure and column chromatography; the same reaction with **11a** gave the corresponding 1,2-H_2 species **13b**, but in only 30% isolated yield. Similarly, **11b** with other Grignard reagents RMgBr gave the corresponding products $[N(PPh_3)_2][8\text{-}R\text{-}3,3,3\text{-}(CO)_3\text{-}1,2\text{-}Me_2\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_8]$ (R = Me (**13c**), $CH_2CH{=}CH_2$ (**13d**), $p\text{-}C_6H_4C{\equiv}CSiMe_3$ (**13e**)).

Spectroscopic and other data characterizing the compounds **13** are presented in Tables 1 and 2. The Grignard-derived organic groups bound to boron gave characteristic resonances at typical positions in both their ^1H and $^{13}C\{^1H\}$ NMR spectra, confirming that these units had been incorporated in the products. Broad resonances at δ 115.4 (**13a**), 115.2 (**13b**), ca. 9.0 (**13c**), 40.2 (**13d**), and 117.5 (**13e**) in the latter set of spectra were assigned as those carbon atoms directly bound to the carborane cage. In $^{11}B\{^1H\}$ NMR spectra of compounds **13**, retention of the mirror symmetry of the precursor compounds **11** was implied by the presence of six peaks with relative intensities 1:1:2:2:2:1 (some coincide). Upon retention of proton coupling, the highest frequency ^{11}B resonance in each case remains a singlet, indicating this as the site of boron substitution. For all five of compounds **13** this vertex resonates within a small range (δ_B 4.4−5.9), and indeed all five spectra are very similar, with the exception that some of the ^{11}B resonances for **13b** are shifted—presumably a consequence of its C(cage)−H, rather than C(cage)−Me, substituents. A single-crystal X-ray diffraction study on compound **13a** confirmed the important features of its structure (Figure 3). The *p*-tolyl group is clearly appended to a β boron atom in the pentagonal $\overline{\mathrm{CCB}B\mathrm{B}}$ face that is bound to manganese (B(8)−C(6) = 1.562(12) Å). By implication, this reasonably confirms the site of substitution for all of compounds **13** and, likewise, for the precursors **11** and their analogues **9** and **10**.

Although, as mentioned earlier, the B−H units of compound **9** appeared to be somewhat deactivated toward electrophiles, this was hoped not to be the case with the compounds **13**. In any event, the α-B−H in the

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[38] Fischer. E. O.; Strametz, H. *Z. Naturforsch., B* **1968**, *23*, 278.

[39] For example: (a) Zakharkin, L. I.; Kovredov, A. I.; Ol'shevskaya, V. A.; Shaugumbekova, Zh. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 1691. (b) Li, J.; Logan, C. F.; Jones, M. *Inorg. Chem.* **1991**, *30*, 4866. (c) Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095. (d) Kultyshev, R. G.; Liu, S.; Leung, H. T.; Liu, J.; Shore, S. G. *Inorg. Chem.* **2003**, *42*, 3199. (e) Rojo, I.; Teixidor, F.; Kivekäs, R.; Sillanpää, R.; Viñas, C. *Organometallics* **2003**, *22*, 4642.

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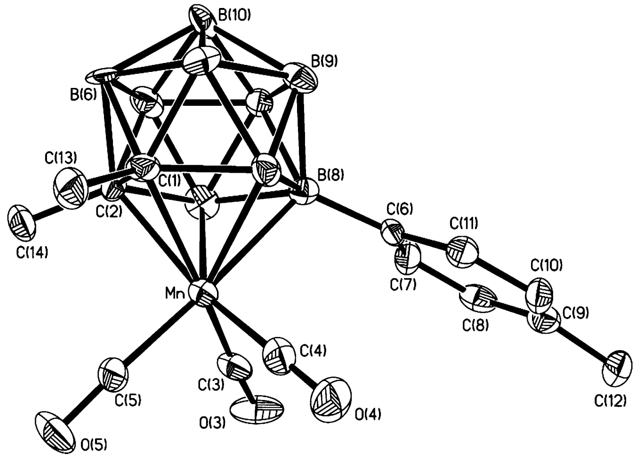

Figure 3. Molecular structure of the anion of compound **13a** showing the crystallographic labeling scheme, drawn as in Figure 1. Selected interatomic distances (Å) and interbond angles (deg): Mn−C(1) = 2.173(8), Mn−C(2) = 2.179(8), Mn−B(4) = 2.212(10), Mn−B(7) = 2.193(9), Mn−B(8) = 2.243(10), Mn−C(3) = 1.788(10), Mn−C(4) = 1.780(10), Mn−C(5) = 1.786(10), C(1)−C(2) = 1.660(11), B(8)−C(6) = 1.562(12), C(3)−O(3) = 1.153(10), C(4)−O(4) = 1.148(9), C(5)−O(5) = 1.153(10); C(6)−B(8)−Mn = 113.3(6), O(3)−C(3)−Mn = 177.2(9), O(4)−C(4)−Mn = 179.4(9), O(5)−C(5)−Mn = 177.1(9).

metal-bound $\overline{\mathrm{CC}B\mathrm{BB}}$ ring is clearly much less hydridic than the *β*-B−H groups, as evidenced by the high regioselectivity for *β*-hydride removal in the formation of compounds **7a**−**e** and **9**−**11**. Hydrides bonded to boron vertexes more distant from the metal center are intuitively expected to be even less reactive. The B−Me species **13c** was chosen for further study because not only was it available in good yield but also the relatively lower steric demands of the Me group would not unduly inhibit further substitution at adjacent sites. These considerations were of greater importance than the electronic properties of this substituent, which might adversely affect the reactivity of the substrate.[32b] Initial studies of the reaction of this compound with CF_3SO_3Me in CH_2Cl_2−THF (1:1) gave only decomposition; the only identifiable manganacarborane isolated from the reaction mixture was small quantites of **13c**. Similarly, this substrate showed no reaction with $[CuCl(PPh_3)]_4/Tl[PF_6]$; presumably the B−Me group effectively blocks the exo-polyhedral binding site.

However, compound **13c** with I_2 in THF did afford a product in which further substitution had taken place. Little or no reaction appeared to occur at room temperature, even after several hours, and optimum conditions appear to require reaction with 2−3 mol equiv of I_2 at reflux temperature for several hours. These conditions are clearly rather more forcing than those required to form compounds **11** and are further indicative of the significantly lower hydridic character of the remaining B−H units in **13**. The product formed in this case is formulated as $[N(PPh_3)_2][4\text{-I-}3,3,3\text{-}(CO)_3\text{-}1,2,8\text{-}Me_3\text{-}\mathit{closo}\text{-}3,1,2\text{-}MnC_2B_9H_7]$ (**14**) on the basis of spectroscopic data (Tables 1 and 2) and by analogy with structural studies discussed below. In both its ^1H and $^{13}C\{^1H\}$ NMR spectra **14** shows two separate C(cage)−Me units, consistent with a loss of molecular mirror symmetry. Similarly, its $^{11}B\{^1H\}$ NMR spectrum shows the cluster to be asymmetric, with nine separate resonances, of which two (*δ* 5.4, ca. −15.5) remain singlets upon retention of proton coupling. Of these two, the one to higher frequency is assigned as the B−Me unit (cf. *δ* 5.3 in **13c**) and the one to lower frequency as B−I (cf. −14.8 in **11b**).

Compound **14** appeared to be unstable, slowly decomposing in solution or during chromatography; this instability also hampered attempts to obtain diffraction-quality crystals so that its molecular structure could be confirmed. A derivative of **14** was therefore sought. Reaction with a Grignard reagent appeared to be an attractive possibility; $p\text{-}MeC_6H_4MgBr$ was chosen, as it had been an effective reagent in the synthesis of compounds **13a**,**b** and the two different boron-bound substituents (and their order of attachment) might readily be distinguished crystallographically. Indeed, it was found that a "one-pot" procedure could be employed, whereby treatment of **13c** first with I_2 and then addition of the Grignard reagent and palladium catalyst without isolation of **14** afforded a product formulated as $[N(PPh_3)_2][4\text{-}(p\text{-}C_6H_4Me)\text{-}3,3,3\text{-}(CO)_3\text{-}1,2,8\text{-}Me_3\text{-}\mathit{closo}\text{-}3,1,2\text{-}MnC_2B_9H_7]$ (**15**).

Compound **15** was characterized by the data presented in Tables 1 and 2. The incorporation of the *p*-tolyl substituent was evident in both ^1H and $^{13}C\{^1H\}$ NMR spectra, with the inequivalence of the two C(cage)−Me units again showing the cluster to lack mirror symmetry. This was also seen in the $^{11}B\{^1H\}$ NMR spectrum, with resonances in a 1:1:1:2:1:1:2 intensity ratio pattern. The two highest frequency resonances, at *δ* 7.2 and 1.9, are tentatively assigned as the B−Me and B−(p-C_6H_4Me) vertexes, respectively. In all of compounds **13** and **14** the organyl-substituted boron atom resonates around *δ* 4−6. The resonance due to B(4), of course, would not necessarily be expected to occur in the same range, as it is an α- rather than a *β*-boron atom. Some local perturbation of the cluster is nevertheless suggested by these peak positions. Arguably, the insertion of the relatively bulky *p*-tolyl group between C−Me and B−Me groups places it in a relatively unfavorable environment. Indeed, it is also likely that rotation about the B−C_6H_4 vector would be hindered; however, the broadness of the compound's NMR spectra precludes any confirmation of this. Nevertheless, such steric interactions almost certainly make some contribution to the instability of the compound.

As with compound **14**, we unfortunately were unable to obtain diffraction-quality crystals of compound **15**. Seeking an alternative strategy to confirm the site of boron−hydride replacement in the reactions of **13c**, further attention was paid to its reactions with other hydride-abstracting systems, and specifically one that would yield a neutral product. After several attempts, such a product was ultimately obtained by treating **13c** with CF_3SO_3Me in CH_2Cl_2−NCMe (1:1). Similar to the reactions of compounds **1**, the product obtained here was again a B−iminium species, namely $[4\text{-}\{(Z)\text{-}N(Me){=}C(H)Me\}\text{-}3,3,3\text{-}(CO)_3\text{-}1,2,8\text{-}Me_3\text{-}\mathit{closo}\text{-}3,1,2\text{-}MnC_2B_9H_7]$ (**16**). The presence of the iminium substituent was readily discernible in ^1H and $^{13}C\{^1H\}$ NMR spectra (Table 2), with characteristic resonances in addition to those for the three cage-bound methyl groups. Similarly, the $^{11}B\{^1H\}$ NMR spectrum showed resonances in the intensity ratio 2:1:1:1:1:3, of which the highest frequency resonance (*δ* 3.7), of integral 2, remained a

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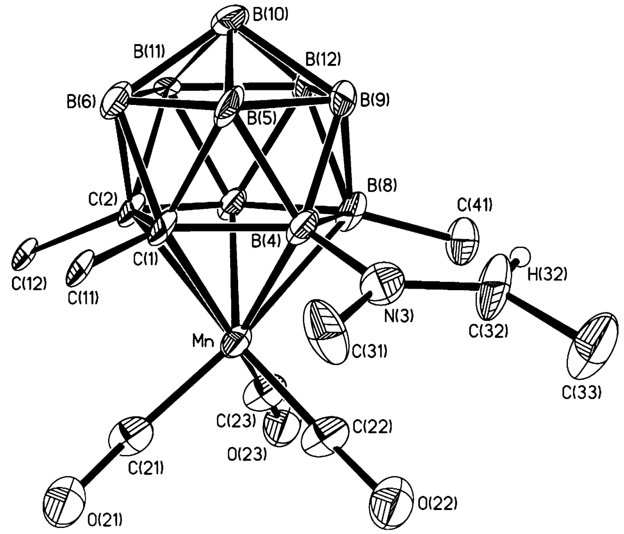

Figure 4. Molecular structure of compound **16** showing the crystallographic labeling scheme, drawn as in Figure 1. Selected interatomic distances (Å) and interbond angles (deg): Mn−C(1) = 2.17(2), Mn−C(2) = 2.155(18), Mn−B(4) = 2.12(2), Mn−B(7) = 2.258(19), Mn−B(8) = 2.236(10), C(1)−C(2) = 1.688(13), Mn−C(21) = 1.784(11), Mn−C(22) = 1.762(19), Mn−C(23) = 1.75(2), C(21)−O(21) = 1.168(10), C(22)−O(22) = 1.20(2), C(23)−O(23) = 1.14(2), B(4)−N(3) = 1.68(2), N(3)−C(32) = 1.291(15), N(3)−C(31) = 1.486(15), C(32)−C(33) = 1.62(3), B(8)−C(41) = 1.596(12); N(3)−B(4)−Mn = 114.2(10), C(32)−N(3)−C(31) = 120.5(11), C(32)−N(3)−B(4) = 118.8(11), C(31)−N(3)−B(4) = 120.7(11), N(3)−C(32)−C(33) = 122.8(12), C(41)−B(8)−Mn = 118.2(6), O(21)−C(21)−Mn = 175(2), O(22)−C(22)−Mn = 178.3(18), O(23)−C(23)−Mn = 179.4(18).

singlet upon retention of ^1H coupling. This corresponds to the two substituted boron atoms and is comparable to the chemical shifts of other similarly functionalized boron vertexes described here.

The spectroscopic data for **16**, however, provided no definitive information as to the geometry (*E* or *Z*) of the iminium substituent. Moreover, as with compounds **14** and **15**, the site of the additional appendage was only confirmed following a single-crystal X-ray diffraction study on compound **16**. Although the crystals were very small and platelike, and diffracted only poorly, the atom connectivity pattern is established beyond doubt (Figure 4). A dimethyliminium group is bonded to B(4), one of the two formally equivalent α boron atoms in the manganese-bound $\overline{\text{CC}B\text{BB}}$ belt. The B(4)−N(3) distance (1.68(2) Å) is longer than the corresponding parameter (1.558(3) Å) in **7d**, while the N(3)−C(32) separation (1.291(15) Å) is numerically longer than that (1.277(4) Å) seen in **7d**, but not significantly so. The *Z* geometry in this substituent is clearly evident: the C(31)−N(3)−C(32)−C33 torsion angle is 1.4(17)°, confirming the cis disposition of the two methyl groups about the C═N bond. The iminium unit is oriented so that these two groups face away from the methyl group bound at the adjacent *β*-boron atom B(8). The B(8)−C(41) connectivity is 1.596(12) Å and is also slightly longer than the B−tolyl distance 1.562(12) Å found in **13a**. The apparent lengthening of the cage-to-substituent distances at both B(4) and B(8) may be indicative of some flexing to lessen steric interactions between these substituents or may simply be due to more subtle electronic or crystal packing effects.

The direct formation of the (*Z*)-iminium substituent in **16** provides a noteworthy contrast to the synthesis of **7d**, in which under the same conditions an (*E*)-iminium group is found. As noted earlier,[15] the hydride abstracting nitrilium cation $[MeC{\equiv}NMe]^+$ may be required to distort as it approaches the carborane surface, forcing the methyl groups into a cisoid geometry and thence giving the (*Z*)-imine. In the case of **7d**, the free imine can isomerize to the more stable *E* form prior to attachment to the boron vertex: this appears not to be the case for **16**. It is likely that the naked α-boron vertex is much less stable, as is suggested by the evident difficulty of hydride abstraction. In this case, it may be argued that the (*Z*)-imine would rapidly coordinate without isomerization. Conversely, the multiple methyl substituents already bound to the cluster surface at adjacent vertexes could also be expected to exercise some stereochemical control over the approach of the imine. It may be that only the *Z* isomer can access the naked boron vertex, even if both *E* and *Z* forms are present in solution. Similar steric considerations might also explain our observation that the $\{MeO(CH_2)_4\}^+$ complex (from CF_3SO_3Me and THF) did not effect B−THF substitution of **13c**: the dimethylimine unit would certainly present fewer steric demands than the oxonium species.

Conclusion

The anion $[3,3,3\text{-}(CO)_3\text{-}closo\text{-}3,1,2\text{-}MnC_2B_9H_{11}]^-$, the dicarbollide analogue of cymantrene $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$, has been known for some four decades and yet had received but scant attention and essentially no derivative chemistry was known. We have, however, now demonstrated that a rich and varied cage substitution is possible via a few relatively simple reactions. The procedures illustrated herein could, in principle, be repeated further to append sequentially a variety of substituents at specific sites on the metallacarborane cage. Such modifications are of general interest in the area of metallacarborane chemistry. Moreover, an attractive area for immediate future attention would be extension of the cage substitution chemistry demonstrated for compounds **1** to the rhenium analogue **2**. Conversely, the extensive array of bi- and polymetallic compounds derived from the anion of **2**[9−11] will likely have further parallels with the compounds **1** beyond the derivatives **4**−**6** presented here.

Experimental Section

General Considerations. Reactions were carried out under an atmosphere of dry oxygen-free nitrogen using Schlenk line techniques. Solvents were distilled from appropriate drying reagents under nitrogen prior to use. Petroleum ether refers to that fraction of boiling point 40−60 °C. Chromatography columns (ca. 15 cm in length and ca. 2 cm in diameter) were packed with silica gel (Acros, 60−200 mesh). NMR spectra were recorded at the following frequencies (MHz): ^1H, 360.1; ^{13}C, 90.6; ^{11}B, 115.5; ^{31}P, 145.8. ^{31}P NMR chemical shifts (*δ*) are positive to high frequency of 85% H_3PO_4 (external). The reagents $[NHMe_3][7,8\text{-}R_2\text{-}nido\text{-}7,8\text{-}$

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C$_2$B$_9$H$_{10}$] (R = H, Me),[40] [MnBr(CO)$_5$],[41] [CuCl(PPh$_3$)]$_4$,[42] [AuCl(PPh$_3$)],[43] and [PdCl$_2$(PPh$_3$)$_2$][44] were prepared according to published procedures; *p*-Me$_3$SiC≡CC$_6$H$_4$MgBr was prepared from *p*-Me$_3$SiC≡CC$_6$H$_4$Br and magnesium turnings in Et$_2$O. Sodium hydride, supplied as a 60% dispersion in oil (Aldrich), was weighed out, washed with petroleum ether (2 × 10 mL), and dried in vacuo immediately prior to use.

Synthesis of [X][3,3,3-(CO)$_3$-1,2-R$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_9$] (X = Cs, N(PPh$_3$)$_2$; R = H, Me). (i) To a two-necked 250 mL round-bottom flask equipped with a stirbar and a condenser was added [NHMe$_3$][*nido*-7,8-C$_2$B$_9$H$_{12}$] (1.4 g, 7.2 mmol). The flask was connected to a Schlenk line, and THF (60 mL) was added. A suspension of NaH (1.5 g, 63 mmol) in THF (100 mL) was added to the solution, and intense effervescence was observed. After the mixture was refluxed for 12 h, the resulting solution of Na$_2$[*nido*-7,8-C$_2$B$_9$H$_{11}$] was cooled to room temperature and allowed to stand without stirring until the excess NaH settled. In another two-necked 250 mL round-bottom flask similarly equipped with a stirbar and a condenser, [Mn(CO)$_3$(NCMe)$_3$]Br[16] was prepared in situ from [MnBr(CO)$_5$] (1.9 g, 6.9 mmol) heated to reflux in NCMe (6 mL) for 1 h. The sodium carborane solution was filtered through a Celite plug (3 cm) directly into the vigorously stirred solution of manganese reagent, and the mixture was then heated to reflux for 10 h. After it was cooled to room temperature, the resultant mixture was filtered in air and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in water (100 mL) and a solution of CsCl (2.3 g, 14 mmol) in H$_2$O (20 mL) added with stirring, giving a pale yellow precipitate that was collected by filtration. This crude product was dissolved in water (1 L), and the solution was slowly concentrated by evaporation under reduced pressure to give Cs[3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{11}$] (**1a**; 1.9 g, 4.7 mmol, 68%) as a yellow microcrystalline solid. The product was filtered off and dried overnight in vacuo at room temperature. IR (THF): $\nu_{\max}$(CO) 1998 vs, 1916 s, 1899 s cm^{-1}.

(ii) A similar reaction using [NHMe$_3$][7,8-Me$_2$-*nido*-7,8-C$_2$B$_9$H$_{10}$] (1.6 g, 7.2 mmol) as the carborane source gave Cs[3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_9$] (**1b**; 1.2 g, 2.7 mmol, 39%) as a yellow powder. IR (THF): $\nu_{\max}$(CO) 1997 vs, 1917 s, 1900 s cm^{-1}.

(iii) Metathesis of compounds **1a**,**b** with [N(PPh$_3$)$_2$]Cl in THF yielded the salts [N(PPh$_3$)$_2$][3,3,3-(CO)$_3$-1,2-R$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_9$] (R = H (**1c**), Me (**1d**)) as yellow powders.

Synthesis of Bimetallic Complexes. (i) Compound **1a** (0.080 g, 0.20 mmol), [CuCl(PPh$_3$)]$_4$ (0.073 g, 0.05 mmol), and Tl[PF$_6$] (0.070 g, 0.20 mmol) were suspended in THF (10 mL) and the mixture stirred for 24 h. Solvent was removed in vacuo and the residue applied to a chromatography column. Elution with CH$_2$Cl$_2$–petroleum ether (1:1) afforded a yellow fraction, from which removal of solvent under reduced pressure gave [3,8-{Cu(PPh$_3$)}-8-μ-H-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**4a**; 0.049 g) as a yellow microcrystalline solid. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 9.2 (br).

(ii) Similarly, compound **1b** (0.080 g, 0.19 mmol), [CuCl(PPh$_3$)]$_4$ (0.067 g, 0.05 mmol), and Tl[PF$_6$] (0.065 g, 0.19 mmol) in THF (10 mL) yielded yellow [3,8-{Cu(PPh$_3$)}-8-μ-H-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**4b**; 0.091 g). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 9.2 (br).

(iii) By a similar procedure, compound **1a** (0.160 g, 0.40 mmol), Ag[BF$_4$] (0.078 g, 0.40 mmol), and PPh$_3$ (0.105 g, 0.40 mmol) stirred together in THF (10 mL) yielded [3,8-{Ag(PPh$_3$)}-8-μ-H-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**5**; 0.238 g) as a pale yellow microcrystalline solid following chromatographic workup using CH$_2$Cl$_2$ as eluant. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 18.1 (vbr d, *J*(AgP) ≈ 740 Hz).

(iv) Similarly, compound **1a** (0.040 g, 0.10 mmol), [AuCl(PPh$_3$)] (0.050 g, 0.10 mmol), and Tl[PF$_6$] (0.035 g, 0.10 mmol) in THF (10 mL) yielded [3,8-{Au(PPh$_3$)}-8-μ-H-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**6**; 0.040 g) as a yellow microcrystalline solid. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 39.4 (br).

Synthesis of [8-L-3,3,3-(CO)$_3$-1,2-R$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (R = H, L = O(CH$_2$)$_4$, SMe$_2$, (*E*)-N(Me)=C(H)Me, (*E*)-N(Me)=C(H)Et; R = Me, L = O(CH$_2$)$_4$). (i) Compound **1a** (0.160 g, 0.40 mmol) was dissolved in CH$_2$Cl$_2$–THF (1:1, 20 mL), and CF$_3$SO$_3$Me (0.15 mL) was added. After the mixture was stirred for 20 h, solvent was removed in vacuo. Column chromatography using CH$_2$Cl$_2$–petroleum ether (3:2) as eluant afforded a yellow fraction. Removal of solvent under reduced pressure gave [8-{O(CH$_2$)$_4$}-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7a**; 0.028 g, 20%) as a yellow microcrystalline solid.

(ii) Similarly, compound **1b** (0.170 g, 0.39 mmol) in CH$_2$Cl$_2$–THF (1:1, 20 mL) and CF$_3$SO$_3$Me (0.15 mL) yielded [8-{O(CH$_2$)$_4$}-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**7b**; 0.034 g) as a pale yellow microcrystalline solid.

(iii) Compound **1a** (0.120 g, 0.30 mmol) was dissolved in SMe$_2$ (20 mL), and concentrated H$_2$SO$_4$ (2 mL) was added. After the mixture was stirred for 24 h, the organic layer was separated, solvent was removed in vacuo, and the residue was applied to a chromatography column. Elution with CH$_2$Cl$_2$–petroleum ether (1:1) afforded a yellow fraction, from which [8-SMe$_2$-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7c**; 0.064 g) was obtained as a yellow solid after removal of solvent under reduced pressure.

(iv) Similar to the synthesis of **7a**, compound **1a** (0.160 g, 0.40 mmol) with CF$_3$SO$_3$Me (0.15 mL) in CH$_2$Cl$_2$–NCMe (1:1, 20 mL) yielded [8-{(*E*)-N(Me)=C(H)Me}-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7d**; 0.095 g) as a yellow microcrystalline solid.

(v) By an analogous procedure, compound **1a** (0.640 g, 1.6 mmol) with CF$_3$SO$_3$Me (ca. 1.0 mL) in CH$_2$Cl$_2$–NCMe (1:1, 80 mL) yielded yellow [8-{(*E*)-N(Me)=C(H)Et}-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7e**; 0.354 g).

Reactions of B–Iminium Compounds. (i) Compound **7d** (0.065 g, 0.20 mmol) and Na[BH$_3$CN] (0.025 g, 0.40 mmol) were stirred in anhydrous MeOH (6 mL) for 24 h. Solvent was removed in vacuo and the residue taken up in the minimum volume (5 mL) of CH$_2$Cl$_2$ and chromatographed. Elution with CH$_2$Cl$_2$–petroleum ether (2:1) gave a single yellow fraction that was evaporated in vacuo to yield [8-{NH(Me)Et}-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7f**; 0.035 g) as a yellow crystalline solid.

(ii) Similarly, compound **7d** (0.142 g, 0.43 mmol) and Na[BH$_3$CN] (0.054 g, 0.86 mmol) in "wet" MeOH (8 mL) gave [8-NH$_2$Me-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7g**; 0.074 g), which was isolated as a yellow crystalline solid following column chromatography using CH$_2$Cl$_2$ as eluant.

(iii) Compound **7d** (0.064 g, 0.20 mmol) was dissolved in THF (4 mL), and PMe$_3$ (1.0 mL of a 1.0 M solution in THF, 1.0 mmol) was added. After the mixture was stirred for 24 h, solvent was removed in vacuo. Column chromatography using CH$_2$Cl$_2$–petroleum ether (4:1) as eluant afforded a yellow fraction. Removal of the solvent under reduced pressure gave [8-{(*Z*)-N(Me)=C(H)Me}-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7h**; 0.035 g) as a yellow crystalline solid.

(iv) With **7e** (0.068 g, 0.20 mmol), an identical reaction and workup using CH$_2$Cl$_2$–petroleum ether (1:1) as eluant gave yellow [8-{(*Z*)-N(Me)=C(H)Et}-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**7j**; 0.058 g).

Synthesis of [N(PPh$_3$)$_2$][8-X-3,3,3-(CO)$_3$-1,2-R$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (R = H, X = Cl, Br, I; R = Me, X = I). (i) Compound **1c** (0.081 g, 0.10 mmol) was dissolved in CH$_2$Cl$_2$ (5 mL), and CF$_3$SO$_3$Me (0.15 mL) was added. After the mixture

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was stirred for 5 h, solvent was removed in vacuo. Column chromatography using neat CH$_2$Cl$_2$ as eluant afforded a yellow fraction from which [N(PPh$_3$)$_2$][8-Cl-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**9**; 0.066 g) was obtained as a yellow solid after removal of solvent under reduced pressure.

(ii) Compound **1a** (0.080 g, 0.20 mmol) was dissolved in THF (5 mL), and a solution of Br$_2$ (25 μL, 0.49 mmol) in THF (2 mL) was added dropwise at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 7 h, and then [N(PPh$_3$)$_2$]Cl (0.115 g, 0.20 mmol) was added and stirring was continued for a further 12 h. Solvent was removed in vacuo and the residue subjected to column chromatography using CH$_2$Cl$_2$−petroleum ether (3:1) as eluant. This afforded a yellow fraction, from which removal of solvent under reduced pressure gave [N(PPh$_3$)$_2$][8-Br-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**10**; 0.130 g) as a yellow solid.

(iii) Similarly, mixture of compound **1a** (0.160 g, 0.40 mmol) in THF (10 mL) with a solution of I$_2$ (0.130 g, 0.51 mmol) in THF (5 mL) and subsequent addition of [N(PPh$_3$)$_2$]Cl (0.260 g, 0.46 mmol) yielded [N(PPh$_3$)$_2$][8-I-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**11a**; 0.354 g) as a yellow solid.

(iv) By the same procedure, mixing compound **1b** (0.160 g, 0.37 mmol) with I$_2$ (0.110 g, 0.45 mmol) and then [N(PPh$_3$)$_2$]Cl (0.230 g, 0.40 mmol) yielded [N(PPh$_3$)$_2$][8-I-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**11b**; 0.343 g) as a yellow solid.

Synthesis of [3,3-(CO)$_2$-3-NO-*closo*-3,1,2-MnC$_2$B$_9$H$_{11}$]. Compound **1c** (0.162 g, 0.20 mmol) was dissolved in freshly distilled MeI (10 mL), the solution was cooled to ca. −90 °C, and [NO][BF$_4$] (0.025 g, 0.21 mmol) was added. The mixture was gradually warmed to room temperature, stirred for 3 h, and then evaporated in vacuo. Column chromatography using first CH$_2$Cl$_2$−petroleum ether (1:1) as eluant afforded an orange fraction which was evaporated in vacuo to give [3,3-(CO)$_2$-3-NO-*closo*-3,1,2-MnC$_2$B$_9$H$_{11}$] (**12b**; 0.012 g) as an orange microcrystalline solid. Further elution using neat CH$_2$Cl$_2$ then afforded a yellow fraction from which was obtained compound **11a** (0.072 g, 35%).

Synthesis of [N(PPh$_3$)$_2$][8-R′-3,3,3-(CO)$_3$-1,2-R$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (R = Me, R′ = *p*-C$_6$H$_4$Me, Me, CH$_2$CH=CH$_2$, *p*-C$_6$H$_4$C≡CSiMe$_3$,; R = H, R′ = *p*-C$_6$H$_4$Me). (i) Compound **11b** (0.144 g, 0.15 mmol) was dissolved in THF (5 mL), and *p*-MeC$_6$H$_4$MgBr (1.5 mL of a 1.0 M solution in Et$_2$O, 1.5 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (0.016 g, 0.023 mmol) were added. After it was stirred for 12 h, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted with CH$_2$Cl$_2$ (3 × 5 mL). The extracts were combined, evaporated to dryness, and then taken up in CH$_2$Cl$_2$−petroleum ether (2:1) and applied to a chromatography column. Elution with the same solvent mixture gave a yellow fraction that was collected and evaporated to yield [N(PPh$_3$)$_2$][8-(*p*-C$_6$H$_4$Me)-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**13a**; 0.114 g) as a yellow powder.

(ii) Similarly, **11a** (0.140 g, 0.15 mmol), *p*-MeC$_6$H$_4$MgBr (1.5 mL of a 1.0 M solution in Et$_2$O, 1.5 mmol), and [PdCl$_2$(PPh$_3$)$_2$] (0.011 g, 0.016 mmol) gave yellow [N(PPh$_3$)$_2$][8-(*p*-C$_6$H$_4$Me)-3,3,3-(CO)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_{10}$] (**13b**; 0.040 g).

(iii) Compound **11b** (0.176 g, 0.18 mmol), MeMgBr (1.2 mL of a 1.5 M solution in THF−toluene, 1.8 mmol), and [PdCl$_2$(PPh$_3$)$_2$] (0.019 g, 0.027 mmol) yielded [N(PPh$_3$)$_2$][3,3,3-(CO)$_3$-1,2,8-Me$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**13c**; 0.119 g) as a yellow solid.

(iv) Compound **11b** (0.144 g, 0.15 mmol), CH$_2$=CHCH$_2$MgBr (1.5 mL of a 1.0 M solution in Et$_2$O, 1.5 mmol), and [PdCl$_2$(PPh$_3$)$_2$] (0.011 g, 0.016 mmol) yielded [N(PPh$_3$)$_2$][8-(CH$_2$CH=CH$_2$)-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**13d**; 0.100 g) as a yellow solid.

(v) Compound **11b** (0.096 g, 0.10 mmol), *p*-Me$_3$SiC≡CC$_6$H$_4$MgBr (∼3 mL of a 0.33 M solution in Et$_2$O, ∼1.0 mmol), and [PdCl$_2$(PPh$_3$)$_2$] (0.007 mg, 0.010 mmol) in THF (3 mL) yielded [N(PPh$_3$)$_2$][8-(*p*-C$_6$H$_4$C≡CSiMe$_3$)-3,3,3-(CO)$_3$-1,2-Me$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$] (**13e**; 0.034 g) as a yellow powder.

Synthesis of Substituted Derivatives of Compound 13c. (i) Compound **13c** (0.101 g, 0.119 mmol) was dissolved in THF (5 mL), the mixture was cooled to −78 °C, and a solution of I$_2$ (0.096 g, 0.378 mmol) in THF (5 mL) was added dropwise. The mixture was heated to reflux for 6 h, cooled to room temperature, and then evaporated to dryness. Extraction of the residue with Et$_2$O (2 × 20 mL), filtration and evaporation of the combined extracts, and then crystallization from CH$_2$Cl$_2$−petroleum ether (1:1, 2 mL, −30 °C) gave [N(PPh$_3$)$_2$][4-I-3,3,3-(CO)$_3$-1,2,8-Me$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_7$] (**14**; 0.053 g) as a yellow microcrystalline solid.

(ii) Compound **14** was prepared as above in situ from **13c** (0.076 g, 0.090 mmol) and I$_2$ (0.076 g, 0.30 mmol) in THF (3 mL total) and used in situ without isolation. To this solution was added *p*-MeC$_6$H$_4$MgBr (1.4 mL, 1.4 mmol) dropwise at −78 °C. The mixture was stirred at room temperature for 1 h, and then [PdCl$_2$(PPh$_3$)$_2$] (0.006 g, 0.009 mmol) was added. After it was stirred for a further 11 h, the reaction mixture was worked up as for compounds **13**. Column chromatography using neat CH$_2$Cl$_2$ afforded a yellow fraction, from which was obtained [N(PPh$_3$)$_2$][4-(*p*-C$_6$H$_4$Me)-3,3,3-(CO)$_3$-1,2,8-Me$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_7$] (**15**) (0.067 g) as a yellow powder after removal of the solvent in vacuo.

(iii) To a solution of **13c** (0.117 g, 0.137 mmol) in CH$_2$Cl$_2$−NCMe (1:1, 5 mL) was added CF$_3$SO$_3$Me (0.15 mL), and the mixture was stirred at room temperature for 20 h. Solvent was removed in vacuo and the residue taken up in the minimum volume (1 mL) of CH$_2$Cl$_2$ and transferred to a chromatography column. Elution with CH$_2$Cl$_2$−petroleum ether (3:1) gave a pale yellow band that was collected and evaporated in vacuo to yield [4-{(*Z*)-N(Me)=C(H)Me}-3,3,3-(CO)$_3$-1,2,8-Me$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_7$] (**16**; 0.026 g) as a yellow solid.

X-ray Crystallographic Structure Determinations. Experimental data for compounds **4a**, **6**, **7d**, **13a**, and **16** are presented in Table 3. For compound **13a**, diffracted intensities were collected at 173(2) K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα X-radiation (λ = 0.710 73 Å). Final unit cell dimensions were determined from the setting angles of 25 accurately centered reflections. Intensity data were corrected for Lorentz, polarization, and X-ray absorption effects, the last using a numerical method based on the measurement of crystal faces. For **4a**, **6**, **7d**, and **16**, X-ray intensity data were collected at 110(2) K on a Bruker-Nonius X8-APEX CCD area-detector diffractometer using Mo Kα X-radiation. Several sets of narrow data "frames" were collected at different values of θ, for various initial values of ϕ and ω, using 0.5° increments of ϕ or ω. The data frames were integrated using SAINT;[45] the substantial redundancy in data allowed an empirical absorption correction (SADABS)[45] to be applied, based on multiple measurements of equivalent reflections.

The structures were solved using conventional direct methods and refined by full-matrix least squares on all F^2 data using SHELXTL version 5.03 and SHELXL-97.[45,46] All non-hydrogen atoms were assigned anisotropic displacement parameters. The locations of the cage carbon atoms were verified by examination of the appropriate internuclear distances and the magnitudes of their isotropic thermal displacement parameters. Hydrogen atoms involved in the agostic-type B−H⇀M interactions (H(8)) in **4a** and **6** were located in difference Fourier syntheses; their positional parameters were refined with fixed isotropic thermal parameters (U_{iso}(H) = 1.2[U_{iso}(parent)]). The remaining hydrogen atoms were included in calculated positions and set riding on their parent atoms with fixed isotropic thermal parameters (U_{iso}(H) = 1.2[U_{iso}(parent)] or U_{iso}(H) = 1.5[U_{iso}(parent)] for methyl hydrogens).

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(45) APEX 2 software, version 1.0-5; Bruker AXS, Madison, WI, 2003.

(46) SHELXTL versions 5.03 and 6.10; Bruker AXS, Madison, WI, 1995 and 2000.

Table 3. Crystallographic Data for 4a, 6, 7d, 13a, and 16

	4a	**6**	**7d**	**13a**	**16**
formula	$C_{23}H_{26}B_9CuMnO_3P$	$C_{23}H_{26}B_9AuMnO_3P$	$C_8H_{17}B_9MnNO_3$	$C_{50}H_{51}B_9MnNO_3P_2$	$C_{11}H_{23}B_9MnNO_3$
fw	597.18	730.60	327.46	928.09	369.53
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$C2^a$
a, Å	9.2571(5)	9.0699(11)	12.9981(12)	9.212(2)	13.001(14)
b, Å	12.9976(7)	13.2594(14)	9.0076(9)	14.065(6)	9.256(10)
c, Å	13.4635(6)	13.6338(16)	13.6019(15)	36.640(12)	15.422(14)
α, deg	63.579(2)	62.765(5)			
β, deg	84.735(2)	84.531(6)	109.397(5)	95.61(2)	103.79(4)
γ, deg	69.717(2)	70.333(6)			
V, Å^3	1357.00(12)	1369.4(3)	1502.1(3)	4725(3)	1802(3)
Z	2	2	4	4	4
ρ_{calcd}, g cm^{-3}	1.462	1.772	1.448	1.305	1.362
μ(Mo Kα), mm^{-1}	1.333	5.896	0.879	0.391	0.741
wR2, R1 (all data) ^{b}	0.1053, 0.0765	0.0387, 0.0181	0.1126, 0.0543	0.1480, 0.1910	0.1997, 0.1588
wR2, R1 ($F_o > 4\sigma(F_o)$)	0.0962, 0.0410	0.0382, 0.0162	0.1078, 0.0388	0.1095, 0.0764	0.1661, 0.0831

[a] Absolute structure not determined: the crystal is a racemic twin (see text). [b] $wR2 = [\sum\{w(F_o{}^2 - F_c{}^2)^2\}/\sum w(F_o{}^2)^2]^{1/2}$; $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

The pendant iminium unit in **7d** was disordered over two distinct sites in the approximate ratio 73:27. This disorder was such that there were two separate positions for the iminium ═C and ═N atoms and the *C*-methyl group of one component coincided with the *N*-methyl group of the other. Nevertheless, it should be noted that the *E* geometry was unequivocally present in both components.

The structure determination for compound **16** presented considerable difficulty. Crystals were very small, platelike, and poorly diffracting, and as a consequence the resulting data set was of only modest quality and many parameters suffered strong correlation. A mixture of constraints and restraints (EADP, DELU, and ISOR cards in SHELXL[45]) were applied to the temperature factors of the $\{C_2B_9Me_2\}$ fragment and of the CO ligands, to allow successful anisotropic refinement. Unlike **7d**, no disorder of the iminium unit was found. Compound **16** is chiral and crystallizes in the chiral space group C_2. However, the crystal was a racemic twin, and hence no information on absolute configuration could be obtained. The compound as synthesized, of course, is a racemate.

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Supporting Information Available: Full details of the crystal structure analyses as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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