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Monocarbollide complexes of molybdenum and tungsten: functionalization through reactions at a cage boron centre‡

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Reactions of the salts $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}closo\text{-}2,1\text{-}MCB_{10}H_{11}]$ (M = Mo or W) with CF_3SO_3Me or H_2SO_4 in the presence of donor molecules L afford zwitterionic molecules $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}L\text{-}closo\text{-}2,1\text{-}MCB_{10}H_{10}]$ [L = OEt_2, $O(CH_2)_4$, *cyclo*-1,4-$O(CH_2)_4O$, SMe_2, $S(CH_2)_4$, *cyclo*-1,4,7-$S_3(CH_2)_6$, $NCBu^t$ or $CNC_6H_3Me_2$-2,6]. The exopolyhedral group L is attached to a β-boron atom in the CB*BB*B ring coordinated to the metal, a feature confirmed by an X-ray crystallographic study of $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}(CNC_6H_3Me_2\text{-}2,6)\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$. The molecules $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}L\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ [L = OEt_2 or $O(CH_2)_4$] in THF (tetrahydrofuran) react with Me_3NO, with addition of $[PPh_4]Br$, to give the salts $[PPh_4][2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}R\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ [R = OEt or $O(CH_2)_3CHO$]. These products on treatment with CF_3SO_3Me in CH_2Cl_2 give the zwitterionic molecules $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{O(Me)R\}\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ (R = Et or Bu^n). Single crystal X-ray diffraction studies established the structures of $[PPh_4][2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}OEt\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ and $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{O(Me)Bu^n\}\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$. In NCMe the reagents $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}closo\text{-}2,1\text{-}MCB_{10}H_{11}]$ react with CF_3SO_3Me to yield $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{N(Me)=C(H)Me\}\text{-}closo\text{-}2,1\text{-}MCB_{10}H_{10}]$ (M = Mo or W), compounds in which an imine substituent is bonded to the cage system, a feature confirmed by an X-ray diffraction study of the tungsten species. Similarly, the compounds $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}closo\text{-}2,1\text{-}MCB_{10}H_{11}]$ react with $CNBu^t$ and CF_3SO_3Me to give a mixture of isomers of $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{N(Bu^t)=C(H)Me\}\text{-}closo\text{-}2,1\text{-}MCB_{10}H_{10}]$ (M = Mo or W) with *E* and *Z* configurations for the $BN(Bu^t)=C(H)Me$ group.

Transition metal complexes where the metal ions are pentahapto coordinated by $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ icosahedral cage frameworks have been extensively studied.[1] In contrast, related species having $[nido\text{-}7\text{-}CB_{10}H_{11}]^{3-}$ fragments as ligands have received very little attention since a few complexes of this kind were reported some three decades ago.[2] This neglect is surprising since the monocarbollide anion with its formal trinegative charge and its mode of coordination is related as a ligand to both $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ and $[C_5H_5]^-$ and thus opens up new possibilities in the design of metallacarbaborane reagents for further syntheses.[3] To redress this imbalance we are synthesizing and investigating the reactivity of 'piano-stool' type complexes where the metal is η^5-ligated on one side by a $[nido\text{-}7\text{-}CB_{10}H_{11}]^{3-}$ fragment and on the other by CO, phosphine or isocyanide groups. In this context we have prepared salts of the anionic complexes $[2,2,2,2\text{-}(CO)_4\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]^-$, $[2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}ReCB_{10}H_{11}]^{2-}$ and $[2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}FeCB_{10}H_{11}]^-$ as well as several derivatives where the CO groups are replaced by other donor molecules.[4]

Although there are electronic relationships between monocarbollide metal carbonyl compounds and their cyclopentadienide analogues, *e.g.* $[2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}FeCB_{10}H_{11}]^-$ *versus* $[Fe(CO)_3(\eta\text{-}C_5H_5)]^+$, it is becoming evident that the cyclopentadienide and monocarbollide complexes display very different chemical behaviour. The chief origin of this difference lies in the non-spectator role of the $[\eta^5\text{-}nido\text{-}7\text{-}CB_{10}H_{11}]^{3-}$ ligand, a feature frequently adopted and which results in the formation of molecules with unusual structures and reactivities. Thus preliminary studies with the compounds $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}L\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]$ **1** (L = CO), **3** (L = PPh_3), and **5** (L = $CNBu^t$) revealed that in reactions with cationic transition metal–ligand fragments zwitterionic products were formed with the electrophilic metal groups attached to cage BH vertices *via* B–H⟶M bonds.[4d] In contrast anionic cyclopentadienide metal carbonyls react with similar substrates generally affording products with metal–metal bonds. Moreover although it has long been known that protonation of the salt of an anion like $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ yields a hydrido complex $[MoH(CO)_3(\eta\text{-}C_5H_5)]$, treatment of **3** with the strong acid $HBF_4{\cdot}OEt_2$ affords a neutral but charge-compensated complex $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}OEt_2\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ **9**,[4c] thus providing a further example demonstrating the tendency for reaction to occur at a BH vertex rather than at the metal centre.

The exopolyhedral attachment of a variety of different organic groups to a boron site in a metallacarbaborane framework is important in the search for new uses for this class of compound.[3] Thus extension of the range of charge-compensated molecules such as **9** opens the way to derivatization of the cage at a specific site. With this in mind we report further work with the molybdenum species and also results with tungsten compounds, the first examples of complexes where this metal is ligated by $[nido\text{-}7\text{-}CB_{10}H_{11}]^{3-}$ groups.

Results and discussion

The tungsten reagent **2** was prepared using a similar procedure to that employed to obtain **1**,[4c] except that $[W(CO)_3(NCEt)_3]$ replaced $[Mo(CO)_3(NCMe)_3]$. The tungsten reagent in EtCN was added to a suspension of $Na_3[nido\text{-}7\text{-}CB_{10}H_{11}]$ in THF (tetrahydrofuran). Carbon monoxide was bubbled through the

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‡ Electronic supplementary information (ESI) available: bond distances and angles for compounds **24**, **28**, **31** and **33b**. See http://www.rsc.org/suppdata/dt/b1/b101003o/

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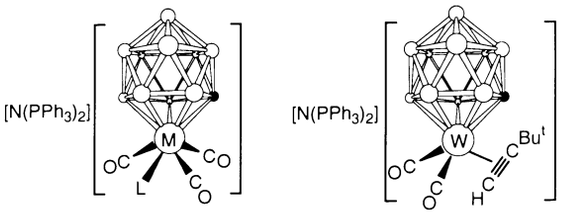
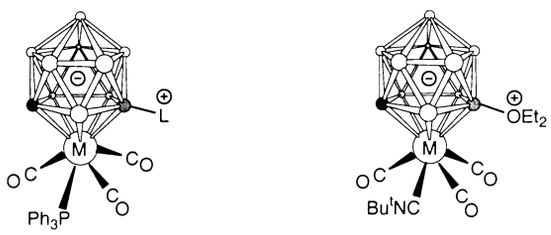


	M	L
1	Mo	CO
2	W	CO
3	Mo	PPh_3
4	W	PPh_3
5	Mo	$CNBu^t$
6	W	$CNBu^t$

	M
7	Mo
8	W

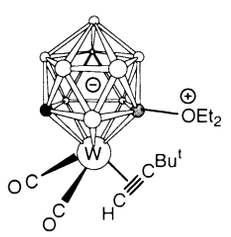
○ BH ● CH

Chart 1



	M
11	Mo
12	W

	M	L
9	Mo	OEt_2
10	W	OEt_2
14	Mo	$O(CH_2)_4$
15	W	$O(CH_2)_4$
16	W	*cyclo*-1,4-$O(CH_2)_4O$
17	Mo	SMe_2
18	Mo	$S(CH_2)_4$
19	W	$S(CH_2)_4$
20	Mo	*cyclo*-$S(CH_2)_2S(CH_2)_2SCH_2CH_2$
21	W	*cyclo*-$S(CH_2)_2S(CH_2)_2SCH_2CH_2$
22	Mo	$NCBu^t$
23	W	$NCBu^t$
24	Mo	$CNC_6H_3Me_2$-2,6
25	W	$CNC_6H_3Me_2$-2,6
26	Mo	$CNBu^t$
27	W	$CNBu^t$



13

○ BH ◍ B ● CH

Chart 2

solution at –78 °C and $HBF_4{\cdot}Et_2O$ added, followed by $[N(PPh_3)_2]Cl$. The salt **2** was isolated from the mixture by column chromatography. We have previously described the preparation of the molybdenum compounds $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}L\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]$ **3** (L = PPh_3) and **5** (L = $CNBu^t$) from **1**. Similarly treatment of **2** in THF with PPh_3 or $CNBu^t$ at room temperatures, in the presence of Me_3NO, to labilize a ligated CO molecule, afforded the complexes $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}L\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{11}]$ **4** (L = PPh_3) and **6** (L = $CNBu^t$), respectively. Compounds **2**, **4** and **6** were characterized by microanalysis and spectroscopic data (Tables 1–3).

Earlier we reported that **1** reacts with $Bu^tC{\equiv}CH$ to afford $[N(PPh_3)_2][2,2\text{-}(CO)_2\text{-}2\text{-}(Bu^tC{\equiv}CH)\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]$ **7**, a species in which the alkyne formally donates four electrons to the metal.[4c] It was found that **2** behaves in a similar manner reacting with the alkyne to afford the salt $[N(PPh_3)_2][2,2\text{-}(CO)_2\text{-}2\text{-}(Bu^tC{\equiv}CH)\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{11}]$ **8**, data for which are given in Tables 1–3. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **8** the resonances for the ligated carbons of the alkyne are observed (δ 177.4 and 190.0) in the chemical shift range expected for an alkyne functioning as a four electron donor.[5] Neither with **7** nor with **8** was there any evidence for insertion of the alkyne into a cage BH group to form a $BCH{=}CHBu^t$ moiety, a process which occurs readily with the labile complexes $[3\text{-}CO\text{-}3\text{-}L\text{-}3\text{-}(Bu^tC{\equiv}CH)\text{-}closo\text{-}3,1,2\text{-}RuC_2B_9H_{11}]$ (L = CO or PPh_3) where the alkynes function as two electron donors to the ruthenium centre.[6]

Synthesis of charge-compensated complexes

Several molybdenum and tungsten zwitterionic compounds of formulation $[2,2,2\text{-}(CO)_3\text{-}2\text{-}L'\text{-}7\text{-}L\text{-}closo\text{-}2,1\text{-}MCB_{10}H_{10}]$ (M = Mo or W, L′ = PPh_3 or $CNBu^t$), akin to complexes **9** and **11**,[4c] were prepared by adding concentrated H_2SO_4 or more usually CF_3SO_3Me to solutions containing mixtures of various donor molecules L and one or other of the compounds **3**–**6**. Nucleophilic substitution at a cage boron atom by sulfur donors facilitated by H_2SO_4 has been observed earlier.[7] The electrophilic reagent CF_3SO_3Me or H_2SO_4 removes H^- from a BH vertex thereby creating a vacant site for the donor molecule to coordinate. In many cases the donor species conveniently function as the solvent for reaction. To examine the scope of the reactions with donors, complexes **3** and **4** were the reagents of choice for the study because they are more stable and more soluble than their precursors **1** and **2**. However, it was also shown that the alkyne tungsten salt **8** when dissolved in CH_2Cl_2–Et_2O reacted with CF_3SO_3Me to give the charge-compensated complex $[2,2\text{-}(CO)_2\text{-}2\text{-}(Bu^tC{\equiv}CH)\text{-}7\text{-}OEt_2\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **13**. Interestingly no reaction of Me^+ occurred at the ligated carbonyl, isocyanide or alkyne groups of the various reactants. Microanalytical and spectroscopic data characterizing the complexes **10**, **12**, **13** and **15**–**25** are given in Tables 1–3.

The NMR data for the new compounds are in agreement with their formulations. In particular the presence of the BL group could be demonstrated for the majority of products from their $^{11}B\text{-}\{^1H\}$ NMR spectra, with its resonance appearing as a singlet in the low field region of the fully coupled spectrum, *e.g.* δ 20.3 (**15**), whereas the other signals became doublets with J(HB) > 100 Hz due to ^1H–^{11}B coupling between boron vertices and exopolyhedral hydrogens (Table 3). Overlapping of peaks in some spectra prevented a safe assignment of all BL signals. Of particular interest is the site of substitution of the donor L on the cage framework. The molecules are asymmetric, as they would be irrespective of whether α or β boron vertices with respect to the carbon in the metal-coordinated CBBBB ring are employed in the bonding to L, and a firm structural assignment could not be made from the NMR data. However, an X-ray diffraction study established[4c] that in the molecule **14** the THF group was coordinated to a boron atom in a β site with respect to the carbon in the CB*BB*B ring ligating the molybdenum. To ensure that this configuration was also the pattern for the new compounds X-ray diffraction studies were carried out on complexes **23** and **24**. The molecular structure of **24** is shown in Fig. 1. A listing of bond distances and angles for this molecule, and those for others reported herein which were studied by X-ray diffraction, has been deposited as Electronic Supplementary Information. The structure of **23** was basically similar. It is immediately apparent from Fig. 1 that the $CNC_6H_3Me_2$-2,6 molecule is attached to a β-boron, with B(3)–C(5) 1.538(5) Å and B(3)–C(5)–N 177.8(3)°. The PPh_3 ligand lies transoid to the isocyanide group [P–Mo–B(3) 149.04(9)°] presumably to reduce steric crowding.

It is evident from the range of charge-compensated complexes prepared that many similar molecules are accessible by the methodology employed, namely treatment of the monocarbollide–molybdenum or –tungsten anionic complexes

Table 1 Analytical and physical data

Compound[a]	Yield (%)	$\tilde{\nu}_{max}$(CO)[b]/cm^{-1}	Analysis (%)[c] C	H	N
2 [N(PPh$_3$)$_2$][2,2,2,2-(CO)$_4$-*closo*-2,1-WCB$_{10}$H$_{11}$]	53	2070, 1980, 1950	51.0 (51.0)	4.4 (4.3)	1.5 (1.5)
4 [N(PPh$_3$)$_2$][2,2,2-(CO)$_3$-2-PPh$_3$-*closo*-2,1-WCB$_{10}$H$_{11}$]	82	2006, 1919, 1896	58.6 (58.8)[d]	5.0 (5.0)	1.2 (1.1)
6 [N(PPh$_3$)$_2$][2,2,2-(CO)$_3$-2-CNBu^t-*closo*-2,1-WCB$_{10}$H$_{11}$]	51	2013,[e] 1939, 1916	54.0 (54.0)[d]	5.1 (5.3)	2.7 (2.7)
8 [N(PPh$_3$)$_2$][2,2-(CO)$_2$-2-(Bu^{t}C≡CH)-*closo*-2,1-WCB$_{10}$H$_{11}$]	80	2018, 1946	54.0 (54.5)	5.3 (5.2)	1.5 (1.4)
10 [2,2,2-(CO)$_3$-2-PPh$_3$-7-OEt$_2$-*closo*-2,1-WCB$_{10}$H$_{10}$]	85	2020, 1940, 1916	42.8 (42.5)	4.8 (4.8)	
12 [2,2,2-(CO)$_3$-2-CNBu^t-7-OEt$_2$-*closo*-2,1-WCB$_{10}$H$_{10}$]	77	2031,[f] 1963, 1932	27.4 (27.1)[g]	5.0 (5.0)	2.4 (2.3)
13 [2,2-(CO)$_2$-2-(Bu^{t}C≡CH)-7-OEt$_2$-*closo*-2,1-WCB$_{10}$H$_{10}$]	60	2038, 1962	28.3 (28.5)[g]	5.5 (5.5)	
15 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{O(CH$_2$)$_4$}-*closo*-2,1-WCB$_{10}$H$_{10}$]	56	2017, 1939, 1915	42.2 (42.6)	4.5 (4.5)	
16 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{*cyclo*-1,4-O(CH$_2$)$_4$O}-*closo*-2,1-WCB$_{10}$H$_{10}$]	67	2020, 1942, 1915	40.9 (41.7)	4.4 (4.4)	
17 [2,2,2-(CO)$_3$-2-PPh$_3$-7-SMe$_2$-*closo*-2,1-MoCB$_{10}$H$_{10}$]	34	2026, 1960, 1919	45.3 (45.4)	4.9 (4.9)	
18 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{S(CH$_2$)$_4$}-*closo*-2,1-MoCB$_{10}$H$_{10}$]	34	2026, 1961, 1919	47.2 (47.3)	5.1 (5.0)	
19 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{S(CH$_2$)$_4$}-*closo*-2,1-WCB$_{10}$H$_{10}$]	43	2020, 1943, 1918	41.8 (41.7)	4.5 (4.4)	
20 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{*cyclo*-1,4,7-S$_3$(CH$_2$)$_6$}-*closo*-2,1-MoCB$_{10}$H$_{10}$]	44	2026, 1958, 1919	44.2 (44.7)	4.9 (4.9)	
21 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{*cyclo*-1,4,7-S$_3$(CH$_2$)$_6$}-*closo*-2,1-WCB$_{10}$H$_{10}$]	22	2020, 1944, 1912	40.3 (40.0)	4.7 (4.4)	
22 [2,2,2-(CO)$_3$-2-PPh$_3$-7-NCBu^t-*closo*-2,1-MoCB$_{10}$H$_{10}$]	30	2026, 1957, 1925	45.0 (45.4)[h]	4.9 (4.9)	1.9 (1.9)
23 [2,2,2-(CO)$_3$-2-PPh$_3$-7-NCBu^t-*closo*-2,1-WCB$_{10}$H$_{10}$]	43	2019, 1942, 1918	41.0 (40.6)[h]	4.4 (4.4)	1.8 (1.7)
24 [2,2,2-(CO)$_3$-2-PPh$_3$-7-(CNC$_6$H$_3$Me$_2$-2,6)-*closo*-2,1-MoCB$_{10}$H$_{10}$]	20	2028,[i] 1962, 1930	53.0 (52.9)	5.0 (4.8)	2.1 (2.0)
25 [2,2,2-(CO)$_3$-2-PPh$_3$-7-(CNC$_6$H$_3$Me$_2$-2,6)-*closo*-2,1-WCB$_{10}$H$_{10}$]	48	2021,[j] 1944, 1922	47.8 (47.0)	4.6 (4.3)	1.9 (1.8)
26 [2,2,2-(CO)$_3$-2-PPh$_3$-7-CNBu^t-*closo*-2,1-MoCB$_{10}$H$_{10}$]	23	2026,[k] 1960, 1928	49.3 (49.5)	5.6 (5.2)	2.1 (2.1)
27 [2,2,2-(CO)$_3$-2-PPh$_3$-7-CNBu^t-*closo*-2,1-WCB$_{10}$H$_{10}$]	19	2019,[l] 1941, 1918	43.6 (43.6)	5.0 (4.6)	1.9 (1.9)
28 [PPh$_4$][2,2,2-(CO)$_3$-2-PPh$_3$-7-OEt-*closo*-2,1-WCB$_{10}$H$_{10}$]	68	2006, 1923, 1904	52.1 (52.1)[h]	4.6 (4.6)	
29 [PPh$_4$][2,2,2-(CO)$_3$-2-PPh$_3$-7-{O(CH$_2$)$_3$CHO}-*closo*-2,1-WCB$_{10}$H$_{10}$]	40	2007, 1919, 1907	53.7 (53.7)[g]	4.9 (4.7)	
30 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{O(Me)Et}-*closo*-2,1-WCB$_{10}$H$_{10}$]	70	2019, 1940, 1918	41.7 (41.7)	4.7 (4.6)	
31 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{O(Me)Bu^n}-*closo*-2,1-WCB$_{10}$H$_{10}$]	50	2019, 1940, 1918	43.5 (43.3)	5.0 (5.0)	
32 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Me)=C(H)Me}-*closo*-2,1-MoCB$_{10}$H$_{10}$]	50	2025, 1954, 1918	45.9 (45.6)[g]	5.0 (4.9)	2.1 (2.1)
33 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Me)=C(H)Me}-*closo*-2,1-WCB$_{10}$H$_{10}$]	46	2017, 1940, 1913	42.4 (41.9)	4.5 (4.7)	1.9 (2.0)
34 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Bu^t)=C(H)Me}-*closo*-2,1-MoCB$_{10}$H$_{10}$]	43	2023, 1954, 1920	49.7 (50.1)	5.7 (5.7)	2.0 (2.1)
35 [2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Bu^t)=C(H)Me}-*closo*-2,1-WCB$_{10}$H$_{10}$]	48	2016, 1938, 1911	44.3 (44.3)	5.0 (5.0)	1.9 (1.8)

[a] All complexes are yellow, except **8** and **13** which are brick red. [b] Measured in CH_2Cl_2; all CO bands are strong; broad medium-intensity bands observed at *ca*. 2550 cm^{-1} in the spectra of all compounds are due to B–H absorptions. [c] Calculated values are given in parentheses. [d] Crystallizes with 0.5 mol equivalent of pentane. [e] ν_{max}(N≡C) 2156 m cm^{-1}. [f] ν_{max}(N≡C) 2168 m cm^{-1}. [g] Crystallizes with 0.5 mol equivalent CH_2Cl_2. [h] Crystallizes with 1.0 mol equivalent CH_2Cl_2. [i] ν_{max}(N≡C) 2242 m cm^{-1}. [j] ν_{max}(N≡C) 2244 m cm^{-1}. [k] ν_{max}(N≡C) 2273 m cm^{-1}. [l] ν_{max}(N≡C) 2274 m cm^{-1}.

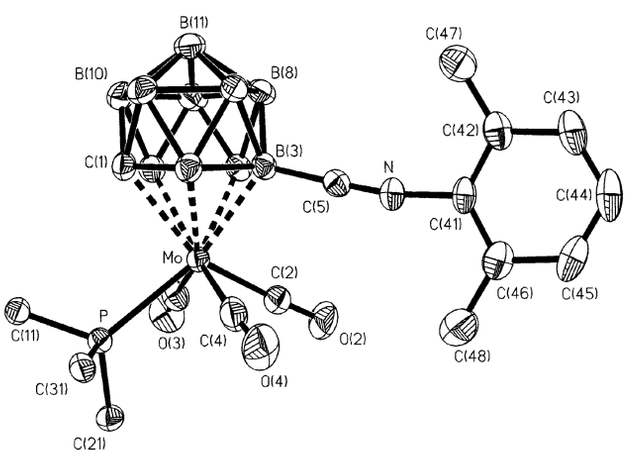


Fig. 1 Structure of **24** showing the crystallographic labeling scheme. In this and in Figs. 2–4 hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the Ph rings are shown. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Mo–B(3) 2.348(4), Mo–B(4) 2.376(4), Mo–B(5) 2.386(4), Mo–B(2) 2.403(4), Mo–C(1) 2.419(3), Mo–P 2.5575(9), B(3)–C(5) 1.538(5), C(5)–N 1.137(4); B(3)–Mo–P 149.04(9), C(1)–Mo–P 88.38(8), C(5)–B(3)–Mo 114.2(2), N–C(5)–B(3) 177.8(3), C(5)–N–C(41) 170.1(3).

with a strong electrophilic reagent in the presence of an oxygen, sulfur or nitrogen donor. Moreover, the structures of the resultant zwitterionic complexes indicate that the BH cage vertices carrying the most hydridic hydrogen are those lying β to the carbon in the CB*BBB* ring. These boron atoms are adjacent to the BH vertex in the non-coordinating B_5 belt which is antipodal to the cage carbon. Significantly no isomers [2,2,2-(CO)$_3$-2-L′-3-L-*closo*-2,1-MCB$_{10}$H$_{10}$] (M = Mo or W, L′ = PPh$_3$ or CNBu^t) with the donor L attached to a boron in an α site with respect to carbon in the CBBBB ring were detected in any of the syntheses, all being regiospecific in nature.

Selected reactions of the charge-compensated complexes

As mentioned earlier, it was of particular interest to determine if any reactivity could be demonstrated for the exopolyhedral groups L without degradation of the cage system. With this in mind attention focused initially on species where the donor atom is oxygen. The latter carries a formal positive charge and therefore adjacent atoms should be susceptible to attack by nucleophiles. In this study the nucleophilic reagent of choice was Me_3NO.

Treatment of complex **10** in THF with Me_3NO produced a mixture which continued to display three CO stretching bands, but these were shifted to lower frequencies than those of **10**, indicating the formation of a more electron rich metallacarbaborane system associated with an anion. After addition of [PPh$_4$]Br the only product isolated was the salt [PPh$_4$][2,2,2-(CO)$_3$-2-PPh$_3$-7-OEt-*closo*-2,1-WCB$_{10}$H$_{10}$] **28**. To establish firmly the structure of this salt a single-crystal X-ray diffraction study was carried out. The anion is shown in Fig. 2. It is immediately apparent that in the reaction of **10** with Me_3NO a nucleophilic attack of the latter on the cage B←OEt$_2$ group took place resulting in cleavage of a C–O bond. A related reaction was observed earlier[8] when the zwitterionic dicarbollide species [1,2-Me$_2$-3,3-(CO)$_2$-3-(η^3-C$_3$H$_5$)-8-OEt$_2$-*closo*-3,1,2-MC$_2$B$_9$H$_8$] (M = Mo or W) on treatment with halide ions afforded salts of the anions [1,2-Me$_2$-3,3-(CO)$_2$-3-(η^3-C$_3$H$_5$)-8-OEt-*closo*-3,1,2-MC$_2$B$_9$H$_8$]$^-$.

The *nido*-9-OEt-7-CB$_{10}$H$_{10}$ cage in complex **28** is coordinated to the tungsten atom by the open CBBBB face in the usual pentahapto manner. As anticipated the ethoxide group is attached to a boron in a β site in the CB*BBB* ring, thereby confirming this geometry for the OEt$_2$ group in its precursor **10**.

Table 2 Hydrogen-1 and carbon-13 NMR data[a]

Compound	^{1}H δ[b]	^{13}C δ[c]
2	7.67–7.46 (m, 30 H, Ph), 1.97 (s, 1 H, cage CH)	217.1 [CO, *J*(WC) = 113], 134.0–126.7 (Ph), 45.8 (cage CH)
4	7.66–7.38 (m, 45 H, Ph), 1.64 (s, 1 H, cage CH)	228.1 [d, CO × 2, *J*(PC) = 23], 228.0 [d, CO, *J*(PC) = 6], 134.2–126.7 (Ph), 48.5 (cage CH)
6	7.68–7.47 (m, 30 H, Ph), 1.91 (s, 1 H, cage CH), 1.50 (s, 9 H, Bu^t)	228.6[d] (CO), 224.5 (CO × 2). 134.0–126.7 (Ph), 59.1 (*C*Me$_3$), 45.5 (cage CH), 30.5 (C*Me*$_3$)
8	11.04 (s, 1 H, C≡CH), 7.66–7.47 (m, 30 H, Ph), 3.94 (s, 1 H, cage CH), 1.45 (s, 9 H, Bu^t)	220.4 (CO), 190.0 (C≡*C*Bu^t), 177.4 (C≡*C*H), 134.0–126.7 (Ph), 45.2 (cage CH), 41.0 (*C*Me$_3$), 31.2 (C*Me*$_3$)
10	7.52–7.27 (m, 15 H, Ph), 4.25 [AB q, 4 H, OCH$_2$, *J*(AB) = 9, *J*(HH) = 7], 1.42 (s, 1 H, cage CH), 1.36 [t, 6 H, Me, *J*(HH) = 7]	227.0 [d, CO, *J*(PC) = 6], 224.7 [d, CO, *J*(PC) = 25], 222.1 [d, CO, *J*(PC) = 25], 133.9–129.0 (Ph), 74.5 (OCH$_2$), 47.6 (cage CH), 12.2 (Me)
12	4.21 [AB q, 4 H, OCH$_2$, *J*(AB) = 7, *J*(HH) = 5], 1.83 (s, 1 H, cage CH), 1.54 (s, 9 H, Bu^t), 1.36 [t, 6 H, Me, *J*(HH) = 7]	225.0, 219.7, 218.5 (CO × 3), 139.8 (br, CN), 75.1 (OCH$_2$), 60.1 (*C*Me$_3$), 43.6 (cage CH), 30.3 (C*Me*$_3$), 12.6 (CH$_2$*Me*)
13	11.40 (s, 1 H, C≡CH), 4.17 [q, 4 H, OCH$_2$, *J*(HH) = 7], 3.56 (s, 1 H, cage CH), 1.53 (s, 9 H, Bu^t), 1.32 [t, 6 H, Me, *J*(HH) = 7]	221.6 (C≡*C*Bu^t), 213.6 (CO), 181.2 (C≡*C*H), 76.8 (OCH$_2$), 43.0 (cage CH), 41.8 (*C*Me$_3$), 31.0 (C*Me*$_3$), 12.8 (CH$_2$*Me*)
15	7.52–7.29 (m, 15 H, Ph), 4.22 (br m, 4 H, OCH$_2$), 2.08 (br m, 4 H, CH$_2$), 1.46 (s, 1 H, cage CH)	227.3 [d, CO, *J*(PC) = 6], 224.9 [d, CO, *J*(PC) = 25], 222.4 [d, CO, *J*(PC) = 24], 133.9–128.9 (Ph), 79.9 (OCH$_2$), 47.7 (cage CH), 24.8 (CH$_2$)
16	7.52–7.26 (m, 15 H, Ph), 4.12, 3.85 (br m × 2, 8 H, OCH$_2$), 1.41 (s, 1 H, cage CH)	227.4 [d, CO, *J*(PC) = 5], 224.9 [d, CO, *J*(PC) = 25], 221.4 [d, CO, *J*(PC) = 24], 133.8–129.0 (Ph), 79.5, 65.2 (OCH$_2$ × 2), 47.8 (cage CH)
17	7.53–7.29 (m, 15 H, Ph), 2.34, 2.28 (2 × s, 6 H, Me), 1.48 (s, 1 H, cage CH)	236.7 [d, CO, *J*(PC) = 6], 232.3 [d, CO, *J*(PC) = 29], 230.9 [d, CO, *J*(PC) = 29], 133.8–129.3 (Ph), 55.8 (cage CH), 26.3, 25.8 (Me)
18	7.53–7.29 (m, 15 H, Ph), 3.19–3.05, 2.13–1.93 (m, 8 H, CH$_2$), 1.48 (s, 1 H, cage CH)	236.6 [d, CO, *J*(PC) = 6], 232.0 [d, CO, *J*(PC) = 29], 231.1 [d, CO, *J*(PC) = 29], 133.9–129.1 (Ph), 56.1 (cage CH), 43.8, 43.4 (SCH$_2$), 30.2, 29.7 (CH$_2$)
19	7.55–7.28 (m, 15 H, Ph), 3.22–3.02, 2.23–1.90 (m, 8 H, CH$_2$), 1.63 (s, 1 H, cage CH)	225.6 [d, CO, *J*(PC) = 6], 223.4 [d, CO, *J*(PC) = 25], 221.9 [d, CO, *J*(PC) = 25], 134.0–129.1 (Ph), 51.7 (cage CH), 43.9, 43.5 (SCH$_2$), 30.2, 29.7 (CH$_2$)
20	7.53–7.29 (m, 15 H, Ph), 3.65–3.34, 3.13–2.75 (m, 12 H, CH$_2$), 1.46 (s, 1 H, cage CH)	236.8 [d, CO, *J*(PC) = 6], 232.8 [d, CO, *J*(PC) = 29], 230.7 [d, CO, *J*(PC) = 29], 136.1–128.3 (Ph), 55.7 (cage CH), 45.2, 44.0, 36.7, 36.1, 32.2, 32.0 (CH$_2$)
21	7.54–7.29 (m, 15 H, Ph), 3.63–3.36, 3.03–2.72 (m, 12 H, CH$_2$), 1.61 (s, 1 H, cage CH)	225.8 [d, CO, *J*(PC) = 6], 224.2 [d, CO, *J*(PC) = 25], 221.6 [d, CO, *J*(PC) = 24], 134.0–129.1 (Ph), 51.0 (cage CH), 45.4, 44.3, 36.6, 36.2, 35.3, 32.1 (CH$_2$)
22	7.55–7.29 (m, 15 H, Ph), 1.48 (s, 9 H, Bu^t), 1.43 (s, 1 H, cage CH)	239.0 [d, CO, *J*(PC) = 6], 233.2 [d, CO, *J*(PC) = 28], 230.6 [d, CO, *J*(PC) = 28], 133.6–128.8 (Ph), 121.1 (N*C*Bu^t), 59.0 (*C*Me$_3$), 54.7 (cage CH), 27.1 (Me)
23	7.49–7.33 (m, 15 H, Ph), 1.52 (s, 1 H, cage CH), 1.49 (s, 9 H, Bu^t)	227.8 [d, CO, *J*(PC) = 5], 224.2 [d, CO, *J*(PC) = 24], 221.8 [d, CO, *J*(PC) = 24], 133.9–129.0 (Ph), 120.4 (N*C*Bu^t), 59.2 (*C*Me$_3$), 49.8 (cage CH), 27.3 (Me)
24	7.52–7.16 (m, 18 H, Ph, C$_6$H$_3$), 2.38 (s, 6 H, Me), 1.58 (s, 1 H, cage CH)	236.8[d] [d, CO, *J*(PC) = 7], 231.7 [d, CO, *J*(PC) = 29], 230.3 [d, CO, *J*(PC) = 29], 137.1–128.7 (Ph), 56.9 (cage CH), 18.5 (Me)
25	7.50–7.17 (m, 18 H, Ph, C$_6$H$_3$), 2.39 (s, 6 H, Me), 1.75 (s, 1 H, cage CH)	225.5[d] [d, CO, *J*(PC) = 5], 223.0 [d, CO, *J*(PC) = 25], 221.2 [d, CO, *J*(PC) = 24], 133.9–128.8 (Ph), 52.2 (cage CH), 18.5 (Me)
26	7.53–7.28 (m, 15 H, Ph), 1.59 (s, 1 H, cage CH), 1.53 (s, 9 H, Bu^t)	237.6[d] [d, CO, *J*(PC) = 6], 232.2 [d, CO, *J*(PC) = 29], 230.5 [d, CO, *J*(PC) = 29], 133.7–128.9 (Ph), 79.8 (N*C*Me$_3$), 56.8 (cage CH), 29.4 (NC*Me*$_3$)
27	7.52–7.37 (m, 15 H, Ph), 1.54 (s, 1 H, cage CH), 1.54 (s, 9 H, Bu^t)	226.3[d] [d, CO, *J*(PC) = 5], 223.5 [d, CO, *J*(PC) = 25], 221.6 [d, CO, *J*(PC) = 25], 133.8–128.9 (Ph), 61.1 (N*C*Me$_3$), 52.1 (cage CH), 29.5 (NC*Me*$_3$)
28	7.92–7.35 (m, 35 H, Ph), 3.24 [q, 2 H, OCH$_2$, *J*(HH) = 7], 1.36 (s, 1 H, cage CH), 0.96 [t, 3 H, Me, *J*(HH) = 7]	228.9 [d, CO, *J*(PC) = 23], 228.3 [d, CO, *J*(PC) = 23], 227.6 [d, CO, *J*(PC) = 6], 136.0–117.2 (Ph), 63.4 (OCH$_2$), 44.1 (cage CH), 17.6 (Me)
29	9.67 [t, 1 H, CHO, *J*(HH) = 2], 7.92–7.36 (m, 35 H, Ph), 3.23 [t, 2 H, OCH$_2$, *J*(HH) = 6], 2.39 [dt, 2 H, C*H*$_2$CHO, *J*(HH) = 2, *J*(HH) = 7], 1.62 [tt, 2 H, OCH$_2$C*H*$_2$, *J*(HH) = 7, 6], 1.31 (s, 1 H, cage CH)	228.7 [d, CO, *J*(PC) = 23], 228.3 [d, CO, *J*(PC) = 23], 227.6 [d, CO, *J*(PC) = 6], 204.3 (CHO), 136.0–117.2 (Ph), 67.3 (OCH$_2$), 44.2 (cage CH), 41.6 (*C*H$_2$CHO), 25.2 (OCH$_2$*C*H$_2$)
30	7.52–7.28 (m, 15 H, Ph), 4.19 [AB, q, 2 H, OCH$_2$, *J*(AB) = 7, *J*(HH) = 7], 3.69 (s, 3 H, OMe), 1.55 (s, 1 H, cage CH), 1.40 [dd, 3 H, CH$_2$*Me*, *J*(HH) = 7, 7]	226.9 [d, CO, *J*(PC) = 5], 224.5 [d, CO, *J*(PC) = 25], 221.9 [d, CO, *J*(PC) = 24], 133.9–129.0 (Ph), 80.9 (OMe), 64.5 (OCH$_2$), 47.7 (cage CH), 12.3 (CH$_2$*Me*)
31	7.52–7.27 (m, 15 H, Ph), 4.06 [AB, t, 2 H, OCH$_2$, *J*(AB) = 11, *J*(HH) = 8], 3.71 (s, 3 H, OMe), 1.75 [tt, 2 H, OCH$_2$C*H*$_2$, *J*(HH) = 8, 8], 1.42 (s, 1 H, cage CH), 1.30 [tq, 2 H, C*H*$_2$Me, *J*(HH) = 8, 8], 0.92 [t, 3 H, CH$_2$*Me*, *J*(HH) = 8]	226.8 [d, CO, *J*(PC) = 5], 224.4 [d, CO, *J*(PC) = 25], 221.9 [d, CO, *J*(PC) = 24], 133.9–128.7 (Ph), 84.2 (OMe), 65.3 (OCH$_2$), 47.7 (cage CH), 28.3 (OCH$_2$*C*H$_2$), 18.1 (*C*H$_2$Me), 13.6 (CH$_2$*Me*)
32	7.72[e] (br m, 1 H, CH), 7.52–7.28 (m, 15 H, Ph), 3.59, *3.39 (s, 3 H, NMe), *2.52, 2.34 [d, 3 H, CMe, *J*(HH) = 6], 1.42 (s, 1 H, cage CH)	239.1 [d, CO, *J*(PC) = 6], *238.5 [d, CO, *J*(PC) = 6], 233.6 [d, CO, *J*(PC) = 30], *232.5 [d, CO, *J*(PC) = 30], *231.5 [d, CO, *J*(PC) = 29], 230.8 [d, CO, *J*(PC) = 29], 175.4, *174.3 (CH), 133.7–129.0 (Ph), 54.3[e] (cage CH), *52.1, 52.0 (NMe), *20.9, 20.5 (C*Me*)
33	7.74[e] (br m, 1 H, CH), 7.52–7.31 (m, 15 H, Ph), 3.59, *3.39 (s, 3 H, NMe), *2.51, 2.36 [d, 3 H, CMe, *J*(HH) = 6], 1.61 (s, 1 H, cage CH)	228.4 [d, CO, *J*(PC) = 5], *227.6 [d, CO, *J*(PC) = 6], 225.0 [d, CO, *J*(PC) = 25], *223.6 [d, CO, *J*(PC) = 24], 222.9 [d, CO, *J*(PC) = 25], *220.9 [d, CO, *J*(PC) = 24], 175.4, *174.6 (CH), 133.9–129.0 (Ph), 52.1 (NMe), 49.8, *49.0 (cage CH), 20.9, *20.3 (C*Me*)

Table 2 (*Contd.*)

Compound	^{1}H δ [b]	^{13}C δ [c]
34	8.22 [e] [q, 1 H, CH, *J*(HH) = 6], 7.53–7.28 (m, 15 H, Ph), *2.72, 2.52 [d, 3 H, Me, *J*(HH) = 6], 1.63, *1.53 (s, 9 H, Bu^{t}), 1.53 [e] (s, 1 H, cage CH)	239.8 [d, CO, *J*(PC) = 6], *238.8 [d, CO, *J*(PC) = 7], 233.3 [d, CO, *J*(PC) = 31], *232.7 [d, CO, *J*(PC) = 29], *231.9 [d, CO, *J*(PC) = 29], 231.1 [d, CO, *J*(PC) = 28], 178.8, *178.1 (NC), 133.7–128.9 (Ph), *73.4, 72.6 (N*C*Me$_3$), 54.0 [e] (cage CH), 32.4 [e] (NC*Me*$_3$), *23.3, 23.1 (C*Me*)
35	8.32, *8.27 [q, 1 H, CH, *J*(HH) = 7], 7.52–7.37 (m, 15 H, Ph), 2.70, *2.54 [d, 3 H, Me, *J*(HH) = 7], 1.62, *1.54 (s, 9 H, Bu^{t}), 1.54 [e] (s, 1 H, cage CH)	229.2 [d, CO, *J*(PC) = 6], *228.0 [d, CO, *J*(PC) = 6], 224.9 [d, CO, *J*(PC) = 26], *224.0 [d, CO, *J*(PC) = 25], *223.3 [d, CO, *J*(PC) = 25], 220.8 [d, CO, *J*(PC) = 24], 179.0, *178.4 (NC), 133.8–128.9 (Ph), *73.3, 72.6 (N*C*Me$_3$), 49.5, *48.4 (cage CH), 32.4 [e] (NC*Me*$_3$), *23.2, 22.8 (C*Me*)

[a] Chemical shifts (δ) in ppm, coupling constants (*J*) in Hertz, measurements at ambient temperatures in CD_2Cl_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] Spectrum weak, resonance for *C*NR nucleus not observed. [e] The peaks due to both isomers coincide to give one peak. Peaks marked with * are assigned to the minor isomer.

Table 3 Boron-11 and phosphorus-31 NMR data [a]

Compound	^{11}B δ [b]	^{31}P δ [c]
2	6.3 (1 B), −5.6 (1 B), −6.7 (2 B), −9.2 (2 B), −14.5 (2 B), −16.4 (2 B)	
4	1.9 (1 B), −6.6 (3 B), −11.1 (2 B), −13.5 (2 B), −17.5 (2 B)	26.5 [*J*(WP) = 173]
6	1.8 (1 B), −7.0 (3 B), −11.8 (2 B), −14.6 (2 B), −17.3 (2 B)	
8	0.5 (1 B), −4.2 (1 B), −5.3 (2 B), −6.0 (2 B), −12.7 (2 B), −15.3 (2 B)	
10	*23.2 (1 B), −1.8 (1 B), −6.7 (1 B), −9.6 (1 B), −10.7 (1 B), −11.7 (1 B), −15.5 (1 B), −17.5 (2 B), −21.9 (1 B)	22.8 [*J*(WP) = 165]
12	*22.5 (1 B), −1.8 (1 B), −7.7 (1 B), −10.4 (1 B), −11.1 (1 B), −12.5 (1 B), −16.0 (1 B), −17.9 (2 B), −22.2 (1 B)	
13	*24.3 (1 B), −2.0 (1 B), −5.3 (2 B), −9.2 (1 B), −11.2 (2 B), −12.0 (1 B), −15.8 (1 B), −17.6 (1 B)	
15	*20.3 (1 B), −2.0 (1 B), −6.9 (1 B), −9.6 (1 B), −10.9 (1 B), −11.9 (1 B), −15.3 (1 B), −17.2 (2 B), −21.9 (1 B)	23.0 [*J*(WP) = 175]
16	*23.9 (1 B), −2.0 (1 B), −7.8 (1 B), −10.2 (2 B), −12.6 (1 B), −15.6 (1 B), −17.8 (2 B), −21.9 (1 B)	22.2 [*J*(WP) = 169]
17	*3.4 (1 B), 2.1 (1 B), −4.1 (1 B), −7.7 (1 B), −8.8 (1 B), −11.0 (1 B), −12.4 (2 B), −16.5 (2 B)	49.1
18	*4.4 (1 B), 2.7 (1 B), −3.7 (1 B), −7.0 (1 B), −9.1 (1 B), −10.9 (1 B), −11.9 (2 B), −16.6 (2 B)	49.2
19	1.7 (2 B), −7.4 (2 B), −9.7 (1 B), −12.5 (1 B), −13.1 (1 B), −14.7 (1 B), −17.3 (2 B)	22.2 [*J*(WP) = 171]
20	*4.0 (1 B), 2.2 (1 B), −4.4 (1 B), −7.2 (1 B), −8.8 (1 B), −11.1 (1 B), −12.4 (2 B), −16.4 (2 B)	49.0
21	1.3 (2 B), −7.8 (3 B), −9.5 (1 B), −13.0 (2 B), −15.2 (1 B), −17.0 (1 B)	22.1 [*J*(WP) = 168]
22	1.0 (2 B), −3.9 (1 B), −5.2 (1 B), −9.1 (1 B), −9.8 (1 B), −11.5 (1 B), −12.3 (1 B), −16.8 (2 B)	48.5
23	0.0 (1 B), −1.0 (1 B), −5.7 (1 B), −7.3 (1 B), −9.7 (1 B), −10.3 (1 B), −14.9 (2 B), −17.2 (2 B)	22.5 [*J*(WP) = 173]
24	3.4 (1 B), −2.5 (1 B), −5.9 (1 B), −8.5 (2 B), −10.4 (3 B), −16.0 (2 B)	48.9
25	2.5 (1 B), −6.2 (3 B), −9.1 (1 B), −11.1 (1 B), −12.0 (1 B), −13.8 (1 B), −16.2 (1 B), *–17.7 (1 B)	22.4 [*J*(WP) = 173]
26	3.1 (1 B), −2.8 (1 B), −6.4 (1 B), −8.7 (2 B), −11.1 (3 B), −15.7 (2 B)	48.8
27	2.1 (1 B), −6.5 (2 B), −9.3 (2 B), −11.6 (2 B), −14.2 (2 B), −17.6 (1 B)	22.5 [*J*(WP) = 175]
28	*20.6 (1 B), −2.3 (1 B), −5.2 (1 B), −8.5 (1 B), −10.4 (1 B), −12.4 (1 B), −15.3 (1 B), −16.5 (1 B), −19.0 (1 B), −24.6 (1 B)	26.5 [*J*(WP) = 164]
29	*20.8 (1 B), −2.3 (1 B), −5.4 (1 B), −8.4 (1 B), −10.5 (1 B), −12.2 (1 B), −15.4 (1 B), −16.5 (1 B), −19.0 (1 B), −25.0 (1 B)	26.2 [*J*(WP) = 164]
30	*23.5 (1 B), −2.0 (1 B), −6.8 (1 B), −10.4 (2 B), −11.9 (1 B), −15.5 (1 B), −17.6 (2 B), −22.0 (1 B)	22.7 [*J*(WP) = 166]
31	*23.6 (1 B), −2.0 (1 B), −6.8 (1 B), −10.4 (2 B), −11.9 (1 B), −15.6 (1 B), −17.7 (2 B), −22.0 (1 B)	22.7 [*J*(WP) = 167]
32	*10.6 (1 B), 0.6 (1 B), −4.2 (1 B), −5.2 (1 B), −9.0 (2 B), −12.0 (1 B), −12.7 (1 B), −16.6 (2 B)	49.3, †49.1
33	*8.7 (1 B), −0.5 (1 B), −5.6 (1 B), −7.5 (1 B), −9.4 (1 B), −10.5 (1 B), −14.6 (1 B), −15.4 (1 B), −17.2 (1 B), −18.0 (1 B)	23.0 [*J*(WP) = 182], †22.3 [*J*(WP) = 178]
34	*11.0 (1 B), 0.6 (1 B), −3.0 (1 B), −4.7 (1 B), −8.9 (2 B), −12.0 (2 B), −12.7 (2 B)	49.7, †49.6
35	*8.6 (1 B), −0.5 (1 B), −5.1 (1 B), −6.3 (1 B), −9.4 (2 B), −14.5 (2 B), −17.2 (2 B)	23.4 [*J*(WP) = 161], †22.7 [*J*(WP) = 166]

[a] Measurements at ambient temperatures in CD_2Cl_2. [b] ^{11}B-{^{1}H} chemical shifts (δ) are positive to high frequency of $BF_3{\cdot}Et_2O$ (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 substituents L (see text) since they occur as singlets in fully coupled ^{11}B spectra. In the ^{11}B spectra of some products the signals overlap with those for a non-substituted boron and the BL resonance could not be unambiguously assigned. [c] ^{31}P-{^{1}H} chemical shifts (δ) are positive to high frequency of H_3PO_4 (external). Peaks marked with † are ascribed to a minor isomer.

The B–O distance [B(3)–O(5) 1.434(7) Å] is significantly shorter than that observed in the molybdenum compound **14** [1.532(2) Å].[4c] The PPh_3 molecule of the *endo*-$W(CO)_3(PPh_3)$ moiety lies transoid to B(3) and B(4) and cisoid to C(1). This arrangement probably reduces steric interaction between the PPh_3 ligand and the ethoxide group in the solid state. A similar orientation of the *endo*-$Mo(CO)_3(PPh_3)$ fragment with respect to the exopolyhedral substituent $CNC_6H_3Me_2$-2,6 molecule was observed in complex **24**.

In order to extend further the kind of reaction which gave **28**, compound **15** was treated with Me_3NO in THF and $[PPh_4]Br$ was added to isolate the expected salt. In compound **15** the CH_2 group to be displaced is anchored to the boron-bound oxygen *via* the CH_2 chain. The ^{1}H and ^{13}C-{^{1}H} NMR spectra of the product isolated showed peaks characteristic for an aldehyde group[9] with resonances at δ 9.67 (intensity corresponding to one proton) and δ 204.3, respectively. The analytical and spectroscopic data (Tables 1–3) for the species identified it as $[PPh_4][2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{O(CH_2)_3CHO\}\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **29**. A suggested pathway for the formation of compound **29** is shown in Scheme 1. It can be inferred that formation of **28** is presumably accompanied by the release of acetaldehyde and $[NHMe_3]^+$ following cleavage of a C–O bond in **10**. Compound **16** was also treated with Me_3NO. Although a reaction took

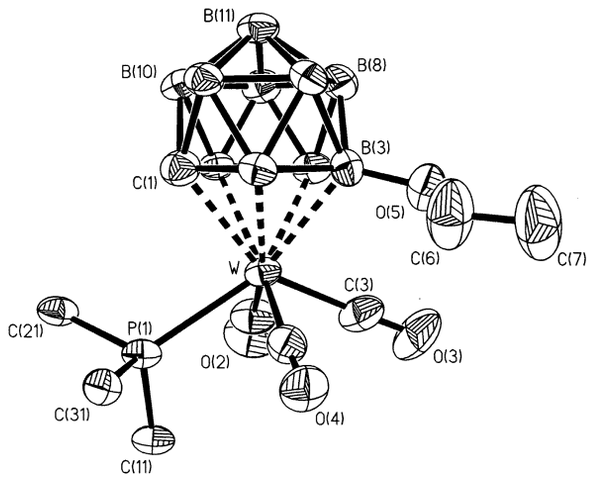


Fig. 2 Structure of the anion of the salt **28**. Selected bond lengths (Å) and angles (°): W–B(4) 2.343(6), W–B(5) 2.354(5), W–C(1) 2.370(5), W–B(2) 2.405(5), W–B(3) 2.419(6), W–P(1) 2.553(2), B(3)–O(5) 1.434(7); C(1)–W–P(1) 84.12(14), B(3)–W–P(1) 151.6(2), C(6)–O(5)–B(3) 120.8(5), W–B(3)–O(5) 116.9(4).

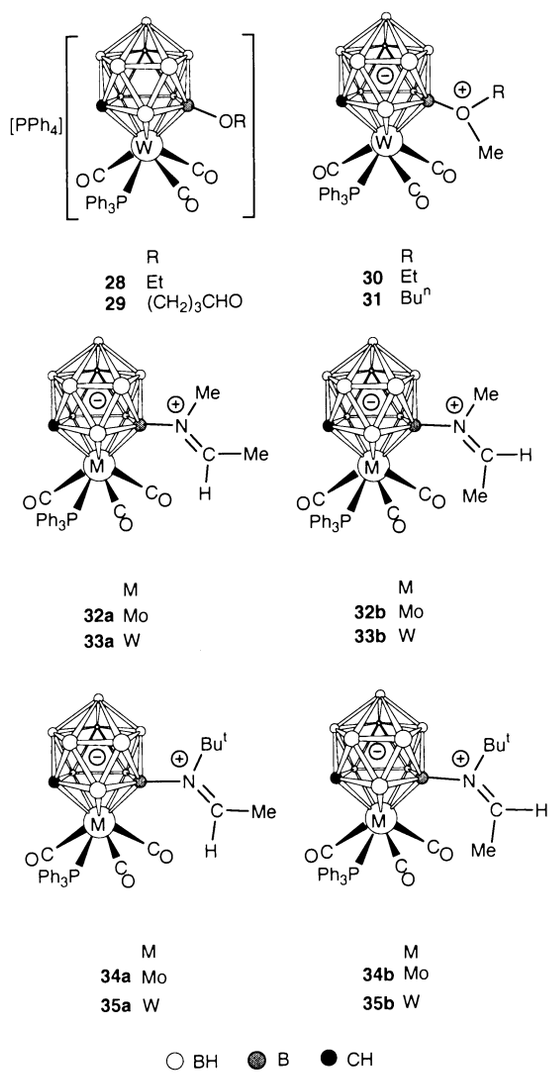
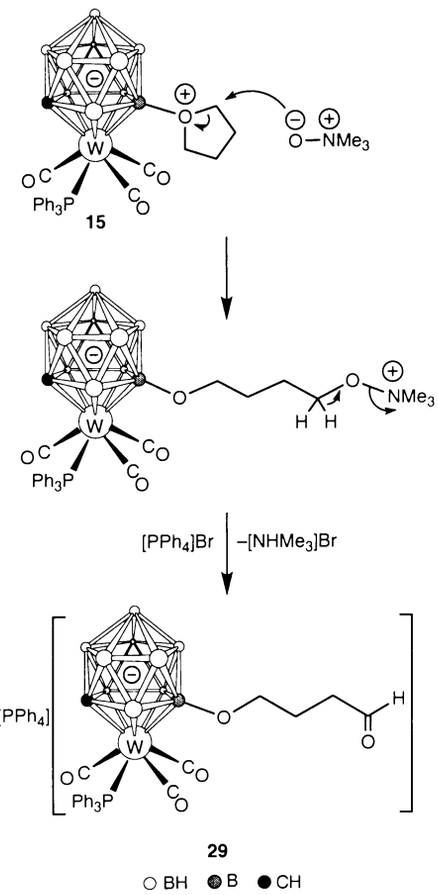


Chart 3

place, a pure product could not be isolated. However, the ^{1}H NMR spectrum of the crude product showed resonances for an aldehyde group in both the ^{1}H and ^{13}C-{^{1}H} NMR spectra.

It was of interest to determine if any of the remaining BH groups in the metal ligating $\overline{\text{CBBBB}}$ ring of the anionic complexes **28** and **29** would be sufficiently hydridic to react with



Scheme 1 Suggested pathway for formation of **29**.

CF_3SO_3Me to afford a zwitterionic complex. Compound **28** was treated with CF_3SO_3Me in a CH_2Cl_2–Et_2O solvent mixture. The alkoxide oxygen proved to be more susceptible to attack by Me^+ than a BH group since the product formed was [2,2,2-$(CO)_3$-2-PPh_3-7-{O(Me)Et}-*closo*-2,1-$WCB_{10}H_{10}$] **30**. Thus in the transformation from **10** to **28** into **30** a diethyl ether substituent on the carbaborane cage is converted into an ethyl methyl ether substituent.

In view of the conversion of **28** into **30**, it was anticipated that treatment of complex **29** with CF_3SO_3Me would yield a cage system with a pendant $BO(Me)(CH_2)_3CHO$ group. However, unexpectedly the product was [2,2,2-$(CO)_3$-2-PPh_3-7-{O(Me)Bu^n}-*closo*-2,1-$WCB_{10}H_{10}$] **31** resulting from attack of Me^+ at the oxygen atoms of both the B–O and aldehyde groups. The absence of an aldehyde group in the product **31** was apparent from the NMR data, the observed resonances being fully in agreement with those expected (Table 2). To establish unequivocally the structure of this unusual product and to confirm the presence of the *n*-butyl chain an X-ray crystallographic study of **31** was undertaken, and the molecule is shown in Fig. 3.

The substituent attached to B(3), a boron in a β site with respect to the carbon C(1) in the $\overline{\text{CB}\textit{BB}\text{B}}$ ring ligating the tungsten, is clearly revealed as an O(Me)Bu^n group. As in **14** and **28**, the PPh_3 molecule in the *endo*-$W(CO)_3(PPh_3)$ moiety lies transoid to B(3) and B(4) and cisoid to C(1).

The pathway for formation of **31** is presently obscure and further studies are in hand. However, it is known that aryl aldehydes can be reduced to methyl arenes by treatment with a $Na[BH_4]$ and CF_3CO_2H mixture.[10] The combination of unreacted **29** as a possible hydride source with CF_3SO_3Me (*cf.* CF_3CO_2H) may serve to act in a similar manner on another molecule of complex **29**. In this respect it should be noted that yields of **31** were never higher than 50%. Furthermore, complex

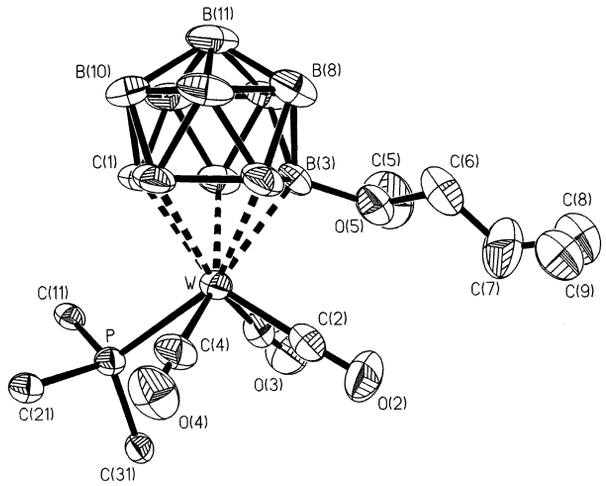


Fig. 3 Structure of **31**. Selected bond lengths (Å) and angles (°): W–B(3) 2.340(9), W–B(4) 2.377(9), W–B(5) 2.379(9), W–C(1) 2.380(8), W–B(2) 2.380(9), W–P 2.546(2), B(3)–O(5) 1.575(11), O(5)–C(5) 1.459(11), O(5)–C(6) 1.476(11); B(3)–W–P 145.8(3), C(1)–W–P 85.8(2), O(5)–B(3)–W 110.9(6), C(5)–O(5)–C(6) 115.8(8), C(5)–O(5)–B(3) 117.6(8), C(6)–O(5)–B(3) 117.5(8).

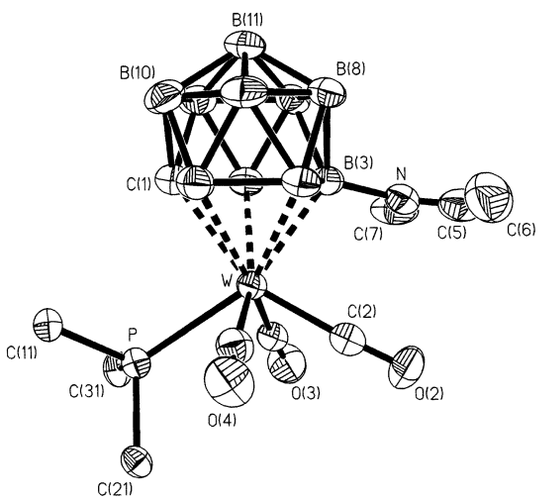


Fig. 4 Structure of **33b**. Selected bond lengths (Å) and angles (°): W–B(3) 2.370(7), W–B(5) 2.375(8), W–B(4) 2.376(7), W–B(2) 2.400(7), W–C(1) 2.403(6), W–P 2.555(2), B(3)–N 1.578(10), N–C(5) 1.129(12), N–C(7) 1.629(11); C(1)–W–P 85.7(2), N–B(3)–W 115.6(4), C(5)–N–B(3) 134.9(12), C(5)–N–C(7) 111.2(11), B(3)–N–C(7) 113.9(7).

29 is technically an aliphatic aldehyde and would not under normal circumstances be expected to undergo such a drastic reduction, making the outcome of this reaction particularly intriguing.

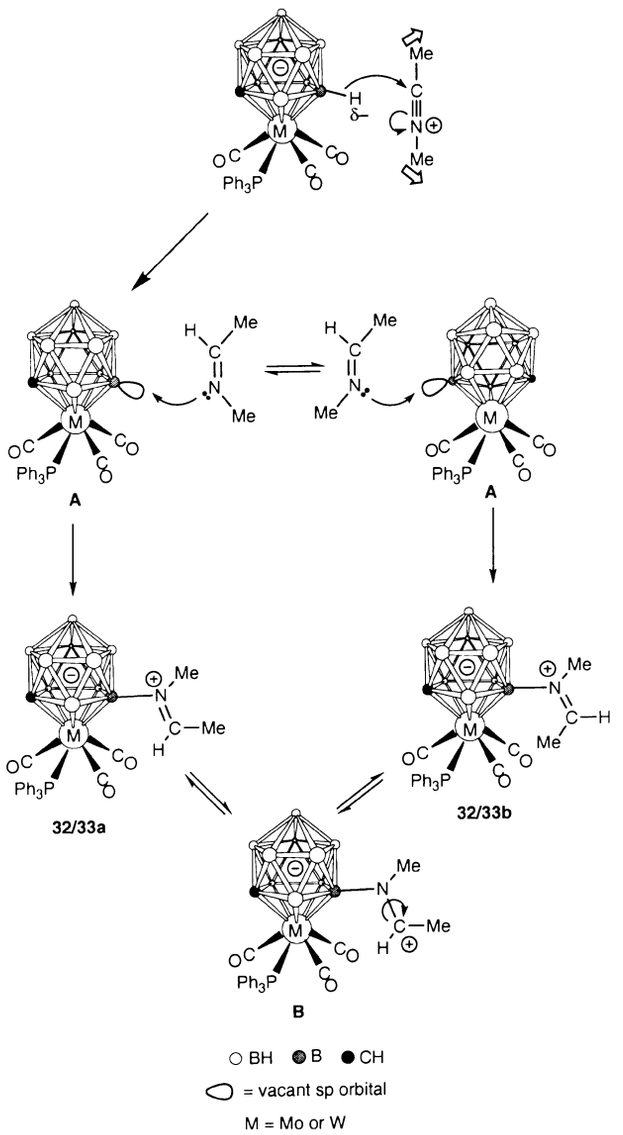
Mention was made earlier of the formation of the species **22** and **23** when the nitrile $NCBu^t$ was the reactant with **3** or **4** and CF_3SO_3Me. Interestingly a very different result was obtained when NCMe was employed. Both **3** and **4** with NCMe and CF_3SO_3Me yielded the novel compounds [2,2,2-$(CO)_3$-2-PPh_3-7-{N(Me)=C(H)Me}-*closo*-2,1-$MCB_{10}H_{10}$] **32** (M = Mo) and **33** (M = W), respectively. The full nature of **33** became apparent following an X-ray diffraction study (Fig. 4).

Atom B(3), lying in a β site in the CB*BB*B ring coordinated to the tungsten atom, carries an N(Me)=C(H)Me substituent. In the pendant iminium group the Me groups have a transoid configuration [torsional angle, C(7)–N–C(5)–C(6) 179.9(8)°]. However, examination of the ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR spectra (Tables 2 and 3) revealed a duplication of many signals. Thus although the *E* form **33b** was that found in the crystal by X-ray diffraction both the *E*- and *Z*-N(Me)=C(H)Me isomers **33a** and **b** are produced in the reaction, formed in a ratio of *ca.* 3 : 2, as deduced from the relative peak intensities. The ^1H NMR spectrum of complex **33** reveals two singlets at δ 3.39 and 3.59 due to the NMe groups of the major and minor isomers and two doublets for CMe groups at δ 2.51 and 2.36 each with ^1H–^1H coupling J(HH) = 6 Hz due to geminal =C(*H*)*Me* coupling in the minor and major species. Unfortunately it could not be determined conclusively which peaks are due to the *cis* and which are due to the *trans* isomers. A broad resonance was observed for the =C(*H*)Me proton and is probably unresolved due to overlap of the signals for the two isomers. It is unlikely, bearing in mind that the complexes **9**–**31** all involve substitution at a β-B vertex, that the isomerism arises by virtue of alternative substitution of N(Me)=C(H)Me at an α vertex. This is supported by the observation of just one singlet in the fully coupled ^{11}B NMR spectrum at δ 8.7 arising from the β-B atom which carries the iminium substituent. The ^{31}P-{^1H} NMR spectrum of complex **33** displayed a resonance with ^{183}W satellites for the major isomer at δ 23.0 [J(WP) = 182 Hz] and a weaker resonance at δ 22.3 [J(WP) = 178 Hz] for the minor species. The molybdenum complex **32** showed similar features in its NMR spectra as those of **33** and can thus be considered to have a similar structure. We recently discovered a related reaction where treatment of [$N(PPh_3)_2$][2,2-$(CO)_2$-2-PPh_3-*closo*-2,1-$FeCB_{10}H_{11}$] with CF_3SO_3Me in NCMe yielded [2,2-$(CO)_2$-2-PPh_3-7-{(*E*)-N(Me)=C(H)Me}-*closo*-2,1-$FeCB_{10}H_{10}$] as a single isomer, no *Z* form being detected.[4e]

A possible pathway for the formation of compounds **32** and **33** is shown in Scheme 2. This involves an initial methylation of NCMe at the nitrogen atom by CF_3SO_3Me giving the *N*-methylnitrilium cation $[MeN{\equiv}CMe]^+$. The formation of *N*-methylnitrilium salts from nitriles and methyl triflate is well established.[11] Once formed the cation $[MeN{\equiv}CMe]^+$ could then abstract H^- from cage BH allowing the N atom of the imine produced to coordinate to the vacant site created on a β-B to yield the observed products. As discussed previously,[4e] because of the steric bulk of the metallacarbaborane the formation of the *Z* isomer of the imine is likely favoured. Prior to coordination to the β-B vertex an opportunity may be afforded for the imine to transform between its geometric isomers. The extent of this interconversion may depend on the lifetime of the intermediate **A** (Scheme 2). Since imines are generally favoured to be *E* over *Z*, as was found with the resulting iminium substituent in [2,2-$(CO)_2$-2-PPh_3-7-{(*E*)-N(Me)=C(H)Me}-*closo*-2,1-$FeCB_{10}H_{10}$], the isomerism may be interrupted by entrapment of the imine by the intermediate **A** in such a way as to give a 3 : 2 distribution of the isomers for both the molybda- and tungsta-carbaboranes. Alternatively, and perhaps more likely, the iminium groups are isomerizing in solution in the products **32** and **33** *via* intermediate **B**. Further spectroscopic measurements did not allow conclusive discernment between these two options.

Failure of the reagent **3** or **4** to react with a combination of $NCBu^t$ and CF_3SO_3Me to afford molecules akin to **32** and **33** is evidently due to the methyl triflate preferentially abstracting H^- from the cage to which molecules of $NCBu^t$ rapidly coordinate yielding **22** and **23**, respectively. If a nitrilium fragment $[MeN{\equiv}CBu^t]^+$ formed reaction would proceed by the pathway indicated in Scheme 2. These results show that $NCBu^t$ is not as readily methylated as NCMe.[11b]

It was of interest to determine in what manner $CNBu^t$, an isomer of $NCBu^t$, would react with **3** or **4** in the presence of CF_3SO_3Me. The isocyanide could conceivably afford an intermediate $[Bu^tN{\equiv}CMe]^+$, or methyl triflate might preferentially remove H^- from cage BH so that a charge-compensated complex in which a $CNBu^t$ molecule is bonded to cage boron would be produced. In practice the products of the reactions were mixtures of the compounds [2,2,2-$(CO)_3$-2-PPh_3-7-$CNBu^t$-*closo*-2,1-$MCB_{10}H_{10}$] [M = Mo (**26**), W (**27**)] and [2,2,2-$(CO)_3$-2-PPh_3-7-{$N(Bu^t)$=C(H)Me}-*closo*-2,1-$MCB_{10}H_{10}$] [M = Mo (**34**), W (**35**)] formed in an approximate 1 : 2 ratio after separation by column chromatography and crystallization. Data character-



Scheme 2 Proposed pathway for formation of the geometric isomers of complexes **32** and **33**.

izing these compounds are given in Tables 1–3. Again NMR data indicated the presence of *E* and *Z* forms of N(Bu^t)=C(H)Me in **34** and **35**. For example, in the ^{1}H NMR spectrum of complex **35** the resonances for the geminal =C(*H*)*Me* group in the major isomer were clearly visible at δ 8.32 and 2.70, respectively [J(HH) = 7 Hz] with those for the minor isomer seen at δ 8.27 and 2.54, respectively [J(HH) = 7 Hz]. As for the complexes **32** and **33**, it is not possible to confidently assign the major isomer as *cis* or *trans*, although based on the complex [2,2-(CO)$_2$-2-PPh$_3$-7-{(*E*)-N(Me)=C(H)Me}-*closo*-2,1-FeCB$_{10}$H$_{10}$] and the general observation of geometric isomerism in imines it would seem that the *trans* form **35b** should be prevalent.

The results with CNBu^t and NCMe show that [Bu^{t}N≡CMe]$^+$ is less readily formed from CF_3SO_3Me than [MeN≡CMe]$^+$. Evidently with CNBu^t a pathway to **26** and **27** is available to at least a degree. It should be noted that with the aryl isocyanide CNC$_6$H$_3$Me$_2$-2,6 the compounds **24** and **25** are the exclusive products, no cage-substituted iminium derivatives being obtained. This is perhaps not surprising since the aryl group would remove electron density away from the isocyanide carbon making it less susceptible to electrophilic attack by Me$^+$.

Conclusion

The syntheses of the neutral but charge-compensated molybdenum and tungsten compounds **9**–**27** demonstrate how a variety of different donor groups may be attached to the metallacarbaborane cage framework in a regiospecific manner at one of the β sites in the $\overline{\text{CB}BB\text{B}}$ ring coordinated to molybdenum or tungsten. The reactions of the tungsten compounds **10** and **15** with Me_3NO, which afford, respectively, **28** and **29,** demonstrate how exopolyhedrally attached ether molecules in the zwitterionic precursors may be transformed into alkoxide groups, the latter subsequently reacting with CF_3SO_3Me to yield products with yet other exopolyhedral substituents on the cage. Importantly this sequence of reactions occurs without degradation of the metallacarbaborane cage system. It has been further shown that the reagents **3** and **4** with NCMe and CF_3SO_3Me give the compounds **32** and **33**, the first examples as far as we are aware of attachment of a reactive imine group to a molybda- or tungsta-carbaborane cage. Clearly the known functionality of this group in organic chemistry[12] merits investigation of its reactivity in these metallacarbaborane molecules also. Finally the syntheses of the molecules **34** and **35** show that isocyanides may also be used as reagents to attach imine groups to the cage. Further studies to exploit these reactions as a way of attaching organic fragments of many types to the *closo*-2,1-MCB$_{10}$ cage systems are clearly merited.

Experimental

General

Solvents were distilled from appropriate drying agents under nitrogen prior to use. Light petroleum 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: ^{1}H 360.1, ^{13}C 90.6, ^{31}P 145.7, and ^{11}B 115.5 MHz. Species with the cations [N(PPh$_3$)$_2$]$^+$ and [PPh$_4$]$^+$ showed ^{31}P-{^{1}H} NMR resonances at δ 21.7 and 23.9, respectively. The salt Na$_3$[*nido*-7-CB$_{10}$H$_{11}$] was synthesized from *nido*-7-NMe$_3$-7-CB$_{10}$H$_{12}$ according to the method of Knoth and co-workers.[13] The compound [W(CO)$_3$(NCEt)$_3$] was prepared as described by Kubas and van der Sluys.[14] The acid HBF$_4$·Et$_2$O (54% solution in Et$_2$O) and the reagent CF_3SO_3Me were used as purchased from Aldrich. The reagent Me_3NO, purchased from Aldrich, was dehydrated completely before use.

Syntheses

[N(PPh$_3$)$_2$][2,2,2,2-(CO)$_4$-*closo*-2,1-WCB$_{10}$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 cm^3) and three small pieces of freshly cut sodium metal (*ca.* 0.30 g) were added. The mixture was refluxed for *ca.* 1 day yielding a white precipitate of Na$_3$[*nido*-7-CB$_{10}$H$_{11}$], after which heating was discontinued. Residual sodium was carefully removed from the suspension of Na$_3$[*nido*-7-CB$_{10}$H$_{11}$] following which *ca.* 80% of the THF was removed *in vacuo*. The compound [W(CO)$_3$(NCEt)$_3$] (2.16 g, 5.00 mmol) in NCEt (30 cm^3) was then added to the Na$_3$[*nido*-7-CB$_{10}$H$_{11}$] suspension *via* a cannula. The resulting mixture was stirred at room temperature for *ca.* 4 h. Following this, CO was bubbled through the solution at −78 °C and HBF$_4$·Et$_2$O (1.38 cm^3, 10.00 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 stirring continued for 2 h. After filtration through a Celite plug, solvent was removed *in vacuo*. The residue was taken up in CH$_2$Cl$_2$ (2 cm^3) and chromatographed. A yellow fraction was eluted with CH$_2$Cl$_2$–light petroleum (4 : 1). The salt [N(PPh$_3$)$_2$][2,2,2,2-(CO)$_4$-*closo*-2,1-WCB$_{10}$H$_{11}$] **2** (2.56 g) was isolated after removal of solvent *in vacuo*.

Complexes $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}L\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{11}]$ (L = PPh_3 or $CNBu^t$) and $[N(PPh_3)_2][2,2\text{-}(CO)_2\text{-}2\text{-}(Bu^tC{\equiv}CH)\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{11}]$. (i) The reagent **2** (0.59 g, 0.61 mmol) was dissolved in THF (15 cm^3) and PPh_3 (0.19 g, 0.73 mmol) and Me_3NO (0.06 g, 0.73 mmol) were added. The mixture was then stirred for 1 h at room temperature, solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 (1 cm^3) and this solution chromatographed. A yellow fraction was eluted with CH_2Cl_2–light petroleum (4 : 1), affording yellow microcrystals of $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{11}]$ **4** (0.60 g) after removal of solvent *in vacuo*.

(ii) Using a similar procedure compound **2** (1.61 g, 1.67 mmol), dissolved in THF (15 cm^3), with addition of $CNBu^t$ (0.20 cm^3, 2.00 mmol) and Me_3NO (0.15 g, 2.00 mmol), gave yellow microcrystals of $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}CNBu^t\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{11}]$ **6** (0.87 g), obtained after removal of solvent *in vacuo*.

(iii) Similarly, as in the synthesis of **4**, compound **2** (0.46 g, 0.49 mmol) in THF (15 cm^3), with $Bu^tC{\equiv}CH$ (71 μL, 0.59 mmol) and Me_3NO (0.08 g, 1.00 mmol) afforded brick red microcrystals of $[N(PPh_3)_2][2,2\text{-}(CO)_2\text{-}2\text{-}(Bu^tC{\equiv}CH)\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{11}]$ **8** (0.39 g) after removal of solvent *in vacuo*.

Zwitterionic complexes $[2,2,2\text{-}(CO)_3\text{-}2\text{-}L'\text{-}7\text{-}L\text{-}closo\text{-}2,1\text{-}MCB_{10}H_{10}]$ (M = Mo or W, L′ = PPh_3 or $CNBu^t$). (i) Compound **4** (0.50 g, 0.42 mmol), in CH_2Cl_2–Et_2O (20 cm^3, 1 : 1), was treated with CF_3SO_3Me (0.24 cm^3, 2.09 mmol) and the mixture stirred for 2 h. Solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2 (1 cm^3) and this solution was chromatographed. A yellow fraction was eluted with CH_2Cl_2–light petroleum (2 : 1) affording yellow microcrystals of $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}OEt_2\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **10** (0.26 g) after removal of solvent *in vacuo*.

(ii) Compound **6** (0.57 g, 0.56 mmol) in CH_2Cl_2–Et_2O (20 cm^3, 1 : 1) was treated with CF_3SO_3Me (0.32 cm^3, 2.80 mmol) and the mixture stirred for 2 h. Solvent was removed *in vacuo* and the residue taken up in CH_2Cl_2 (1 cm^3) and chromatographed. A yellow fraction was eluted with CH_2Cl_2–light petroleum (3 : 1), giving yellow microcrystals of $[2,2,2\text{-}(CO)_3\text{-}2\text{-}CNBu^t\text{-}7\text{-}OEt_2\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **12** (0.24 g) after removal of solvent *in vacuo*.

(iii) Similarly, compound **8** (0.39 g, 0.39 mmol) in CH_2Cl_2–Et_2O (20 cm^3, 1 : 1) with CF_3SO_3Me (0.22 cm^3, 1.95 mmol) yielded brick red microcrystals of $[2,2\text{-}(CO)_2\text{-}2\text{-}(Bu^tC{\equiv}CH)\text{-}7\text{-}OEt_2\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **13** (0.12 g).

(iv) Compound **4** (0.50 g, 0.42 mmol) was dissolved in CH_2Cl_2-THF (20 cm^3, 1 : 1) and CF_3SO_3Me (0.24 cm^3, 2.09 mmol) added. The mixture was stirred for 2 h, solvent removed *in vacuo*, the residue dissolved in CH_2Cl_2 (1 cm^3) and the solution was chromatographed. A yellow fraction was eluted with CH_2Cl_2–light petroleum (2 : 1) affording yellow microcrystals of $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{O(CH_2)_4\}\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **15** (0.17 g) after removal of solvent *in vacuo*.

(v) Similarly, compound **4** (0.50 g, 0.42 mmol), dissolved in CH_2Cl_2-1,4-dioxane (20 cm^3, 1 : 1), with CF_3SO_3Me (0.24 cm^3, 2.09 mmol) afforded yellow microcrystals of $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{cyclo\text{-}1,4\text{-}O(CH_2)_4O\}\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **16** (0.21 g) after elution of the chromatography column with CH_2Cl_2–light petroleum (3 : 1) and removal of solvent *in vacuo*.

(vi) Compound **3** (0.30 g, 0.27 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and SMe_2 (0.5 cm^3) added followed by concentrated H_2SO_4 (0.1 cm^3). The mixture was stirred at room temperature overnight. After removal of solvent *in vacuo*, the residue was dissolved in the minimum amount of CH_2Cl_2 and chromatographed. A yellow fraction was eluted with CH_2Cl_2–light petroleum (3 : 2), affording yellow crystals of $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}SMe_2\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ **17** (0.06 g) after removal of solvent and crystallization from CH_2Cl_2–light petroleum.

(vii) Similarly **3** (0.30 g, 0.27 mmol) in CH_2Cl_2 (20 cm^3) with SC_4H_8 (tetrahydrothiophene) (0.5 cm^3) and concentrated H_2SO_4 (0.1 cm^3) gave yellow crystals of $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{S(CH_2)_4\}\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ **18** (0.06 g).

(viii) Compound $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{S(CH_2)_4\}\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **19** (0.053 g) was similarly obtained by treating **4** (0.20 g, 0.17 mmol) with SC_4H_8 (0.5 cm^3) and concentrated H_2SO_4 (0.1 cm^3).

(ix) Similarly **3** (0.30 g, 0.27 mmol) and $S_3(CH_2)_6$ (1,4,7-trithiacyclononane) (0.15 g, 0.83 mmol) were dissolved in CH_2Cl_2 (20 cm^3) and concentrated H_2SO_4 (0.1 cm^3) was added. After stirring for 12 h, solvent was removed *in vacuo* and the residue chromatographed. Elution with CH_2Cl_2–light petroleum (2 : 1) gave a yellow fraction. Removal of solvent *in vacuo* followed by crystallization from CH_2Cl_2–Et_2O afforded yellow microcrystals of $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{cyclo\text{-}1,4,7\text{-}S_3(CH_2)_6\}\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ **20** (0.09 g).

(x) Similarly **4** (0.30 g, 0.25 mmol), $S_3(CH_2)_6$ (0.13 g, 0.72 mmol) and concentrated H_2SO_4 (0.1 cm^3) gave yellow microcrystals of $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{cyclo\text{-}1,4,7\text{-}S_3(CH_2)_6\}\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **21** (0.05 g).

(xi) A mixture of $NCBu^t$ (1 cm^3) and CF_3SO_3Me (0.10 cm^3, 0.85 mmol) was added to a stirred solution of compound **3** (0.25 g, 0.23 mmol) in CH_2Cl_2 (10 cm^3), forming a yellow solution. After stirring for 12 h, solvent was removed *in vacuo*, and the residue taken up in CH_2Cl_2 and chromatographed using CH_2Cl_2–light petroleum (1 : 1) as eluant. A yellow fraction was collected, affording $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}NCBu^t\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ **22** (0.04 g) after removal of solvent *in vacuo*.

(xii) Compound $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}NCBu^t\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **23** (0.13 g) was prepared as described for **22**, except that **4** (0.50 g, 0.42 mmol) was used instead of **3**.

(xiii) Compound **3** (0.50 g, 0.45 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and $CNC_6H_3Me_2$-2,6 (xylyl isocyanide) (0.09 g, 0.68 mmol) and CF_3SO_3Me (0.08 cm^3, 0.68 mmol) were added. After stirring for 1 h at room temperature, work up as for **22** afforded $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}(CNC_6H_3Me_2\text{-}2,6)\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ **24** (0.06 g).

(xiv) Similarly **4** (0.50 g, 0.42 mmol) was treated with $CNC_6H_3Me_2$-2,6 (0.10 g, 0.76 mmol) and CF_3SO_3Me (0.10 cm^3, 0.85 mmol) to give yellow microcrystals of $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}(CNC_6H_3Me_2\text{-}2,6)\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **25** (0.16 g) eluted from the column with CH_2Cl_2–light petroleum (2 : 1).

The salts $[PPh_4][2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}R\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ [R = OEt or $O(CH_2)_3C(H)O$] and their reactions with CF_3SO_3Me. (i) Compound **10** (0.30 g, 0.41 mmol) was dissolved in THF (15 cm^3), the reagent Me_3NO (0.05 g, 0.62 mmol) was added and the mixture stirred for 30 min at room temperature. After removal of solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 (15 cm^3), $[PPh_4]Br$ (0.17 g, 0.41 mmol) added, and the mixture stirred for 1 h. Solvent was removed *in vacuo*, the residue taken up in CH_2Cl_2 (1 cm^3) and chromatographed. A yellow fraction was eluted with CH_2Cl_2-THF (4 : 1), affording yellow microcrystals of the salt $[PPh_4][2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}OEt\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **28** (0.29 g) after removal of solvent *in vacuo*.

(ii) The compound $[PPh_4][2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{O(CH_2)_3CHO\}\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **29** (0.18 g) was obtained from **15** (0.30 g, 0.41 mmol) using the same procedure as for **28**.

(iii) A sample of compound **28** (0.30 g, 0.29 mmol) in CH_2Cl_2 (15 cm^3) was treated with CF_3SO_3Me (0.17 cm^3, 1.44 mmol). The mixture was stirred for 30 min at room temperature. Solvent was removed *in vacuo*, the residue taken up in CH_2Cl_2 (1 cm^3) and chromatographed. A yellow fraction was eluted with CH_2Cl_2–light petroleum (2 : 1), affording $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}\{O(Me)Et\}\text{-}closo\text{-}2,1\text{-}WCB_{10}H_{10}]$ **30** (0.14 g) after removal of solvent *in vacuo*.

Table 4 Data for crystal structure analyses of compounds **24**, **28**, **31** and **33b**

	24	**28**	**31**	**33b**·0.5(pentane)
Chemical formula	$C_{31}H_{34}B_{10}MoNO_3P$	$C_{48}H_{50}B_{10}O_4P_2W$	$C_{27}H_{37}B_{10}O_4PW$	$C_{27.5}H_{38}B_{10}NO_3PW$
M	703.60	1044.77	748.49	753.51
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$
a/Å	8.5591(14)	10.298(4)	11.916(2)	23.042(3)
b/Å	11.8898(12)	10.916(2)	13.606(2)	21.716(3)
c/Å	18.484(2)	23.439(3)	20.455(2)	17.268(3)
α/°	104.286(9)	78.861(14)		
β/°	97.586(12)	83.08(2)	92.272(10)	129.571(14)
γ/°	104.489(11)	75.48(2)		
U/Å^3	1726.9(4)	2495.4(10)	3313.9(7)	6660(2)
Z	2	2	4	8
μ(Mo-Kα)/cm^{-1}	4.60	24.20	35.66	35.47
T/*K*	293	293	293	293
Reflections measured	6495	6886	5492	11846
Independent reflections	6050	6447	5210	5794
R(int)	0.0227	0.0283	0.0293	0.0518
*wR*2 (all data), *R*1 [a]	0.0877, 0.0376	0.0705, 0.0297	0.0818, 0.0438	0.0724, 0.0393

[a] $F_o > 4\sigma(F_o)$.

(iv) The salt **29** (0.30 g, 0.28 mmol) in CH_2Cl_2 (15 cm^3) was treated with CF_3SO_3Me (0.16 cm^3, 1.38 mmol) and the mixture stirred for 2 h at room temperature. After removal of solvent, the residue was taken up in CH_2Cl_2 (1 cm^3) and the solution chromatographed. A yellow fraction was eluted with CH_2Cl_2–light petroleum (2 : 1), affording [2,2,2-(CO)$_3$-2-PPh$_3$-7-{O(Me)Bu^n}-*closo*-2,1-WCB$_{10}$H$_{10}$] **31** (0.10 g) following removal of solvent *in vacuo*.

Compounds [2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Me)=C(H)Me}-*closo*-2,1-MCB$_{10}$H$_{10}$] (M = Mo or W). (i) Compound **3** (0.50 g, 0.45 mmol) was dissolved in CH_2Cl_2–MeCN (15 cm^3, 2 : 1), CF_3SO_3Me (0.08 cm^3, 0.68 mmol) added, and the mixture stirred for 2 h. Solvent was removed *in vacuo*, the residue taken up in CH_2Cl_2 (1 cm^3) and the solution chromatographed. A yellow fraction was eluted with CH_2Cl_2–light petroleum (2 : 1), affording yellow microcrystals of [2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Me)=C(H)Me}-*closo*-2,1-MoCB$_{10}$H$_{10}$] **32** (0.14 g) after removal of solvent *in vacuo*.

(ii) Similarly, the reagent **4** (0.30 g, 0.25 mmol) was treated with CF_3SO_3Me (0.10 cm^3, 0.85 mmol) in CH_2Cl_2–MeCN (25 cm^3, 4 : 1) and the mixture stirred overnight. The compound [2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Me)=C(H)Me}-*closo*-2,1-WCB$_{10}$H$_{10}$] **33** (0.083 g) was obtained after chromatography using CH_2Cl_2–light petroleum (2 : 1) as eluant.

[2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Bu^t)=C(H)Me}-*closo*-2,1-MCB$_{10}$H$_{10}$] and [2,2,2-(CO)$_3$-2-PPh$_3$-7-CNBu^t-*closo*-2,1-MCB$_{10}$H$_{10}$] (M = Mo or W). (i) Compound **3** (0.50 g, 0.45 mmol) was dissolved in CH_2Cl_2 (15 cm^3), and CNBu^t (0.08 cm^3, 0.68 mmol) and CF_3SO_3Me (0.08 cm^3, 0.68 mmol) were added. The mixture was stirred for 1 h at room temperature following which solvent was removed *in vacuo*. The residue was taken up in CH_2Cl_2 (1 cm^3) and the solution chromatographed. A yellow fraction was eluted with CH_2Cl_2–light petroleum (2 : 1) affording sequentially fractions containing **34** and **26**. After removal of solvent *in vacuo*, the compounds [2,2,2-(CO)$_3$-2-PPh$_3$-7-CNBu^t-*closo*-2,1-MoCB$_{10}$H$_{10}$] **26** (0.067 g) and [2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Bu^t)=C(H)Me}-*closo*-2,1-MoCB$_{10}$H$_{10}$] **34** (0.13 g) were purified by fractional crystallization by dissolving the microcrystals in CH_2Cl_2 layered with light petroleum.

(ii) Compounds [2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Bu^t)=C(H)Me}-*closo*-2,1-WCB$_{10}$H$_{10}$] **35** and [2,2,2-(CO)$_3$-2-PPh$_3$-7-CNBu^t-*closo*-2,1-WCB$_{10}$H$_{10}$] **27** were prepared in a similar manner. Compound **4** (0.50 g, 0.42 mmol) was treated with CNBu^t (0.10 cm^3, 0.85 mmol) and CF_3SO_3Me (0.10 cm^3, 0.85 mmol) in CH_2Cl_2 (20 cm^3) added. The mixture was stirred overnight. After removal of solvent, the residue was taken up in the minimum of CH_2Cl_2 and chromatographed using CH_2Cl_2–light petroleum (1 : 1) as eluant. The complexes [2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Bu^t)=C(H)Me}-*closo*-2,1-WCB$_{10}$H$_{10}$] **35** (0.15 g) and [2,2,2-(CO)$_3$-2-PPh$_3$-7-CNBu^t-*closo*-2,1-WCB$_{10}$H$_{10}$] **27** (0.06 g) were sequentially collected from the column, and purified for microanalysis by fractional crystallization as described for their molybdenum analogues.

Crystallography

Experimental data for **24**, **28**, **31** and **33b** are given in Table 4. Diffracted intensities were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα X-radiation. Final unit cell dimensions were determined from the setting angles of 25 accurately centered reflections. The data were corrected for Lorentz, polarization and X-ray absorption effects, the latter using a numerical method based on the measurements of crystal faces (**24**, **28** and **31**), or a semi-empirical method based on azimuthal scans of *ψ* data (**33b**).

The structures were solved by direct methods while successive Fourier difference syntheses were used to locate all non-hydrogen atoms using SHELXTL version 5.03.[15] Refinements were made by full-matrix least squares on all F^2 data using SHELXL 97.[16] Anisotropic thermal parameters were included for all non-hydrogen atoms. For all structures, cage carbon atoms were assigned by comparison of the bond lengths to adjacent boron atoms in conjunction with the magnitudes of their isotropic thermal parameters. All hydrogen atoms were included in calculated positions and allowed to ride on their parent boron or carbon atoms with fixed isotropic thermal parameters ($U_{iso} = 1.2U_{iso}$ of the parent atom or $U_{iso} = 1.5U_{iso}$ for methyl protons).

Compound **33b** co-crystallized with one-half molecule of pentane per asymmetric unit. The solvent molecule was disordered across the two fold rotation axis at Wyckoff position 4*e* ($\frac{1}{2}$, $y + \frac{1}{2}$, $\frac{1}{4}$). All carbon atoms in the pentane molecule were refined with equivalent anisotropic thermal parameters and the C(91)–C(92) distance was fixed at 1.50(5) Å. All calculations were carried out on Dell PC computers.

CCDC reference numbers (for **23**, **24**, **28**, **31** and **33b**) 157559–157563.

See http://www.rsc.org/suppdata/dt/b1/b101003o/ for crystallographic data in CIF or other electronic format.

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