Allyl(carbaborane) Complexes of Group 6 Metals: Preparation and Reactivity

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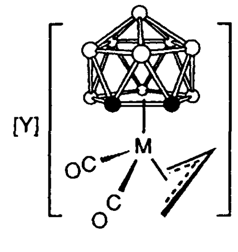
Treatment of thf (tetrahydrofuran) solutions of $[MBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ (M = Mo or W) with $Na_2[7,8\text{-}C_2B_9H_9R'_2]$ (R' = H or Me), followed by addition of $[N(PPh_3)_2]Cl$ or $[NEt_4]Cl$, afforded the salts $[Y][M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)]$ [Y = $N(PPh_3)_2$, R' = Me, M = Mo **1a** or W **1b**; Y = NEt_4, R' = H, M = Mo **1c**] in high yield. These species may be synthesised, but in lower yield, from allyl bromide and $Tl_2[M(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)]$ generated *in situ*. Protonation of the salts **1a** and **1b** with $HBF_4\cdot Et_2O$ in the presence of CO or PPh_3 yielded the compounds $[M(CO)_2L_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (M = Mo **2a** or W **2b**, L = CO; M = Mo **2c** or W **2e**, L = PPh_3). The synthesis of **2c** was accompanied by formation of the tricarbonyl species $[Mo(CO)_3(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **2d**. Treatment of the salt **1c** with $HBF_4\cdot Et_2O$ in the presence of buta-1,3-diene afforded the species $[Mo(CO)_2(\eta^4\text{-}C_4H_6)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ **5**. When reactions of **1a**–**c** with $HBF_4\cdot Et_2O$ were carried out in the presence of alkynes, the bis(alkyne) complexes $[M(CO)(RC_2R)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)]$ (M = Mo, R = R' = Me **6a**; M = W, R = Ph, R' = Me **6b**; M = Mo, R = Me, R' = H **6c**) are formed. The compounds **6a** and **6c** can also be obtained from reactions between $Tl_2[Mo(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)]$ generated *in situ*, MeC≡CMe, and $AgBF_4$. Reaction of the complex **6a** with PMe_2Ph gives the species $[Mo(CO)(PMe_2Ph)(MeC_2Me)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **6e**. Treatment of the reagent $Tl_2[Mo(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ with $AgBF_4$ in the presence of $[W(\equiv CC_6H_4\text{-}Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ afforded the dimetal complex $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **7**.

We report herein the synthesis of the salts $[Y][M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)]$ [Y = $N(PPh_3)_2$, R' = Me, M = Mo **1a** or W **1b**; Y = NEt_4, R' = H, M = Mo **1c**], and the protonation ($HBF_4\cdot Et_2O$) of these species in the presence of CO, PPh_3 or RC≡CR (R = Me or Ph). The anionic complexes $[M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)]^-$ are isolobal with the neutral complexes $[M(CO)_2(\eta^3\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$,[1] and it was anticipated that protonation of the former would remove the allyl group as $MeCH{=}CH_2$ and release a reactive moiety $M(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)$ having a vacant co-ordination site at the formally 14-electron metal centre.† Studies on the protonation of the salts **1** in the presence of donor substrate molecules are related to similar reactions of the reagents $[Y][M(\equiv CR)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)]$ (R = alkyl or aryl).[2] The latter on treatment with acids afford a multitude of products in the presence of different substrates, and the structures of the complexes isolated indicate that an initial step in the reaction profile involves formation of an alkylidene species $M({=}CHR)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)$, formally having 16 electrons at the metal centre. Also relevant to the results reported herein are the dianionic complexes $[M(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]^{2-}$, first prepared by Hawthorne and co-workers[3] and recently used in several syntheses, and the monoanionic η^3-allyliron complexes $[Fe(CO)(\eta^3\text{-}C_3H_4R\text{-}2)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]^-$ (R = H or Me).[4]

Results and Discussion

The *in situ* generation of $Tl_2[M(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (M = Mo or W) in thf (tetrahydrofuran) solutions, from $[M(CO)_3(NCMe)_3]$ and $Tl[\textit{closo}\text{-}3,1,2\text{-}TlC_2B_9H_9Me_2]$, followed by addition of allyl bromide and $[N(PPh_3)_2]Cl$, gives the salts $[N(PPh_3)_2][M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (M = Mo **1a** or W **1b**) in *ca.* 40% yield. The relatively poor yields are due to difficulties in purification associated with the formation of $[N(PPh_3)_2][7,8\text{-}C_2B_9H_{10}Me_2]$ as a side product, and this led us to develop an alternative and high-yield synthesis involving reaction of the allylmetal complexes $[MBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ (M = Mo or W) in thf with $Na_2[7,8\text{-}C_2B_9H_9Me_2]$, followed by addition of $[N(PPh_3)_2]Cl$. Similar methodology, employing $Na_2[7,8\text{-}C_2B_9H_{11}]$, $[MoBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$, and $[NEt_4]Cl$, afforded $[NEt_4][Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ **1c**. Data characterising the salts **1** are given in Tables 1–3.



○ BH

	M	Y	●
1a	Mo	$N(PPh_3)_2$	CMe
1b	W	$N(PPh_3)_2$	CMe
1c	Mo	NEt_4	CH

The IR spectra of the salts **1** display two CO stretching bands (Table 1). The NMR data for the complexes are in agreement with the formulations proposed. Thus the ^1H NMR spectrum of **1a** (Table 2) shows a singlet at δ 1.95 for the two cage CMe groups. There are two doublets for the $\eta^3\text{-}C_3H_5$ ligand. The resonances at δ 1.10 with $J(H_aH_c)$ 10 Hz is assigned to the *anti*-protons (H_a), and the other signal at δ 2.92 with

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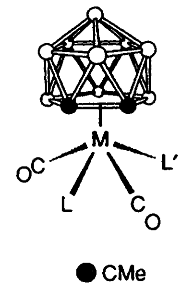
† In this paper Mo or W atoms form with $[\textit{nido}\text{-}7,8\text{-}C_2B_9H_9R'_2]^{2-}$ anions *closo*-1,2-dicarba-3-metalladodecaborane structures. However, in the formulae the carbaborane group is designated as $\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2$ in order to emphasise its pentahapto ligand properties in which it formally acts as a four-electron donor, related to the five-electron donor $\eta^5\text{-}C_5H_5$.

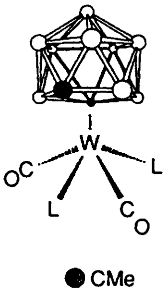
Table 1 Analytical[a] and other data for the new compounds

Compound	Colour	Yield (%)	$\nu_{max}(CO)$[b]/cm^{-1}	Analysis (%) C	Analysis (%) H
1a $[N(PPh_3)_2][Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Yellow	78	1920vs, 1830s	[c] 61.0 (60.6)	6.2 (5.7)
1b $[N(PPh_3)_2][W(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Yellow	84	1910vs, 1816s	[d] 55.0 (55.2)	5.5 (5.1)
1c $[NEt_4][Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$	Yellow	75	1928vs, 1832s	[e] 39.9 (39.5)	8.6 (8.0)
2a $[Mo(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Yellow	80	2097vs, 2034 (sh), 2013vs (br)	26.4 (26.1)	4.4 (4.1)
2b $[W(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Yellow	86	2096vs, 2025 (sh), 2003vs (br)	20.9 (21.1)	3.5 (3.3)
2c $[Mo(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Yellow	59	1943s, 1857vs	[f] 58.2 (58.0)	5.6 (5.3)
2d $[Mo(CO)_3(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$[g]	Yellow		2033vs, 1960vs, 1945vs		
2e $[W(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Yellow	66	1933s, 1842vs	[h] 51.3 (51.1)	4.4 (4.7)
5 $[Mo(CO)_2(\eta^4\text{-}C_4H_6)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$	Yellow	54	2037vs, 1987s	29.0 (28.4)	5.1 (5.1)
6a $[Mo(CO)(MeC_2Me)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Yellow	70	2036vs	[f] 36.2 (37.3)	7.5 (6.5)
6b $[W(CO)(PhC_2Ph)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Yellow	79	2069vs	53.9 (54.4)	5.3 (4.8)
6c $[Mo(CO)(MeC_2Me)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$	Yellow	75	2037vs	35.7 (36.2)	6.7 (6.4)
6d $[Mo(CO)(PPh_3)(PhC_2Ph)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Green	98	1945s (br)	[h] 56.7 (56.4)	6.0 (5.2)
6e $[Mo(CO)(PMe_2Ph)(MeC_2Me)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Blue	80	1937vs	42.3 (42.8)	7.0 (6.8)
7 $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Green	46	2007vs, 1960vs, 1940 (sh)	34.6 (34.7)	3.9 (3.9)

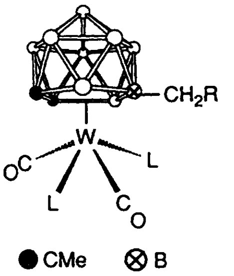
[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2. For all carbaborane compounds there is a broad band at 2550 cm^{-1} due to B–H absorptions. [c] N, 1.6 (1.6%). [d] N, 1.4 (1.4%). [e] N, 3.1 (3.1%). [f] Crystallised with 0.5 CH_2Cl_2. [g] Formed as a mixture with compound **2c**, see text. [h] Crystallised with 1 CH_2Cl_2.



	M	L	L′
2a	Mo	CO	CO
2b	W	CO	CO
2c	Mo	PPh$_3$	PPh$_3$
2d	Mo	CO	PPh$_3$
2e	W	PPh$_3$	PPh$_3$



	L
3a	CO
3b	PPh$_3$



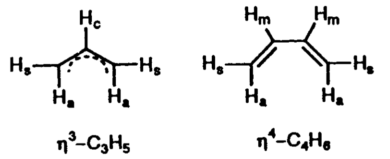
	L	R
4a	CO	Me
4b	CO	C_6H_4Me-4
4c	CO	C_6H_4OMe-2
4d	PPh$_3$	C_6H_4Me-4
4e	PHPh$_2$	C_6H_4OMe-2

$J(H_sH_c)$ 7 Hz is assigned to the *syn*-protons (H_s). The central methine proton (H_c) of the ligand appears as a triplet of triplets at δ 4.13. In comparison, in the spectrum of $[N(PPh_3)_2][Fe(CO)(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ there are doublets at δ 1.15 [H_a, $J(H_aH_c)$ 11 Hz] and 2.62 [H_s, $J(H_sH_c)$ 7 Hz], and a multiplet at δ 3.96 for H_c.[4] In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **1a**, resonances for the two CO ligands are observed at δ 240.6, while peaks at δ 58.0 and 29.2 are assigned to *C*Me and C*Me* nuclei of the carbaborane cage, respectively. Signals at δ 75.3 and 47.8 may be ascribed to the CH and CH_2 fragments of the $\eta^3\text{-}C_3H_5$ ligand. The IR and NMR data for **1b** and **1c** are similar to those of **1a**. Spectroscopic data for the complexes $[M(CO)_2(\eta^3\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ (M = Mo or W) reveal that they are formed as a mixture of two conformers (*exo* and *endo*) which differ in orientation of the $\eta^3\text{-}C_3H_5$ ligand.[5] Thus these species show four rather than two CO stretching bands in their IR spectra and display dynamic ^1H NMR spectra. The ^1H NMR spectrum of **1a** measured at room temperature and at 190 K showed no pattern of peaks indicating fluxional behaviour. Evidently for the salts **1** only one conformer exists for the $\eta^3\text{-}C_3H_5$ group in the anions, and for steric reasons this may well be the *exo* form shown.

Protonation of CO-saturated CH_2Cl_2 solutions of compound **1a** with $HBF_4{\cdot}Et_2O$ at −78 °C yielded, after column chromatography on silica at −20 °C, the complex $[Mo(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **2a**, characterised by the data given in Tables 1–3. Protonation of **1b** under similar conditions afforded **2b**. Interestingly, the latter is a polytopal isomer of $[W(CO)_4(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$ **3a**, obtained by treating $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ with $HBF_4{\cdot}Et_2O$.[6] This is an unusual reaction since it involves loss of a $BCH_2C_6H_4Me$-4 fragment. Compound **2b** is also closely related to the complexes $[W(CO)_4\{\eta^5\text{-}7,8\text{-}C_2B_9H_8(CH_2R)\text{-}10\text{-}Me_2\text{-}7,8\}]$ (R = Me **4a**, C_6H_4Me-4 **4b** or C_6H_4OMe-2 **4c**), prepared by treating CO-saturated CH_2Cl_2 solutions of the salts $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ with $HBF_4{\cdot}Et_2O$.[7]

When compound **1a** was treated with $HBF_4{\cdot}Et_2O$, in the presence of PPh_3, a chromatographically inseparable mixture of $[Mo(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **2c** and $[Mo(CO)_3(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **2d** was formed. However, by crystallisation from CH_2Cl_2–light petroleum pure **2c** was obtained. In contrast, protonation of **1b** with $HBF_4{\cdot}Et_2O$ in the presence of PPh_3 affords $[W(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **2e** as the only product.

Table 2 Hydrogen-1 and carbon-13 NMR data[a] for the new compounds



Compound	δ (^{1}H)[b]	δ (^{13}C)[c]
1a	1.10 [d, 2 H, H_a, *J*(H_aH_c) 10], 1.95 (s, 6 H, Me), 2.92 [d, 2 H, H_s, *J*(H_sH_c) 7], 4.13 [t of t, 1 H, H_c, *J*(HH) 10, 7], 7.47–7.68 (m, 30 H, Ph)	240.6 (CO), 134.0–126.7 (Ph), 75.3 (CH), 58.0 (br, *C*Me), 47.8 (CH_2), 29.2 (C*Me*)
1b	1.20 [d of t, 2 H, H_a, *J*(H_aH_c) 9, *J*(H_aH_s) 1], 2.29 (s, 6 H, Me), 2.94 [d of t, 2 H, H_s, *J*(H_sH_c) 6, *J*(H_sH_a) 1], 3.74 [t of t, 1 H, H_c, *J*(HH) 9, 6], 7.49–7.69 (m, 30 H, Ph)	231.2 [WCO, *J*(WC) 160], 134.1–126.7 (Ph), 67.4 (CH), 57.2 (br, *C*Me), 40.6 (CH_2), 31.6 (C*Me*)
1c	1.15 [d of t, 2 H, H_a, *J*(H_aH_c) 10, *J*(H_aH_s) 1], 1.33 [t, br, 12 H, NCH_2*Me*, *J*(HH) 7], 1.83 (s, br, 2 H, CH), 2.98 [d of t, 2 H, H_s, *J*(H_sH_c) 7, *J*(H_sH_a) 1], 3.23 [q, 8 H, NCH_2, *J*(HH) 7], 3.37 [t of t, 1 H, H_c, *J*(HH) 10, 7]	242.0 (CO), 78.6 (CH), 53.0 (CH_2N), 45.0 (CH_2), 42.0 (br, CH of $C_2B_9H_{11}$), 7.7 (*Me*CH_2N)
2a	2.25 (s, 6 H, Me)	220.8 (CO), 77.3 (br, *C*Me), 32.9 (C*Me*)
2b	2.46 (s, 6 H, Me)	209.5 (CO), 72.2 (br, *C*Me), 33.4 (C*Me*)
2c	0.93 (s, 6 H, Me), 7.10–7.54 (m, br, 30 H, Ph)	[d] 134.3–128.5 (Ph), 68.8 (br, *C*Me), 27.4 (C*Me*)
2d	2.08 (s, 6 H, Me), 7.29–7.58 (m, br, 15 H, Ph)	232.6 [d, CO, *J*(PC) 8], 230.7 [d, 2 × CO, *J*(PC) 34], 134.3–128.7 (Ph), 73.8 (br, *C*Me), 31.9 (C*Me*)
2e	1.04 (s, 6 H, Me), 7.10–7.95 (m, br, 30 H, Ph)	[d] 134.1–128.4 (Ph), 64.7 (br, *C*Me), 27.7 (C*Me*)
5[e]	2.22 [d, 2 H, H_a, *J*(H_aH_m) 9], 3.37 (s, br, 2 H, CH), 3.77 [d, 2 H, H_s, *J*(H_sH_m) 7], 6.12 (m, 2 H, H_m)	229.2 (CO), 94.2 (=CH), 61.4 (=CH_2), 48.0 (br, CH of $C_2B_9H_{11}$)
6a	1.60 (s, 6 H, Me), 2.72 [q, 6 H, ≡CMe, *J*(HH) 1], 3.00 [q, 6 H, ≡CMe, *J*(HH) 1]	223.4 (CO), 174.6, 150.6 (C≡C), 69.5 (br, *C*Me), 27.1 (C*Me*), 18.3, 15.9 (≡C*Me*)
6b	1.76 (s, 6 H, Me), 7.20–7.86 (m, 20 H, Ph)	211.5 (CO), 178.2, 162.0 (C≡C), 136.9–127.2 (Ph), 68.8 (br, *C*Me), 27.7 (C*Me*)
6c	2.72 (s, 6 H, Me), 2.80 (s, 6 H, Me), 2.88 (s, br, 2 H, CH)	225.2 (CO), 164.3, 143.2 (C≡C), 50.3 (br, CH of $C_2B_9H_{11}$), 15.9 (2 × Me)
6d[f]	1.26 (s, 3 H, Me), 1.81 (s, 3 H, Me), 6.68–7.90 (m, 25 H, Ph)	236.4 [d, CO, *J*(PC) 16], 214.3 [d, C≡C, *J*(PC) 7], 207.0 [d, C≡C, *J*(PC) 7], 136.4–127.7 (Ph), 75.1, 72.6 (br, *C*Me), 29.5, 28.7 (C*Me*)
6e[g]	1.61 [d, 3 H, PMe, *J*(PH) 10], 1.65 (s, 3 H, Me), 1.69 [d, 3 H, PMe, *J*(PH) 10], 1.80 (s, 3 H, Me), 2.48 (s, 3 H, ≡CMe), 3.12 (s, 3 H, ≡CMe), 7.22–7.44 (m, 5 H, Ph)	234.9 [d, CO, *J*(PC) 14], 216.8 [d, C≡C, *J*(PC) 8], 206.1 [d, C≡C, *J*(PC) 6], 137.7–128.9 (Ph), 73.7, 68.2 (br, *C*Me), 30.1, 28.8 (C*Me*), 21.2, 19.1 (≡C*Me*), 18.0 [d, PMe, *J*(PC) 9], 17.6 [d, PMe, *J*(PC) 7]
7	−8.10 [q, br, 1 H, BHW, *J*(BH) 55], 1.89, 2.00, 2.56 (s × 3, Me-4 and CMe), 5.46 (s, 5 H, C_5H_5), 6.94, 7.41 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	380.1 (μ-C), 226.1, 217.8, 213.3 (CO), 161.4–121.4 (C_6H_4), 92.5 (C_5H_5), 71.2, 69.7 (br, *C*Me), 31.6, 31.3 (C*Me*), 21.0 (Me-4)

[a] Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz. [b] Measured at ambient temperatures in CD_2Cl_2 unless otherwise stated. Proton resonances for terminal BH groups occur as broad unresolved peaks in the range δ *ca.* −2 to +3. [c] Hydrogen-1 decoupled, measured at ambient temperatures in CD_2Cl_2 unless otherwise stated. Chemical shifts are positive to high frequency of $SiMe_4$. [d] Signals due to carbonyl carbon nuclei are not seen due to ^{31}P–^{13}C coupling and poor solubility. [e] Measured in $(CD_3)_2CO$. [f] Measured at 200 K. [g] Measured at 240 K.

The analytical and spectroscopic data for compounds **2c** and **2e** (Tables 1–3) are in agreement with the formulations shown. The absence of CO resonances in the ^{13}C-{^1H} NMR spectra of these products is attributed to measurements on insufficiently concentrated solutions, due to the relative insolubility of the compounds giving rise to weak spectra in which the intensity of the signals would be expected to be reduced by ^{31}P–^{13}C coupling. However, both compounds display two CO bands in their IR spectra.

Complex **2e** is an isomer of the compound [$W(CO)_2(PPh_3)_2(\eta^5$-7,9-$C_2B_9H_9Me_2)$] **3b**, obtained by treating [NEt_4][$W(\equiv CC_6H_4Me$-4$)(CO)_2(\eta^6$-7,9-$C_2B_{10}H_{10}Me_2)$] with $HBF_4 \cdot Et_2O$, in the presence of PPh_3. As in the synthesis of **3a**, referred to above, a $BCH_2C_6H_4Me$-4 fragment is released in this reaction, and both processes proceed *via* the intermediacy of species [$W(CO)_2L_2\{\eta^6$-7,9-$C_2B_{10}H_9(CH_2C_6H_4Me$-4)-11-$Me_2$-7,9$\}$].[6] Both **2e** and **3b** display two CO stretching bands in their IR spectra at very similar frequencies (**2e**, 1933 and 1842; **3b**, 1935 and 1845 cm^{-1}). Complex **2e** is also structurally related to the compounds [$W(CO)_2L_2\{\eta^5$-7,8-$C_2B_9H_8(CH_2R)$-10-Me_2-7,8$\}$] (L = PPh_3, R = C_6H_4Me-4 **4d**; L = $PHPh_2$, R = C_6H_4OMe-2 **4e**),[7] prepared by protonating ($HBF_4 \cdot Et_2O$) the salts [NEt_4][$W(\equiv CR)(CO)_2(\eta^5$-7,8-$C_2B_9H_9Me_2)$] in the presence of PPh_3 and $PHPh_2$, respectively. An X-ray diffraction study on **4d** revealed that the PPh_3 groups are transoid to one another,[7a] and we assume that **2e** has a similar arrangement. The ^{31}P-{^1H} NMR spectrum of **2e** has a single resonance at δ 24.7 [*J*(WP) 186 Hz] to be compared with corresponding singlet peaks in the spectra of **4d** [δ 15.54, *J*(WP) 172 Hz][7a] and **4e** [δ 15.2, *J*(WP) 186 Hz].[7b] In contrast, the spectrum of **3b** has two doublet resonances [δ 15.0, *J*(PP) 29, *J*(WP) 170; δ 18.3, *J*(PP) 29, *J*(WP) 195 Hz],[6] a feature we ascribe to restricted rotation in this species about an axis through the metal atom and the centroid of the η^5-CBCBB ring. This could lead to a conformer in which the P atoms of a transoid P–W–P group lie in different sites with respect to the CMe vertices in the pentagonal ring.

Although compound **2d** was not isolated free of **2c**, its spectroscopic properties are in complete agreement with its formulation. There are three CO stretching bands in the IR spectrum (Table 1), similar to those seen in the spectrum of the tricarbonyl species [$W(CO)_3(PPh_3)\{\eta^5$-7,8-$C_2B_9H_8(CH_2C_6H_4OMe$-2)-10-Me_2-7,8$\}$].[7b] The ^1H NMR spectrum of **2d** (Table 2) showed a singlet (δ 2.08) for the cage Me groups. The CMe fragments were revealed in the ^{13}C-{^1H} NMR spectrum with peaks at δ 73.8 (*C*Me) and 31.9 (C*Me*), and there were as

Table 3 Boron-11 and phosphorus-31 NMR[a] data for the new compounds

Compound	δ (^{11}B)[b]	δ (^{31}P)[c]
1a	−5.0 (1 B), −7.9 (2 B), −10.2 (3 B), −11.9 (2 B), −13.6 (1 B)	
1b	−5.2 (1 B), −7.7 (2 B), −9.3 (3 B), −11.3 (2 B), −12.5 (1 B)	
1c	−4.8 (1 B), −11.2 (2 B), −12.4 (2 B), −14.2 (2 B), −17.2 (1 B), −22.2 (1 B)	
2a	3.3 (1 B), −0.2 (1 B), −2.1 (2 B), −3.6 (1 B), −5.1 (2 B), −5.6 (2 B)	
2b	2.7 (1 B), −2.7 (2 B), −3.7 (1 B), −4.5 (1 B), −6.1 (2 B), −7.8 (2 B)	
2c	−0.2 (2 B), −4.6 to −7.2 (vbr, 7 B)	61.2
2d	−0.2 (2 B), −4.6 to −7.2 (vbr, 7 B)	51.9
2e[d]	−4.3 to −12.7 (vbr, 9 B)	24.7 [*J*(WP) 186 Hz]
5[e]	3.9 (1 B), 1.8 (1 B), 0.7 (3 B), −8.4 (2 B), −12.8 (2 B)	
6a	2.1 (1 B), −5.0 (2 B), −8.2 (3 B), −9.0 (3 B)	
6b	6.0 (1 B), −3.5 (3 B), −5.8 (2 B), −8.5 (1 B), −11.7 (2 B)	
6c	−3.2 (1 B), −5.4 (2 B), −8.3 (1 B), −11.1 (2 B), −15.5 (3 B)	
6d	2.3 (1 B), −2.0 to −12.0 (8 B)	57.6
6e	1.2 (1 B), −1.8 (2 B), −5.0 (2 B), −5.7 (2 B), −7.8 (1 B), −9.4 (1 B)	25.8
7[f]	21.2 [1 B, BHW, *J*(HB) 55 Hz], −4.8 (2 B), −6.6 (3 B), −8.6 (2 B), −10.9 (1 B)	

[a] Chemical shifts (δ) in ppm. [b] Hydrogen-1 decoupled, measured at ambient temperatures in CD_2Cl_2 unless otherwise stated. Chemical shifts 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. [c] Hydrogen-1 decoupled, measured at ambient temperatures in CD_2Cl_2. Chemical shifts are positive to high frequency of 85% H_3PO_4 (external). [d] Measured in $CDCl_3$–Me_2CO (1:4). [e] Measured in $(CD_3)_2CO$. [f] *J*(HB) measured from a fully coupled ^{11}B NMR spectrum.

expected two CO resonances; δ 232.6 [d, *J*(PC) 8] and 230.7 [d, *J*(PC) 34 Hz], with relative intensity 1:2.

The reaction between compound **1c** and $HBF_4\cdot Et_2O$ in the presence of buta-1,3-diene affords the complex $[Mo(CO)_2(\eta^4\text{-}C_4H_6)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ **5**, identified by the data given in the Tables. As expected, the IR spectrum shows two CO stretching bands (2037 and 1987 cm^{-1}). In the ^{1}H NMR spectrum there are two doublets for the $\eta^4\text{-}C_4H_6$ ligand. One at δ 2.22, with $J(H_aH_m)$ 9 Hz, is assigned to the *anti*-protons (H_a) and the other at δ 3.77, with $J(H_sH_m)$ 7 Hz, is assigned to the *syn*-protons (H_s). The multiplet at δ 6.12 is attributed to the two equivalent CH protons (H_m). The two cage CH groups give rise to a broad signal at δ 3.37. Correspondingly, in the ^{13}C-{^{1}H} NMR spectrum there is a broad peak at δ 48.0 assigned to these groups. The CO ligands resonate at δ 229.2, and the signals for the $\eta^4\text{-}C_4H_6$ group are seen at δ 94.2 (CH) and 61.4 (CH_2).

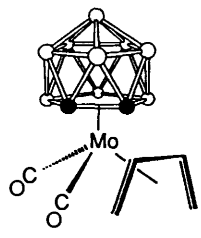
Protonation reactions in the presence of alkynes were next investigated. Treatment of compound **1a** in CH_2Cl_2 at *ca.* −78 °C with $HBF_4\cdot Et_2O$ in the presence of MeC≡CMe gave the bis(alkyne)monocarbonyl complex $[Mo(CO)(MeC_2Me)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **6a**, in good yield. This species was first isolated, but in poorer yield (*ca.* 30%), from the reaction between $Tl_2[Mo(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$, $AgBF_4$ and MeC≡CMe. In this reaction the thallium salt undergoes a two-electron oxidation with $AgBF_4$ to generate the $Mo(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)$ moiety, which reacts with the alkyne to give **6a**. It is noteworthy that the anion $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$, isolobal with $[Mo(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]^{2-}$, readily undergoes a one-electron oxidation to afford $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$, and that the latter in the presence of $AgBF_4$ and MeC≡CMe undergoes a further one-electron oxidation to yield the salt $[Mo(CO)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$.[8] The relationship between the cation of the latter product (Scheme 1, **A**) and the neutral complex **6a** [Scheme 1, **B** (R = Me)] is apparent since the ligands $\eta\text{-}C_5H_5$ and $\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2$ are mapped isolobally.[3b]

Protonation of the salt **1b** in CH_2Cl_2 with $HBF_4\cdot Et_2O$, in the presence of PhC≡CPh, affords $[W(CO)(PhC_2Ph)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **6b**. In this reaction an unstable intermediate was observed with ν_{max}(CO) at 2059 and 1988 cm^{-1}. This may be the mono(alkyne)dicarbonyl species $[W(CO)_2(PhC_2Ph)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$, since the stable complex $[W(CO)_2(PhC_2Ph)(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$,[6] prepared by protonating $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ with $HBF_4\cdot Et_2O$ in the presence of PhC≡CPh, displays CO stretching bands at 2055 and 1994 cm^{-1}. The complex **6c** was obtained by treating **1c** with $HBF_4\cdot Et_2O$ and MeC≡CMe.

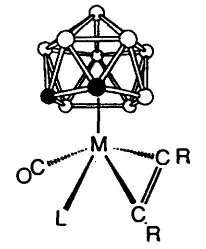
The spectroscopic data for the complexes **6a**–**6c** (Tables 1–3) are as expected. Each complex shows one CO absorption in its IR spectrum (Table 1). The ^{1}H NMR spectrum of **6a** (Table 2) shows a resonance for the cage CMe groups at δ 1.60, and two quartets [*J*(HH) 1 Hz] at δ 2.72 and 3.00 are assigned to the two pairs of non-equivalent CMe groups of the alkyne ligands. The latter are evidently not rotating on the NMR time-scale about an axis through the metal and the midpoint of the C≡C bond. In the ^{13}C-{^{1}H} NMR spectrum there is a peak for the CO group at δ 223.4, and a broad signal at δ 69.5 due to the cage carbon vertices. A resonance at δ 27.1 is assigned to the Me groups of the carbaborane cage,[2] and peaks at δ 18.3 and 15.9 are due to methyl groups of the but-2-yne ligands. Of interest are the peaks for the ligated carbon atoms of the latter at δ 174.6 and 150.6. These occur in the chemical shift range for alkynes donating formally three electrons to the molybdenum centre,[9] and the observation of two signals again indicates that the alkyne molecules are not rotating on the NMR time-scale. The data may be compared with the single resonances for the alkyne-carbon nuclei seen in the spectra of the complexes $[W(CO)(PhC_2Ph)_2\{\eta^5\text{-}7,8\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)\text{-}10\text{-}Me_2\text{-}7,8\}]$ (δ 178.2)[7a] and $[W(CO)_2(PhC_2Ph)(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$ (δ 206.0),[6] species wherein the PhC≡CPh ligands evidently rotate and formally donate three and four electrons, respectively, to the tungsten centres.

Unexpectedly, protonation of the salt **1a** with $HBF_4\cdot Et_2O$ in the presence of two equivalents of PhC≡CPh did not yield $[Mo(CO)(PhC_2Ph)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$. No stable complex was isolated from this reaction mixture. However, as mentioned above, an intermediate presumed to be $[W(CO)_2(PhC_2Ph)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ was observed during the synthesis of **6b**. A similar intermediate mono(alkyne)dicarbonylmolybdenum species [ν_{max}(CO) at 2060 and 1999 cm^{-1}] was observed during the protonation of **1a** in the presence of PhC≡CPh. If solutions containing this complex are treated with PPh_3 the green compound $[Mo(CO)(PPh_3)(PhC_2Ph)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **6d** is obtained in high yield. This product, with an $M(CO)(PR_3)(PhC_2Ph)$ group ligated by the *nido*-C_2B_9 fragment, is structurally related to the complex $[W(CO)(PMe_3)(PhC_2Ph)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)\text{-}10\text{-}Me_2\text{-}7,8\}]$, obtained by treating $[W(CO)_2(PhC_2Ph)_2\{\eta^5\text{-}7,8\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)\text{-}10\text{-}Me_2\text{-}7,8\}]$ with PMe_3.[7a]

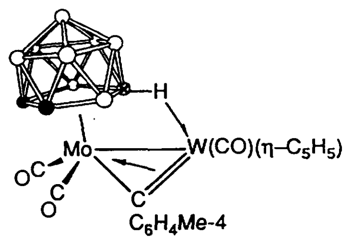
Treatment of compound **6a** with PMe_2Ph affords $[Mo(CO)(PMe_2Ph)(MeC_2Me)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **6e**, and data



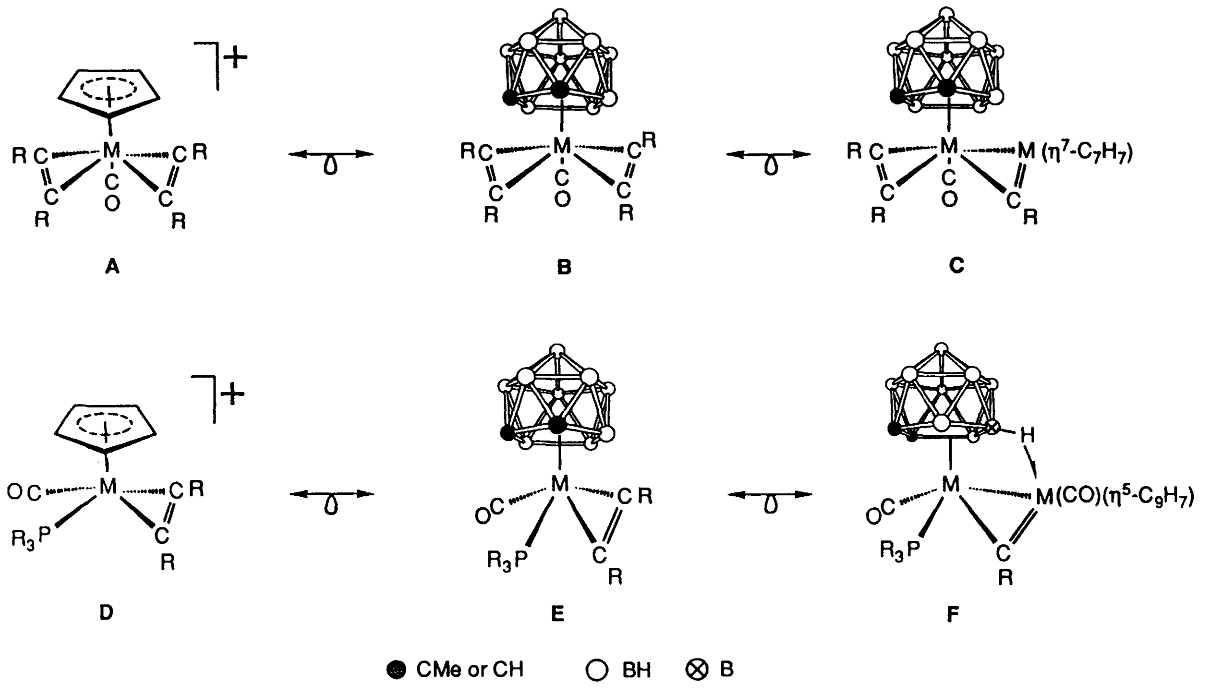
5 ● CH



	M	L	R	●
6a	Mo	MeC≡CMe	Me	CMe
6b	W	PhC≡CPh	Ph	CMe
6c	Mo	MeC≡CMe	Me	CH
6d	Mo	PPh₃	Ph	CMe
6e	Mo	PMe₂Ph	Me	CMe



7 ● CMe ⊗ B



Scheme 1 M = Mo or W, R = alkyl or aryl, η^5-C_9H_7 = indenyl

characterising this product, and **6d**, are given in the Tables. Due to the dynamic behaviour of both complexes, a property shared with $[W(CO)(PMe_3)(PhC_2Ph)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8(CH_2C_6H_4\text{-}Me\text{-}4)\text{-}10\text{-}Me_2\text{-}7,8\}]$,[7a] the ^1H and ^{13}C-$\{^1H\}$ NMR data (Table 2) were recorded at low temperatures so that limiting spectra could be measured. In the ^1H NMR spectrum of **6d** there are two resonances (δ 1.26 and 1.81) for the non-equivalent cage CMe groups, and correspondingly in the ^{13}C-$\{^1H\}$ NMR spectrum there are four peaks for these moieties at δ 75.1 and 72.6 (*C*Me) and δ 29.5 and 28.7 (C*Me*). Two doublet [*J*(PC) 7 Hz] resonances at δ 214.3 and 207.0 are ascribed to the Ph*C*$_2$Ph nuclei, the chemical shifts being in accord with the alkyne functioning as a four-electron donor.[9] A CO resonance is seen as a doublet at δ 236.4 [*J*(PC) 16 Hz]. The ^{31}P-$\{^1H\}$ NMR spectrum has a resonance at δ 57.6. The spectroscopic data for **6e** are also in agreement with its formulation.

The reaction of $Tl_2[Mo(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ in thf with $AgBF_4$ in the presence of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ gave the green dimetal complex $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **7**. The latter is an isomer of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$, a complex, however, in which the molybdenum atom carries the η-C_5H_5 group and the tungsten atom a *nido*-7,9-$C_2B_9H_9Me_2$ cage.[10] This species is formed, together with $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}\text{-}Me_2)]$, when $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^6\text{-}7,9\text{-}C_2B_{10}\text{-}H_{10}Me_2)]$ is protonated with $HBF_4{\cdot}Et_2O$ in the presence of $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$.

The IR spectrum of compound **7** displays three CO stretching bands (2007, 1960 and 1940 cm^{-1}), similar to those observed (2002, 1952 and 1920 cm^{-1}) for the closely related $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$.[10] In the ^1H NMR spectrum of compound **7** the presence of the exopolyhedral B–H→W bridge bond is evidenced by a broad quartet signal at δ −8.1 [*J*(BH) 55 Hz]. Correspondingly, in a fully coupled ^{11}B NMR spectrum there is a diagnostic doublet resonance for this group at δ 21.2 [*J*(HB) 55 Hz].[2,10] In the ^{13}C-$\{^1H\}$ NMR spectrum the three non-equivalent CO groups give rise to peaks at δ 226.1, 217.8 and 213.3. Resonances for the non-equivalent cage CMe fragments occur at δ 71.2 and 69.7 (*C*Me) and δ 31.6 and 31.3 (C*Me*). A peak at δ 380.1 is assigned to the ligated carbon of the bridging alkylidyne group. The chemical shift is in the range expected for a dimetal species which is electronically unsaturated (32 valence electrons) with the $(\eta\text{-}C_5H_5)(OC)W{\equiv}CC_6H_4Me\text{-}4$ formally donating four electrons to the molybdenum centre.[11]

Noteworthy isolobal relationships exist between several of the complexes reported herein, and those described previously. We referred earlier to the mapping (Scheme 1) of cationic species of type **A** {*e.g.* $[\mathrm{Mo(CO)(MeC_2Me)_2(\eta\text{-}C_5H_5)}]^+$} with neutral compounds of type **B** (*e.g.* **6a**). These bis(alkyne) complexes are in turn related to dimetal products of type **C** {*e.g.* $[\mathrm{MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(MeC_2Me)(\eta^7\text{-}C_7H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)}]$[12]} as a result of substituting the CR group by an $\mathrm{Mo(\eta^7\text{-}C_7H_7)}$ fragment. Similarly, structural relationships exist between the three classes of monoalkyne complex of types **D** {*e.g.* $[\mathrm{Mo(CO)(PPh_3)(PhC_2Ph)(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$[13]}, **E** (*e.g.* **6d**) and **F** {*e.g.* $[\mathrm{MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})}]$ ($\mathrm{C_9H_7}$ = indenyl)[14]}, as a consequence of the isolobal mapping of the ligands $\eta\text{-}\mathrm{C_5H_5}$ and $\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_9R'_2}$ (R' = H or Me),[3a,b] and the groups CR and $\mathrm{MoL_2(\eta^5\text{-}C_9H_7)}$ (L = CO or agostic B–H→Mo).[15] These relationships are serving as useful guidelines for employment of the reagents **1** in the syntheses to be described in subsequent papers.

Experimental

All reactions were conducted under an atmosphere of dry nitrogen, using Schlenk-line techniques. Solvents were distilled from appropriate drying agents under nitrogen before use. Light petroleum refers to that fraction of b.p. 40–60 °C. Chromatography columns (*ca.* 15 cm in length and 2 cm in diameter unless otherwise stated) were packed with silica gel (Aldrich, 70–230 mesh) or with alumina (Aldrich, Brockmann activity III). The reagents $[\mathrm{MBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)}]$ (M = Mo or W),[16] $\mathrm{Tl_2}[\mathrm{Mo(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)}]$ (R = Me or H),[3b] and $[\mathrm{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)}]$[17] were prepared by literature methods. Tetrafluroboric acid was an 85% solution of $\mathrm{HBF_4{\cdot}Et_2O}$ in $\mathrm{Et_2O}$, as supplied by Aldrich. The NMR measurements were made using a Bruker AMX 360 spectrometer (frequencies of measurement: ^{11}B, 115.5; ^{13}C, 90.6; and ^{31}P, 145.8 MHz) and the IR spectra were recorded with a Bruker IFS 25 instrument. Analytical and other data for the new compounds are given in Table 1.

Preparation of the Complexes $[\mathrm{Y}][\mathrm{M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)}]$ [Y = $\mathrm{N(PPh_3)_2}$ *or* $\mathrm{NEt_4}$, M = Mo *or* W, R' = Me *or* H].—*Method* 1. (*i*) A thf (30 cm^3) solution of $[\mathrm{MoBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)}]$ (2.64 g, 7.40 mmol) at room temperature was treated with a thf (30 cm^3) solution of $\mathrm{Na_2}[7,8\text{-}\mathrm{C_2B_9H_9Me_2}]$. The latter was generated from $[\mathrm{NHMe_3}][7,8\text{-}\mathrm{C_2B_9H_{10}Me_2}]$ (1.50 g, 6.80 mmol) and NaH (60% dispersion in mineral oil, 1.50 g, 37.50 mmol; washed with 2 × 20 cm^3 thf) at refluxing temperature for 12 h. After stirring the mixture for 0.5 h, $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ (4.27 g, 7.40 mmol) was added and stirring was continued for 0.5 h, after which solvent was removed *in vacuo*. The residue was extracted with $\mathrm{CH_2Cl_2}$ (10 cm^3) and the solution chromatographed on silica at −20 °C. Elution with $\mathrm{CH_2Cl_2}$–light petroleum (3:1) gave a yellow eluate. After solvent was removed *in vacuo*, the crude product was recrystallised from $\mathrm{CH_2Cl_2}$–light petroleum (1:15, 30 cm^3) and dried *in vacuo* to give yellow *microcrystals* of $[\mathrm{N(PPh_3)_2}][\mathrm{Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)}]$ **1a** (4.71 g).

(*ii*) Using the same procedure as for compound **1a**, treatment of $[\mathrm{WBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)}]$ (1.05 g, 2.40 mmol) with $\mathrm{Na_2}[7,8\text{-}\mathrm{C_2B_9H_9Me_2}]$ {generated from $[\mathrm{NHMe_3}][7,8\text{-}\mathrm{C_2B_9H_{10}Me_2}]$ (0.50 g, 2.30 mmol) and NaH (60% dispersion in mineral oil, 0.50 g, 12.50 mmol, washed with 2 × 10 cm^3 thf)} in thf at room temperature, followed by addition of $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ (1.43 g, 2.50 mmol), yielded yellow *microcrystals* of $[\mathrm{N(PPh_3)_2}][\mathrm{W(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)}]$ **1b** (1.85 g).

(*iii*) Similarly, treatment of $[\mathrm{MoBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)}]$ (1.32 g, 3.70 mmol) with $\mathrm{Na_2}[7,8\text{-}\mathrm{C_2B_9H_{11}}]$, obtained from $[\mathrm{NHMe_3}][7,8\text{-}\mathrm{C_2B_9H_{12}}]$ (0.70 g, 3.60 mmol) and NaH (60% dispersion in mineral oil, 0.70 g, 17.50 mmol, washed with 2 × 10 cm^3 of thf), in thf at room temperature, followed by addition of $[\mathrm{NEt_4}]\mathrm{Cl}$ (0.70 g, 3.80 mmol), gave yellow *microcrystals* of $[\mathrm{NEt_4}][\mathrm{Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})}]$ **1c** (1.23 g).

Method 2. A mixture of $\mathrm{Tl}[\mathit{closo}\text{-}3,1,2\text{-}\mathrm{TlC_2B_9H_9Me_2}]$ (0.20 g, 0.35 mmol) and $[\mathrm{Mo(CO)_3(NCMe)_3}]$ (0.10 g, 0.35 mmol) was stirred in thf (20 cm^3) for 1 h, thereby generating an orange solution of the salt $\mathrm{Tl_2}[\mathrm{Mo(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)}]$. The latter was cooled to −78 °C and allyl bromide (0.30 cm^3, 3.50 mmol) was added. The reaction mixture was warmed to room temperature and stirred overnight. The salt $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ (0.21 g, 0.37 mmol) was then added and the mixture was stirred for 1 h. Compound **1a** was isolated (*ca.* 0.12 g) by following the work-up procedure described in (*i*) above.

Protonation Reactions of the Complexes $[\mathrm{Y}][\mathrm{M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)}]$.—(*i*) A $\mathrm{CH_2Cl_2}$ (50 cm^3) solution of compound **1a** (0.10 g, 0.11 mmol) was saturated with a stream of CO at −78 °C. To this solution was added $\mathrm{HBF_4{\cdot}Et_2O}$ (0.02 cm^3, 0.15 mmol), and the mixture was then stirred at room temperature for 0.5 h, with the CO source maintained. Solvent was removed *in vacuo*, the residue was extracted with $\mathrm{CH_2Cl_2}$–light petroleum (1:1, 10 cm^3) and the extracts chromatographed on silica at −20 °C. Elution with the same solvent mixture gave a yellow eluate. Solvent was removed *in vacuo* and the product was dried *in vacuo* to give yellow *microcrystals* of $[\mathrm{Mo(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)}]$ **2a** (0.03 g).

(*ii*) Similarly, treatment of compound **1b** (0.10 g, 0.10 mmol) with $\mathrm{HBF_4{\cdot}Et_2O}$ (0.02 cm^3, 0.15 mmol) under a CO atmosphere at −78 °C afforded yellow *microcrystals* of $[\mathrm{W(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)}]$ **2b** (0.04 g).

(*iii*) A $\mathrm{CH_2Cl_2}$ (20 cm^3) solution of compound **1a** (0.10 g, 0.11 mmol) and $\mathrm{PPh_3}$ (0.08 g, 0.31 mmol) was treated with $\mathrm{HBF_4{\cdot}Et_2O}$ (0.02 cm^3, 0.15 mmol) at room temperature. The mixture was stirred for 5 h, solvent was removed *in vacuo*, the residue was extracted with $\mathrm{CH_2Cl_2}$ (10 cm^3), and the solution chromatographed on silica at −20 °C. Elution with $\mathrm{CH_2Cl_2}$–light petroleum (1:1) gave a yellow eluate. Solvent was removed *in vacuo* to give a mixture of $[\mathrm{Mo(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)}]$ **2c** and $[\mathrm{Mo(CO)_3(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)}]$ **2d**. Crystallisation of this mixture from $\mathrm{CH_2Cl_2}$–light petroleum (1:2, 15 cm^3) afforded yellow *microcrystals* of **2c** (0.05 g).

(*iv*) Using the same procedure as above, treatment of a mixture of the salt **1b** (0.10 g, 0.10 mmol) and $\mathrm{PPh_3}$ (0.06 g, 0.23 mmol) in $\mathrm{CH_2Cl_2}$ (20 cm^3) with $\mathrm{HBF_4{\cdot}Et_2O}$ (0.02 cm^3, 0.15 mmol) at room temperature for 1 h yielded yellow *microcrystals* of $[\mathrm{W(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)}]$ **2e** (0.06 g).

(*v*) A $\mathrm{CH_2Cl_2}$ solution (10 cm^3) of compound **1c** (0.20 g, 0.44 mmol) was saturated with buta-1,3-diene at −78 °C. To this solution $\mathrm{HBF_4{\cdot}Et_2O}$ (0.06 cm^3, 0.44 mmol) was added and the mixture stirred at room temperature for 4 h. The solvent and excess of butadiene were removed *in vacuo*, the residue was dissolved in $\mathrm{CH_2Cl_2}$ (2 cm^3), and the solution chromatographed on alumina. Elution with $\mathrm{CH_2Cl_2}$–light petroleum (3:1) yielded a single yellow band which was collected. Solvent was removed *in vacuo* and the residue crystallised from $\mathrm{CH_2Cl_2}$–light petroleum (1:2, *ca.* 15 cm^3) to give yellow *microcrystals* of $[\mathrm{Mo(CO)_2(\eta^4\text{-}C_4H_6)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})}]$ **5** (0.08 g).

(*vi*) But-2-yne (0.06 g, 1.10 mmol) was condensed into a $\mathrm{CH_2Cl_2}$ solution (10 cm^3) of compound **1a** (0.20 g, 0.22 mmol) at −78 °C, and $\mathrm{HBF_4{\cdot}Et_2O}$ (0.03 cm^3, 0.22 mmol) was added. Immediately the solution darkened to a deep red colour. The mixture was slowly warmed to ambient temperature, then stirred for 2 h, the colour changing to straw yellow. Solvent was removed *in vacuo*, and the residue was dissolved in $\mathrm{CH_2Cl_2}$–light petroleum (1:1, 5 cm^3) and chromatographed on alumina. Elution with the same solvent mixture yielded a single yellow band which was collected. After removal of the solvent *in vacuo*, the residue was crystallised from $\mathrm{CH_2Cl_2}$–light petroleum (1:4, *ca.* 20 cm^3) to give yellow *microcrystals* of $[\mathrm{Mo(CO)(MeC_2Me)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)}]$ **6a** (0.06 g).

(*vii*) A $\mathrm{CH_2Cl_2}$ (20 cm^3) solution of compound **1b** (0.10 g, 0.10 mmol) to which $\mathrm{PhC{\equiv}CPh}$ (0.04 g, 0.22 mmol) had been added was treated with $HBF_4{\cdot}Et_2O$ (0.02 cm^3, 0.15 mmol) at room temperature. The mixture turned red instantly, and displayed in the IR spectrum strong ν_{max}(CO) bands at 2059 and 1988 cm^{-1}. This solution slowly (0.5 h) turned yellow, and showed one CO stretch at 2069 cm^{-1}. Solvent was removed *in vacuo*, and the residue was extracted with CH_2Cl_2–light petroleum (1 : 1, 10 cm^3) and the extract chromatographed on silica at −20 °C. Elution initially with CH_2Cl_2–light petroleum (1 : 5) removed excess of PhC≡CPh. Further elution with CH_2Cl_2–light petroleum (1 : 1) gave a yellow eluate. Solvent was removed *in vacuo*, and the product was washed with light petroleum (2 × 1 cm^3) and dried *in vacuo* to give yellow *microcrystals* of [W(CO)($PhC_2Ph)_2$(η^5-7,8-$C_2B_9H_9Me_2$)] **6b** (0.06 g).

(*viii*) Following a similar procedure to that described for compound **6a**, the reaction between **1c** (0.20 g, 0.44 mmol), but-2-yne (0.12 g, 2.20 mmol) and $HBF_4{\cdot}Et_2O$ (0.06 cm^3, 0.44 mmol) yielded yellow *microcrystals* of [Mo(CO)($MeC_2Me)_2$(η^5-7,8-$C_2B_9H_{11}$)] **6c** (0.12 g).

Synthesis of the Complexes [Mo(CO)L(RC_2R)(η^5-7,8-$C_2B_9H_9Me_2$)] (L = PPh_3 *or* PMe_2Ph, R = Ph *or* Me).—(*i*) A CH_2Cl_2 (20 cm^3) solution of compound **1a** (0.10 g, 0.11 mmol) and PhC≡CPh (0.02 g, 0.11 mmol) was treated with $HBF_4{\cdot}Et_2O$ (0.02 cm^3, 0.15 mmol) at 0 °C. The solution instantly turned brown. After stirring for 5 min, PPh_3 (0.04 g, 0.15 mmol) was added, whereupon the solution slowly turned green. After warming to room temperature the mixture was stirred for 0.5 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (1 : 1, 10 cm^3) and chromatographed on silica at −20 °C. Elution with the same solvent mixture gave a green eluate. After removal of solvent *in vacuo*, the residue was washed with light petroleum (0.5 cm^3) and dried *in vacuo* to give green *microcrystals* of [Mo(CO)(PPh_3)(PhC_2Ph)(η^5-7,8-$C_2B_9H_9Me_2$)] **6d** (0.08 g).

(*ii*) To a CH_2Cl_2 solution (10 cm^3) of compound **6a** (0.10 g, 0.25 mmol), PMe_2Ph (0.03 g, 0.25 mmol) was added, and the mixture stirred overnight. Solvent was removed *in vacuo* from the resultant blue solution. The residue was dissolved in CH_2Cl_2 (2 cm^3) and chromatographed on alumina. Elution using CH_2Cl_2 yielded a single blue band, the eluate from which was collected. Removal of solvent *in vacuo* and crystallisation of the residue from CH_2Cl_2–light petroleum (1 : 4, *ca.* 20 cm^3) gave blue *microcrystals* of [Mo(CO)(PMe_2Ph)(MeC_2Me)(η^5-7,8-$C_2B_9H_9Me_2$)] **6e** (0.09 g).

Oxidation Reactions of Tl_2[Mo(CO)$_3$(η^5-7,8-$C_2B_9H_9Me_2$)].—(*i*) A mixture of Tl[*closo*-3,1,2-$TlC_2B_9H_9Me_2$] (0.20 g, 0.35 mmol) and [Mo(CO)$_3$(NCMe)$_3$] (0.10 g, 0.35 mmol) was stirred in thf for 1 h, affording an orange solution of the salt Tl_2[Mo(CO)$_3$(η^5-7,8-$C_2B_9H_9Me_2$)]. The solution was cooled to −78 °C and but-2-yne (0.10 g, 1.80 mmol) and $AgBF_4$ (0.14 g, 0.74 mmol) were added. The reaction mixture was warmed to room temperature and stirred for 4 h. Compound **6a** (0.05 g) was obtained following the work-up procedure described above.

(*ii*) An orange solution of Tl_2[Mo(CO)$_3$(η^5-7,8- $C_2B_9H_9Me_2$)] (0.35 mmol) was generated as in (*i*). It was cooled to −78 °C, and [W(≡CC_6H_4Me-4)(CO)$_2$(η-C_5H_5)] (0.14 g, 0.35 mmol) and $AgBF_4$ (0.14 g, 0.70 mmol) were added. The reaction mixture was warmed to room temperature and stirred for 6 h, the solution becoming dark green. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (2 cm^3) and chromatographed on alumina. Elution with CH_2Cl_2 yielded a green band which was collected. After removal of solvent *in vacuo*, the residue was crystallised from CH_2Cl_2–light petroleum (1 : 4, 10 cm^3) to give green *microcrystals* of [MoW(μ-CC_6H_4Me-4)(CO)$_3$(η-C_5H_5)(η^5-7,8-$C_2B_9H_9Me_2$)] **7** (0.11 g).

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