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Synthesis of the complexes $[N(PPh_3)_2][M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ (M = Mo or W): crystal structure of $[N(PPh_3)_2][WBr(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$

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Abstract

Treatment of the compounds $[MBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ (M = Mo or W) with $Na_2[7,9\text{-}C_2B_{10}H_{10}Me_2]$ in tetrahydrofuran, followed by addition of $[N(PPh_3)_2]Cl$, affords the salts $[N(PPh_3)_2][M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$. Reactions of $[N(PPh_3)_2]_2[M(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ with an excess of allyl bromide generate the complexes $[N(PPh_3)_2][MBr(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ *via* an allyl-coupling process. The structure of the latter (M = W) has been determined by X-ray diffraction. The preparation of the molybdenum salt $[N(PPh_3)_2][MoBr(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ by this route was accompanied by the formation of small amounts of the complex $[N(PPh_3)_2][MoBr(CO)_3(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$ resulting from ejection of a BH vertex from the cage. Indeed, it was observed that in CH_2Cl_2 solutions, the former species was slowly converted into the latter at ambient temperatures. Protonation (aqueous HBr) of the salts $[N(PPh_3)_2][M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ in the presence of an atmosphere of CO also yields the compounds $[N(PPh_3)_2][MBr(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$, but if the molybdenum compound is protonated in the absence of CO the complex $[N(PPh_3)_2][MoBr(CO)_3(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$ is formed directly. The NMR data for the new compounds are reported and discussed, as are the possible pathways of their formation.

Key words: Molybdenum; Tungsten; Crystal structure; Cage compound; Carborane; Allyl

1. Introduction

We have recently described the synthesis of the allyl(carborane)-molybdenum and -tungsten 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**)] [1a], and have reported their reactivity towards acids ($HBF_4 \cdot Et_2O$ [1a] or HI [1b]). Thus treatment of the compounds $[MBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ with $Na_2[7,8\text{-}C_2B_9H_9Me_2]$ in THF (tetrahydrofuran), followed by addition of $[N(PPh_3)_2]Cl$, affords the complexes **1** in high yield. These species may also be prepared, but in appreciably lower yield, from allyl bromide, $Tl_2[M(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ and $[N(PPh_3)_2]Cl$. The salts **1** are proving to be good precursors for the synthesis of other molybdenum- and tungsten-carborane compounds [1]. For example, if **1a** is treated with $HBF_4 \cdot Et_2O$ in the presence of the alkyne $Me_3SiC{\equiv}CH$ the complex $[Mo(CO)(\eta\text{-}Me_3SiC_2H)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**2**) is initially formed, but this product subsequently rearranges to $[Mo(CO)(\eta\text{-}Me_3SiC_2H)\{\eta^5,\eta^2\text{-}7,8\text{-}C_2B_9H_8\text{-}Me_2\text{-}10\text{-}[C(H){=}C(H)SiMe_3]\}]$ (**3**) [1c].

In parallel with these studies, we are engaged in a continuing investigation of salts of the anionic complexes $[W({\equiv}CR)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]^-$ and $[W({\equiv}CR)(CO)_2(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]^-$ (R = alkyl, aryl, or alkynyl) [2]. In the former species, the tungsten atom is pentahapto coordinated by the open pentagonal face of a *nido*-eleven vertex carborane cage, whilst in the latter the metal is ligated in the hexahapto manner by a *nido*-twelve vertex cage. Subtle reactivity differences are displayed by these η^5- and η^6-tungsten systems [3], and this prompted us to prepare, as described herein, the salts $[N(PPh_3)_2][M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ [M = Mo (**4a**) and W (**4b**)], in the hope that these compounds would serve as

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useful reagents for further work, and show reactivity patterns different from those of the salts **1**.

2. Results and discussion

Treatment of [MoBr(CO)$_2$(NCMe)$_2$(η^3-C$_3$H$_5$)] with Na$_2$[7,9-C$_2$B$_{10}$H$_{10}$Me$_2$] in THF at room temperature, followed by addition of [N(PPh$_3$)$_2$]Cl, and column chromatography on silica at −20°C, gave the complex [N(PPh$_3$)$_2$][Mo(CO)$_2$(η^3-C$_3$H$_5$)(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)] (**4a**) in high yield, as expected. The salt [N(PPh$_3$)$_2$]-[W(CO)$_2$(η^3-C$_3$H$_5$)(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)] (**4b**) was similarly prepared from [WBr(CO)$_2$(NCMe)$_2$(η^3-C$_3$H$_5$)], Na$_2$[7,9-C$_2$B$_{10}$H$_{10}$Me$_2$] and [N(PPh$_3$)$_2$]Cl. The compounds **4** were well characterised by data listed in Tables 1 and 2.

In the IR spectra of the salts **4** there are two CO-stretching bands, and these occur at appreciably higher frequency than those for the complexes **1**. Thus for **4a**, the absorptions are at 1947vs cm^{-1} and 1877s cm^{-1}, whereas in the spectrum of **1a** they are at 1920vs cm^{-1} and 1830s cm^{-1}. This implies that the η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$ group donates less electron density to the metal centre than the η^5-7,8-C$_2$B$_9$H$_9$Me$_2$ cage. Such differences in IR spectra have been observed previously for these *nido*-cages; for example, the CO-stretching bands for the anion [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-7,8-C$_2$B$_9$H$_9$Me$_2$)]$^-$ [ν_{max}(CO) at 1956 cm^{-1} and 1874 cm^{-1}] [4] occur at a lower frequency than those for [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)]$^-$ [ν_{max}(CO) at 1990 cm^{-1} and 1930 cm^{-1}] [5].

The NMR spectra of the species **4** (Table 2), measured at ambient temperatures, indicated dynamic behaviour, which is a common feature for metal complexes containing an MC$_2$B$_{10}$ framework [3c,5,6]. In mononuclear metal complexes, this fluxionality involves movement of the cage CMe groups, which can flip synchronously from one side of the mean plane through the facial B$_4$ group to the other. Thus in the ^{1}H NMR spectrum of **4a** the two non-equivalent cage CMe groups give rise to a single peak at $\delta = 2.04$ rather than two resonances. This peak at $\delta = 2.04$ remains broad at 190 K indicating dynamic behavior even at this temperature, which is unusual for these systems. There are two doublets at $\delta = 1.12$ [$J(H_aH_c) = 10$ Hz] and 2.45 [$J(H_sH_c) = 7$ Hz] which are assignable to the *anti*- and *syn*-protons [Table 2, (H$_a$) and (H$_s$)] of the η^3-C$_3$H$_5$ group [1a]. The centre proton (H$_c$) of this ligand resonates as a triplet of triplets at $\delta = 4.66$ [J(HH) = 10 Hz and 7 Hz].

The ^{13}C{^{1}H} NMR spectrum of **4a** shows a single resonance at $\delta = 234.4$ for the two carbonyl ligands, in accord with the fluxionality, and for the same reason there are only two rather than four peaks for the CMe fragments of the cage, at $\delta = 85.5$ (*C*Me) and 34.8 (C*Me*). Signals for the η^3-C$_3$H$_5$ ligand (Table 2) are as expected [1a]. Complex **4b** has similar ^{1}H and ^{13}C{^{1}H} NMR spectra to those of **4a**.

Since complexes **1a** or **1b** can also be prepared, as mentioned earlier, from allyl bromide, Tl$_2$[M(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_9$Me$_2$)] (M = Mo or W), and [N(PPh$_3$)$_2$]Cl, it was of interest in this study to investigate whether the reagents **4** could be made from the di-anions [M(CO)$_3$(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)]$^{2-}$ in a similar manner. Accordingly, the species [N(PPh$_3$)$_2$]$_2$[Mo(CO)$_3$-(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)] was treated with an excess of allyl bromide at room temperature for 12 h. The product of this reaction was a yellow compound which was unexpectedly different from **4a**, as indicated by the IR spectrum [ν_{max}(CO) at 2044 cm^{-1} and 1977 cm^{-1}]. This product was identified as [N(PPh$_3$)$_2$][MoBr-(CO)$_3$(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)] (**5a**) by the microanalytical and NMR data listed in Tables 1 and 2. A tungsten analogue [N(PPh$_3$)$_2$][WBr(CO)$_3$(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)] (**5b**) was similarly prepared, and its structure was firmly established by a single-crystal X-ray diffraction study.

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

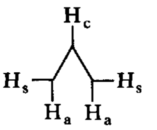
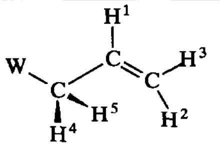
Compound		Colour	Yield (%)	ν_{max}(CO) [b]/cm^{-1}	Analysis (%)		
					C	H	N
4a	[N(PPh$_3$)$_2$][Mo(CO)$_2$(η^3-C$_3$H$_5$)(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)]	Yellow	63	1947vs, 1877s	58.9 (59.8)	5.7 (5.7)	1.6 (1.6)
4b	[N(PPh$_3$)$_2$][W(CO)$_2$(η^3-C$_3$H$_5$)(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)]	Yellow	76	1942vs, 1870s	55.5 (54.5)	5.4 (5.2)	1.4 (1.4)
5a	[N(PPh$_3$)$_2$][MoBr(CO)$_3$(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)]	Yellow	84	2044vs, 1977vs,br	52.8 (53.2)	5.1 (4.8)	1.4 (1.4)
5b	[N(PPh$_3$)$_2$][WBr(CO)$_3$(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)]	Yellow	95	2038vs, 1962vs,br	48.4 (48.7)	5.0 (4.4)	1.4 (1.3)
6a	[N(PPh$_3$)$_2$][MoBr(CO)$_3$(η^5-7,9-C$_2$B$_9$H$_9$Me$_2$)]	Orange	66	2026vs, 1943sh, 1928vs	[c] 52.5 (52.2)	4.8 (4.6)	1.4 (1.4)
7b [d]	[N(PPh$_3$)$_2$][W(CO)$_3$(η^1-C$_3$H$_5$)(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)]	Pale green		2009vs, 1940vs, 1919vs			

[a] Calculated values are given in parentheses. [b] Measured in CH$_2$Cl$_2$. For all carborane compounds there is a broad band at 2550 cm^{-1} resulting from B–H absorptions. [c] Crystallised with 0.5 molecules of CH$_2$Cl$_2$. [d] Isolated as a very unstable species with unidentified impurities, see text.

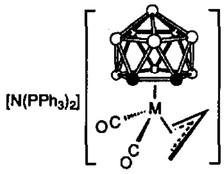
The structure of the anion of **5b** is shown in Fig. 1, and selected bond lengths and angles are listed in Table 3. The tungsten atom is coordinated on one side by three CO molecules (W–C–O average 177°) and by a bromide ligand [W–Br 2.704(1) Å]. On the other side the metal is ligated by the *nido*-$C_2B_{10}H_{10}Me_2$ group in the usual hexahapto manner [5,6b,c,7]. The open CBCBBB face of the *nido*-C_2B_{10} cage is distinctly non-planar, as evidenced by appreciable differences in the connectivities between the tungsten atom and the six ring atoms: W(1)–C(1) 2.445(6), W(1)–B(2) 2.465(8), W(1)–C(3) 2.224(7), W(1)–B(4) 2.467(8), W(1)–B(5) 2.449(7), W(1)–B(6) 2.353(6) Å. Atom C(3), associated with the shortest distance to the metal, is the cage vertex with the lowest connectivity in the framework. Moreover, the B(2) ··· B(8) [1.94(1) Å] and B(4) ··· B(8) [2.00(1) Å] separations, represented by dashed lines in Fig. 1, involve the high coordinate B(8) vertex and result in two quadrilateral faces about C(3). The low coordinate C(3) atom displays relatively short distances to B(2) [1.56(1) Å] and B(4) [1.53(1) Å]. The bonding of the carborane cage to the tungsten in the anion of **5b** is very similar to that in the anion $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]^-$. In the latter [5], the W–C (cage) distances are 2.26(1) Å and 2.56(1) Å; a difference of 0.30 Å, compared with 0.22 Å in **5b**.

The spectroscopic data for the complexes **5** are in agreement with the structure of **5b** established by X-ray diffraction. Thus in a limiting low temperature (220 K) ^1H NMR spectrum of **5a** there are two singlet resonances at $\delta = 1.77$ and 2.46 for the two non-equivalent cage methyl groups. Correspondingly, in the $^{13}C\{^1H\}$ NMR spectrum there are four resonances for the CMe groups at $\delta = 73.0$ and 62.5 (*C*Me), and at $\delta = 33.6$ and 32.8 (C*Me*). The three non-equivalent carbonyl

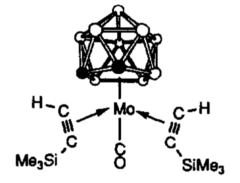
TABLE 2. ^1H, ^{13}C and ^{11}B NMR data for the new compounds [a]

Compound	 η^3-C_3H_5 δ (^1H) [b]	 η^1-C_3H_5 δ (^{13}C) [c]	δ (^{11}B) [d]
4a	1.12 [d, 2H, H_a, $J(H_aH_c) = 10$]; 2.04 (br s, 6H, Me); 2.45 [d, 2H, H_s, $J(H_sH_c) = 7$]; 4.66 [t of t, 1H, H_c, $J(HH) = 10, 7$]; 7.46–7.66 (m, 30H, Ph)	234.4 (CO), 134.1–126.8 (Ph), 85.5 (br, *C*Me), 75.6 (CH), 46.2 (CH_2), 34.8 (Me)	5.1 (1B), 1.4 (2B), −1.4 (1B), −3.2 (1B), −4.6 (2B), −7.6 (2B), −10.2 (1B)
4b	1.27 [d, 2H, H_a, $J(H_aH_c) = 10$]; 2.24 (br s, 6H, Me); 2.34 [d, 2H, H_s, $J(H_sH_c) = 7$]; 4.25 [t of t, 1H, H_c, $J(HH) = 10, 7$]; 7.45–7.68 (m, 30H, Ph)	223.0 (CO), 134.1–126.8 (Ph), 86.2 (br, *C*Me), 69.7 (CH), 38.4 (CH_2), 36.1 (Me)	4.5 (1B), −0.6 (1B), −1.3 (1B), −3.0 (1B), −4.6 (1B), −5.8 (3B), −7.0 (1B), −12.2 (1B)
5a [e]	1.77 (s, 3H, Me); 2.46 (s, 3H, Me); 7.41–7.64 (m, 30H, Ph)	234.7, 222.2, 216.1 (CO), 133.4–125.9 (Ph), 73.0, 62.5 (br, *C*Me), 33.6, 32.8 (Me)	11.2 (vbr, 1B), 3.1 (2B), 0.3 (2B), −1.5 (2B), −4.6 (2B), −12.4 (vbr, 1B)
5b [f]	1.95 (s, 3H, Me); 2.61 (s, 3H, Me); 7.43–7.63 (m, 30H, Ph)	223.2, 213.3, 207.1 (CO), 133.6–126.1 (Ph), 77.3, 67.6 (br, *C*Me), 34.3, 32.8 (Me)	8.6 (1B), 2.7 (2B), −0.7 (4B), −5.1 (2B), −12.7 (1B)
6a	1.59 (s, 6H, Me); 7.46–7.67 (m, 30H, Ph)	239.6 (CO), 229.5 (2 × CO), 134.1–126.8 (Ph), 68.4 (vbr, *C*Me), 31.5 (Me)	−3.9 (1B), −4.8 (1B), −5.3 (2B), −7.1 (2B), −10.6 (2B), −13.4 (1B)
7b [g]	4.42 [d of d, 1H, H^3, $J(H^3H^1) = 10$, $J(H^3H^2) = 3$]; 4.75 [d of d of t, 1H, H^2, $J(H^2H^1) = 17$, $J(H^2H^3) = 3$, $J(H^2H^4) = J(H^2H^5) = 1$]; 6.11 [d of d of t, 1H, H^1, $J(H^1H^2) = 17$, $J(H^1H^3) = 10$, $J(H^1H^4) = J(H^1H^5) = 9$]		

[a] Measured in CD_2Cl_2 at ambient temperatures unless otherwise stated. Chemical shifts (δ) in ppm and coupling constants (J) in Hz. [b] Proton resonances for terminal B–H groups occur as broad unresolved peaks in the range δ *ca.* −2 to +3. [c] Hydrogen-1 decoupled. Chemical shifts are positive to high frequency of $SiMe_4$. [d] Hydrogen-1 decoupled. 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. [e] Measured at 220 K. [f] Measured at 240 K. [g] Only peaks caused by the η^1-C_3H_5 group in the ^1H NMR spectrum are listed because of the instability of **7b** and the presence of impurities in the sample.



M
1a Mo
1b W



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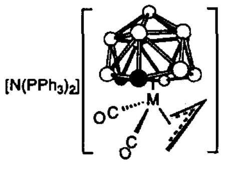
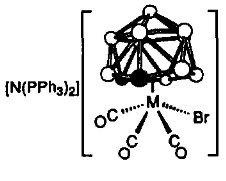
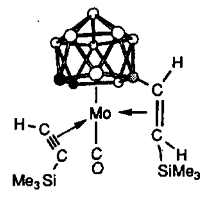


M
4a Mo
4b W

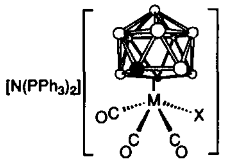


M
5a Mo
5b W

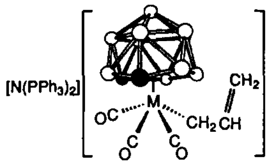


3

● CMe ○ BH ◉ B



M X
6a Mo Br
6b W I



M
7a Mo
7b W

● CMe ○ BH

ligands give signals at $\delta = 234.7$, 222.2, and 216.1. The NMR data for **5b** are similar to those of **5a** (Table 2).

During the preparation of the salt **5a**, a small amount of another species was detected in the product by IR spectroscopy. If a CH_2Cl_2 solution of **5a** was stirred at ambient temperatures for 10 days, this species could be isolated pure, and was identified as $[N(PPh_3)_2][MoBr(CO)_3(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$ (**6a**) by the data given in Tables 1 and 2. However, no similar product was observed in the reaction mixture in the synthesis of **5b**. The molybdenum complex **6a** is closely related to the tungsten species $[N(PPh_3)_2][WI(CO)_3(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$ (**6b**), the structure of which has been determined by X-ray diffraction [3b]. Compound **6b** was previously prepared by protonating $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ with aqueous HI solution; in this synthesis formally loss of both a BH vertex and a $C(H)C_6H_4Me\text{-}4$ fragment occurred. Evidently loss of a BH vertex occurs in the formation of **6a** from **5a**, a feature discussed further below.

The IR spectrum of **6a** shows three CO-stretching bands at 2026, 1943, and 1928 cm^{-1}, very similar to

TABLE 3. Selected bond lengths (Å) and angles (°) for $[N(PPh_3)_2][WBr(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ (**5b**)

W(1)-C(1)	2.445(6)	W(1)-B(2)	2.465(8)	W(1)-C(3)	2.224(7)	W(1)-B(4)	2.467(8)
W(1)-B(5)	2.449(7)	W(1)-B(6)	2.353(6)	W(1)-C(5)	1.967(6)	W(1)-C(6)	1.983(8)
W(1)-C(7)	1.990(7)	W(1)-Br	2.704(1)	C(1)-B(2)	1.712(9)	C(1)-B(6)	1.70(1)
C(1)-B(7)	1.69(1)	C(1)-B(11)	1.719(9)	C(1)-C(2)	1.56(1)	B(2)-C(3)	1.56(1)
B(2)-B(7)	1.766(9)	B(2) ··· B(8)	1.94(1)	C(3)-B(4)	1.53(1)	C(3)-B(8)	1.788(9)
C(3)-C(4)	1.548(9)	B(4)-B(5)	1.78(1)	B(4) ··· B(8)	2.00(1)	B(4)-B(9)	1.796(9)
B(5)-B(6)	1.83(1)	B(5)-B(9)	1.75(1)	B(5)-B(10)	1.741(9)	B(6)-B(10)	1.82(1)
B(6)-B(11)	1.81(1)	B(7)-B(8)	1.87(1)	B(8)-B(9)	1.86(1)	B(8)-B(12)	1.779(9)
C(5)-O(5)	1.167(9)	C(6)-O(6)	1.15(1)	C(7)-O(7)	1.17(1)		
C(1)-W(1)-B(2)	40.8(2)	B(2)-W(1)-C(3)	38.5(3)	C(3)-W(1)-B(4)	37.7(3)		
B(4)-W(1)-B(5)	42.4(2)	C(1)-W(1)-B(6)	41.4(3)	C(5)-W(1)-C(6)	76.0(3)		
C(5)-W(1)-C(7)	106.8(3)	C(6)-W(1)-C(7)	75.1(3)	C(5)-W(1)-Br	75.0(2)		
C(6)-W(1)-Br	127.2(2)	C(7)-W(1)-Br	72.5(2)	B(2)-C(1)-B(6)	121.2(5)		
C(1)-B(2)-C(3)	119.1(6)	B(2)-C(3)-B(4)	123.4(5)	C(3)-B(4)-B(5)	119.1(6)		
B(4)-B(5)-B(6)	116.3(6)	C(1)-B(6)-B(5)	113.8(5)	B(2)-B(8)-C(3)	49.3(4)		
B(2)-B(8)-B(4)	87.3(4)	C(3)-B(8)-B(4)	47.3(4)	B(2)-B(8)-B(7)	55.1(4)		
C(3)-B(8)-B(7)	102.9(5)	C(3)-B(8)-B(9)	101.0(5)	B(7)-B(8)-B(9)	104.4(5)		
C(3)-B(8)-B(12)	136.3(6)	B(4)-B(8)-B(12)	106.9(5)	W(1)-C(5)-O(5)	175.9(6)		
W(1)-C(6)-O(6)	179.5(4)	W(1)-C(7)-O(7)	175.8(6)				

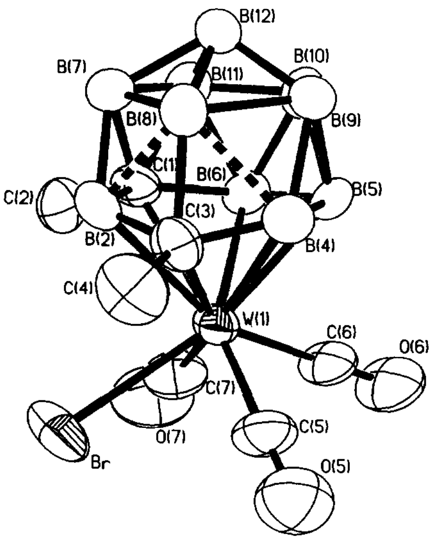


Fig. 1. ORTEP view of the anion of the salt $[N(PPh_3)_2][WBr(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ (**5b**), showing the crystallographic atom-labelling scheme. Thermal ellipsoids are shown at 50% probability level.

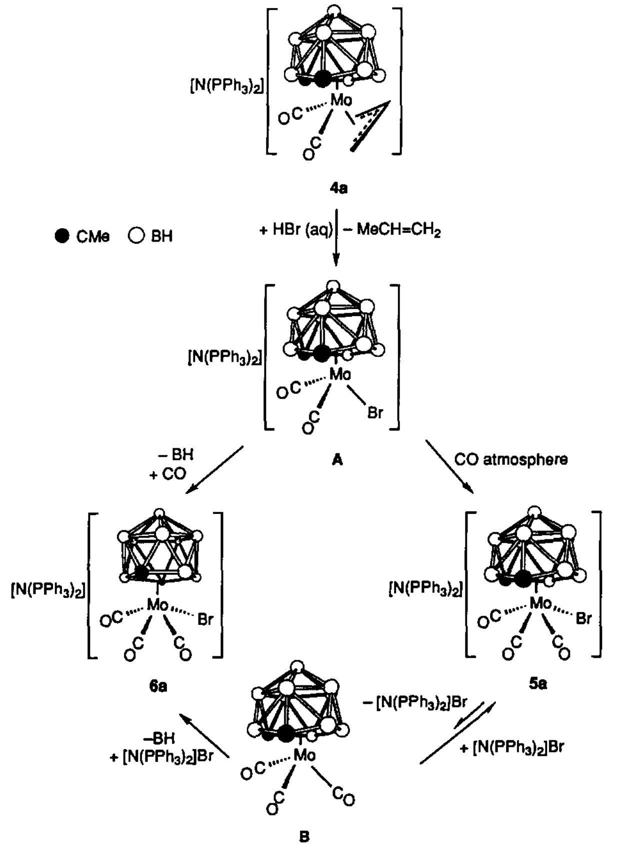
those of **6b** (2013, 1930, and 1910 cm^{-1}) [3b]. The relatively lower frequencies of the CO bands for **6a** as compared with those for **5a** suggest that the η^5-7,9-$C_2B_9H_9Me_2$ group is a better electron donor than the η^6-7,9-$C_2B_{10}H_{10}Me_2$ ligand. In the ^1H NMR spectrum of **6a**, there is only one resonance ($\delta = 1.59$) for the two CMe groups, because they are equivalent as a result of the anion having a plane of symmetry through the Mo and Br atoms, the CO ligand transoid to the Br atom, and the boron atom between the two carbons in the open face of the cage. Correspondingly, the $^{13}C\{^1H\}$ NMR spectrum shows two signals for the CMe groups at $\delta = 68.4$ (*C*Me) and 31.5 (C*Me*). The resonances at $\delta = 239.6$ and 229.5 are assigned to the three carbonyl ligands. Since the latter signal is appreciably more intense, it can be ascribed to the two equivalent transoid carbonyl groups of the $MoBr(CO)_3$ moiety.

Treatment of $[Y]_2[M(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ [Y = Tl or $N(PPh_3)_2$, M = Mo or W] with allyl bromide affords only the allyl complexes **1a** or **1b**. Formation of the bromo complexes **5a** and **5b** from the corresponding reaction between allyl bromide and $[N(PPh_3)_2]_2[M(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ is therefore interesting. These reactions may proceed through intermediates $[N(PPh_3)_2][M(\eta^1\text{-}CH_2CH{=}CH_2)(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ [M = Mo (**7a**) or W (**7b**)] having σ-bonded allyl groups, which might react with the allyl bromide present in the solutions to yield the complexes **5** with loss of $CH_2{=}C(H)CH_2CH_2C(H){=}CH_2$. There is ample precedent for allyl group coupling of this kind in allylnickel chemistry, for example, the reaction between $[Ni_2(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_4Me\text{-}2)_2]$ and $CH_2{=}C(Me)CH_2Br$ gives $NiBr_2$ and $CH_2{=}C(Me)CH_2CH_2C(Me){=}CH_2$ [8].

In the synthesis of the complexes **5**, described above, monitoring the reactions by IR spectroscopy revealed the presence of intermediates which were very unstable and therefore could not be isolated in pure form. However, the intermediates displayed three CO-stretching bands in their IR spectra (see Experimental section), as expected for the formulations proposed. An attempt was made to isolate the proposed intermediate **7b**, which is more stable than **7a**, by employing one mole equivalent of allyl bromide in the reaction. Selected ^1H NMR data suggests the presence of an η^1-C_3H_5 ligand. Thus although signals for the WCH_2 group were obscured by other peaks, resonances due to a vinyl group were clearly discernible with characteristic signals at $\delta = 4.42$ [d of d, C(H)=C(*H*)H, *J*(*cis*-HH) = 10 Hz, *J*(*gem*-HH) = 3 Hz]; 4.75 [d of d of t, C(H)=C(H)*H*, *J*(*trans*-HH) = 17 Hz, *J*(*gem*-HH) = 3 Hz, *J*(H–CH_2) = 1 Hz and 1 Hz]; 6.11 [d of d of t, C(*H*)=C(H)H, *J*(*trans*-HH) = 17 Hz, *J*(*cis*-HH) = 10 Hz, *J*(H–CH_2) = 9 Hz and 9 Hz].

As reported previously [1b], when the salts **1a** and **1b** are protonated with aqueous HI, in the presence of an atmosphere of CO, the salts $[N(PPh_3)_2][MoI(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ and $[N(PPh_3)_2][WI(CO)_3(\eta^5\text{-}2,8\text{-}C_2B_9H_9Me_2)]$ are formed. In the tungsten species the cage has rearranged from an η^5-*nido*-7,8-C_2B_9 configuration in the precursor to an η^5-*nido*-2,8-C_2B_9 framework in the product. It was, therefore, of interest to investigate the protonation of complexes **4a** and **4b**. Treatment of these compounds with aqueous HBr solution in the presence of CO, gave the salts **5a** and **5b** respectively, in excellent yields. As mentioned above, compound **5a** degrades slowly in solution to afford **6a** by loss of a BH fragment. However, if the above reactions were carried out in the absence of CO, in the case of **4a**, complex **6a** was isolated and **5a** was not observed. In contrast, in the protonation of **4b**, complex **5b** formed as the major product, together with an unidentified carborane-containing species.

These results parallel our earlier observations concerning protonation reactions of the alkylidyne(carborane)tungsten complex $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ [3a,c]. Thus, in the presence of CO, protonation of the latter initially gives a 4 : 1 mixture of $[W(CO)_4\{\eta^6\text{-}7,9\text{-}C_2B_{10}H_9Me_2\text{-}11\text{-}(CH_2C_6H_4Me\text{-}4)\}]$ and $[W(CO)_4(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$, whereas in the absence of CO only the latter species having a *nido*-11-vertex C_2B_9 cage is obtained. Furthermore, it was observed that $[W(CO)_4\{\eta^6\text{-}7,9\text{-}C_2B_{10}H_9Me_2\text{-}11\text{-}(CH_2C_6H_4Me\text{-}4)\}]$ slowly converts to $[W(CO)_4(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$ in CH_2Cl_2 solution, a



Scheme 1.

process involving loss of a BH fragments as well as a $C(H)C_6H_4Me$-4 moiety [3c].

A possible pathway for loss of a BH fragment in some of the reactions discussed above is summarised in Scheme 1. Thus, when complex **4a** is protonated with aqueous HBr solution, release of propene would occur [1a], and an unstable 16-electron intermediate **A** might form. In the absence of a CO atmosphere, intermediate **A** might eliminate a BH vertex and then subsequently scavenge a molecule of CO from other species in the solution to form **6a**, in which the metal has the stable 18-electron shell. The driving force for loss of the BH fragment could be the formation of the η^5-7,9-$C_2B_9H_9Me_2$ group which is a better electron donor, as discussed above, than the η^6-7,9-$C_2B_{10}H_{10}Me_2$ ligand present in **A**. Alternatively, if an atmosphere of CO is present, the species **A** could afford the 18-electron molybdenum complex **5a** before it has time to collapse with loss of a BH fragment to yield **6a**. In solution, complex **5a** could form the 16-electron species **B** through loss of bromide as $[N(PPh_3)_2]Br$. Like the intermediate **A**, species **B** could then eject a BH fragment and react with bromide from $[N(PPh_3)_2]Br$ to form **6a**, as shown.

3. Experimental details

All reactions were conducted under 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) were packed with silica gel (Aldrich, 70–230 mesh). The reagents $[MBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ [9] and $[N(PPh_3)_2]_2[M(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ (M = Mo or W) [10] were prepared by literature methods. The NMR measurements were made using a Bruker AMX 360 spectrometer (frequencies of measurement: ^{11}B, 115.5 MHz and ^{13}C, 90.6 MHz), and IR spectra were recorded with a Bruker IFS 25 FT-IR instrument. Analytical and other data for the new compounds are given in Table 1.

3.1. Preparation of the compounds $[N(PPh_3)_2][M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$

(i) To a THF (20 cm^3) solution of 1,2-$C_2B_{10}H_{10}Me_2$- (0.20 g, 1.16 mmol) were added Na cuttings (*ca.* 0.4 g, 17.4 mmol) and a trace amount of $C_{10}H_8$, and the mixture was stirred at room temperature for 2 h. The solution of $Na_2[7,9\text{-}C_2B_{10}H_{10}Me_2]$ so formed was then added to a THF (20 cm^3) solution of $[MoBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ (0.45 g, 1.27 mmol) at room temperature. The mixture was stirred for 0.5 h, $[N(PPh_3)_2]Cl$ (0.70 g, 1.22 mmol) was added and the mixture was stirred for a further 1 h. Solvent was removed *in vacuo*, the residue was extracted with CH_2Cl_2 (10 cm^3) and the extract chromatographed at −20°C. Elution with CH_2Cl_2 gave a yellow-brown eluate. Solvent was removed *in vacuo* and the product was washed with Et_2O (2 × 10 cm^3) and dried *in vacuo* to afford yellow *microcrystals* of $[N(PPh_3)_2][Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ (**4a**) (0.66 g).

(ii) Similarly, yellow *microcrystals* of $[N(PPh_3)_2][W(CO)_2(\eta^3\text{-}C_3H_5)(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ (**4b**) (0.87 g) were isolated from the reaction between $[WBr(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ (0.55 g, 1.24 mmol) and $Na_2[7,9\text{-}C_2B_{10}H_{10}Me_2]$ (1.16 mmol) using the procedure described above, with addition of $[N(PPh_3)_2]Cl$ (0.70 g, 1.22 mmol).

3.2. Reactions of the salts $[N(PPh_3)_2]_2[M(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ with allyl bromide

(i) A THF (20 cm^3) solution of $[N(PPh_3)_2]_2[Mo(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ (0.10 g, 0.07 mmol) was treated with allyl bromide (0.2 cm^3, 2.31 mmol) at room temperature. Reaction occurred instantly, and after 10 min an intermediate with $\nu_{max}(CO)$ at 2008vs, 1950vs and 1925vs cm^{-1} was observed. The mixture was stirred at room temperature for 12 h. Solvent was removed *in vacuo*, and the residue was extracted with CH_2Cl_2 : light petroleum (10 cm^3, 3 : 2) and chromatographed 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 $[N(PPh_3)_2][MoBr(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ (**5a**) (0.03 g).

(ii) Yellow *microcrystals* of $[N(PPh_3)_2][WBr(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ (**5b**) (0.03 g) were obtained by the same procedure from $[N(PPh_3)_2]_2[W(CO)_3(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ (0.10 g, 0.07 mmol) and allyl bromide (0.2 cm^3, 2.31 mmol). After 10 min the reaction mixture showed $\nu_{max}(CO)$ at 2006vs, 1942s and 1918vs cm^{-1}.

3.3. *Protonation of the complexes* $[N(PPh_3)_2][M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ *with aqueous HBr solution*

(i) A CH_2Cl_2 (20 cm^3) solution of **4a** (0.10 g, 0.11 mmol) at room temperature was saturated with CO gas and treated with HBr (0.50 cm^3, 48% aqueous solution, 4.42 mmol). The mixture was stirred for 0.5 h under CO. Solvent was removed *in vacuo*, and the complex **5a** (0.09 g) was then isolated, as described above.

(ii) Similarly, a CH_2Cl_2 (20 cm^3) solution of **4b** (0.10 g, 0.10 mmol) was saturated with CO at room temperature and treated with HBr (0.50 cm^3, 48% aqueous solution, 4.42 mmol). The mixture was stirred for 0.5 h under CO. Solvent was removed *in vacuo*, and the complex **5b** (0.10 g) was isolated, as described above.

(iii) A CH_2Cl_2 (20 cm^3) solution of **4a** (0.10 g, 0.11 mmol) was treated with HBr (0.50 cm^3, 48% aqueous solution, 4.42 mmol) at room temperature. The mixture was stirred for 0.5 h, and solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 : light petroleum (10 cm^3, 3 : 2) and the extract chromatographed at −20°C. Elution with the same solvent mixture gave an orange eluate. Solvent was removed *in vacuo* and the product was dried *in vacuo* to give orange *microcrystals* of $[N(PPh_3)_2][MoBr(CO)_3(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$ (**6a**) (0.07 g).

Complex **6a** can also be prepared by stirring a CH_2Cl_2 solution of **5a** at room temperature for 10 days. The yield by this method is *ca.* 60%.

3.4. *Crystal structure determination*

Light yellow rectangular crystals of complex **5b** were grown from CH_2Cl_2 : light petroleum (1 : 5), and that chosen for study had dimensions *ca.* 0.13 mm × 0.28 mm × 0.36 mm. Diffracted intensities were collected with an Enraf-Nonius CAD4-F diffractometer (292 K, Mo–Kα X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.71073 Å). Of the 4658 data collected (ω-2θ scans, 3.0° ≤ 2θ ≤ 40.0°), 3900 unique data had $F \geq 4\sigma(F)$, and only these were used for structure solution and refinement. The data were corrected for Lorentz, polarisation and X-ray absorption effects, the latter by a method based upon azimuthal scan data [11].

TABLE 4. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2 × 10^3) for the anion of complex **5b**

Atom	x	y	z	U_{eq} [a]
W(1)	1113(1)	4608(1)	3024(1)	45(1)
C(1)	198(7)	3985(4)	1673(4)	48(1)
B(2)	2097(7)	4205(5)	1802(4)	48(1)
C(3)	3026(7)	3979(5)	2504(4)	55(1)
B(4)	2526(8)	3192(5)	2880(4)	52(1)
B(5)	589(7)	2887(5)	2848(4)	44(1)
B(6)	−675(7)	3431(5)	2247(4)	45(1)
B(7)	1148(8)	3248(5)	1084(4)	54(1)
B(8)	2616(8)	2914(5)	1761(4)	51(1)
B(9)	1580(8)	2132(5)	2238(4)	52(1)
B(10)	−304(8)	2189(6)	1983(4)	59(1)
B(11)	−557(8)	2835(6)	1271(4)	58(1)
B(12)	996(8)	2146(5)	1306(5)	57(1)
C(2)	−604(7)	4711(5)	1293(4)	64(1)
C(4)	4677(7)	4394(5)	2678(5)	77(1)
C(5)	2457(7)	5071(5)	3986(4)	69(1)
O(5)	3321(7)	5317(5)	4536(4)	107(1)
C(6)	−113(8)	4381(5)	3802(4)	71(1)
O(6)	−824(6)	4243(4)	4251(3)	101(1)
C(7)	−451(7)	5512(5)	3023(4)	70(1)
O(7)	−1413(7)	6003(5)	2981(4)	118(1)
Br	2441(1)	6292(1)	2933(1)	86(1)

[a] Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.5. *Crystal data*

$C_{43}H_{46}B_{10}BrNO_3P_2W$, M = 1058.6, triclinic, space group $P\bar{1}$, a = 9.081(3) Å, b = 14.4939(10) Å, c = 18.2993(16) Å, α = 103.474(6)°, β = 96.956(14)°, γ = 93.554(13)°, U = 2311.9(8) Å^3, Z = 2, D_c = 1.521 g cm^{-3}, $F(000)$ = 1048, μ(Mo–Kα) = 35.14 cm^{-1}.

The structure was solved by conventional heavy-atom methods, and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. All hydrogen atoms were included at geometrically calculated positions (C–H 0.96 Å and B–H 1.10 Å) and allowed to ride on the parent carbon or boron [12] atom with fixed isotropic thermal parameters (U_{iso} = 0.08 and 0.06 Å^2, respectively). Calculations were performed using the SHELXTL-PC package of programs [11]. Refinement by blocked full-matrix least-squares converged at R = 0.038 (R' = 0.041) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0020|F|^2]$ gave a satisfactory analysis of variance. Atom coordinates for the anion of **5b** are listed in Table 4. Atomic scattering factors are from Ref. 13. The final electron-density difference synthesis showed no peaks greater than 1.36 e Å^{-3} or less than -0.95 e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles. Observed and calculated structure factors are available from the authors.

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