Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 110.[1] Synthesis of Compounds with Tungsten–Copper or –Gold Bonds; Crystal Structure of $[NEt_4][W_2Cu(\mu\text{-}CC{\equiv}CBu^t)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]\cdot Et_2O$ ‡

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Treatment of the reagents $[NEt_4][W({\equiv}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ in CH_2Cl_2 with 1 equivalent of CuCl or [AuCl(tht)] (tht = tetrahydrothiophene) affords the labile complexes $[NEt_4][WMCl(\mu\text{-}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (M = Cu or Au, R = C_6H_4Me-4 or $C{\equiv}CBu^t$). Use of 2 equivalents of CuCl yields the stable tungstendicopper species $[NEt_4][WCu_2Cl_2(\mu_3\text{-}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, which may also be obtained by adding 1 equivalent of CuCl to the tungsten–copper dimetal compounds in CH_2Cl_2. Reactions of the salts $[NEt_4][WCuCl(\mu\text{-}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ with CNR′ in CH_2Cl_2 in the presence of $TlBF_4$ yields the neutral complexes $[WCu(\mu\text{-}CR)(CO)_2(CNR')(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4Me-4 or $C{\equiv}CBu^t$, R′ = $C_6H_3Me_2$-2,6; R = $C{\equiv}CBu^t$, R′ = Bu^t). The trimetal compounds $[NEt_4][W_2M(\mu\text{-}CR)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ (M = Cu, R = C_6H_4Me-4 or $C{\equiv}CBu^t$; M = Au, R = $C{\equiv}CBu^t$) have been prepared by treating, in CH_2Cl_2, 2 equivalents of the reagents $[NEt_4][W({\equiv}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ with 1 equivalent of CuCl or [AuCl(tht)] in the presence of $TlBF_4$. An X-ray diffraction study of the salt $[NEt_4][W_2Cu(\mu\text{-}CC{\equiv}CBu^t)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ revealed a novel structure in the crystal. The anion has a W_2Cu spine [W–Cu 2.602(1) and 2.764(1) Å, W–Cu–W 152.7(1)°] with each metal–metal bond asymmetrically bridged by a $CC{\equiv}CBu^t$ group [μ-C–W 1.85(1), μ-C–Cu(av.) 2.08(1) Å; W-μ-C–$CCBu^t$(av.) 169.5(1)°]. The shorter of the two W–Cu separations is also spanned by a $C_2B_9H_9Me_2$ cage. As expected the latter is η^5 co-ordinated to the tungsten atom, but it also forms an exopolyhedral B–H$\rightharpoonup$Cu three-centre two-electron bridge bond employing the boron atom β to the carbon atoms in the pentagonal CCB*B*B face of the cage [μ-B–W 2.36(1), μ-B–Cu 2.33(1) Å]. The other tungsten atom is ligated by a $C_2B_9H_9Me_2$ group in the normal η^5 bonding mode, and both tungstens carry two terminally bound CO groups. The reaction between $[W({\equiv}CC{\equiv}CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Pt(nb)_3]$ (nb = norbornene = bicyclo[2.2.1]heptene) affords the compound $[W_2Pt(\mu\text{-}CC{\equiv}CBu^t)_2(CO)_4(\eta\text{-}C_5H_5)_2]$. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR data for the new compounds are reported and discussed.

In previous papers[1,2] in this series we have shown that the alkylidynetungsten compounds $[W({\equiv}CR)(CO)_2L]$ {R = alkyl, alkynyl or aryl; L = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$, $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate] or $XC(pz)_3$ (X = C_6F_5Au or BF_3)} add metal–ligand fragments to afford numerous di-, tri- or polynuclear metal complexes. Parallel studies have been initiated with the anionic complexes $[W({\equiv}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]^-$ (R′ = Me or H). With these reagents the carbaborane ligand frequently plays an interesting non-spectrator role, which generally takes the form of the cage adopting an η^5 co-ordination mode to the tungsten *via* its open pentagonal face while simultaneously forming an exopolyhedral B–H$\rightharpoonup$M (metal) bond with another metal centre.[3]

The majority of complexes isolated when employing either $[W({\equiv}CR)(CO)_2L]$ or $[W({\equiv}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ as reagents for preparing polynuclear metal compounds have bonds between tungsten and another transition element.[4] However, some tungsten–copper and –gold species have also been prepared by adding $Cu(\eta\text{-}C_5Me_5)$, $M(PPh_3)$ (M = Cu or Au) or AuX (X = Cl or C_6F_5) fragments to C≡W groups.[5–7] The latter also co-ordinate to Au or Cu atoms derived from the reagents [AuCl(tht)][5b,d] (tht = tetrahydrothiophene) or $[Cu(NCMe)_4][PF_6]$,[7] respectively. Examples of compounds recently isolated containing W–Au bonds include the species $[WAuX(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ **1** [X = Cl, $Mn(CO)_5$, $Co(CO)_4$ or $Rh(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)$], $[WRh_2Au_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **2**,[8] $[MoWCoAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **3**[9] and $[W_2Au(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **4**.[5e] In this paper we describe the synthesis of several new di- and tri-metal compounds containing W–Cu bonds, as well as some species with W–Au linkages.

Results and Discussion

Treatment of CH_2Cl_2 solutions of the reagents $[NEt_4][W({\equiv}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4Me-4 or $C{\equiv}CBu^t$) with CuCl or [AuCl(tht)] affords the complexes $[NEt_4][WMCl(\mu\text{-}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5a** (M = Cu, R = C_6H_4Me-4), **5b** (M = Cu, R = $C{\equiv}CBu^t$), **5c** (M = Au, R = C_6H_4Me-4) and **5d** (M = Au, R = $C{\equiv}CBu^t$). All four compounds readily decompose, both in solution and in the solid state, and consequently satisfactory microanalytical data were not obtained. However, these species could be identified by their spectroscopic properties leaving no doubt of their formation.

In their IR spectra they display the expected two CO

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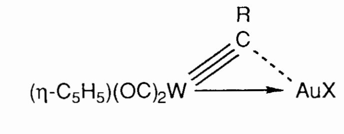
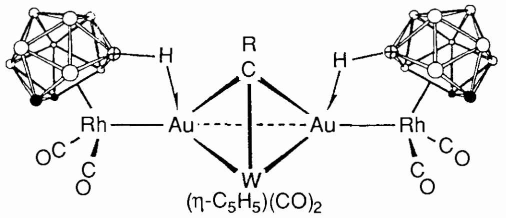
‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



	X
1a	Cl
1b	Mn(CO)$_5$
1c	Co(CO)$_4$
1d	Rh(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)



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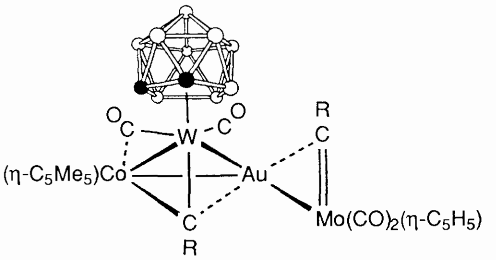

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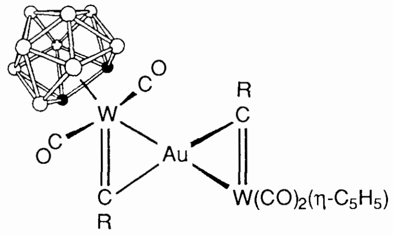

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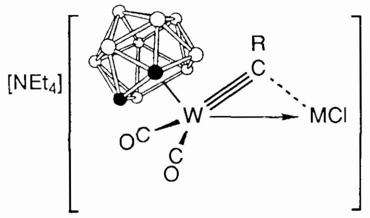
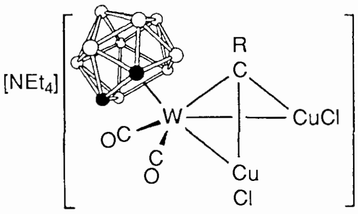
● CMe ○ BH ⊕ B

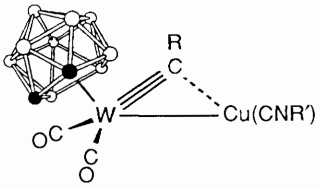
R = C_6H_4Me-4



	M	R
5a	Cu	C$_6$H$_4$Me-4
5b	Cu	C≡CBu^t
5c	Au	C$_6$H$_4$Me-4
5d	Au	C≡CBu^t



	R
6a	C$_6$H$_4$Me-4
6b	C≡CBu^t



	R	R′
7a	C$_6$H$_4$Me-4	C$_6$H$_3$Me$_2$-2,6
7b	C≡CBu^t	C$_6$H$_3$Me$_2$-2,6
7c	C≡CBu^t	Bu^t

stretching bands (Table 1), and these absorptions occur at somewhat higher frequencies than those seen in the spectra of the tungsten precursors. Thus in the spectrum of [NEt$_4$][W(≡CC≡CBu^t)(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)] the carbonyl bands are observed[10] at 1886 and 1968 cm^{-1}, and these absorptions may be compared with those for the compounds **5b** (1916 and 1988 cm^{-1}) and **5d** (1932 and 2000 cm^{-1}). In addition, the spectrum of compound **5b** shows a C≡C stretch at 2134 cm^{-1}, confirming that the CuCl fragment is ligated by the C≡W group and not the C≡C bond.

The ^{1}H and ^{13}C-{^{1}H} NMR spectra (Table 2) were necessarily measured on freshly prepared solutions. In the ^{13}C-{^{1}H} spectra of the tungsten–gold complexes resonances for the alkylidyne μ-C nuclei are seen at δ 283.1 (**5c**) and 244.0 (**5d**), and these signals may be compared with those for the W≡CR groups in the precursors at δ 298.3 (R = C$_6$H$_4$Me-4)[5d] and 269.0 (R = C≡CBu^t).[10] It is noteworthy that resonances for CR nuclei are appreciably more shielded if the substituent R is the alkynyl group C≡CBu^t rather than alkyl or aryl.[11a] It is also interesting to compare the ^{13}C-{^{1}H} NMR chemical shift of the μ-C group in the neutral complex [WAu(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (δ 292.9)[5d] with that for the salt **5c** (283.1). The μ-C resonance for the tungsten–copper species **5a** was not observed, probably because of the

Table 1 Analytical[a] and physical data for the complexes

Compound	Colour	Yield (%)	ν_{max}(CO)[b]/cm^{-1}	Analysis (%) C	H	N
5a $[\mathrm{NEt_4}][\mathrm{WCuCl}(\mu\text{-}\mathrm{CC_6H_4Me}\text{-}4)(\mathrm{CO})_2(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$[c]	Orange	84	1983vs, 1910s			
5b $[\mathrm{NEt_4}][\mathrm{WCuCl}(\mu\text{-}\mathrm{CC{\equiv}CBu^t})(\mathrm{CO})_2(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$[c]	Red	97	1988s, 1916vs			
5c $[\mathrm{NEt_4}][\mathrm{WAuCl}(\mu\text{-}\mathrm{CC_6H_4Me}\text{-}4)(\mathrm{CO})_2(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$[c]	Brown	97	1991vs, 1923s			
5d $[\mathrm{NEt_4}][\mathrm{WAuCl}(\mu\text{-}\mathrm{CC{\equiv}CBu^t})(\mathrm{CO})_2(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$[c]	Brown	98	2000vs, 1932vs			
6a $[\mathrm{NEt_4}][\mathrm{WCu_2Cl_2}(\mu_3\text{-}\mathrm{CC_6H_4Me}\text{-}4)(\mathrm{CO})_2(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$	Orange	89	2009vs, 1947s	30.9 (31.7)	5.8 (5.1)	1.6 (1.7)
6b $[\mathrm{NEt_4}][\mathrm{WCu_2Cl_2}(\mu_3\text{-}\mathrm{CC{\equiv}CBu^t})(\mathrm{CO})_2(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$	Red	97	2009vs, 1949s	30.2 (30.7)	6.3 (5.4)	1.8 (1.7)
7a $[\mathrm{WCu}(\mu\text{-}\mathrm{CC_6H_4Me}\text{-}4)(\mathrm{CO})_2(\mathrm{CNC_6H_3Me_2}\text{-}2,6)\text{-}(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$	Orange	57	[d] 1995vs, 1924vs	38.7 (39.6)	4.4 (4.5)	1.7 (2.0)
7b $[\mathrm{WCu}(\mu\text{-}\mathrm{CC{\equiv}CBu^t})(\mathrm{CO})_2(\mathrm{CNC_6H_3Me_2}\text{-}2,6)(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$	Red	69	[e] 1999vs, 1930vs	37.4 (38.4)	4.2 (4.8)	1.6 (2.0)
7c $[\mathrm{WCu}(\mu\text{-}\mathrm{CC{\equiv}CBu^t})(\mathrm{CO})_2(\mathrm{CNBu^t})(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$	Red	70	[f] 1998vs, 1928vs	34.4 (33.8)	4.4 (5.2)	1.8 (2.2)
8a $[\mathrm{NEt_4}][\mathrm{W_2Cu}(\mu\text{-}\mathrm{CC_6H_4Me}\text{-}4)_2(\mathrm{CO})_4(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})_2]$	Brown	43	1987vs, 1916vs	36.4 (36.0)	6.3 (5.4)	1.5 (1.1)
8b $[\mathrm{NEt_4}][\mathrm{W_2Cu}(\mu\text{-}\mathrm{CC{\equiv}CBu^t})_2(\mathrm{CO})_4(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})_2]$	Red	61	[g] 1991s, 1926vs	[h] 36.4 (36.4)	5.7 (6.3)	0.9 (1.1)
8c $[\mathrm{NEt_4}][\mathrm{W_2Au}(\mu\text{-}\mathrm{CC{\equiv}CBu^t})_2(\mathrm{CO})_4(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})_2]$	Red	55	[g] 2001vs, 1936s	30.4 (30.1)	4.7 (5.2)	0.8 (1.1)
9 $[\mathrm{W_2Pt}(\mu\text{-}\mathrm{CC{\equiv}CBu^t})_2(\mathrm{CO})_4(\eta\text{-}\mathrm{C_5H_5})_2]$	Brown	83	1950vs, 1840m (br)	34.2 (33.9)	2.8 (2.9)	

[a] Calculated values are given in parentheses. [b] Measured in $\mathrm{CH_2Cl_2}$, unless otherwise stated. [c] Compounds unstable, see text. [d] ν_{max}(NC) at 2183 cm^{-1}. [e] ν_{max}(NC) at 2184 cm^{-1}. [f] ν_{max}(NC) at 2177 cm^{-1}. [g] Measured in $\mathrm{Et_2O}$. [h] Crystallised with 1 molecule of $\mathrm{Et_2O}$.

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

Compound	^{1}H (δ)	^{13}C[b] (δ)
5a	1.25 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, J(HH) 7, J(NH) 2], 2.22 (s, 6 H, CMe), 2.30 (s, 3 H, Me-4), 3.14 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, J(HH) 7], 7.14, 7.67 [$(\mathrm{AB})_2$ 4 H, $\mathrm{C_6H_4}$, J(AB) 8]	[c,d]220.7 (CO), 140.9 [$\mathrm{C^1(C_6H_4)}$], 139.2, 130.1, 128.8 ($\mathrm{C_6H_4}$), 64.6 (CMe), 30.6 (CMe), 21.7 (Me-4), 7.7 ($\mathrm{NCH_2}\mathit{Me}$)
5b	1.30 (s, 9 H, $\mathrm{Bu^t}$), 1.31 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, J(HH) 7, J(NH) 2], 2.14 (s, 6 H, CMe), 3.23 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, J(HH) 7]	248.3 (vbr, μ-C), 220.6 (CO), 103.2 (vbr, $\mathrm{C{\equiv}}\mathit{C}\mathrm{Bu^t}$), 99.8 ($\mathit{C}\mathrm{{\equiv}CBu^t}$), 64.5 ($\mathit{C}$Me), 52.7 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 30.3 (C$\mathit{Me}$), 29.8 ($\mathrm{C}\mathit{Me}_3$), 29.2 ($\mathit{C}\mathrm{Me_3}$), 7.6 ($\mathrm{NCH_2}\mathit{Me}$)
5c	1.29 (mbr, 12 H, $\mathrm{NCH_2}\mathit{Me}$), 2.37 (s, 6 H, CMe), 2.38 (s, 3 H, Me-4), 3.17 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, J(HH) 7], 7.21, 7.87 [$(\mathrm{AB})_2$, 4 H, $\mathrm{C_6H_4}$, J(AB) 8]	283.1 (μ-C), 221.2 (CO), 149.0 [$\mathrm{C^1(C_6H_4)}$], 141.6, 130.9, 129.0 ($\mathrm{C_6H_4}$), 67.0 (CMe), 53.3 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 31.5 (C$\mathit{Me}$), 21.6 (Me-4), 7.8 ($\mathrm{NCH_2}\mathit{Me}$)
5d	1.33 (s, 9 H, $\mathrm{Bu^t}$), 1.36 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, J(HH) 7, J(NH) 2], 2.35 (s, 6 H, CMe), 3.25 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, J(HH) 7]	244.0 (μ-C), 219.8 (CO), 108.4 ($\mathrm{C{\equiv}}\mathit{C}\mathrm{Bu^t}$), 98.3 ($\mathit{C}\mathrm{{\equiv}CBu^t}$), 67.5 ($\mathit{C}$Me), 52.8 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 30.4 (C$\mathit{Me}$), 30.0 ($\mathrm{C}\mathit{Me}_3$), 29.8 ($\mathit{C}\mathrm{Me_3}$), 7.8 ($\mathrm{NCH_2}\mathit{Me}$)
6a	1.30 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, J(HH) 7, J(NH) 2], 2.12 (s, 6 H, CMe), 2.30 (s, 3 H, Me-4), 3.22 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, J(HH) 7], 7.11, 7.75 [$(\mathrm{AB})_2$, 4 H, $\mathrm{C_6H_4}$, J(AB) 8]	[c]215.4 (CO), 151.5 [$\mathrm{C^1(C_6H_4)}$], 139.8, 130.3, 128.6 ($\mathrm{C_6H_4}$), 67.8 (CMe), 52.8 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 30.9 (C$\mathit{Me}$), 21.7 (Me-4), 7.6 ($\mathrm{NCH_2}\mathit{Me}$)
6b	1.33 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, J(HH) 7, J(NH) 2], 1.41 (s, 9 H, $\mathrm{Bu^t}$), 2.32 (s, 6 H, CMe), 3.26 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, J(HH) 7]	219.4 (μ-C), 214.9 (CO), 115.0 ($\mathrm{C{\equiv}}\mathit{C}\mathrm{Bu^t}$), 104.1 ($\mathit{C}\mathrm{{\equiv}CBu^t}$), 67.2 (br, CMe), 53.2 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 31.3 (C$\mathit{Me}$), 30.9 ($\mathrm{C}\mathit{Me}_3$), 30.5 ($\mathit{C}\mathrm{Me_3}$), 8.0 ($\mathrm{NCH_2}\mathit{Me}$)
7a	2.16 (s, 6 H, CMe), 2.25 (s, 6 H, $\mathrm{Me_2}$-2,6), 2.31 (s, 3 H, Me-4), 7.11, 7.57 (m, 7 H, $\mathrm{C_6H_4}$ and $\mathrm{C_6H_3}$)	282.7 (μ-C), 218.1 (CO), 151.8 [$\mathrm{C^1(C_6H_4)}$], 146.9 (br, CN), 139.8–124.6 ($\mathrm{C_6H_4}$ and $\mathrm{C_6H_3}$), 65.1 (CMe), 30.3 (CMe), 21.5 (Me-4), 18.3 ($\mathrm{Me_2}$-2,6)
7b	1.22 (s, 9 H, $\mathrm{Bu^t}$), 2.20, 2.51 (s × 2, 12 H, CMe and $\mathrm{Me_2}$-2,6), 7.21–7.38 (m, 3 H, $\mathrm{C_6H_3}$)	248.6 (br, μ-C), 218.6 (CO), 147.5 (CN), 136.1, 130.8, 128.5, 125.2 ($\mathrm{C_6H_3}$), 103.2 (br, $\mathrm{C{\equiv}}\mathit{C}\mathrm{Bu^t}$), 100.5 ($\mathit{C}\mathrm{{\equiv}CBu^t}$), 65.5 ($\mathit{C}$Me), 30.5 (C$\mathit{Me}$), 29.7 ($\mathrm{C}\mathit{Me}_3$ and $\mathit{C}\mathrm{Me_3}$)
7c	1.35 (s, 9 H, $\mathrm{Bu^t}$), 1.38 (s, 9 H, $\mathrm{CNBu^t}$), 2.18 (s, 6 H, CMe)	249.4 (br, μ-C), 220.0 (CO), 135.0 (br, CN), 102.3 (br, $\mathrm{C{\equiv}}\mathit{C}\mathrm{Bu^t}$), 100.2 ($\mathit{C}\mathrm{{\equiv}CBu^t}$), 65.0 ($\mathit{C}$Me), 57.7 ($\mathrm{N}\mathit{C}\mathrm{Me_3}$), 30.6 (C$\mathit{Me}$), 30.0, 29.8 (2 × $\mathrm{C}\mathit{Me}_3$), 29.7 ($\mathrm{C{\equiv}C}\mathit{C}\mathrm{Me_3}$)
8a	1.24 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, J(HH) 7, J(NH) 2], 2.20 (sbr, 12 H, CMe), 2.30 (s, 6 H, Me-4), 3.17 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, J(HH) 7], 6.95–7.20 (mbr, 8 H, $\mathrm{C_6H_4}$)	289.7 (μ-C), 222.0 (CO), 150.7 [$\mathrm{C^1(C_6H_4)}$], 139.9, 129.6, 128.7 ($\mathrm{C_6H_4}$), 64.7 (CMe), 52.9 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 30.5 (C$\mathit{Me}$), 21.8 (Me-4), 7.7 ($\mathrm{NCH_2}\mathit{Me}$)
8b	1.33 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, J(HH) 7, JNH) 2], 1.35 (s, 18 H, $\mathrm{Bu^t}$), 2.18 (s, 12 H, CMe), 3.17 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, J(HH) 7]	253.8 (μ-C), 221.5 [CO, J(WC) 171], 101.8 ($\mathrm{C{\equiv}}\mathit{C}\mathrm{Bu^t}$), 100.3 [$\mathit{C}\mathrm{{\equiv}CBu^t}$, J(WC) 52], 65.5 (CMe), 53.0 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 30.7 (C$\mathit{Me}$), 29.5 ($\mathit{C}\mathrm{Me_3}$), 7.8 ($\mathrm{NCH_2}\mathit{Me}$)
8c	1.32 (s, 18 H, $\mathrm{Bu^t}$), 1.36 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, J(HH) 7, J(NH) 2], 2.33 (s, 12 H, CMe), 3.21 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, J(HH) 7]	254.1 [μ-C, J(WC) 153], 218.7 [CO, J(WC) 166], 108.3 ($\mathrm{C{\equiv}}\mathit{C}\mathrm{Bu^t}$), 96.9 [$\mathit{C}\mathrm{{\equiv}CBu^t}$, J(WC) 44], 52.3 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 30.4 (C$\mathit{Me}$), 29.4 ($\mathrm{C}\mathit{Me}_3$), 28.7 ($\mathit{C}\mathrm{Me_3}$), 7.1 ($\mathrm{NCH_2}\mathit{Me}$)
9	1.28 (s, 18 H, $\mathrm{Bu^t}$), 5.73 (s, 10 H, $\mathrm{C_5H_5}$)	271.6 [μ-C, J(PtC), 853, J(WC) 168], 224.0 [CO, J(WC) 172], 218.0 [CO, J(WC) 180], 115.1 ($\mathrm{C{\equiv}}\mathit{C}\mathrm{Bu^t}$), 95.9 [$\mathit{C}\mathrm{{\equiv}CBu^t}$, J(PtC) 51, J(WC) 32], 92.1 ($\mathrm{C_5H_5}$), 29.5 ($\mathit{C}\mathrm{Me_3}$), 29.4 ($\mathrm{C}\mathit{Me}_3$)

[a] Chemical shifts δ in ppm, coupling constants in Hz. Measurements in $\mathrm{CD_2Cl_2}$ at ambient temperatures. [b] Hydrogen-1 decoupled to high frequency of $\mathrm{SiMe_4}$ (0.0 ppm). [c] Signal due to μ-C nucleus not observed due to quadrupolar coupling by ^{63}Cu and ^{65}Cu. [d] Peak due to $\mathrm{N}\mathit{C}\mathrm{H_2Me}$ nucleus obscured by solvent signal.

quadrupolar effect of ^{n}Cu (n = 63 or 65) nuclei, or through dissociation of the CuCl fragment. The μ-C signal for compound **5b** occurs at δ 248.3, but it is very broad.

Comparison of the chemical shifts for the $\mathrm{C{\equiv}}\mathit{C}\mathrm{Bu^t}$ nuclei in the ^{13}C-{^{1}H} NMR spectra of the compounds **5b** and **5d** with previous results is of interest. In complexes containing a terminally bound $\mathrm{W{\equiv}CC{\equiv}CBu^t}$ group the $\mathrm{C{\equiv}}\mathit{C}\mathrm{Bu^t}$ nucleus is less deshielded than the $\mathit{C}\mathrm{{\equiv}CBu^t}$ nucleus. Thus $[\mathrm{NEt_4}][\mathrm{W}(\mathrm{{\equiv}CC{\equiv}CBu^t})(\mathrm{CO})_2(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$ shows resonances at δ 99.2 due to $\mathit{C}\mathrm{{\equiv}CBu^t}$ and at 91.0 due to $\mathrm{C{\equiv}}\mathit{C}\mathrm{Bu^t}$,[10] while the

Table 3 Selected internuclear distances (Å) and angles (°) for $[NEt_4][W_2Cu(\mu\text{-}CC\equiv CBu^t)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]\cdot Et_2O$ **8b**

W(1)–Cu	2.764(1)	W(1)–C(30)	1.85(1)	W(1)–C(3)	1.99(1)	W(1)–C(4)	1.96(1)
W(1)–C(1)	2.42(1)	W(1)–C(2)	2.48(1)	W(1)–B(3)	2.43(1)	W(1)–B(4)	2.38(1)
W(1)–B(5)	2.36(2)	W(2)–Cu	2.602(1)	W(2)–C(40)	1.85(1)	W(2)–C(5)	1.97(1)
W(2)–C(6)	1.98(1)	W(2)–C(1′)	2.41(1)	W(2)–C(2′)	2.47(1)	W(2)–B(3′)	2.43(1)
W(2)–B(4′)	2.36(1)	W(2)–B(5′)	2.42(1)	Cu–C(30)	2.05(1)	Cu–C(40)	2.10(1)
Cu–B(4′)	2.33(1)	Cu–H(4′)	1.78(10)	C(30)–C(31)	1.42(1)	C(31)–C(32)	1.19(2)
C(32)–C(33)	1.47(2)	C(40)–C(41)	1.40(2)	C(41)–C(42)	1.18(2)	C(42)–C(43)	1.54(2)
C(3)–O(3)	1.16(2)	C(4)–O(4)	1.17(2)	C(5)–O(5)	1.18(2)	C(6)–O(6)	1.17(1)
C(1)–C(2)	1.64(1)	C(1)–B(5)	1.73(2)	C(2)–B(3)	1.70(1)	B(3)–B(4)	1.80(2)
B(4)–B(5)	1.80(2)	C(1′)–C(2′)	1.66(1)	C(1′)–B(5′)	1.71(1)	C(2′)–B(3′)	1.72(2)
B(3′)–B(4′)	1.77(2)	B(4′)–B(5′)	1.82(2)	B(4′)–H(4′)	1.1(1)		
Cu–W(1)–C(30)	48.0(3)	Cu–W(1)–C(3)	69.3(3)	C(30)–W(1)–C(3)	97.2(4)	Cu–W(1)–C(4)	116.6(3)
C(30)–W(1)–C(4)	81.2(5)	C(3)–W(1)–C(4)	86.3(5)	Cu–W(2)–C(40)	53.1(3)	Cu–W(2)–C(5)	134.9(4)
C(40)–W(2)–C(5)	82.1(5)	Cu–W(2)–C(6)	90.1(3)	C(40)–W(2)–C(6)	90.6(5)	C(5)–W(2)–C(6)	85.7(5)
W(1)–Cu–W(2)	152.7(1)	W(1)–Cu–C(30)	41.9(3)	W(2)–Cu–C(30)	161.5(3)	W(1)–Cu–C(40)	128.2(3)
W(2)–Cu–C(40)	44.8(3)	C(30)–Cu–C(40)	121.0(4)	W(1)–Cu–H(4′)	108(3)	W(2)–Cu–H(4′)	83(3)
W(1)–C(30)–Cu	90.1(4)	W(1)–C(30)–C(31)	168.9(8)	Cu–C(30)–C(31)	101.0(6)	C(30)–C(31)–C(32)	177(1)
C(31)–C(32)–C(33)	178(1)	W(2)–C(40)–Cu	82.1(4)	W(2)–C(40)–C(41)	170(1)	Cu–C(40)–C(41)	108(1)
C(40)–C(41)–C(42)	178(1)	C(41)–C(42)–C(43)	177(1)	W(1)–C(3)–O(3)	177(1)	W(1)–C(4)–O(4)	177(1)
W(2)–C(5)–O(5)	177(1)	W(2)–C(6)–O(6)	179(1)				

corresponding signals for $[W(\equiv CC\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ occur at δ 100.1 and 88.9 respectively.[11a] In dimetal compounds with $\mu\text{-}CC\equiv CBu^t$ groups this pattern is reversed, for example, for $[WRh(\mu\text{-}CC\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (C_9H_7 = indenyl) the shifts are δ 102.5 ($\mathit{C}\equiv CBu^t$) and 123.0 ($C\equiv \mathit{C}Bu^t$),[11b] with the $\mathit{C}Bu^t$ resonance being the more deshielded. Although this is also the pattern for the compounds **5b** and **5d** the signals are closer together, *viz.* for **5b** δ 99.8 and 103.2 and for **5d** δ 98.3 and 108.4. This may reflect weaker binding of the MCl fragments to the C≡W groups in these complexes, compared with the attachment of the $Rh(CO)(\eta^5\text{-}C_9H_7)$ moiety to the C≡W bond in the aforementioned tungsten–rhodium compound.

The tungsten–gold complexes **5c** and **5d** are clearly related to the species **1a**, and to the compounds $[WAu(\mu\text{-}CR)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = $C_6H_4Me\text{-}4$[5d] or $C\equiv CBu^t$[12]). An X-ray diffraction study on $[WAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ revealed a μ-C–Au separation of 2.19(3) Å and a μ-C–W distance [1.88(3) Å] only marginally longer than that found [1.826(7) Å] for the C≡W triple bond in $[PPh_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$.[13] Moreover, in the tungsten–gold complex the $W\text{-}\mu\text{-}C\text{-}C^1(C_6H_4Me\text{-}4)$ angle [163(2)°] is large, deviating by only *ca.* 17° from 180°. These features show that in $[WAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$[5d] the alkylidyne group asymmetrically bridges the W–Au bond. It is likely that the alkylidyne ligands in the salts **5** also semi-bridge the W–Cu or W–Au bonds, and may well be essentially terminally bound to the W atoms, with the MCl groups attached perhaps by a W→M donor bond.

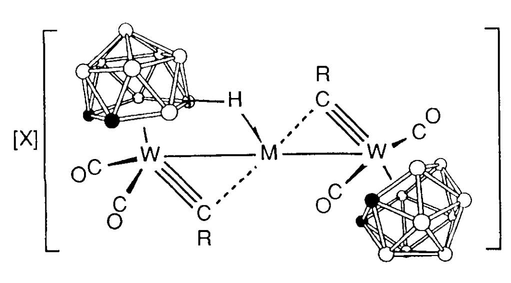
Reaction of 2 equivalents of CuCl with the reagents $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ affords the tungstendicopper compounds $[NEt_4][WCu_2Cl_2(\mu_3\text{-}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **6a** (R = $C_6H_4Me\text{-}4$) and **6b** (R = $C\equiv CBu^t$), in essentially quantitative yield. These complexes, which were more stable than the species **5**, were characterised by the data given in Tables 1 and 2. Surprisingly, addition of ⩾ 2 equivalents of [AuCl(tht)] to the salts $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ did not yield analogous tunstendigold species.

The 'butterfly' $\mu_3\text{-}CWCu_2$ core atom arrangement invoked for the compounds **6**, probably exists also in the previously reported complex $[WCu_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$.[5a] In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of the latter the μ_3-C resonance is relatively deshielded at δ 275.5. Unfortunately, the μ_3-C signal for complex **6a** was not observed, but that for **6b** is much more shielded at δ 219.4. However, this difference is very probably due to the presence of the $\mu_3\text{-}CC\equiv CBu^t$ group. Thus in the $^{13}C\text{-}\{^1H\}$ NMR spectrum of $[WCo_2(\mu_3\text{-}CC\equiv CBu^t)(CO)_8(\eta\text{-}C_5H_5)]$ the μ_3-C resonance is at δ 218.8,[11a] a very similar value to that found for complex **6b**. The latter also shows peaks at δ 115.0 ($C\equiv \mathit{C}Bu^t$) and 104.1 ($\mathit{C}\equiv CBu^t$). The compound $[WCo_2(\mu_3\text{-}CC\equiv CBu^t)(CO)_8(\eta\text{-}C_5H_5)]$ exhibits corresponding signals at δ 115.9 ($C\equiv \mathit{C}Bu^t$) and 98.2 ($\mathit{C}\equiv CBu^t$).[11a]

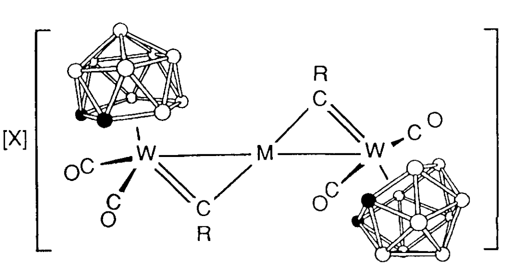
The $^{11}B\text{-}\{^1H\}$ NMR spectra of the complexes **6** are unusual. They consist of two resonances; a sharp signal at δ *ca.* −5 of intensity corresponding to one or perhaps two borons, and a very broad resonance at δ *ca.* −8 corresponding to seven or eight borons. Normally $^{11}B\text{-}\{^1H\}$ NMR measurements made at 128.0 MHz on complexes of the kind under discussion show several reasonably resolved but broad peaks spread over the region δ −5 to −12. A possible explanation for the spectra of the complexes **6** is that in solution there is a rapidly reversible equilibrium between the structure shown and one containing exopolyhedral $B\text{-}H\rightharpoonup Cu$ bonds, and these equilibrate at a rate comparable with the NMR time-scale. We have observed previously that the cluster compounds $[NEt_4][WCo_2(\mu_3\text{-}CR)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = alky or aryl) contain $B\text{-}H\rightharpoonup Co$ bonds. The WCo_2 triangle is bridged on one side by the CR group and the other by the $C_2B_9H_9Me_2$ cage which is η^5 coordinated to the tungsten while forming two $B\text{-}H\rightharpoonup Co$ bonds.[14] In these tungstendicobalt species, however, the presence of the $B\text{-}H\rightharpoonup Co$ linkages is readily detected by ^1H and by $^{11}B\text{-}\{^1H\}$ NMR spectroscopy. The idea that the complexes **6** are stabilised to some degree by $B\text{-}H\rightharpoonup Cu$ bonds is reasonable, in view of other results described below, as well as the clear demonstration by Hawthorne and co-workers[15] of exopolyhedral $B\text{-}H\rightharpoonup Cu$ bonds in the cluster compounds $[N(PPh_3)_2][M_2Cu_2(\mu\text{-}CO)_4(CO)_2(\eta^5\text{-}C_2B_9H_{11})_2]$ (M = Mo or W).

Treatment of compound **5a** or **5b** in CH_2Cl_2 with the halide-abstracting reagent $TlBF_4$ in the presence of $CNC_6H_3Me_2\text{-}2,6$ yields the complexes $[WCu(\mu\text{-}CR)(CO)_2(CNC_6H_3Me_2\text{-}2,6)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **7a** (R = $C_6H_4Me\text{-}4$) and **7b** (R = $C\equiv CBu^t$). A similar synthesis employing salt **5b** and $CNBu^t$ affords $[WCu(\mu\text{-}CC\equiv CBu^t)(CO)_2(CNBu^t)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **7c**. The complexes **7** are much more robust than their precursors **5a** and **5b**, and they were characterised by the data listed in Tables 1 and 2. In addition to displaying two CO absorptions in their IR spectra, the complexes **7** show NC stretching bands at 2183 (**7a**), 2184 (**7b**) and 2177 cm^{-1} (**7c**). The spectra of compounds **7b** and **7c** also display C≡C absorptions at 2135 cm^{-1}.

In the $^{13}C\text{-}\{^1H\}$ NMR spectra of the complexes **7** there are diagnostic peaks for the ligated carbons of the isocyanide groups at δ 146.9 (**7a**), 147.5 (**7b**) and 135.0 (**7c**). In addition, the



A



B

● CMe ○ BH ⊕ B

	X	M	R
8a	NEt_4	Cu	C_6H_4Me-4
8b	NEt_4	Cu	$C{\equiv}CBu^t$
8c	NEt_4	Au	$C{\equiv}CBu^t$
8d	$N(PPh_3)_2$	Au	C_6H_4Me-4

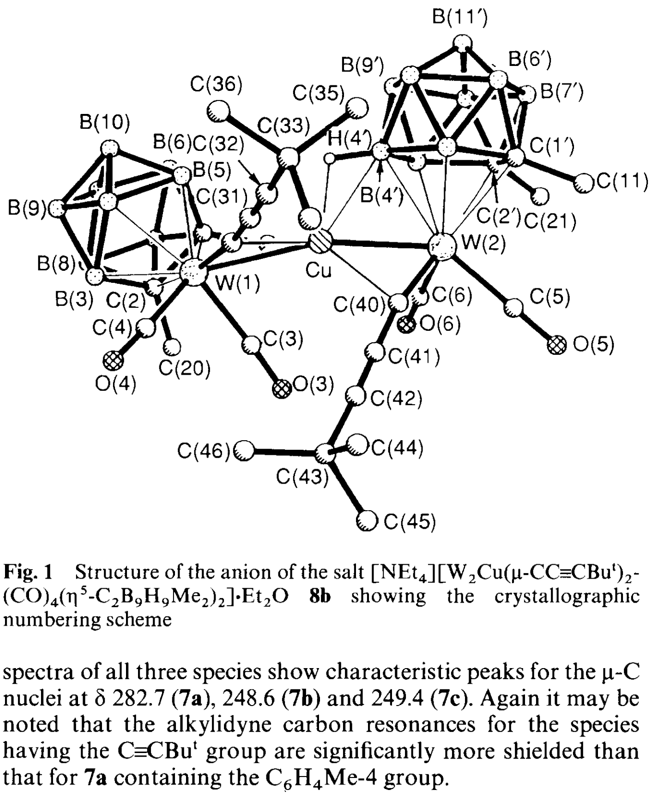


Fig. 1 Structure of the anion of the salt $[NEt_4][W_2Cu(\mu\text{-}CC{\equiv}CBu^t)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]\cdot Et_2O$ **8b** showing the crystallographic numbering scheme

spectra of all three species show characteristic peaks for the μ-C nuclei at δ 282.7 (**7a**), 248.6 (**7b**) and 249.4 (**7c**). Again it may be noted that the alkylidyne carbon resonances for the species having the $C{\equiv}CBu^t$ group are significantly more shielded than that for **7a** containing the C_6H_4Me-4 group.

Treatment of CuCl in CH_2Cl_2 with 2 equivalents of $[NEt_4][W({\equiv}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ in the presence of $TlBF_4$ gives the trimetal complex $[NEt_4][W_2Cu(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8a**. A similar synthesis using CuCl and $[NEt_4][W({\equiv}CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ affords $[NEt_4][W_2Cu(\mu\text{-}CC{\equiv}CBu^t)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8b**, while the complex $[NEt_4][W_2Au(\mu\text{-}CC{\equiv}CBu^t)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8c** was obtained employing [AuCl(tht)] as the precursor. The three compounds **8a**–**8c** are closely related to the species $[N(PPh_3)_2][W_2Au(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8d** obtained previously from the reaction between [AuCl(tht)] and 2 equivalents of $[N(PPh_3)_2][W({\equiv}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$.[5d] The compounds **8a** and **8b** could similarly be prepared from **5a** and **5b**, respectively, and 1 equivalent of $[NEt_4][W({\equiv}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4Me-4 or $C{\equiv}CBu^t$), in the presence of a slight excess of $TlBF_4$. A similar reaction with compound **5d** yields **8c**.

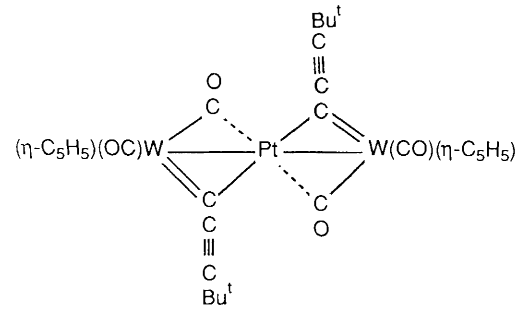
Data for the new compounds **8a**–**8c** are given in Tables 1 and 2. A single-crystal X-ray diffraction study was carried out on complex **8b**. The results are summarised in Table 3, and the structure of the anion is shown in Fig. 1. Each metal–metal bond [W(1)–Cu 2.764(1), W(2)–Cu 2.602(1) Å] forming the WCuW spine of the anion is bridged asymmetrically by a $CC{\equiv}CBu^t$ group [W(1)–C(30) 1.85(1), Cu–C(30) 2.05(1); W(2)–C(40) 1.85(1), Cu–C(40) 2.10(1) Å]. The μ-C–W separations differ little from that found [1.826(7) Å] for the C≡W triple bond in $[PPh_4][W({\equiv}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$.[13] Moreover, the angles W(1)–C(30)–C(31) [168.9(8)°] and W(2)–C(40)–C(41) [170(1)°] are large, and this feature, like the W(1)–C(30) and W(2)–C(40) separations, indicates that the C≡W groups are little changed by formation of the W–Cu bonds. As mentioned above, similar structural features have been observed in $[WAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$,[5d] and occur also in several other dimetal complexes including $[WPt(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_8Me_2)(CO)_2(PEt_3)]$ [μ-C–W 1.88(2) Å, W–μ-C–$C^1(C_6H_3Me_2$-2,6) 175(1)°].[16] In contrast, in many other dimetal compounds containing μ-CR groups the bonding is essentially symmetrical, resulting in longer μ-C–W distances and smaller W–μ-C–CR angles. For example, in $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ the parameters are μ-C–W 1.91(1) Å and W–μ-C–$C^1(C_6H_4Me$-4) 150(1)°.[17]

An interesting feature of the structure of complex **8b** is the presence of the exopolyhedral B(4′)–H(4′)–Cu linkage spanning the shorter of the two W–Cu bonds. The presence of the H(4′) atom was detected in the Fourier difference syntheses, and is undoubtedly responsible for the relatively short W(2)–Cu connectivity compared with W(1)–Cu. Moreover, the cage-ligating W(2) has slipped so that the distance Cu–B(4′) [2.33(1) Å] is comparable with W(2)–B(4′) [2.36(1) Å]. As mentioned earlier, the existence of B–H⟶Au three-centre two-electron bonds has been firmly established in other structures.[15]

In the trimetallatetrahedrane structure $[W_2Cu(\mu_3\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_4(PPh_3)(\eta\text{-}C_5H_5)_2]$[7] and in the 'butterfly' structure $[WPtCu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$[5a] the W–Cu distances are 2.625(average) and 2.648(3) Å, respectively. These distances are comparable with the W(2)–Cu bond [2.602(1) Å] in **8b**. As expected the W(1)–Cu bond [2.764(1) Å] is appreciably longer since it is only weakly bridged by the $CC{\equiv}CBu^t$ group. In general bridging ligands, except hydrogen, shorten metal–metal bonds.

Each tungsten atom in the anion of **8b** carries two essentially linearly bound CO groups (W–C–O 177–179°). Within the $C\text{–}C{\equiv}CBu^t$ fragments, the C≡C bonds [C(31)–C(32) 1.19(2), C(41)–C(42) 1.18(2) Å] are typical for such linkages. However, the C–C distances [C(30)–C(31) 1.42(1), C(40)–C(41) 1.40(2) Å] are relatively short.

Compound **8b** is a member of a large family of trimetal complexes in which a metal atom (Ni, Pt or Au) is ligated by



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two C≡M (M = Mo or W) groups, and X-ray studies have been carried out previously on five of these species.[18] In the salt **8b** the dihedral angle between the $\overline{\text{W(1)CuC(30)}}$ and $\overline{\text{W(2)CuC(40)}}$ rings is 74°. In the previously determined structures these angles range from 60 to 130°, and in the complex $[W_2Au(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ it is 62°.[5b] In the latter the W–Au–W angle is 163° whereas the bend in the W–Cu–W spine of the anion **8b** is 152.7(1)°, and is thus more pronounced.

The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of complex **8b** show (Table 2) all the expected resonances, except that the ^1H spectrum does not reveal a high-field signal for the B–H⇀Cu group. In many complexes containing B–H⇀metal bonds the ^1H NMR spectrum reveals a quartet resonance [*J*(BH) *ca.* 80 Hz] in the range δ −0.2 to −12.0.[8] Moreover, B–H⇀metal linkages are often revealed in $^{11}B\text{-}\{^1H\}$ spectra by a peak in the range δ 10–30, whereas resonances for B–H two-centre fragments are somewhat more shielded. However, a number of dimetal species containing B–H⇀metal groups are known which do not reveal the expected NMR signals.[8,10] Thus the pentanuclear metal compound **2**, the structure of which has been established by X-ray diffraction, does not show a resonance for the B–H⇀Au groups in its ^1H NMR spectrum.[8] However, the $^{11}B\text{-}\{^1H\}$ NMR spectrum does have a peak at δ 7.5, which became a doublet [*J*(BH) 79 Hz] in a proton-coupled ^{11}B spectrum. These data are indicative of the presence of the B–H⇀Au groups in complex **2**. In contrast, the $^{11}B\text{-}\{^1H\}$ NMR spectrum of compound **8b** shows broad peaks at δ −5.5, −9.3, −11.5 and −13.0, typical for a C_2B_9 cage system in which a boron atom is not engaged in exopolyhedral bonding.

A possible explanation for these results is that whereas in the crystal compound **8b** adopts a structure of type **A**, in solution dynamic behaviour occurs involving a lifting of the B–H⇀Cu interaction to give a structure **B** in which the cage adopts a spectator role. Rapid equilibration could then occur between **B** and structures containing B–H⇀Cu bonds, and these need not involve the same carbaborane cage. Moreover, the B–H⇀Cu bonds generated could involve boron atoms in the face of the cage which are either α or β to the carbon atoms in the pentagonal $\overline{\text{CCBBB}}$ faces. Switching between α and β BH sites has been implicated in the chemistry of tungsten–iridium species with B–H⇀Ir bonds.[19] If these processes were fast on the NMR time-scale for compound **8b** the absence of NMR signals for the B–H⇀Cu group would be explained, as would an averaging of the resonances for the CMe and Bu^t groups. The ground-state structure determined by X-ray diffraction would be expected to show eight signals for the cage CMe groups, whereas only two are seen at δ 65.5 (*C*Me) and 30.7 (C*Me*). Even if the B–H⇀Cu interactions were exchanging rapidly four resonances would be anticipated. Hence there is almost certainly a second fluxional process, possibly one in which the two $\overline{\text{W}(\mu\text{-C})\text{Cu}}$ planes twist past each other through 180°. The $^{13}C\text{-}\{^1H\}$ NMR spectrum was measured at −60 °C, but was found to be virtually the same as the room-temperature spectrum, except that the μ-C resonance (δ 253.8) showed ^{183}W satellites [*J*(WC) 173 Hz].

Presumably compound **8c** has a solid-state structure similar to **8b**, and possibly those of **8a** and **8d** are also similar. However, the alternative structures **A** and **B** are likely to be delicately balanced, and so the $\mu\text{-}CC_6H_4Me\text{-}4$ species might conceivably have structure **B** in the ground state. An X-ray diffraction study of compound **8a** or **8d** could resolve this matter.

The presence of the B–H⇀Cu bond in **8b** undoubtedly enhances the stability of the compound. It should be noted that the isolobal complex $[W_2Cu(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ is highly labile, decomposing very readily.[7] However, the fact that in the salt **8b** the copper atom is part of an anion, and is therefore more electron rich, may also favour the stability of this complex.

We have also investigated the reaction between $[W(\equiv CC\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Pt(nb)_3]$ (nb = norbornene = bicyclo[2.2.1]heptene) and have thereby isolated the complex $[W_2Pt(\mu\text{-}CC\equiv CBu^t)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ **9**, data for which are given in Tables 1 and 2. The IR spectrum shows two CO stretching bands at 1950 and 1840 cm^{-1}. The latter frequency implies that two of the carbonyl ligands semi-bridge the W–Pt bonds. This is a general feature of complexes of the type $[W_2Pt(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5R'_5)_2]$ (R = alkyl or aryl, R′ = H or Me).[17,20] However, as mentioned above, all the CO ligands in compound **8b** are terminally bound to the W atoms, as they are also in $[W_2Au(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ [ν_{max}(CO) at 2024 and 1969 cm^{-1}].[5b] Thus these two complexes are exceptions to the general pattern.

The $^{13}C\text{-}\{^1H\}$ NMR spectrum of complex **9** is of interest. The important peaks are those due to the nuclei μ-C [δ 271.6, *J*(PtC) 853, *J*(WC) 168], C≡*C*Bu^t (115.1), and *C*≡CBu^t [95.9, *J*(PtC) 51, *J*(WC) 32 Hz]. The strong $^{195}Pt\text{–}^{13}C$ coupling on the μ-C resonance indicates that the CC≡CBu^t group symmetrically bridges the W–Pt bond. For $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ the $^{195}Pt\text{–}^{13}C$ coupling of 830 Hz is comparable, and the X-ray diffraction study revealed very similar μ-C–W and μ-C–Pt distances (1.90–2.01 Å).[17] Also supporting the suggestion that in compound **9** the CC≡CBu^t groups are symmetrically bridging the W–Pt bonds is the observation that the C≡*C*Bu^t and *C*≡CBu^t ^{13}C NMR resonances are well separated, with the former signal being the more deshielded. We referred earlier to the spectrum of $[WRh(\mu\text{-}CC\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ which also shows disparate C≡CBu^t peaks at δ 102.5 (*C*≡CBu^t) and 123.0 (C≡*C*Bu^t),[11b] in agreement with essentially symmetrical bridging of the metal–metal bond by the alkylidyne group. Symmetrical bridging by the CC≡CBu^t group in compound **9** would result in appreciable bending of the W–μ-C–CCBu^t angles compared with those observed for complex **8b** (see earlier discussion). This in turn may be responsible for the observation in the $^{13}C\text{-}\{^1H\}$ NMR spectra of appreciably different $^{183}W\text{–}C^{13}C\equiv CBu^t$ couplings between the two species: 52 for **8b** and 32 Hz for **9**.

Experimental

The experimental procedures, and the instrumentation used for the spectroscopic measurements, have been described in previous papers in this series. Light petroleum refers to that fraction of b.p. 40–60 °C. The reagent $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ was prepared by the method used to obtain the Ph analogue.[21] The compounds $[NEt_4][W(\equiv CC\equiv CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$,[10] $[W(\equiv CC\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$,[11a] $[Pt(nb)_3]$[22] and $[AuCl(tht)]$[23] were prepared as described in the literature. The $^{11}B\text{-}\{^1H\}$ NMR chemical shifts were measured in CD_2Cl_2, and are positive to high frequency of $BF_3\cdot Et_2O$ (external). Analytical and other data for the new compounds are given in Table 1.

Reactions of the Complexes $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ *with* CuCl *and* [AuCl(tht)].—(*i*) The reagent $[NEt_4][W\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.12 g, 0.19 mmol) in CH_2Cl_2 (15 cm^3) was treated with CuCl (0.019 g, 0.19

mmol), and the mixture was stirred for *ca.* 30 min. Solvent was removed *in vacuo*, and the residue was washed with light petroleum (2 × 15 cm^3) giving orange *microcrystals* of $[NEt_4][WCuCl(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5a** (0.12 g).

A similar preparation employing an excess of CuCl (0.019 g, 0.19 mmol) with $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.06 g, 0.07 mmol) in CH_2Cl_2 (15 cm^3) gave orange *microcrystals* of $[NEt_4][WCu_2Cl_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **6a** (0.071 g).

(*ii*) The compound $[NEt_4][W(\equiv CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.25 g, 0.40 mmol) was treated with CuCl (0.039 g, 0.39 mmol) in CH_2Cl_2 (15 cm^3), and the mixture was stirred for *ca.* 30 min. Solvent was removed *in vacuo*, and the residue was washed with Et_2O (2 × 20 cm^3) giving red *microcrystals* of $[NEt_4][WCuCl(\mu\text{-}CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5b** (0.28 g).

The compound $[NEt_4][WCu_2Cl_2(\mu_3\text{-}CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **6b** (0.32 g) was similarly obtained from $[NEt_4][W(\equiv CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.25 g, 0.40 mmol) and CuCl (0.08 g, 0.79 mmol) in CH_2Cl_2 (15 cm^3).

(*iii*) The reagent $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.63 g, 0.99 mmol) in CH_2Cl_2 (5 cm^3) was treated with [AuCl(tht)] (0.32 g, 1.00 mmol), and the mixture was stirred for 15 min. Solvent was reduced in volume *in vacuo* to *ca.* 2 cm^3, and hexane (*ca.* 10 cm^3) was added dropwise, thereby yielding a brown precipitate. Removal of the supernatant liquid with a syringe and washing the residue with hexane (2 × 20 cm^3) gave brown *microcrystals* of $[NEt_4][WAuCl(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5c** (0.84 g).

(*iv*) Using a similar procedure, the complex $[NEt_4][WAuCl(\mu\text{-}CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5d** (0.84 g) was obtained from $[NEt_4][W(\equiv CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.62 g, 0.99 mmol) and [AuCl(tht)] (0.32 g, 1.00 mmol). Compound **5d** could not be obtained crystalline.

Synthesis of the Complexes $[WCu(\mu\text{-}CR)(CO)_2(CNR')(\eta^5\text{-}C_2B_9H_9Me_2)]$.—(*i*) The reagent $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.12 g, 0.19 mmol) in CH_2Cl_2 (15 cm^3) was treated first with CuCl (0.02 g, 0.20 mmol), and then $TlBF_4$ (0.70 g, 0.24 mmol, excess) and $CNC_6H_3Me_2$-2,6 (0.03 g, 0.23 mmol) were added simultaneously. The mixture was stirred for *ca.* 12 h and filtered. The solution thus obtained was reduced in volume *in vacuo* to *ca.* 3 cm^3, and chromatographed on a Florisil column (2 × 15 cm) at −50 °C. Elution with CH_2Cl_2 removed a red fraction which was reduced in volume to *ca.* 1 cm^3. Addition of light petroleum (*ca.* 5 cm^3) and cooling to −30 °C gave orange *microcrystals* of $[WCu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(CNC_6H_3Me_2\text{-}2,6)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **7a** (0.08 g), after removal of the supernatant liquid.

(*ii*) Similarly, $[NEt_4][W(\equiv CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.25 g, 0.40 mmol) in CH_2Cl_2 (15 cm^3) was treated with CuCl (0.039 g, 0.39 mmol), $TlBF_4$ (0.25 g, 0.86 mmol) and $CNC_6H_3Me_2$-2,6 (0.052 g, 0.40 mmol). After stirring the mixture for 12 h, solvent was removed *in vacuo*, and the residue was extracted with Et_2O (3 × 20 cm^3). The extracts were combined and reduced in volume *in vacuo* to *ca.* 1 cm^3, and light petroleum (10 cm^3) was added. Cooling to −30 °C gave red *microcrystals* of $[WCu(\mu\text{-}CC{\equiv}CBu^t)(CO)_2(CNC_6H_3Me_2\text{-}2,6)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **7b** (0.19 g), after removal of supernatant liquid and drying *in vacuo*.

(*iii*) The compound $[WCu(\mu\text{-}CC{\equiv}CBu^t)(CO)_2(CNBu^t)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **7c** (0.18 g) was obtained using a similar method to that for **7b**, employing $[NEt_4][W(\equiv CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.25 g, 0.40 mmol), CuCl (0.039 g, 0.39 mmol), $TlBF_4$ (0.25 g, 0.86 mmol), and $CNBu^t$ (0.045 cm^3, 0.40 mmol).

Synthesis of the Compounds $[NEt_4][W_2M(\mu\text{-}CR)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$.—(*i*) The reagent $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.12 g, 0.19 mmol) in CH_2Cl_2 (*ca.* 15 cm^3) was treated with CuCl (0.01 g, 0.10 mmol) and with an excess of $TlBF_4$ (0.05 g, 0.17 mmol). The mixture was stirred for 1 h, after which the resulting suspension was filtered. The solution thus obtained was reduced in volume *in vacuo* to *ca.* 2 cm^3, and light petroleum was added dropwise until precipitation of $[NEt_4][BF_4]$ commenced. The mixture was stirred for a further 10 min, following which it was filtered and the resulting solution treated with light petroleum (*ca.* 30 cm^3). Removal of solvent *in vacuo* gave a brown powder which was washed with light petroleum (20 cm^3) to give brown *microcrystals* of $[NEt_4][W_2Cu(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8a** (0.049 g).

(*ii*) Similarly, the compound $[NEt_4][W(\equiv CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.50 g, 0.80 mmol) in CH_2Cl_2 (20 cm^3) was treated with CuCl (0.039 g, 0.39 mmol) and an excess of $TlBF_4$ (0.25 g, 0.86 mmol). The mixture was stirred for 30 min, after which the solvent was removed *in vacuo*. The residue was extracted with Et_2O (3 × 20 cm^3). The combined extracts were slowly evaporated yielding red *microcrystals* of $[NEt_4][W_2Cu(\mu\text{-}CC{\equiv}CBu^t)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8b** (0.29 g).

(*iii*) The complex $[NEt_4][W_2Au(\mu\text{-}CC{\equiv}CBu^t)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8c** (0.18 g) was prepared from $[NEt_4][W(\equiv CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.31 g, 0.50 mmol), [AuCl(tht)] (0.08 g, 0.25 mmol), and $TlBF_4$ (0.25 g, 0.86 mmol), using the procedure described for the preparation of compound **8b**.

Preparation of the Complex $[W_2Pt(\mu\text{-}CC{\equiv}CBu^t)_2(CO)_4(\eta\text{-}C_5H_5)_2]$.—A mixture of the reagents $[W(\equiv CC{\equiv}CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (0.40 g, 1.01 mmol) and $[Pt(nb)_3]$ (0.24 g, 0.50 mmol) in light petroleum (20 cm^3) was stirred for 1 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (*ca.* 5 cm^3) and chromatographed on an alumina column (3 × 15 cm). Elution with CH_2Cl_2 removed a brown fraction. The volume of solvent was reduced *in vacuo* to *ca.* 2 cm^3, and light petroleum (*ca.* 20 cm^3) was added. Cooling to −30 °C afforded brown *microcrystals* of $[W_2Pt(\mu\text{-}CC{\equiv}CBu^t)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ **9** (0.41 g), after removal of solvent *in vacuo*.

Crystal-structure Determination of Compound **8b**.—Ruby prisms of complex **8b** were grown from an Et_2O solution at −20 °C. Diffracted intensities were collected at 298 K on a Siemens R3m/V four-circle diffractometer from a crystal of dimensions *ca.* 0.20 × 0.30 × 0.40 mm, which was sealed under nitrogen in a glass capillary. Of the 10 080 unique reflections collected (Wyckoff ω scans, $2\theta \leqslant 50°$), 6815 had $F \geqslant 4\sigma(F)$, and only these were used for structure solution and refinement, after corrections for Lorentz, polarisation and X-ray absorption effects.[24]

Crystal data. $C_{34}H_{68}B_{18}CuNO_4W_2{\cdot}Et_2O$, $M = 1236.7$, triclinic, space group $P\bar{1}$, $a = 11.642(2)$, $b = 14.563(2)$, $c = 17.250(3)$ Å, $\alpha = 86.95(1)$, $\beta = 76.84(1)$, $\gamma = 89.00(1)°$, $U = 2\,844(1)$ Å^3, $Z = 2$, $D_c = 1.44$ g cm^{-3}, $F(000) = 1204$, Mo-Kα X-radiation (graphite monochromator), $\lambda = 0.710\,73$ Å, $\mu(\text{Mo-K}\alpha) = 45.3$ cm^{-1}.

The structure was solved by first finding the metal atoms by direct methods, and subsequently locating the C, B, N, O and H(4′) atoms by Fourier-difference syntheses. The C*Me*$_3$ atoms were found to be disordered in a 60:20:20 ratio for C(34)–C(36), and in a 33:33:33 ratio for the group C(44)–C(46). As a result of this disorder no H atoms were included for the Bu^t groups. The remaining H atoms, except H(4′) which was fully refined, were included in calculated positions [C–H 0.96, $U_{iso} = 0.08$; B–H 1.1 Å, $U_{iso} = 1.2\ U_{iso}(B)$ Å^2, using the program BHGEN[25]]. All non-hydrogen atoms, except the C*Me*$_3$ carbons, were refined anisotropically. Refinement by full-matrix least squares led to $R = 0.044$ ($R' = 0.043$), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,5|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks $\geqslant 0.81$ or $\leqslant -0.62$ e Å^{-3}.

All calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.[24] Scattering factors with corrections for anomalous dispersion

Table 4 Atomic positional parameters (fraction coordinates × 10^4) for compound **8b**, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
W(1)	3020(1)	448(1)	2829(1)
W(2)	2162(1)	3896(1)	3430(1)
Cu	2958(1)	2346(1)	2827(1)
C(30)	4093(9)	1332(6)	2328(6)
C(31)	5051(10)	1864(7)	1883(7)
C(32)	5829(10)	2322(8)	1491(7)
C(33)	6775(13)	2884(10)	981(9)
C(34)	7717(26)	3049(22)	1433(17)
C(34A)	7067(63)	3636(48)	1698(43)
C(34B)	8024(61)	2473(51)	1175(45)
C(35)	6222(25)	3816(19)	764(19)
C(35A)	6628(73)	3858(53)	1260(55)
C(35B)	5990(64)	3613(50)	451(46)
C(36)	7348(23)	2333(16)	219(15)
C(36A)	7889(63)	2200(46)	635(48)
C(36B)	6773(52)	2586(37)	100(32)
C(40)	3393(9)	3195(6)	3663(6)
C(41)	4369(10)	2804(7)	3903(7)
C(42)	5206(11)	2495(8)	4106(7)
C(43)	6294(12)	2048(10)	4347(9)
C(44)	7362(25)	2674(23)	3978(26)
C(44A)	7175(59)	1990(53)	3559(41)
C(44B)	7257(30)	2685(23)	4460(29)
C(45)	6137(50)	2285(42)	5246(18)
C(45A)	6610(49)	2747(35)	5026(32)
C(45B)	5740(43)	1441(37)	5167(32)
C(46)	6378(41)	1056(29)	4110(33)
C(46A)	5985(34)	1089(26)	4650(28)
C(46B)	6801(43)	1388(34)	3636(25)
C(3)	2808(10)	869(7)	3929(7)
O(3)	2677(9)	1065(6)	4588(5)
C(4)	4467(12)	−154(7)	2997(7)
O(4)	5338(9)	−528(7)	3058(7)
C(5)	2477(11)	4630(7)	4281(8)
O(5)	2715(10)	5074(6)	4774(6)
C(6)	1026(11)	3221(8)	4287(7)
O(6)	356(9)	2815(7)	4790(6)
C(1)	938(9)	336(6)	2857(7)
C(10)	304(10)	1125(7)	3333(8)
C(2)	1319(9)	−600(6)	3313(6)
C(20)	1055(11)	−701(8)	4206(6)
B(3)	2474(11)	−1136(7)	2721(7)
B(4)	2803(12)	−487(8)	1781(7)
B(5)	1805(12)	482(6)	1903(8)
B(6)	394(13)	31(10)	2065(11)
B(7)	67(12)	−622(9)	2974(9)
B(8)	1029(13)	−1551(7)	2866(8)
B(9)	1950(13)	−1485(8)	1886(8)
B(10)	1513(14)	−501(9)	1410(8)
B(11)	408(15)	−1171(10)	2098(10)
C(1′)	2082(9)	5264(6)	2598(6)
C(11)	2522(11)	6082(7)	2983(7)
C(2′)	716(9)	4881(6)	2928(6)
C(21)	−124(11)	5303(9)	3658(8)
B(3′)	633(10)	3759(8)	2689(8)
B(4′)	2061(10)	3465(8)	2148(7)
B(5′)	3000(10)	4465(8)	2081(7)
B(6′)	2372(13)	5372(8)	1582(8)
B(7′)	956(13)	5620(9)	2126(8)
B(8′)	93(12)	4687(9)	2160(10)
B(9′)	933(11)	3799(8)	1634(8)
B(10′)	2378(12)	4222(8)	1275(7)
B(11′)	1160(13)	4963(10)	1286(9)
N	7228(9)	7923(7)	831(6)
C(51)	7218(18)	8751(11)	1338(11)
C(52)	6696(20)	9618(13)	1017(15)
C(53)	6153(15)	7691(15)	700(17)
C(54)	5226(17)	7338(16)	1497(12)
C(55)	7852(15)	7168(11)	1291(10)
C(56)	8051(18)	6360(13)	886(12)
C(57)	7999(16)	8130(12)	26(9)
C(58)	9265(16)	8450(14)	13(12)
O(01)	6697(13)	6433(11)	3263(9)
C(01)	5944(25)	5666(19)	3528(17)
C(02)	6092(24)	5080(19)	3074(16)
C(03)	6918(25)	6953(20)	3761(17)
C(04)	7577(18)	7645(14)	3648(13)

were taken from ref. 26. Atom coordinates are listed in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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