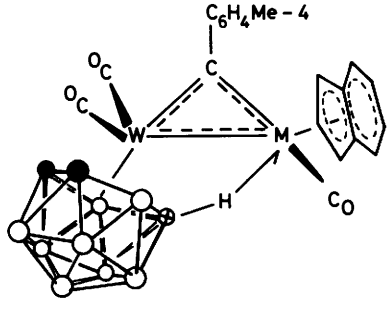
Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 58.[1] Some Reactions of the Compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (M = Mo or W); Crystal Structures of the Complexes $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(L)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ $[L = N_2C(C_6H_4Me\text{-}4)_2$ or O] *

Judith A. K. Howard, Alun P. James, Alasdair N. de M. Jelfs, Christine M. Nunn, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (M = Mo or W) react with the diazoalkanes N_2CR_2 (R = C_6H_4Me-4 or Ph) in diethyl ether at room temperature to afford the dimetal complexes $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(N_2CR_2)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$. The molecular structure of the compound with M = W and R = C_6H_4Me-4 has been established by *X*-ray diffraction. The tungsten–tungsten bond [2.777(1) Å] is bridged by the *p*-tolylmethylidyne ligand [μ-C–W 1.975(5) and 2.081(5) Å] and by a three-centre two-electron B–H⟶W bond formed by one tungsten atom and a BH fragment in the pentagonal face of the η^5-$C_2B_9H_9Me_2$ group attached to the other tungsten centre. The latter also carries two terminally bound CO ligands. The tungsten atom which is part of the B–H⟶W system is bonded by the indenyl ligand and a monodentate $N_2C(C_6H_4Me\text{-}4)_2$ group [W–N 1.768(5) Å, W–N–N 166.8(4)°]. The compounds $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(L)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ [L = O or NC_6H_4Me-4] have been prepared by treating $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ with aqueous H_2O_2 and $N_3C_6H_4Me$-4, respectively. The n.m.r. spectra [^1H, ^{13}C-{^1H}, and ^{11}B-{^1H}] of all the new compounds are reported, and display features indicative of the presence of μ-CC_6H_4Me-4 groups and three-centre two-electron B–H⟶M (M = Mo or W) bonds.

In a previous paper[2] we have described the synthesis and structures of the dimetal compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1a**, M = Mo; **1b**, M = W) in which the metal–metal linkages are bridged by a *p*-tolylmethylidyne group, and by a B–H⟶M three-centre two-electron bond. Treatment of complexes (**1**) with PMe_3 affords the species $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2a**, M = Mo; **2b**, M = W) in which B–H⟶M bridges are no longer present. Both types of compound, (**1**) and (**2**), formally possess 32 valence electrons and are thus unsaturated.

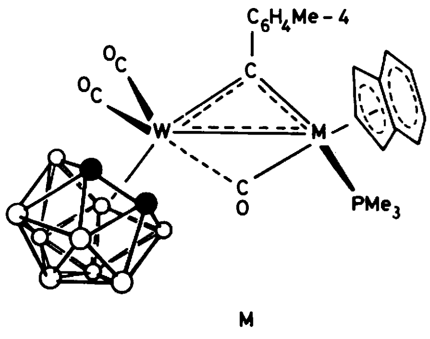
Herein we describe reactions of complexes (**1**) with the diazo-compounds N_2CR_2 (R = C_6H_4Me-4 or Ph), and also reactions of (**1b**) with aqueous hydrogen peroxide and with the azide $N_3C_6H_4Me$-4. These reactions were studied in order to develop the chemistry of the formally electronically unsaturated species (**1**).



	M	●	○	⊕
(**1a**)	Mo	CMe	BH	B
(**1b**)	W	CMe	BH	B

Results and Discussion

The compounds (**1**) react with $N_2C(C_6H_4Me\text{-}4)_2$ in diethyl ether at room temperature to afford the complexes $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{N_2C(C_6H_4Me\text{-}4)_2\}(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3a**, M = Mo; **3b**, M = W). Similarly, the diazo-compound N_2CPh_2 reacts with (**1**) to give the analogous



	M
(**2a**)	Mo
(**2b**)	W

---

* 1,1-Dicarbonyl-2-(diazodi-*p*-tolylmethane)-2-(η^5-indenyl)-μ-[7′—11′-η-nonahydro-7′,8′-dimethyl-7′,8′-dicarba-*nido*-undecaborato-(2−)-$B^{7'-11'}$(W^1),$H^{10'}$(W^2)]-μ-(*p*-tolylmethylidyne)-ditungsten-(*W*–*W*) and 1,1-dicarbonyl-2-(η^5-indenyl)-μ-[7′—11′-η-nonahydro-7′,8′-dimethyl-7′,8′-dicarba-*nido*-undecaborato(2−)-$B^{7'-11'}$(W^1),$H^{10'}$-(W^2)]-2-oxo-μ-(*p*-tolylmethylidyne)-ditungsten (*W*–*W*) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

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

Compound[b]	Colour	Yield (%)	$\nu(BH)$[c]/cm^{-1}	$\nu(CO)$[c]/ cm^{-1}	Analysis (%) C	H	N
(**3a**) $[MoW(\mu-CR)(CO)_2(N_2CR_2)(\eta^5-C_9H_7)(\eta^5-C_2B_9H_9Me_2)]$	Red	87	2 563m br	1 975s, 1 908s	47.7 (48.6)	4.5 (4.6)	2.9 (3.0)
(**3b**) $[W_2(\mu-CR)(CO)_2(N_2CR_2)(\eta^5-C_9H_7)(\eta^5-C_2B_9H_9Me_2)]$	Red	50	2 559w br	1 975s, 1 909s	44.4 (44.5)	4.2 (4.2)	2.7 (2.5)
(**3c**) $[MoW(\mu-CR)(CO)_2(N_2CPh_2)(\eta^5-C_9H_7)(\eta^5-C_2B_9H_9Me_2)]$	Red	81	2 564m br	1 977s, 1 911s	46.4 (47.5)	4.2 (4.3)	3.1 (3.1)
(**3d**) $[W_2(\mu-CR)(CO)_2(N_2CPh_2)(\eta^5-C_9H_7)(\eta^5-C_2B_9H_9Me_2)]$	Red	72	2 569m br	1 977s, 1 910s	42.7 (43.4)	4.0 (3.9)	2.6 (2.8)
(**3f**) $[W_2(\mu-CR)(CO)_2(O)(\eta^5-C_9H_7)(\eta^5-C_2B_9H_9Me_2)]$	Brown	37	2 570w br	1 966s, 1 929s	33.7 (33.8)	3.5 (3.6)	
(**3g**) $[W_2(\mu-CR)(CO)_2(NR)(\eta^5-C_9H_7)(\eta^5-C_2B_9H_9Me_2)]$	Brown	62	[d]2 567m br	[d]1 978s, 1 915s	38.3 (39.7)	4.4 (4.0)	1.9 (1.6)

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. Data for (**3e**) are given in ref. 2. [c] In CH_2Cl_2 unless otherwise stated. [d] In Et_2O.

Table 2. N.m.r. data[a] for the dimetal compounds

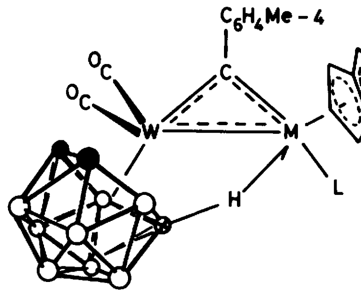
Compound	^1H (δ)[b]	^{13}C (δ)[c]	^{11}B (δ)[d]
(**3a**)	−7.21 [m, 1 H, B(μ-H)Mo], 1.98 (s, 3 H, Me), 2.13 (s, 3 H, Me), 2.41 (s, 6 H, 2 × Me-4), 2.48 (s, 3 H, Me-4), 5.65 [t, 1 H, C_9H_7, *J*(HH) 4], 5.74 (s, 1 H, C_9H_7), 6.17 (s, 1 H, C_9H_7), 6.89—7.49 (m, 16 H, C_6H_4 and C_9H_7)	320.1 (μ-C), 219.6 [WCO, *J*(WC) 158], 218.9 [WCO, *J*(WC) 164], 158.9 [$C^1(C_6H_4)$], 156.0 [$N_2C(C_6H_4$-Me-4$)_2$], 141.7—118.1 (C_6H_4 and C_9H_7), 108.1, 93.3, 84.1 (C_9H_7), 30.5 (2 × C*Me*), 21.5 (2 × Me-4), 21.3 (Me-4)	18.9 [1 B, B(μ-H)Mo], −9.3 (8 B)
(**3b**)	−6.92 [m, 1 H, B(μ-H)W], 1.95 (s, 3 H, Me), 2.13 (s, 3 H, Me), 2.39 (br, 6 H, 2 × Me-4), 2.48 (s, 3 H, Me-4), 5.71 (m, 1 H, C_9H_7), 5.98 (m, 1 H, C_9H_7), 6.32 (m, 1 H, C_9H_7), 6.92—7.47 (m, 16 H, C_6H_4 and C_9H_7)	[e]316.4 [μ-C, *J*(WC) 104], 219.3 (WCO), 160.0 [$C^1(C_6H_4)$], 157.8 [$N_2C(C_6H_4Me$-4$)_2$], 141.7—118.5 (C_6H_4 and C_9H_7), 105.7, 89.9, 79.2 (C_9H_7), 63.3, 59.9 (*C*Me), 30.8, 30.6 (C*Me*), 21.4 (2 × Me-4), 21.1 (Me-4)	20.6 [1 B, B(μ-H)W], −7.9 (8 B)
(**3c**)	−6.34 [m, 1 H, B(μ-H)Mo], 1.91 (s, 3 H, Me), 2.05 (s, 3 H, Me), 2.41 (s, 3 H, Me-4), 5.47 (m, 1 H, C_9H_7), 5.63 (s, 1 H, C_9H_7), 6.02 (s, 1 H, C_9H_7), 6.79—7.48 (m, 18 H, C_6H_4, Ph, and C_9H_7)	320.6 (μ-C), 219.4 [WCO, *J*(WC) 158], 218.2 [WCO, *J*(WC) 180], 158.3 [$C^1(C_6H_4)$], 155.4 (N_2*C*Ph_2), 136.4—118.2 (C_6H_4, Ph, and C_9H_7), 107.8, 93.0, 83.8 (C_9H_7), 30.2 (C*Me*), 21.1 (Me-4)	18.8 [1 B, B(μ-H)Mo], −8.5 (8 B)
(**3d**)	−6.78 [br, 1 H, B(μ-H)W], 1.95 (s, 3 H, Me), 2.13 (s, 3 H, Me), 2.50 (s, 3 H, Me-4), 5.71 [t, 1 H, C_9H_7, *J*(HH) 3], 6.00 (m, 1 H, C_9H_7), 6.32 (m, 1 H, C_9H_7), 6.94—7.80 (m, 18 H, C_6H_4, Ph, and C_9H_7)	[e]316.7 (μ-C), 219.0 (WCO), 159.9 [$C^1(C_6H_4)$], 156.5 (N_2*C*Ph_2), 136.3—118.3 (C_6H_4, Ph, and C_9H_7), 105.8, 89.9, 79.3 (C_9H_7), 63.2, 60.0 (*C*Me), 30.7, 30.5 (C*Me*), 21.1 (Me-4)	20.6 [1 B, B(μ-H)W], −8.4 (8 B)
(**3f**)	−5.16 [br, 1 H, B(μ-H)W, *J*(BH) *ca.* 60], 1.95 (s, 3 H, Me), 2.12 (s, 3 H, Me), 2.54 (s, 3 H, Me-4), 6.43 [t, 1 H, C_9H_7, *J*(HH) 3], 6.58 (m, 1 H, C_9H_7), 7.00—7.65 (m, 9 H, C_6H_4 and C_9H_7)	302.8 (μ-C), 218.8, 215.8 (WCO), 158.7—121.2 (C_6H_4 and C_9H_7), 107.8, 93.1, 83.8 (C_9H_7), 31.2, 31.0 (C*Me*), 21.6 (Me-4)	19.6 [1 B, B(μ-H)W], −6.9 (8 B)
(**3g**)	−6.18 [br, 1 H, B(μ-H)W], 1.94, 2.10, 2.25, 2.47 (s × 4, 12 H, Me and Me-4), 6.39 (m, 1 H, C_9H_7), 6.46 [t, 1 H, C_9H_7, *J*(HH) 3], 6.57—7.18 (m, 9 H, C_6H_4 and C_9H_7), 7.38, 7.54 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[e]310.1 [μ-C, *J*(WC) 102], 219.1 [WCO, *J*(WC) 178], 218.4 [WCO, *J*(WC) 160], 159.4—119.6 (C_6H_4 and C_9H_7), 104.4, 91.2, 78.5 (C_9H_7), 63.0, 60.2 (*C*Me), 30.6, 30.4 (C*Me*), 21.1 (Me-4)	[f]20.7 [1 B, B(μ-H)W], −8.0 (8 B)

[a] Chemical shifts in p.p.m., coupling constants in Hz, measurements at room temperature unless otherwise stated. [b] Measured in CD_2Cl_2. [c] Hydrogen-1 decoupled chemical shifts are positive to high frequency of $SiMe_4$ (0.0 p.p.m.), with measurements in CD_2Cl_2–CH_2Cl_2. [d] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $BF_3 \cdot Et_2O$ (external), with measurements in CD_2Cl_2 unless otherwise stated. [e] Measured at −40 °C. [f] In $CDCl_3$.

complexes $[MW(\mu-CC_6H_4Me-4)(CO)_2(N_2CPh_2)(\eta^5-C_9H_7)(\eta^5-C_2B_9H_9Me_2)]$ (**3c**, M = Mo; **3d**, M = W). Analytical and other data for (**3a**)—(**3d**) are given in Table 1. Discussion of the n.m.r. data (Table 2) is deferred, however, until the results of a single-crystal *X*-ray diffraction study on (**3b**) are described.

The structure of compound (**3b**) is shown in Figure 1, and selected internuclear parameters are given in Table 3. The *p*-tolylmethylidyne and carbaborane ligands adopt the same bonding modes towards the W_2 fragment as they do in the precursor (**1b**).[2] However, the dimensions of the C(40)W(1)W(2) ring in (**3b**) are somewhat different from those in (**1b**), with the indenyl-ligated tungsten atom in the former complex distinctly less strongly bonded to the μ-C–W fragment [W(1)–W(2) 2.777(1) (**3b**), 2.660(2) (**1b**); W(1)–μ-C 2.081(5) (**3b**), 1.94(2) Å (**1b**)]. Moreover, in (**3b**) the W(2)–C(40) separation [1.975(5) Å] corresponds to that expected for a C=W bond in dimetal systems,[3] whereas the analogous distance in (**1b**) [2.08(2) Å] is distinctly longer. Whereas (**1b**) is a 32 valence electron complex, as discussed below, (**3b**) is best regarded as a saturated 34 valence electron compound, and this difference correlates with the observed changes in the μ-CW_2 ring dimensions.

The W(2) atom in (**3b**) carries two terminal CO groups, and is bonded to the open pentagonal face of the carbaborane ligand. The latter forms a B(4)–H(4)⟶W(1) bridge, a feature which is



	M	L
(3a)	Mo	$N_2C(C_6H_4Me\text{-}4)_2$
(3b)	W	$N_2C(C_6H_4Me\text{-}4)_2$
(3c)	Mo	N_2CPh_2
(3d)	W	N_2CPh_2
(3e)	W	PMe_3
(3f)	W	O
(3g)	W	NC_6H_4Me-4

●	○	⊕
CMe	BH	B

revealed in the n.m.r. spectra of the complex described below. The W(1) atom carries the indenyl group which displays the commonly observed 'slippage' of this ligand with the W(1) to C(27), C(28), and C(29) distances being distinctly shorter than the W(1)–C(21) and W(1)–C(26) separations (see Table 3). The 'slippage' of the indenyl ligand is less pronounced in the precursor (**1b**).[2]

Of particular interest is the presence of the monodentate $N_2C(C_6H_4Me\text{-}4)_2$ ligand on W(1). The W(1)–N(1) [1.768(5) Å], N(1)–N(2) [1.31(1) Å], and N(2)–C(5) [1.30(1) Å] distances suggest bond orders between two and three for the tungsten–nitrogen separation, between one and two for N(1)–N(2), and two for N(2)–C(5).[4] The angles W(1)–N(1)–N(2) [166.8(4)°] and N(1)–N(2)–C(5) [122.7(5)°] indicate essentially *sp* and sp^2 hybridisation at N(1) and N(2), respectively. The σ co-ordination mode of the diazoalkane ligand in (**3b**) has recently been observed in the titanium complex $[Ti(NNCPh_2)(PMe_3)(\eta\text{-}C_5H_5)_2]$,[5] and previously in the compounds $[Mn\{NNC(CO_2Me)_2\}(CO)_2(\eta\text{-}C_5H_5)]$[6] and $[Mo_2(OPr^i)_6(NNCPh_2)_2(py)]$ (py = pyridine).[7]

Complex (**3b**) showed no tendency to lose nitrogen and form a carbene complex, as do the diazoalkane-bridged species $[Mo_2(\mu\text{-}NNCR_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (R = Ph or C_6H_4Me-4).[8] Treatment of (**3b**) with PMe_3 displaces the diazoalkane ligand and forms the complex $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3e**), a result previously described.[2]

The spectroscopic data for the four compounds (**3a**)—(**3d**) are very similar, indicating that these species must all have the same structure as that established for (**3b**) by the *X*-ray diffraction study. For all the compounds the i.r. spectra in the carbonyl stretching region show two bands, as expected (Table 1). The ^1H n.m.r. spectra all display (Table 2) a characteristic high-field signal for the B–H⇀M (M = Mo or W) bridge system, *e.g.* at δ −7.21 for (**3a**). Moreover, in accord with the presence in these complexes of the unique boron atom involved in the B–H⇀M bridge, the $^{11}B\text{-}\{^1H\}$ n.m.r. spectra all show a similar pattern, consisting of a resonance due to this unique boron nucleus (δ 18.8—20.6 p.p.m.) and a broad unresolved band corresponding to eight boron nuclei (δ −7.9 to −9.3 p.p.m.).

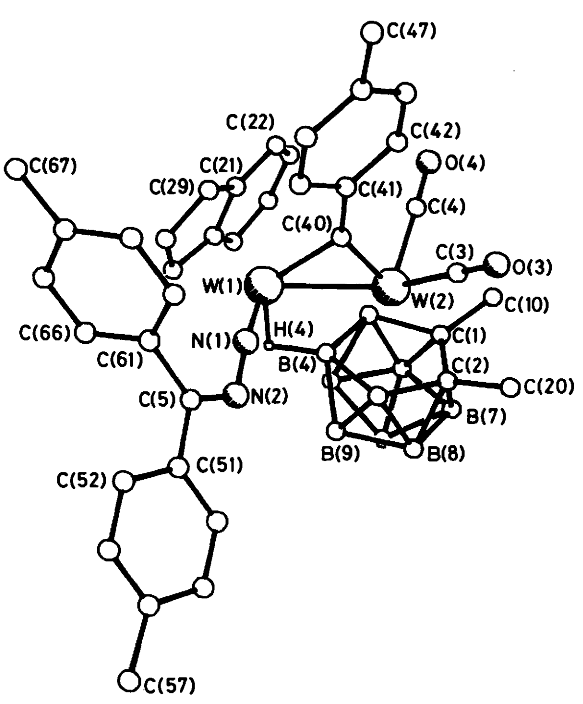


Figure 1. The molecular structure of $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{N_2C(C_6H_4Me\text{-}4)_2\}(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3b**) showing the crystallographic atom-labelling scheme

The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (Table 2) display characteristic signals for alkylidyne–carbon nuclei edge-bridging a metal–metal bond,[3] *e.g.* at δ 316.4 p.p.m. [*J*(WC) 104 Hz] for (**3b**). Whereas the spectra of (**3a**) and (**3c**) show two distinct CO resonances, as expected, those of (**3b**) and (**3d**) show only one peak under the conditions of measurement (50 MHz). However, it will be noted from the data in Table 3 that the peak separations for the CO signals in (**3a**) and (**3c**) are very small, suggesting that in the spectra of (**3b**) and (**3d**) the two resonances are coincident. Samples of complexes (**3c**) and (**3d**) were prepared from $N_2{}^{13}CPh_2$ in order to make an unambiguous n.m.r. assignment for the $N_2\mathit{C}Ph_2$ nuclei in these species (Table 2). Compounds (**3a**) and (**3b**) show dynamic behaviour involving rotation about the N–C bonds [N(2)–C(5) of Figure 1], thereby making the Me groups of the $NC(C_6H_4Me\text{-}4)_2$ fragment equivalent. Thus the ^1H n.m.r. spectra of (**3a**) and (**3b**) when measured at ambient temperatures show one peak for the Me-4 substituents of the diazoalkane ligand. However, measurement of the spectrum of (**3b**) at −40 °C resulted in disappearance of the broad peak observed at δ 2.39 (6 H) for the $C(C_6H_4\mathit{Me}\text{-}4)_2$ group in the room-temperature spectrum and the appearance of two signals, each corresponding to three protons, at δ 2.31 and 2.54. Other features in the spectrum, apart from the aromatic region, do not change over the same temperature range. The rotation process is even more facile for (**3a**), since measurement of the ^1H spectrum at −40 °C only resulted in a broadening of the resonance corresponding to 6 H seen as a sharp singlet at δ 2.41 in the room-temperature spectrum.

During the studies described herein it was observed that (**1b**) reacted with oxygen, but it was not possible to isolate a pure product by this route. It was found, however, that if (**1b**) were treated with aqueous hydrogen peroxide the oxotungsten complex $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(O)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3f**) could be isolated. The nature of this compound only became confirmed after an *X*-ray diffraction

Table 3. Selected internuclear distances (Å) and angles (°) for the complexes $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(L)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ [L = $N_2C(C_6H_4Me\text{-}4)_2$ (**3b**) or O (**3f**)]

	(3b)	(3f)		(3b)	(3f)
W(1)–W(2)	2.777(1)	2.761(1)	W(1)–C(40)	2.081(5)	2.086(7)
W(2)–C(2)	2.475(6)	2.461(8)	W(2)–B(3)	2.376(7)	2.348(9)
W(1)–B(4)	2.470(6)	2.444(8)	W(1)–H(4)	1.87(4)	2.08(10)
W(2)–C(4)	1.986(7)	1.962(9)	W(1)–C(21)	2.559(7)	2.607(8)
W(1)–C(28)	2.303(8)	2.284(8)	W(1)–C(29)	2.358(7)	2.319(8)
C(4)–O(4)	1.15(1)	1.16(1)	W(1)–N(1)	1.768(5)	
W(1)–O(5)		1.699(6)	W(2)–C(1)	2.474(5)	2.469(9)
W(2)–C(40)	1.975(5)	1.951(7)	W(2)–B(5)	2.356(7)	2.349(9)
W(2)–B(4)	2.256(6)	2.227(9)	W(2)–C(3)	1.979(6)	2.001(9)
B(4)–H(4)*	1.27(5)	1.21(10)	W(1)–C(27)	2.330(7)	2.323(9)
W(1)–C(26)	2.513(6)	2.595(8)	C(3)–O(3)	1.16(1)	1.14(1)
C(40)–C(41)	1.48(1)	1.47(1)	N(2)–C(5)	1.30(1)	
N(1)–N(2)	1.31(1)				
W(1)–W(2)–C(40)	48.4(2)	48.9(2)	W(2)–W(1)–C(40)	45.2(1)	44.8(2)
W(2)–C(40)–C(41)	142.6(4)	144.6(6)	W(2)–C(3)–O(3)	177.5(6)	176.0(9)
N(1)–N(2)–C(5)	122.7(5)		N(2)–C(5)–C(51)	116.4(5)	
W(1)–C(40)–W(2)	86.4(2)	86.2(3)	W(1)–C(40)–C(41)	130.9(4)	129.0(5)
W(2)–C(4)–O(4)	178.1(5)	176.6(8)	W(1)–N(1)–N(2)	166.8(4)	
N(2)–C(5)–C(61)	122.8(5)		W(2)–W(1)–O(5)		107.8(2)

* H(4) positions refined for both (**3b**) and (**3f**).

study. The structure of (**3f**) (Figure 2) proved to be very similar to that of (**3b**) with the diazoalkane ligand in the latter replaced by an oxygen atom in the former. Because of the closely related nature of the structures the interatomic parameters for (**3f**) are therefore shown together with those of (**3b**) in Table 3.

In (**3f**) the W(1)–O(5) distance [1.699(6) Å] is relatively short, suggesting considerable multiple-bond character involving donation of the *p*π electrons on oxygen into the empty π orbitals on the tungsten.[9] In the cluster compound $[FeW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_5(O)(\eta\text{-}C_5H_5)_2]$[10] the W=O distance [1.726(7) Å] is somewhat longer. As with (**3b**), the presence of the B–H⇀W bridge system in (**3f**) produces some slippage and fold distortions of the C_2B_9 cage. These distortions have been defined[11] in terms of three parameters: (*i*) a slip distance (Δ) from the perpendicular through the centroid of the non-bonded pentagonal B_5 girdle to the metal atom, and (*ii*) two fold angles θ and φ representating the angles between the perpendicular through the centroid of the B(6)B(7)B(8)B(9)B(10) ring and planes defined by B(5)C(1)C(2)B(3) and B(3)B(4)B(5) (Figures 1 and 2), respectively. For (**3b**) the values are Δ 0.25 Å, θ 0.9°, and φ 0.2°, and for (**3f**) Δ 0.22 Å, θ 1.7°, and φ 0.5°. These parameters are very similar to those found previously for (**1b**)[2] and for $[RuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$, the latter having a three-centre two-electron B–H⇀Ru bond.[12]

The spectroscopic properties of (**3f**) are in accord with the structure found in the solid state. The i.r. spectrum shows two CO stretching bands (Table 1), and there are two signals for these ligands in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum (Table 2). The latter also displays the expected resonance for the bridging alkylidyne–carbon nucleus at 302.8 p.p.m. The ^1H n.m.r. spectrum has a resonance at δ −5.16 characteristic for the B–H⇀W group, and in accord with this observation the $^{11}B\text{-}\{^1H\}$ spectrum has a peak for one boron nucleus at δ 19.6 p.p.m.

We have also investigated the reaction between (**1b**) and the azide $N_3C_6H_4Me\text{-}4$ and have thereby obtained the *p*-tolylimido–tungsten complex $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(NC_6H_4Me\text{-}4)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3g**). Formation of (**3g**), however, required more forcing conditions (in toluene at 90 °C) than those which afforded compounds (**3a**)—(**3f**). The data obtained for (**3g**) (Tables 1 and 2) are in accord with a structure similar to those of the other new compounds described herein. The ^1H n.m.r. spectrum showed the customary high-field signal (at δ −6.18) for the B–H⇀W group, and the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum had the diagnostic resonance for the μ-C nucleus at δ 310.1 p.p.m.

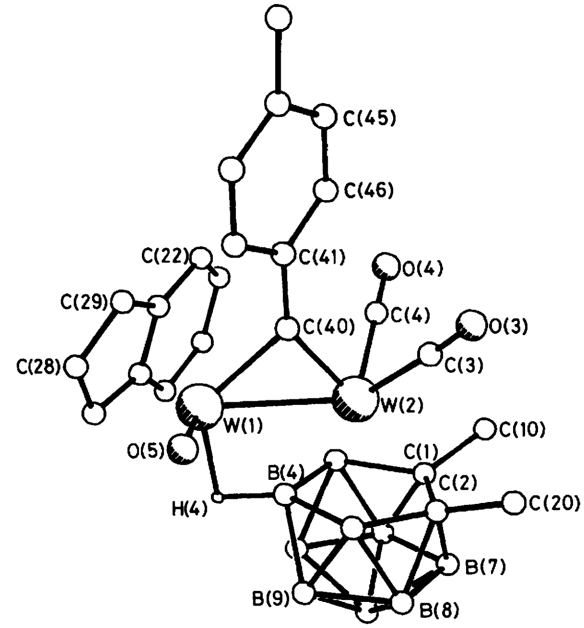


Figure 2. The molecular structure of $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(O)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3f**) showing the crystallographic atom-labelling scheme

The compounds (**3a**)—(**3d**), and (**3f**) and (**3g**), are best regarded as 34 valence electron species. This assumes that the ligand L formally contributes four electrons to the dimetal system by transfer of *p*π electrons on the ligating N or O atoms into vacant π orbitals on the metal centre. An important feature of the ^{13}C-$\{^1H\}$ n.m.r. spectra of the new compounds is that the resonances for the μ-C nuclei lie in the range δ 303—321 p.p.m., as expected for electronically saturated complexes.[3] In contrast, the resonances for the ligated μ-C groups in the 32 valence electron compounds **(1a)** and **(1b)** are significantly more deshielded at δ 381.7 and 367.6 p.p.m., respectively. Moreover, the trimethylphosphine complex **(3e)** displays a signal (δ 353.1 p.p.m.) for its μ-C group appreciably more deshielded than the corresponding signals in the ^{13}C-$\{^1H\}$ n.m.r. spectra of the compounds listed in Table 2. In **(3e)** there are no lone pairs of electrons on the ligating phosphorus atom to engage in multiple bonding with the tungsten atom. We have discussed earlier[13] the interesting correlation between chemical shifts of bridging alkylidyne carbon nuclei and the degree of electronic unsaturation of dimetal compounds. Unsaturated 32 electron species show ^{13}C-$\{^1H\}$ n.m.r. resonances for μ-C groups *ca.* 40—80 p.p.m. more deshielded than those of their saturated counterparts.

Several canonical forms may be employed to describe the electron distribution in the complexes **(3a)**—**(3d)**, and **(3f)** and **(3g)**, and there are numerous possibilities for electron delocalization involving variable electron contributions from the ligand L, the indenyl group, and the carbaborane cage. The work reported earlier,[2] and that described herein, illustrate an interesting difference in reactivity pattern for the compounds **(1)**. With PMe_3 the unsaturated 32 valence electron dimetal compounds **(2)** are formed which no longer possess a three-centre two-electron $B-H \rightharpoonup M$ bond. In contrast, the compounds **(1)** react with the reagents N_2CR_2 (R = C_6H_4Me-4 or Ph), H_2O_2, and $N_3C_6H_4Me$-4 to produce 34 valence electron dimetal complexes which retain the $B-H \rightharpoonup M$ bridge system.

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. The compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (M = Mo or W) were prepared as previously described,[2] and the diazo-compounds $N_2C(C_6H_4Me\text{-}4)_2$ and N_2CPh_2 by standard methods.[7] Analytical and other data for the new compounds are given in Table 1.

Reactions of $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (M = Mo *or* W) *with Diazo-compounds.*—(*i*) Compound **(1a)** (0.37 g, 0.50 mmol) and $N_2C(C_6H_4Me\text{-}4)_2$ (0.11 g, 0.50 mmol) were stirred together in diethyl ether (10 cm^3) for 30 min. Solvent was removed *in vacuo* and the residue washed with light petroleum (2 × 5 cm^3). Crystallisation of the residue from diethyl ether–light petroleum (10 cm^3, 1:2) at *ca.* −20 °C afforded dark red *crystals* of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{N_2C(C_6H_4Me\text{-}4)_2\}(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(3a)** (0.41 g).

In a similar synthesis, compound **(1a)** (0.37 g, 0.50 mmol) and N_2CPh_2 (0.10 g, 0.50 mmol) were stirred together in diethyl ether (10 cm^3) for 30 min. Dark red *crystals* of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(N_2CPh_2)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(3c)** (0.37 g) were obtained, as described for **(3a)**.

(*ii*) A mixture of **(1b)** (0.15 g, 0.18 mmol) and $N_2C(C_6H_4Me\text{-}4)_2$ (0.04 g, 0.18 mmol) in diethyl ether–dichloromethane (20 cm^3, 3:1) was stirred for 30 min, and then filtered through an alumina pad (*ca.* 3 cm). Solvent was removed *in vacuo*, and the residue crystallised from dichloromethane–diethyl ether (*ca.* 3 cm^3, 1:5) giving $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{N_2C(C_6H_4Me\text{-}4)_2\}(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(3b)** (0.10 g).

The compound $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(N_2CPh_2)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(3d)** (0.23 g) was similarly prepared from **(1b)** (0.26 g, 0.32 mmol) and N_2CPh_2 (0.062 g, 0.32 mmol).

Synthesis of the Oxo-complex $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(O)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$.—A toluene (10 cm^3) solution of **(1b)** (0.11 g, 0.13 mmol) was treated with 0.5 cm^3 of aqueous hydrogen peroxide (30%, 100 volume), and the mixture stirred for 10 min. Sodium carbonate (*ca.* 1 g) was added, and the mixture stirred for a further 5 min, and then filtered. All volatile material was removed *in vacuo*, and the residue was crystallised from dichloromethane–diethyl ether (*ca.* 1 cm^3, 1:1) affording brown *crystals* of $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(O)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(3f)** (0.04 g).

Synthesis of the Complex $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(NC_6H_4Me\text{-}4)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$.—A mixture of **(1b)** (0.50 g, 0.61 mmol) and $N_3C_6H_4Me$-4 (0.16 g, 1.21 mmol) in toluene (10 cm^3) was heated at 90 °C for 6 h. Solvent was removed *in vacuo*, and the residue dissolved in diethyl ether and chromatographed on an alumina column (*ca.* 2 × 20 cm). Elution with diethyl ether afforded a yellow-brown eluate which after removal of solvent *in vacuo* gave brown *crystals* of $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(NC_6H_4Me\text{-}4)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(3g)** (0.34 g).

Crystal Structure Determinations and Refinements.—Crystals were grown as deep red [**(3b)**] or brown prisms [**(3f)**] by diffusion of diethyl ether into dichloromethane solutions of the compounds. Crystals for study [**(3b)**, *ca.* 0.5 × 0.3 × 0.2 mm; **(3f)**, *ca.* 0.4 × 0.3 × 0.3 mm] were sealed under nitrogen in Lindemann glass capillaries. Diffracted intensities were collected on a Nicolet *P3m* diffractometer at 293 K, operating in the θ—2θ scan mode. For **(3b)**, 6 981 unique intensities were measured within the range $3.0 \leqslant 2\theta \leqslant 52°$ and 6 588 satisfied the criterion $I \geqslant 4\sigma(I)$. Only these were used in the structure solution and refinement, after correction for Lorentz, polarisation, and *X*-ray absorption effects, the latter by an empirical method based upon azimuthal scan data.[14] For **(3f)**, 5 839 unique intensities were collected ($3.0 \leqslant 2\theta \leqslant 55°$), with 4 307 satisfying the criterion $I \geqslant 3\sigma(I)$, and only these were used in the structure solution after similar corrections to those for **(3b)** had been applied.

Crystal data for **(3b)**. $C_{38}H_{43}B_9N_2O_2W_2 \cdot 0.5C_4H_{10}O$, M = 1 051.8, triclinic, a = 8.870(2), b = 21.499(7), c = 11.175(3) Å, α = 90.61(3), β = 96.17(2), γ = 98.46(2)°, U = 2 095(1) Å^3, Z = 2, D_c = 1.68 g cm^{-3}, $F(000)$ = 1 030, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 56.43 cm^{-1}.

Crystal data for **(3f)**. $C_{23}H_{29}B_9O_3W_2$, M = 818.5, monoclinic, a = 11.066(3), b = 12.13(1), c = 20.133(5) Å, β = 93.11(2)°, U = 2 699(2) Å^3, Z = 4, D_c = 2.01 g cm^{-3}, $F(000)$ = 1 536, space group $P2_1/c$ (no. 14), μ(Mo-K_α) = 87.23 cm^{-1}.

The metal atoms were located by direct methods, and all remaining non-hydrogen atoms were found by conventional difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically apart from those [O(7), C(71), and C(72)] of a poorly defined diethyl ether solvent molecule located disordered about a centre of inversion in **(3b)** (one solvent molecule per unit cell). These atoms were fixed in position and given isotropic thermal parameters in the refinement. For **(3b)** the hydrogen atoms of the carbaborane cage were located and their positional parameters were refined ($U_{iso.}$ 0.03 Å^2). For **(3f)** the hydrogen atoms on the carbaborane cage were all located, their positional parameters refined, and all cage hydrogen atoms, apart from H(4), given a common isotropic thermal parameter ($U_{iso.}$ 0.04 Å^2). For both **(3b)** and **(3f)** all non-cage hydrogen atoms were included in calculated 'riding' positions [C–H 0.96 Å, $U_{iso.} = 1.2 \times U_{eqiv.}(C)$]. Refinement by full-matrix least squares led to convergence for **(3b)** at

Table 4. Atomic positional parameters (fractional co-ordinates) (× 10^4), with estimated deviations in parentheses for (**3b**)·$0.5Et_2O$

Atom	x	y	z	Atom	x	y	z
W(1)	2 363(1)	2 499(1)	1 644(1)	N(2)	4 727(6)	1 649(2)	1 167(4)
W(2)	2 905(1)	3 521(1)	167(1)	C(5)	5 448(7)	1 306(3)	1 916(5)
C(3)	4 888(7)	4 089(3)	315(5)	C(51)	6 275(7)	852(3)	1 386(5)
C(4)	2 043(7)	4 242(3)	809(5)	C(52)	6 989(7)	422(3)	2 095(6)
O(3)	6 076(5)	4 405(2)	419(4)	C(53)	7 670(8)	−32(3)	1 563(7)
O(4)	1 514(6)	4 649(2)	1 197(5)	C(54)	7 705(7)	−78(3)	316(7)
C(40)	3 624(6)	3 397(3)	1 871(5)	C(55)	7 034(8)	362(3)	−377(6)
C(41)	4 620(6)	3 706(3)	2 921(5)	C(56)	6 326(8)	817(3)	130(6)
C(42)	4 928(7)	4 355(3)	3 081(5)	C(57)	8 410(9)	−594(3)	−235(8)
C(43)	5 950(7)	4 646(3)	4 021(5)	C(61)	5 393(7)	1 343(3)	3 246(5)
C(44)	6 730(7)	4 290(3)	4 828(5)	C(62)	6 379(8)	1 803(3)	3 946(5)
C(45)	6 425(7)	3 634(3)	4 694(6)	C(63)	6 331(9)	1 817(3)	5 196(6)
C(46)	5 388(7)	3 348(3)	3 765(5)	C(64)	5 352(8)	1 377(4)	5 761(6)
C(47)	7 877(10)	4 611(4)	5 835(7)	C(65)	4 419(9)	924(4)	5 052(7)
C(1)	1 546(7)	3 676(3)	−1 835(5)	C(66)	4 449(8)	898(4)	3 800(6)
C(2)	3 145(7)	3 411(3)	−2 008(5)	C(67)	5 356(11)	1 379(4)	7 116(6)
C(10)	1 408(8)	4 372(3)	−1 981(6)	B(3)	3 309(8)	2 742(3)	−1 240(6)
C(20)	4 559(8)	3 859(3)	−2 347(6)	B(4)	1 597(8)	2 585(3)	−533(6)
C(21)	473(7)	2 890(3)	2 946(6)	B(5)	483(8)	3 200(4)	−921(6)
C(22)	−8(9)	3 492(4)	2 957(7)	B(6)	7(9)	3 147(4)	−2 500(7)
C(23)	−1 300(9)	3 573(4)	2 232(7)	B(7)	1 678(11)	3 300(4)	−3 187(6)
C(24)	−2 108(8)	3 098(4)	1 482(8)	B(8)	2 804(9)	2 709(4)	−2 819(6)
C(25)	−1 658(7)	2 522(4)	1 393(7)	B(9)	1 793(10)	2 173(3)	−1 882(7)
C(26)	−345(6)	2 398(3)	2 169(6)	B(10)	25(9)	2 448(4)	−1 689(7)
C(27)	340(8)	1 846(3)	2 361(6)	B(11)	784(11)	2 516(4)	−3 102(7)
C(28)	1 532(9)	1 993(4)	3 311(6)	O(7)	0	0	5 000
C(29)	1 728(8)	2 640(4)	3 614(6)	C(71)	314	9 255	4 436
N(1)	3 817(5)	2 030(2)	1 512(4)	C(72)	1 098	9 356	3 638

Tabel 5. Atomic positional parameters (fractional co-ordinates) (× 10^4), with estimated deviations in parentheses for (**3f**)

Atom	x	y	z	Atom	x	y	z
W(1)	2 403(1)	1 051(1)	3 858(1)	C(27)	3 359(7)	797(8)	4 903(4)
W(2)	894(1)	2 583(1)	3 228(1)	C(26)	3 344(7)	1 980(8)	4 926(4)
C(40)	2 500(6)	2 062(6)	3 024(4)	C(25)	2 806(9)	2 737(11)	5 361(5)
C(41)	3 454(7)	2 129(7)	2 548(4)	C(24)	3 009(13)	3 831(13)	5 254(8)
C(42)	4 044(7)	1 187(7)	2 346(4)	C(23)	3 693(15)	4 206(11)	4 734(8)
C(43)	4 915(8)	1 236(8)	1 866(4)	C(22)	4 162(10)	3 504(9)	4 301(6)
C(44)	5 235(7)	2 222(7)	1 596(4)	B(3)	−573(8)	1 225(8)	3 389(5)
C(45)	4 675(9)	3 156(8)	1 805(5)	B(4)	362(7)	1 627(8)	4 111(4)
C(46)	3 792(8)	3 111(8)	2 277(5)	B(5)	116(8)	3 050(8)	4 253(4)
C(47)	6 142(8)	2 269(9)	1 058(4)	B(6)	−1 430(10)	3 186(10)	4 457(6)
C(1)	−949(9)	3 417(7)	3 651(4)	B(7)	−2 328(10)	2 796(11)	3 748(6)
C(2)	−1 321(7)	2 380(8)	3 160(5)	B(8)	−2 086(9)	1 395(11)	3 605(6)
C(10)	−1 101(9)	4 611(9)	3 392(6)	B(9)	−1 024(8)	885(9)	4 212(5)
C(20)	−1 852(9)	2 577(10)	2 459(5)	B(10)	−626(9)	2 026(10)	4 748(5)
C(3)	829(8)	2 702(9)	2 235(4)	B(11)	−2 130(10)	1 898(11)	4 429(6)
C(4)	1 659(7)	4 042(7)	3 253(4)	O(5)	2 160(5)	−182(5)	3 474(3)
C(21)	4 015(7)	2 381(7)	4 409(4)	O(4)	2 100(7)	4 907(6)	3 301(4)
C(29)	4 445(7)	1 422(8)	4 065(4)	O(3)	850(7)	2 731(9)	1 669(3)
C(28)	4 138(7)	480(8)	4 423(5)				

$R = 0.034$ ($R' = 0.036$) and for (**3f**) at $R = 0.036$ ($R' = 0.035$), with a weighting scheme of the form $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$, with $g = 0.000\ 08$ [(**3b**)] and 0.000 55 [(**3f**)] giving a satisfactory analysis. The final electron-density difference synthesis showed no residual peaks $\leqslant 1.3$ e Å^{-3} [for (**3b**)] and $\leqslant 0.8$ e Å^{-3} [for (**3f**)]. Scattering factors and corrections for anomalous dispersion were from ref. 15. All computations were carried out on an 'Eclipse' (Data General) computer with the SHELXTL system of programs.[14] Atomic co-ordinates for (**3b**) and (**3f**) are given in Tables 4 and 5, respectively.

Acknowledgements

We thank the S.E.R.C. for support and for research studentships (to A. P. J. and C. M. N.), and Shell Research Ltd. for a C.A.S.E. award.

References

1 Part 57, P. G. Byrne, M. E. Garcia, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, preceding paper.
2 M. Green, J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 81.
3 J. A. Abad, L. W. Bateman, J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2075.
4 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123.
5 L. B. Kool, M. D. Rausch, H. G. Alt, M. Herberhold, A. F. Hill, U. Thewalt, and B. Wolf, *J. Chem. Soc., Chem. Commun.*, 1986, 408.

6 W. A. Herrmann, G. Kriechbaum, M. L. Ziegler, and P. Wulknitz, *Chem. Ber.*, 1981, **114**, 276.

7 M. H. Chisholm, K. Folting, J. C. Huffmann, and A. L. Ratermann, *J. Chem. Soc., Chem. Commun.*, 1981, 1229; *Inorg. Chem.*, 1984, **23**, 2303.

8 L. Messerle and M. D. Curtis, *J. Am. Chem. Soc.*, 1980, **102**, 7789.

9 I. Feinstein-Jaffe, D. Gibson, S. J. Lippard, R. R. Schrock, and A. Spool, *J. Am. Chem. Soc.*, 1984, **106**, 6305.

10 L. Busetto, J. C. Jeffery, R. M. Mills, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 101.

11 D. M. P. Mingos, M. I. Forsyth, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1978, 1363.

12 M. Green, J. A. K. Howard, A. N. de M. Jelfs, O. Johnson, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 73.

13 M. Green, J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1986, 1697.

14 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *P*3*m* *X*-ray system, University of Cambridge, 1976; updated, Göttingen, 1981.

15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 11th June 1986; *Paper* 6/1184