Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 52.[1] Synthesis and Reactions of the Compounds $[RuW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4Me-4 or Me); Crystal Structures of $[RuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ and $[N(PPh_3)_2][RuW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta\text{-}C_5H_5)]$ *

Michael Green, Judith A. K. Howard, Alasdair N. de M. Jelfs, Owen Johnson, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Treatment of the compounds $[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4Me-4 or Me) with $[Ru(CO)(NCMe)_2(\eta\text{-}C_5H_5)][BF_4]$ in CH_2Cl_2 affords the dimetal complexes $[RuW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$. The structure of the product with R = C_6H_4Me-4 has been established by a single-crystal *X*-ray diffraction study. The Ru–W bond [2.803(2) Å] is spanned by the *p*-tolymethylidyne group [Ru–μ-C 2.220(7); W–μ-C, 1.890(6) Å]. The tungsten atom carries two CO ligands and the $\eta^5\text{-}C_2B_9H_9Me_2$ cage. The ruthenium atom is ligated by a CO group and the cyclopentadienyl anion, and also by the unique B–H bond of the open pentagonal face of the icosahedral $\eta^5\text{-}C_2B_9H_9Me_2$ fragment [B–Ru, 2.400(7); B–H, 1.33; Ru–H, 1.67 Å]. Deprotonation of $[RuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$, on basic alumina or by n-butyl-lithium, in the presence of $[N(PPh_3)_2]Cl$ gives the salt $[N(PPh_3)_2][RuW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta\text{-}C_5H_5)]$ which was structurally characterised by *X*-ray diffraction. The structure of the anion [Ru–W, 2.748(1); Ru–μ-C, 2.100(6); W–μ-C, 1.941(5) Å] is very similar to that of its neutral precursor, the major difference being replacement of the B–H$\rightharpoonup$Ru three-centre two-electron bond by a direct B–Ru linkage [2.155(6) Å]. The $C_2B_9H_8Me_2$ cage thus adopts an unusual μ-σ,η^5 bonding mode at the WRu centre. Some reactions of the ruthenium–tungsten dimetal species are described, and spectroscopic data are reported and discussed.

In the preceding paper[1] we described the synthesis of the salts $[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1**, R = C_6H_4-Me-4 or Me). We also reported their use as reagents for preparing dimetal compounds with tungsten bonded to gold or rhodium, the metal–metal bonds in the products being bridged by alkylidyne groups. The anions of (**1**) are isolobal with the neutral species $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$. The latter are known to react with a variety of low-valent metal–ligand fragments to give dimetal or metal cluster compounds containing tungsten and other transition elements.[2] It is to be anticipated therefore, that the complexes (**1**) will be precursors to many compounds with heteronuclear metal–metal bonds, and in extending our studies we have investigated reactions with the ruthenium salt $[Ru(CO)(NCMe)_2(\eta\text{-}C_5H_5)][BF_4]$.[3] This work was prompted by the observation that the salts (**1**) with $[M(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (M = Mo or W, C_9H_7 = indenyl)[4] afford novel dimetal compounds $[MW(\mu\text{-}CR)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9\text{-}Me_2)]$ containing three-centre two-electron B–H$\rightharpoonup$M bonds in addition to bridging alkylidyne groups.[5]

Results and Discussion

Treatment of the compounds (**1**) with $[Ru(CO)(NCMe)_2(\eta\text{-}C_5H_5)][BF_4]$ in CH_2Cl_2 at room temperature affords the crystalline complexes $[RuW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2a**, R = C_6H_4Me-4; **2b**, R = Me). The i.r. spectra of these products show three bands in the terminal carbonyl stretching region with almost identical patterns, indicating that the compounds are isostructural. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (Table 1) display resonances characteristic for alkylidyne-carbon nuclei [(**2a**), δ 276.7; (**2b**), 285.3 p.p.m.], but the chemical shifts are outside the range (δ 300—430 p.p.m.) normally associated with alkylidyne ligands bridging a dimetal centre.[6] The ^1H n.m.r. spectra showed resonances [(**2a**), δ −11.48; (**2b**), −11.60] at high field, and the chemical shifts and the appearance of these signals as quartets ($^{11}B\text{-}^1H$ coupling) suggested the presence of B–H$\rightharpoonup$Ru groups in these molecules. Further discussion of the n.m.r. data is deferred, however, until the results of the *X*-ray diffraction study are described.

The structure of (**2a**) is shown in Figure 1, and selected internuclear distances and angles are listed in Table 2. It is immediately evident that the Ru–W bond is bridged by the *p*-tolylmethylidyne group, the dimensions of the three-membered ring being Ru–W 2.803(2), Ru–C(01) 2.220(7), and W–C(01) 1.890(6) Å. The metal–metal bond distance is intermediate between those found[7] in $[RuW(\mu\text{-}Cl)(\mu\text{-}CMe)(Cl)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ [2.769(1) Å] and $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ [2.835(1) and 3.026(1) Å]. The Ru–C(01) separation [2.220(7) Å] is significantly longer than the Ru–μ-C distance in $[RuW(\mu\text{-}Cl)(\mu\text{-}CMe)(Cl)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ [2.021(9) Å].[7] Moreover, in (**2a**) the Ru–μ-C distance is longer than the Ru–μ-C bonds in the diruthenium compounds $[Ru_2(\mu\text{-}CR_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ [R = Me, 2.113(4); R = H, 2.093(5) Å, average][8] and $[Ru_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ [2.030(7) Å, average],[9] containing alkylidene and vinylidene groups, respectively. The relatively long Ru–C(01) distance perhaps indicates the presence of a weak σ bond. It is accompanied by a relatively short W–C(01) separation

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* 1,2,2-Tricarbonyl-1-(η-cyclopentadienyl)-μ-[7′—11′-η-nonahydro-7′,8′-dimethyl-7′,8′-dicarba-*nido*-undecaborato(2−)-$C^{7',8'}$, $B^{9'-11'}$(W), $H^{10'}$(Ru)]-μ-(*p*-tolylmethylidyne)rutheniumtungsten (*Ru–W*) and bis(triphenylphosphine)iminium 1,2,2-tricarbonyl-1-(η-cyclopentadienyl)-μ-[σ,7′—11′-η-octahydro-7′,8′-dimethyl-7′,8′-dicarba-*nido*-undecaborato(3−)-$C^{7',8'}$, $B^{9'-11'}$(W), $B^{10'}$(Ru)]-μ-(*p*-tolylmethylidyne)-rutheniumtungstate (*Ru–W*) respectively.

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

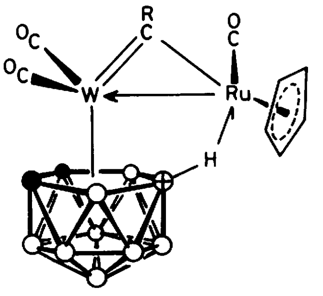
Table 1. Hydrogen-1, carbon-13, and boron-11 n.m.r. data[a] for the ruthenium–tungsten compounds

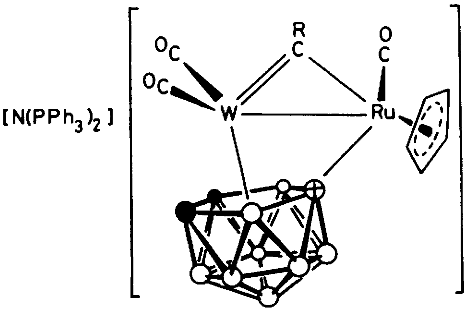
Compound	^{1}H(δ)[b,c]	^{13}C(δ)[d]	^{11}B(δ)[e]
(**2a**)	-11.48 [q, 1 H, B(μ-H)Ru, *J*(BH) 70], 2.09 (s, 3 H, CMe), 2.28 (s, 6 H, CMe and Me-4), 5.22 (s, 5 H, C_5H_5), 7.19 and 7.40 [$(AB)_2$ system, 4 H, C_6H_4, *J*(AB) 8]	276.7 [μ-C, *J*(WC) 132], 225.4 [WCO, *J*(WC) 187], 220.1 [WCO, *J*(WC) 162], 197.9 (RuCO), 154.7 [$C^1(C_6H_4)$], 137.1, 129.1, 128.6 (C_6H_4), 90.3 (C_5H_5), 61.9, 60.6 (*C*Me), 30.0, 29.4 (C*Me*), 21.1 (Me-4)	19.5 [s, 1 B, B(μ-H)Ru], -7.6 (br, 8 B)
(**2b**)	-11.60 [q, 1 H, B(μ-H)Ru, *J*(BH) 62], 2.04, 2.28 (2 × s, 6 H, CMe), 2.70 (s, 3 H, μ-CMe), 5.39 (s, 5 H, C_5H_5)	[f] 285.3 [μ-C, *J*(WC) 131], 225.7 [WCO, *J*(WC) 187], 221.6 [WCO, *J*(WC) 162], 199.4 (RuCO), 90.2 (C_5H_5), 62.0, 59.8 (*C*Me), 47.0 (μ-C*Me*)	[g] 18.8 [s, 1 B, B(μ-H)Ru], -8.0, -15.3 (v br, 8 B)
(**3a**)	2.03, 2.20, 2.24 (3 × s, 9 H, CMe and Me-4), 4.94 (s, 5 H, C_5H_5), 7.07—7.69 (m br, 34 H, C_6H_4 and Ph)	312.6 [μ-C, *J*(WC) 125], 232.7 [WCO, *J*(WC) 187], 227.6 [WCO, *J*(WC) 162], 208.9 (RuCO), 158.6 [$C^1(C_6H_4)$], 133.7—125.4 (C_6H_4 and Ph), 89.7 (C_5H_5), 58.6, 56.7 (*C*Me), 30.4, 29.7 (C*Me*), 21.1 (Me-4)	45.9 [s, 1 B, BRu], -8.3, -17.4 (v br, 8 B)
(**5**)	1.63 [d, 9 H, MeP, *J*(PH) 8], 2.30, 2.31 (2 × s, 6 H, CMe and Me-4), 2.62 [d, 3 H, CMe, *J*(PH) 3], 5.07 (s, 5 H, C_5H_5), 5.95 [s, 1 H, C*H*(C_6H_4Me-4)], 7.16, 7.63 [$(AB)_2$ system, 4 H, C_6H_4, *J*(AB) 8]	208.2 [d, WCO, *J*(PC) 6], 202.7 [d, WCO, *J*(PC) 6], 199.2 (RuCO), 137.7, 136.2, 129.3, 126.8 (C_6H_4), 89.5 (C_5H_5), 39.5 (C*Me*), 34.9 [d, C*Me*, *J*(PC) 12], 28.9 [*C*H(C_6H_4Me-4)], 20.9 (Me-4), 15.4 [d, PMe_3, *J*(PC) 24]	65.4 [s, 1 B, BC(H)C_6H_4Me-4], 20.3 (br, 1 B), 6.0 (br, 1 B), -4.5 (br, 4 B), -14.8 (br, 2 B)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at room temperature unless otherwise stated. [b] Measured in CD_2Cl_2. [c] Resonances for B–H protons not resolved, due to ^{11}B–^{1}H coupling, and occurring as very broad signals in the range *ca.* δ 0—5. [d] Hydrogen-1 decoupled, chemical shifts to high frequency of $SiMe_4$, measured in CD_2Cl_2–CH_2Cl_2 at −40 °C. [e] Hydrogen-1 decoupled, chemical shifts to high frequency of $BF_3\cdot Et_2O$ (external). [f] Measured in $(CD_3)_2CO$–thf at −40 °C. Signal for C*Me* groups obscured by solvent peaks. [g] Measured in $(CD_3)_2CO$–thf at room temperature.

$[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$

	R
(**1a**)	C_6H_4Me-4
(**1b**)	Me





⊕ B ○ BH ● CMe

	R
(**2a**)	C_6H_4Me-4
(**2b**)	Me

	R
(**3a**)	C_6H_4Me-4
(**3b**)	Me

[1.890(6) Å], which may be compared with that [1.82(2) Å] in the mononuclear tungsten compound [W(≡CC_6H_4Me-4)$(CO)_2(\eta\text{-}C_5H_5)$].[10] Moreover, W–C(01) is appreciably shorter than the corresponding distances found [1.91(2)—1.967(6) Å] by *X*-ray diffraction in several compounds containing the dimetal ring system $\overline{\text{M}(\mu\text{-CC}_6\text{H}_4\text{Me-4})\text{W}}$ (M = Ti, Co, Rh, Ru, or Pt).[7,11] Furthermore, the short W–C(01) distance is associated with a W–C(01)–C(02) angle [152.6(5)°] appreciably larger than the corresponding angles [137.9(7)—146(1)°] in related dimetal compounds.[7,11] However, in the compound [RhW(μ-CC_6H_4Me-4)$(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)$][1] the W–$\mu$-C separation [1.880(6) Å] and the W–μ-C–C^1(C_6H_4Me-4) angle [153.9(4)°] are similar to those in (**2a**).

The ruthenium atom in (**2a**) carries a terminal carbonyl group [Ru–C(5)–O(5) 176.2(6) Å], and the cyclopentadienyl ligand. The tungsten atom has two effectively linear carbonyl groups [W–C(1)–O(1) 175.6(6), W–C(2)–O(2) 174.6(6)°], and is also ligated by the η^5-$C_2B_9H_9Me_2$ cage. Interestingly, one hydrogen atom [H(1)] in the latter forms a bridge to the ruthenium (1.67 Å), thus accounting for the quartet resonance in the ^{1}H n.m.r.

Table 2. Selected bond distances (Å) and interbond angles (°) for $[RuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2a**) and $[N(PPh_3)_2][RuW(\mu\text{-}C_6H_4Me\text{-}4)(\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta\text{-}C_5H_5)]$ (**3a**)

	(2a)	**(3a)**[a]		**(2a)**	**(3a)**		**(2a)**	**(3a)**		**(2a)**	**(3a)**
Ru–W	2.803(2)	2.748(1)	W–C(1)	2.030(7)	1.989(7)	W–C(2)	1.968(7)	1.949(7)	W–B(1)	2.248(8)	2.226(7)
W–B(2)	2.372(8)	2.364(7)	W–C(3)	2.488(6)	2.544(6)	W–C(4)	2.472(6)	2.506(6)	W–B(5)	2.371(8)	2.356(8)
W–C(01)	1.890(6)	1.941(5)	Ru–C(01)	2.220(7)	2.100(6)	Ru–C(5)	1.864(7)	1.822(6)	Ru–C(cp)[b]	2.231(8)	2.289(5)
Ru–B(1)	2.400(7)	2.155(6)	Ru–H(1)	1.67		B(1)–H(1)	1.33		C(01)–C(02)	1.464(9)	1.462(7)
C(1)–O(1)	1.121(8)	1.142(9)	C(2)–O(2)	1.158(9)	1.169(9)	C(5)–O(5)	1.156(10)	1.151(8)			
Ru–W–C(1)	129.1(2)	125.7(2)	Ru–W–C(2)	96.1(2)	102.7(2)	C(1)–W–C(2)	91.8(3)	90.5(3)	Ru–W–C(01)	52.1(2)	49.6(2)
C(1)–W–C(01)	79.1(3)	81.0(2)	C(2)–W–C(01)	83.9(3)	83.5(2)	B(1)–W–C(01)	105.2(3)	98.0(2)	W–Ru–C(5)	101.6(2)	97.7(2)
W–Ru–B(1)	50.5(2)	52.3(2)	C(5)–Ru–B(1)	95.1(3)	83.6(2)	W–Ru–C(01)	42.2(2)	44.8(1)	C(5)–Ru–C(01)	87.3(3)	92.7(2)
B(1)–Ru–C(01)	90.8(3)	95.5(2)	Ru–C(5)–O(5)	176.2(6)	177.6(5)	W–C(1)–O(1)	175.6(6)	176.0(6)	W–C(2)–O(2)	174.6(6)	175.3(6)
W–B(1)–Ru	74.1(2)	77.7(2)	W–C(01)–Ru	85.6(2)	85.6(2)	W–C(01)–C(02)	152.6(5)	149.3(4)	Ru–C(01)–C(02)	121.4(4)	124.8(3)
Ru–H(1)–B(1)	106.0(3)										

[a] P–N distance (mean) 1.566(6) Å; P–N–P 147.1(4)°. [b] Mean value, cp = $\eta\text{-}C_5H_5$.

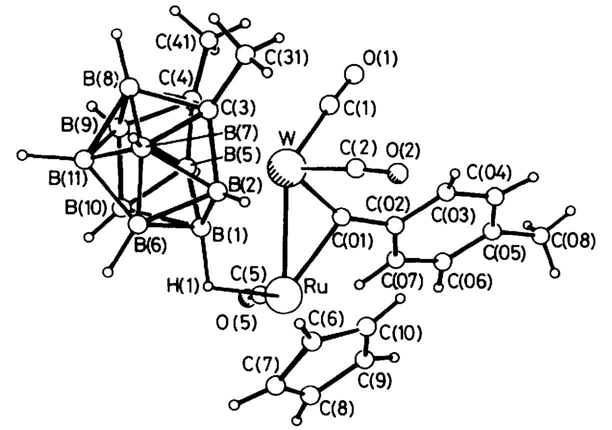


Figure 1. The molecular structure of $[RuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2a**) showing the atom-numbering scheme

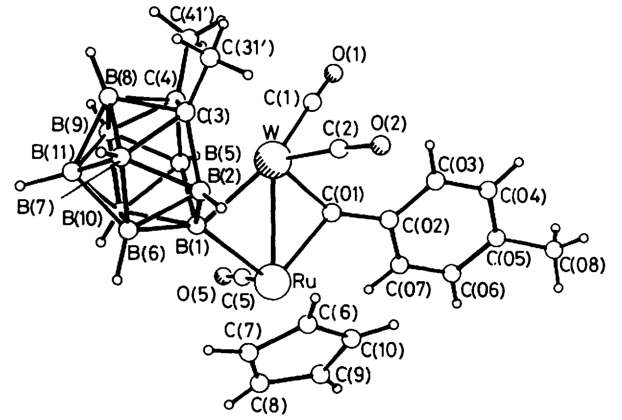
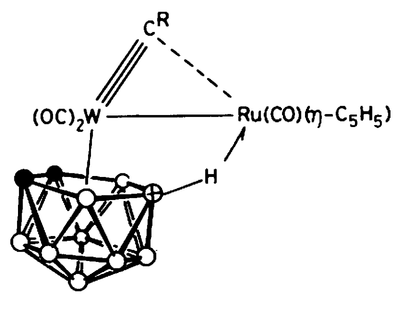


Figure 2. The molecular structure of the anion of $[N(PPh_3)_2][RuW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta\text{-}C_5H_5)]$ (**3a**) showing the atom-numbering scheme

spectrum at δ −11.48, mentioned earlier. The Ru–B(1) distance [2.400(7) Å], though appreciably longer than W–B(1) [2.248(8) Å] is not much greater than the other W–B separations [W–B(2), 2.372(8); W–B(5), 2.371(8) Å].

As mentioned in the Introduction, we have previously observed carbaborane cage bonding in a heteronuclear dimetal system similar to that in (**2a**) in 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).[5] Moreover, earlier Hawthorne and co-workers[12] had shown that *exo*-polyhedral B–H→Rh bridge bonding occurs in the homonuclear dimetal compounds $[Rh_2(PR_3)_2(\eta^5\text{-}C_2B_9H_{11})_2]$ (PR_3 = PPh_3, PEt_3, or PMe_2Ph). The presence of the B–H→M (M = Mo, W, Rh, or Ru) three-centre two-electron bonds in these various complexes produces a 'slippage' of the metal atom from above the centroid of the open pentagonal face of the carbaborane ligand towards the unique boron atom. *X*-Ray diffraction studies have revealed similar distortions in certain mononuclear metal carbaborane complexes.[13] The 'slippage' of the pentagonal girdle of the icosahedral ligand is accompanied by a 'folding' of the C_2B_3 face about the two equivalent boron atoms [B(2) and B(5) of Figure 1]. These slip and fold distortions have been defined[14] 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*) fold angles θ and φ representing the angles between the perpendicular through the centroid of the B(6), B(7), B(8), B(9), and B(10) ring and the planes defined by B(2)C(3)C(4)B(5) and by B(2)B(1)B(5) (Figure 1), respectively. For compound (**2a**), the parameters are Δ 0.24 Å, θ 1.4°, and φ 0.3°. The relatively large Δ value and the small values of θ and φ suggest that these distortions are due to the effect of the B–H→Ru interaction rather than any electronic effects in the bonding of tungsten to the cage ligand.

Compounds (**2a**) and (**2b**) have similar spectroscopic properties, and therefore it is very likely that they have similar structures. Thus the $^{11}B\text{-}\{^1H\}$ n.m.r. spectra of both species (Table 1) show a low-field signal for a unique boron nucleus [(**2a**), δ 19.5; (**2b**) 18.8 p.p.m.], and this resonance may be assigned to the B–H→Ru groups. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra, measured at −40 °C, reveal three peaks in each spectrum for the carbonyl groups (Table 1). Moreover, the appearance of $^{183}W\text{-}^{13}C$ satellite signals on two of the resonances enable these to be assigned to the two CO ligands attached to the tungsten. We referred earlier to the resonances for the μ-*C*R groups at δ 276.7 (**2a**) and 285.3 p.p.m. (**2b**). These signals also show $^{183}W\text{-}^{13}C$ couplings of 132 and 131 Hz, respectively. As mentioned above, the μ-*C*R resonance in the spectrum of (**2a**) is more shielded than any observed previously in dimetal complexes,[6,11] with the exception of those found in the gold–tungsten complexes $[AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9R'_2)]$ (R = C_6H_4Me-4, R′ = Me or H; R = Me, R′ = Me)[1] and $[AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)][PF_6]$ (R = C_6H_4Me-4 or Me).[15] The effect seems not to be due to the presence of the B–H→Ru groups in (**2**) since in 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), which have similar B–H→M bonding, the signals for the μ-CC_6H_4Me-4 nuclei occur within the normal range at δ 381.7 (M = Mo) and 367.6 p.p.m. (M = W). It seems probable that the chemical shifts observed for the μ-C nuclei in the ^{13}C-{^1H} n.m.r. spectra of (**2**) are a consequence of the nature of the W(μ-CR)Ru ring bonding. In order to provide an 18-electron configuration at the ruthenium and tungsten centres we have chosen to regard the metal–metal linkages as involving donation of an electron pair from ruthenium to tungsten. The usual assumptions are made that the carbaborane ligand is formally a four-electron donor, that the agostic[16] B–H⟶Ru interaction contributes an electron pair to the ruthenium, and the μ-CR groups provide three electrons for the bridge system. However, as discussed above, the *X*-ray diffraction results for (**2a**) revealed that the μ-C atom was very much closer to the tungsten than to the ruthenium, and consequently should be regarded as semi-bridging the metal–metal vector. In an extreme view, if the CR ligands in (**2**) were terminally bound to the tungsten, then the two metal centres could acquire 18-electron closed-shell configurations without invoking a Ru–C bond, see below.



The concept of a semi-bridging alkylidyne ligand in a dimetal complex has been discussed earlier[1,15] in the context of the *X*-ray diffraction and ^{13}C-{^1H} n.m.r. data for the complexes $[AuW(\mu-CR)(CO)_2(PPh_3)(\eta^5-C_2B_9H_9R'_2)]$ (R = C_6H_4Me-4, R′ = Me or H; R = Me, R′ = Me) and $[AuW(\mu-CR)(CO)_2(PPh_3)(\eta-C_5H_5)][PF_6]$ (R = C_6H_4Me-4 or Me). Probably the electron distribution in (**2**) lies between the extremes of Ru–W and Ru⟶W bonding, substantial electron delocalisation being possible *via* the ligands.

In the synthesis of (**2a**) the complex was purified by column chromatography on Florisil. In an experiment in which an attempt was made to isolate (**2a**) after chromatography on basic alumina, a different product, (**3a**), was obtained which was salt-like in character. It was suspected that the new compound resulted from deprotonation of (**2a**), and a better synthesis was devised involving treatment of the latter in CH_2Cl_2 with $[N(PPh_3)_2]Cl$ followed by n-butyl-lithium. The compound (**3a**) was established as the species $[N(PPh_3)_2][RuW(\mu-CC_6H_4Me-4)(\mu-\sigma,\eta^5-C_2B_9H_8Me_2)(CO)_3(\eta-C_5H_5)]$ by a single-crystal *X*-ray diffraction study.

The structure of the anion of (**3a**) is shown in Figure 2, and selected internuclear distances and angles are listed in Table 2, adjacent to those of (**2a**) for comparison. The results confirm that deprotonation of (**2a**) occurs at the B–H⟶Ru bridge, and in accord with this result the ^1H n.m.r. spectrum of (**3a**) shows no high-field resonance characteristic of a B–H⟶M bond. In (**3a**) there is a σ bond between B(1) and the ruthenium atom [B(1)–Ru 2.155(6) Å]. Apart from this feature, the structure of the anion of (**3a**) is very similar to that of its precursor (**2a**). However, the formation of the B(1)–Ru σ bond results in further slippage of the open pentagonal face of the carbaborane ligand with Δ = 0.32 Å, θ = 1.3°, and φ = 0.8°, respectively. The Ru–W vector and the B(1)B(2)C(3)C(4)B(5) mean plane deviate by 7.6° from being parallel, whereas for (**2a**) the corresponding angle is only 1.5°. It is thus more obvious that in (**3a**) slippage is due to the *exo*-polyhedral boron–ruthenium interaction.

The dimensions of the Ru(μ-C)W ring in (**3a**) [Ru–W 2.748(1), Ru–C(01) 2.100(6), W–C(01) 1.941(5) Å, with W–C(01)–C(02) 149.3(4)°] show that the μ-CC_6H_4Me-4 ligand is less asymmetrically bridging, with tighter bonding of the W≡C fragment to the ruthenium than in (**2a**). The W–μ-C separation for (**3a**) is within the range previously found for several complexes containing a W(μ-C)M ring system, and corresponds to a formal W=C bond.[7,11] Moreover, for an 18-electron closed-shell configuration at each metal centre it is not necessary to invoke a Ru⟶W donor bond.

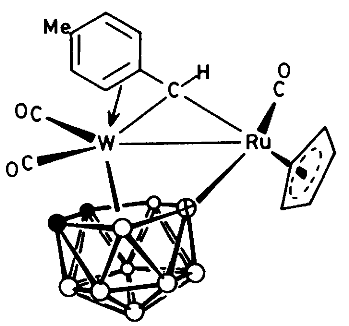
The three carbonyl groups in (**3a**) are essentially terminally bound to their respective metal centres [W–C(1)–O(1) 176.0(6), W–C(2)–O(2) 175.3(6), and Ru–C(5)–O(5) 177.6(5)°]. The $[N(PPh_3)_2]^+$ counter ion is non-linear [P–N–P 147.1(4)°], with an N–P (average) distance of 1.566(6) Å. These data are as expected. In a variety of salts containing the cation $[N(PPh_3)_2]^+$ the P–N–P angle occurs in the range 135—180°.[17]

Having established the structure of (**3a**), it was possible to interpret the spectroscopic data. A ^{31}P-{^1H} n.m.r. spectrum showed a resonance at 21.1 p.p.m. (rel. to 85% H_3PO_4, external), characteristic for the cation. The i.r. spectrum showed three bands (1 939, 1 898, and 1 852 cm^{-1}) in the CO stretching region, these absorptions being *ca.* 70 cm^{-1} to lower frequency of the three CO bands in (**2a**), as expected for an anionic complex. The ^{11}B-{^1H} n.m.r. spectrum of (**3a**) (Table 1) showed the presence of a unique boron at δ 45.9 p.p.m., and this signal may be ascribed to the B–Ru group. The other boron resonances were very broad. The ^{13}C-{^1H} n.m.r. spectrum was informative with peaks at δ 312.6 [*J*(WC) 125], 232.7 [*J*(WC) 187], 227.6 [*J*(WC) 162], and 208.9 p.p.m. The signal at 312.6 p.p.m. is in the region for a μ-C nucleus bridging two metal centres.[6,11] The peaks at δ 232.7 and 227.6 may be ascribed to the CO groups bound to the tungsten, and the signal at 208.9 p.p.m. to the Ru(CO) group.

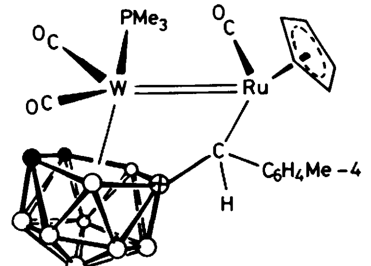
An attempt to prepare (**3b**) by treating (**2b**) with $[N(PPh_3)_2]Cl$, followed by n-butyl-lithium was unsuccessful since no product could be isolated. However, the observation of CO bands in the i.r. spectrum at 1 934s, 1 892s, and 1 846s cm^{-1} suggested that (**3b**) was formed, since this band pattern is very similar to that shown by (**3a**).

It was anticipated that protonation of (**3a**) with $HBF_4 \cdot Et_2O$ would yield (**2a**). However, in CH_2Cl_2 the reaction followed a different course. A colour change from brown to red was observed, and the i.r. spectrum of the solution showed three major bands in the carbonyl stretching region at 1 985, 1 946, and 1 917 cm^{-1}. It was not possible to isolate a stable product from the solution, but n.m.r. measurements [^1H, ^{13}C-{^1H}, and ^{11}B-{^1H}] revealed the absence of signals attributable to B–H⟶Ru, M–H (M = Ru or W), or bridging alkylidyne groups. Indeed, observation of a resonance in the ^{11}B-{^1H} n.m.r. spectrum at δ 58.8 p.p.m. suggested that the unstable product formed by protonation of (**3a**) retained the B–Ru linkage present in the latter. This suggests that protonation of the anion of (**3a**) occurs at the bridging carbon atom rather than at the B–Ru bond, to afford a species having the structure (**4**), although resonances in the ^1H and ^{13}C-{^1H} n.m.r. spectra could not be unequivocally assigned. It has been observed previously[18] that protonation of dimetal compounds with bridging *p*-tolylmethylidyne groups affords products in which the $C(H)C_6H_4Me$-4 fragment adopts the bonding mode shown in (**4**).

Protonation of (**3a**) with CF_3CO_2H also failed to yield a stable neutral complex, although the reaction followed a different course than when $HBF_4 \cdot Et_2O$ was used, since a ^{13}C-{^1H} n.m.r. spectrum of the mixture showed a resonance



(4)



(5)

○ BH ⊕ B ● CMe

for a μ-CC_6H_4Me-4 group (δ 291.4 p.p.m.). There was no signal in the ^1H n.m.r. spectrum for a B–H⇀Ru group, and the ^{11}B-{^1H} n.m.r. spectrum had a resonance at δ 62.7 p.p.m. suggestive of a B–Ru bond.

The reactivity of (**2a**) towards the tertiary phosphines PMe_3, P(cyclo-$C_6H_{11})_3$, PPh_3, and $P(OMe)_3$ was studied. No reaction appeared to occur with PPh_3 or $P(OMe)_3$, but P(cyclo-$C_6H_{11})_3$ affords a yellow precipitate which had an i.r. spectrum indicating that it was the salt [PH(cyclo-$C_6H_{11})_3$][RuW(μ-CC_6H_4-Me-4)(μ-σ,η^5-$C_2B_9H_8Me_2$)$(CO)_3$(η-C_5H_5)]. Treatment of (**2a**) in diethyl ether with one equivalent of PMe_3 gave a red crystalline complex formulated as [RuW{μ-σ,η^5-CH(C_6H_4-Me-4)($C_2B_9H_8Me_2$)}$(CO)_3(PMe_3)$(η-C_5H_5)] (**5**). Unfortunately, crystals of (**5**) suitable for *X*-ray diffraction were not obtained, and hence the structure proposed is based on spectroscopic data.

The ^{31}P-{^1H} n.m.r. spectrum of (**5**) showed a characteristic resonance for a W(PMe_3) group at δ −36.5 with the expected ^{183}W–^{31}P coupling (244 Hz). Surprisingly, the i.r. spectrum showed only one very broad CO stretching band, but the presence of three carbonyl ligands was firmly established by the ^{13}C-{^1H} n.m.r. spectrum (Table 1). Resonances at 208.2, 202.7, and 199.2 p.p.m. are assigned to the two W(CO) and Ru(CO) groups, respectively. The W(CO) signals occur as doublets due to ^{31}P–^{13}C coupling (6 Hz). Characteristic peaks for the *p*-tolyl group are observed in both the ^1H and ^{13}C-{^1H} n.m.r. spectra, while the presence of the μ-CH group is indicated by signals at δ 5.95 in the ^1H spectrum, and at 28.9 p.p.m. in the ^{13}C-{^1H} spectrum. A signal at 65.4 p.p.m. in the ^{11}B-{^1H} n.m.r. spectrum is assigned to the $BCH(C_6H_4Me$-4) group. The unusual bridging ligand invoked for (**5**) has been established by *X*-ray diffraction in the compound [MoW{μ-σ,η^3-CH(C_6H_4Me-4)($C_2B_9H_8Me_2$)}$(CO)_3$(η-EtC_2Et)(η^5-C_9H_7)].[5] Moreover, the latter is formed by addition of a nucleophilic ligand (EtC_2Et) to the tungsten centre in [MoW(μ-C_6H_4Me-4)-$(CO)_3$(η^5-C_9H_7)(η^5-$C_2B_9H_9Me_2$)], a process similar to the addition of the donor ligand PMe_3 to the tungsten centre of (**2a**). It seems likely, therefore, that other examples of insertion of bridging alkylidyne groups into B–H bonds, activated by a B–H⇀M interaction, will be observed.

Table 3. Atomic positional parameters (fractional co-ordinates × 10^4), with estimated standard deviations in parentheses, for complex (**2a**)

Atom	*x*	*y*	*z*
W	4 423(1)	6 246(1)	3 491(1)
Ru	5 723(1)	8 165(1)	4 201(1)
C(6)	6 553(7)	9 919(9)	3 719(3)
C(7)	6 405(7)	10 545(8)	4 196(3)
C(8)	7 217(7)	9 711(9)	4 557(3)
C(9)	7 862(6)	8 576(8)	4 294(4)
C(10)	7 441(7)	8 739(9)	3 785(3)
C(5)	5 350(6)	7 263(8)	4 797(3)
O(5)	5 166(6)	6 757(7)	5 181(2)
C(1)	4 551(6)	3 973(8)	3 426(3)
O(1)	4 696(5)	2 722(5)	3 408(3)
C(2)	5 617(6)	6 563(8)	2 972(3)
O(2)	6 329(5)	6 866(7)	2 679(2)
B(1)	3 502(7)	8 226(9)	3 842(3)
B(5)	2 578(7)	6 554(9)	3 944(3)
C(4)	2 029(6)	5 976(7)	3 366(3)
C(3)	2 492(6)	7 077(8)	2 933(3)
B(2)	3 453(7)	8 519(9)	3 175(3)
B(6)	2 411(7)	9 576(9)	3 544(3)
B(10)	1 873(7)	8 384(8)	4 021(3)
B(9)	966(7)	6 915(9)	3 718(4)
B(8)	896(7)	7 209(9)	3 074(3)
B(7)	1 785(8)	8 836(10)	2 959(4)
B(11)	821(8)	8 779(9)	3 470(4)
C(41)	1 657(6)	4 327(8)	3 250(3)
C(31)	2 625(8)	6 439(9)	2 412(3)
C(01)	5 970(6)	5 858(7)	3 905(2)
C(02)	7 117(6)	4 947(7)	4 065(3)
C(07)	7 625(7)	4 792(8)	4 561(3)
C(06)	8 673(7)	3 832(8)	4 692(3)
C(05)	9 253(6)	3 015(7)	4 331(3)
C(04)	8 747(6)	3 166(8)	3 837(3)
C(03)	7 702(6)	4 117(8)	3 704(3)
C(08)	10 395(7)	2 004(10)	4 482(4)

The results described in this paper further confirm the 'non-spectator' nature of the carbaborane ligand in chemistry based on use of the salts (**1**) in the synthesis of dimetal complexes. Indeed, in the presence of bridging alkylidyne groups involvement of the η^5-$C_2B_9H_9Me_2$ ligand in reactions may be the norm rather than the exception.

Experimental

The experimental techniques employed and the instrumentation used are described in the preceding paper.[1] Light petroleum refers to that fraction of b.p. 40—60 °C. The compounds [$N(PPh_3)_2$][W(≡CR)$(CO)_2$(η^5-$C_2B_9H_9Me_2$)] (R = C_6H_4Me-4 or Me)[1] and [Ru(CO)$(NCMe)_2$(η-C_5H_5)]-[BF_4][3] were prepared by methods previously described.

Synthesis of the Complexes [RuW(μ-CR)$(CO)_3$(η-C_5H_5)(η^5-$C_2B_9H_9Me_2$)] (R = C_6H_4Me-4 *or* Me).—(*i*) A mixture of (**1a**) (0.90 g, 0.86 mmol) and [Ru(CO)$(NCMe)_2$(η-C_5H_5)][BF_4] (0.31 g, 0.86 mmol) in CH_2Cl_2 (10 cm^3) was stirred for 11 h. Solvent was removed *in vacuo*, and the residue extracted with Et_2O (4 × 20 cm^3). The combined extracts were concentrated to *ca.* 30 cm^3, and chromatographed on a Florisil column (2 × 20 cm^3, 100—200 mesh), eluting with Et_2O. A green-brown fraction was collected, and solvent was removed *in vacuo* giving dark brown *microcrystals* of [RuW(μ-CC_6H_4Me-4)-$(CO)_3$(η-C_5H_5)(η^5-$C_2B_9H_9Me_2$)] (**2a**) (0.18 g, 30%) (Found: C, 32.5; H, 3.9. $C_{20}H_{27}B_9O_3RuW$ requires C, 34.4; H, 3.9%);

Table 4. Atomic positional parameters (fractional co-ordinates $\times 10^4$), with estimated standard deviations in parentheses, for the salt (**3a**)

Atom	x	y	z	Atom	x	y	z
W	1 722(1)	3 342(1)	5 653(1)	C(12)*	6 335(3)	3 374(4)	−2 171(5)
Ru	1 244(1)	1 721(1)	4 299(1)	C(13)	6 523	4 205	−2 512
C(8)*	1 262(4)	732(3)	2 743(4)	C(14)	7 340	4 761	−2 288
C(9)	399	848	2 872	C(15)	7 970	4 485	−1 722
C(10)	392	1 747	2 789	C(16)	7 783	3 653	−1 381
C(6)	1 252	2 188	2 609	C(11)	6 965	3 097	−1 605
C(7)	1 789	1 560	2 581	C(22)*	6 677(2)	622(3)	−2 764(4)
C(01)	584(3)	2 585(3)	5 278(4)	C(23)	6 276	−78	−3 575
C(02)	−357(3)	2 454(4)	5 328(5)	C(24)	5 389	−216	−3 803
C(03)	−763(4)	3 174(4)	5 567(5)	C(25)	4 904	347	−3 222
C(04)	−1 646(4)	3 062(5)	5 531(6)	C(26)	5 305	1 047	−2 412
C(05)	−2 179(4)	2 215(5)	5 243(5)	C(21)	6 191	1 185	−2 183
C(06)	−1 791(4)	1 486(5)	5 069(6)	C(32)*	5 687(3)	1 356(3)	420(4)
C(07)	−902(4)	1 603(4)	5 120(5)	C(33)	5 229	1 411	1 389
C(08)	−3 151(4)	2 105(7)	5 118(7)	C(34)	5 134	2 240	1 941
C(1)	1 099(4)	3 758(4)	6 974(6)	C(35)	5 498	3 015	1 524
O(1)	720(4)	3 946(4)	7 734(5)	C(36)	5 956	2 960	555
C(2)	1 296(4)	4 147(4)	4 835(6)	C(31)	6 051	2 130	3
O(2)	1 051(4)	4 591(3)	4 278(4)	P(2)	8 225(1)	1 631(1)	74(1)
C(5)	1 219(4)	1 014(4)	5 348(5)	C(42)*	7 276(3)	−81(3)	−105(3)
O(5)	1 224(3)	552(3)	5 990(4)	C(43)	6 891	−867	274
B(1)	2 508(4)	2 349(4)	5 019(5)	C(44)	6 986	−936	1 380
B(2)	2 931(4)	3 385(5)	4 513(6)	C(45)	7 466	−219	2 107
C(3)	3 294(4)	4 166(4)	5 639(6)	C(46)	7 851	568	1 728
C(31′)	3 362(4)	5 158(4)	5 648(7)	C(41)	7 755	637	622
C(4)	3 124(4)	3 738(4)	6 744(5)	C(52)*	9 803(2)	1 154(3)	0(3)
C(41′)	3 032(5)	4 337(5)	7 819(6)	C(53)	10 607	1 107	−446
B(5)	2 656(4)	2 638(4)	6 505(5)	C(54)	10 813	1 383	−1 456
B(6)	3 581(4)	2 557(5)	4 494(7)	C(55)	10 215	1 706	−2 019
B(7)	4 064(4)	3 723(6)	4 863(7)	C(56)	9 411	1 753	−1 572
B(8)	4 175(5)	3 962(6)	6 296(7)	C(51)	9 205	1 477	−563
B(9)	3 776(5)	2 982(5)	6 835(7)	C(62)*	7 878(3)	2 663(4)	1 974(4)
B(10)	3 399(5)	2 091(5)	5 714(6)	C(63)	8 071	3 367	2 855
B(11)	4 355(5)	2 915(6)	5 583(8)	C(64)	8 884	3 941	2 955
N(1)	7 622(3)	1 814(4)	−841(4)	C(65)	9 506	3 811	2 175
P(1)	6 752(1)	2 055(1)	−1 122(1)	C(66)	9 313	3 107	1 294
				C(61)	8 500	2 533	1 194

* Pivot atom of a rigid group; remaining atoms in the group have identical standard deviations.

$\nu_{max.}$(CO) at 2 008m, 1 987s, and 1 914s cm^{-1}; $\nu_{max.}$(BH) at 2 567 cm^{-1} (in Et_2O).

(*ii*) A mixture of (**1b**) (1.63 g, 1.69 mmol) and $[Ru(CO)(NCMe)_2(\eta-C_5H_5)][BF_4]$ (0.61 g, 1.69 mmol) in CH_2Cl_2 (15 cm^3) was stirred for 5 h. Diethyl ether (10 cm^3) was added, and the solution chromatographed on Florisil. Elution with Et_2O gave a green eluate. Solvent was removed *in vacuo*, and the residue was washed with Et_2O (4 × 5 cm^3) giving grey-green *microcrystalline* $[RuW(\mu-CMe)(CO)_3(\eta-C_5H_5)(\eta^5-C_2B_9H_9Me_2)]$ (**2b**) (0.65 g, 61%) (Found: C, 27.0; H, 3.6. $C_{14}H_{23}B_9O_3RuW$ requires C, 27.1; H, 3.7%); $\nu_{max.}$(CO) at 2 005m, 1 978s, and 1 907s cm^{-1}; $\nu_{max.}$(BH) at 2 563w cm^{-1} (in thf).

Synthesis of the Salt $[N(PPh_3)_2][RuW(\mu-CC_6H_4Me-4)(\mu-\sigma,\eta^5-C_2B_9H_8Me_2)(CO)_3(\eta-C_5H_5)]$.—The compounds (**1a**) (0.66 g, 0.64 mmol) and $[Ru(CO)(NCMe)_2(\eta-C_5H_5)][BF_4]$ (0.23 g, 0.64 mmol) were stirred together in CH_2Cl_2 (10 cm^3) for 12 h. The salt $[N(PPh_3)_2]Cl$ (0.42 g, 0.64 mmol) was added, and the mixture was treated with $LiBu^n$ (0.64 mmol, 0.40 cm^3 of a 1.67 mol dm^{-3} solution) dropwise, with vigorous stirring for a further 3 h. Solvent was removed *in vacuo*, and the residue extracted with Et_2O–CH_2Cl_2 (1 : 1, 20 cm^3). The extracts were chromatographed on an alumina column (2 × 20 cm^3, Brockman activity II), eluting with the same solvent mixture. A yellow solution was collected, solvent was removed *in vacuo*, and the residue crystallised from CH_2Cl_2–light petroleum (1 : 1, 4 cm^3) affording brown *microcrystals* of $[N(PPh_3)_2][RuW(\mu-CC_6H_4Me-4)(\mu-\sigma,\eta^5-C_2B_9H_8Me_2)(CO)_3(\eta-C_5H_5)]$ (**3a**) (0.10 g, 12%) (Found: C, 54.4; H, 4.8; N, 1.0; P, 5.0. $C_{56}H_{56}B_9NO_3P_2RuW$ requires C, 54.5; H, 4.6; N, 1.1; P, 5.0%); $\nu_{max.}$(CO) at 1 939s, 1 898s, and 1 852s cm^{-1}; $\nu_{max.}$(BH) at 2 550w cm^{-1} (in CH_2Cl_2).

Compound (**3a**) can be prepared (30% yield) by treating (**2a**) and $[N(PPh_3)_2]Cl$ in CH_2Cl_2 with one equivalent of $LiBu^n$ (1.6 mol dm^{-3} in n-hexane).

Reaction of $[RuW(\mu-CC_6H_4Me-4)(CO)_3(\eta-C_5H_5)(\eta^5-C_2B_9H_9Me_2)]$ *with* PMe_3.—A Et_2O (5 cm^3) solution of (**2a**) (0.13 g, 0.19 mmol) was treated with PMe_3 (0.19 mmol). The mixture was stirred (10 min), and then cooled to −20°C for 1 h. The supernatant liquid was removed with a syringe and the red crystals washed with Et_2O (2 × 5 cm^3) and dried *in vacuo* giving $[RuW\{\mu-\sigma,\eta^5-CH(C_6H_4Me-4)(C_2B_9H_8Me_2)\}(CO)_3(PMe_3)(\eta-C_5H_5)]$ (**5**) (0.10 g, 71%) (Found: C, 35.0; H, 4.0. $C_{23}H_{36}B_9O_3PRuW$ requires C, 35.7; H, 4.7%); $\nu_{max.}$(CO) at 1 981s br; $\nu_{max.}$(BH) at 2 554w cm^{-1} (in CH_2Cl_2); $^{31}P-\{^1H\}$ n.m.r. (in CD_2Cl_2), δ −36.5 p.p.m. [J(WP) 244 Hz], rel. to 85% H_3PO_4 (external).

Crystal Structure Determination.—Crystals of (**2a**) grow as black needles from Et_2O, those of (**3a**) as black spheroids from CH_2Cl_2–light petroleum. Crystals for study [(**2a**), 0.15 ×

0.25 × 0.70 mm; (**3a**) 0.40 × 0.40 × 0.40 mm] were sealed in Lindemann glass capillaries under nitrogen. Diffracted intensities were collected (ω—2θ scans) in the range $2.9 \leqslant 2\theta \leqslant 50°$ at 200 K for (**2a**) and at 298 K for (**3a**), on a Nicolet *P*3*m* four-circle diffractometer. For (**2a**), of 5 106 intensities, 3 925 had $I \geqslant 3\sigma(I)$, where $\sigma(I)$ is the standard deviation in I based on counting statistics. Only these data were used in the final refinement of the structure, after all the data had been corrected for Lorentz polarisation effects, and a numerical correction applied for *X*-ray absorption.[19] Correspondingly for (**3a**), of 9 895 intensities, 8 530 had $I \geqslant 3\sigma(I)$ and only these were used in structure refinement, after similar corrections had been applied.

Crystal data for (**2a**). $C_{20}H_{27}B_9O_3RuW$, $M = 697.6$, monoclinic, $a = 10.317(6)$, $b = 8.872(6)$, $c = 26.89(2)$ Å, $\beta = 95.47(6)°$, $U = 2\,450(3)$ Å^3, $D_c = 1.90$ g cm^{-3}, $Z = 4$, $F(000) = 1\,336$, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 54.40$ cm^{-1}.

Crystal data for (**3a**). $[C_{36}H_{30}NP_2]^+[C_{20}H_{26}B_9O_3RuW]^-$, $M = 1\,235.2$, triclinic, $a = 15.816(7)$, $b = 15.537(6)$, $c = 12.323(4)$ Å, $\alpha = 99.23(3)$, $\beta = 89.79(3)$, $\gamma = 102.25(3)°$, $U = 2\,919(2)$ Å^3, $Z = 2$, $D_c = 1.41$ g cm^{-3}, $F(000) = 1\,234$, space group $P\bar{1}$ (no. 2), $\mu(\text{Mo-}K_\alpha) = 23.59$ cm^{-1}.

Structure solutions and refinements. The structures were solved by heavy-atom methods, and all non-hydrogen atoms were located from difference Fourier calculations. All refinements, by blocked-cascade least-squares techniques, were performed on a Data General 'Eclipse' computer with the SHELXTL system of programs.[19] Hydrogen atoms attached to the boron atoms of the carbaborane cages and those in the *p*-tolyl group of (**2a**) were located from difference Fourier calculations; all other hydrogen atoms were incorporated at calculated 'riding' positions (C–H 0.96 Å) with fixed isotropic thermal parameters (1.2 times $U_{\text{eq.}}$ for the carbon atom to which they were attached). Weighting schemes applied were of the form $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$ where $g = 0.000\,15$ for (**2a**) and 0.000 28 for (**3a**). The final difference electron-density synthesis for (**2a**) showed residual peaks < 3 e Å^{-3} close to the two metal atoms, while in (**3a**) peaks were < 1.5 e Å^{-3}. Scattering factors for W were taken from ref. 20, while those for all other atoms are included in the programs of ref. 19. Refinement converged at $R = 0.0397$ ($R' = 0.0428$) for (**2a**), and $R = 0.0419$ ($R' = 0.0452$) for (**3a**).

The interacting hydrogen, H(1), in compound (**2a**) was located from a difference Fourier synthesis but its position was not refined. Atomic co-ordinates for (**2a**) and (**3a**) are listed in Tables 3 and 4, respectively.

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