Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 51.[1] Alkylidyne(carbaborane)tungsten-gold and -rhodium Complexes; Crystal Structures of $[AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$, $[RhW(\mu\text{-}CR)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, and $(RhW[\mu\text{-}CR)(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9(C_7H_9)H_8Me_2\}]$ (R = C_6H_4Me-4) [*]

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Reactions between the bromo(alkylidyne)tungsten complex $[W(\equiv CR)Br(CO)_4]$ (R = C_6H_4Me-4) and the salts $Na_2[7,8\text{-}C_2B_9H_9R'_2]$ (R′ = Me or H), followed by treatment with $[N(PPh_3)_2]Cl$ afford the compounds $[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]$ (**1a**, R′ = Me; **1b**, R′ = H). The salt $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1c**) was prepared from $[W(\equiv CMe)Br(CO)_4]$ and $Tl_2[7,8\text{-}C_2B_9H_9Me_2]$, with subsequent addition of $[NEt_4]Cl$. Treatment of (**1a**) or (**1b**) with $[AuCl(PPh_3)]$, in the presence of $TlPF_6$, yields the gold–tungsten complexes $[AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9R'_2)]$ (**2a**, R′ = Me; **2b**, R′ = H). Similarly, (**1c**) with $[AuCl(PPh_3)]$ affords $[AuW(\mu\text{-}CMe)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2c**). The structure of (**2a**) has been established by *X*-ray diffraction. The Au–W bond [2.780(8) Å] is asymmetrically bridged by the CC_6H_4Me-4 group [μ-C–Au 2.19(3), μ-C–W 1.88(3) Å]. Treatment of $[AuCl(tht)]$ (tht = tetrahydrothiophene) with (**1a**) gives the salt $[N(PPh_3)_2][AuW_2(\mu\text{-}CR)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ (**3**). The rhodium–tungsten compound $[RhW(\mu\text{-}CR)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4a**) has been prepared by two routes: from the reaction between (**1a**) and $[RhCl(PPh_3)_3]$ or from (**1a**) and $[Rh(PPh_3)_2(cod)][PF_6]$ (cod = cyclo-octa-1,5-diene). The latter with (**1b**) yields $[RhW(\mu\text{-}CR)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})]$ (**4b**). Compounds (**1a**) and (**1b**) react with $[Rh(PPh_3)_2(nbd)][PF_6]$ [nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)] to give the complexes $[RhW(\mu\text{-}CR)(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9(C_7H_9)H_8R'_2\}]$ [**5a**, R′ = Me; **5b**, (two isomers), R′ = H]. The structures of (**4a**) and (**5a**) have been established by *X*-ray diffraction. Both molecules have Y-shaped $WRhP_2$ cores with the Rh–W bonds [**4a**, 2.681(1), **5a**, 2.662(2) Å] bridged by CC_6H_4Me-4 groups [**4a**, μ-C–Rh 2.068(5), μ-C–W 1.880(6); **5a**, μ-C–Rh 2.12(2), μ-C–W 1.84(2) Å], and semibridged by a CO ligand [W–C–O, **4a**, 160.2(5); **5a**, 156(1)°]. In (**4a**), the tungsten atom is ligated by a terminal CO group and the $\eta^5\text{-}C_2B_9H_9Me_2$ cage. In (**5a**), the tungsten also carries a terminal CO group but the carbaborane ligand has a C_7H_9 [nortricyclene (tricyclo[2.2.1.$0^{2,6}$]heptane)] fragment attached to the unique boron atom in the open face of the cage. Thus in the formation of (**5a**) an unprecedented hydroboration reaction has occurred, a cage B–H bond having added to the norbornadiene ligand with concomitant C–C bond formation. In contrast, treatment of the norbornadiene-containing salt $[Rh(dppe)(nbd)][PF_6]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with (**1a**) gives $[RhW(\mu\text{-}CR)(CO)_2(dppe)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4c**). Reactions of (**4a**) with PEt_3, PMe_2Ph, dppe, and CO are reported. Examination of the $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the complexes (**4**) and (**5**) reveal that they undergo dynamic behaviour in solution and possible mechanisms are described and discussed.

The compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) shows a reactivity pattern towards low-valent transition-metal complexes similar to that of an alkyne. This property has enabled many heteronuclear dimetal complexes to be prepared, the bonds between tungsten and the various transition elements being bridged by the *p*-tolylmethylidyne group.[2] Within the framework of the isolobal model,[3] this chemistry is capable of development in several different ways. Thus the *p*-tolylmethylidyne group in $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ can be replaced by ethylidyne,[4] or the tungsten by molybdenum.[5] The products obtained from reactions between these species and low-valent metal fragments have their own unique properties. Especially interesting results are to be anticipated, however, when the cyclopentadienyl anion in the alkylidyne–tungsten compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me) is replaced by one or other of the groups $\eta\text{-}C_5Me_5$, $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate], and $\eta^5\text{-}C_2B_9H_9R'_2$ (R′ = Me or H).[6] We have initiated studies with the hydrotris(pyrazol-1-yl)borato ligand,[7] and in this paper we describe some work on complexes in which tungsten is ligated by carbaborane groups.[†]

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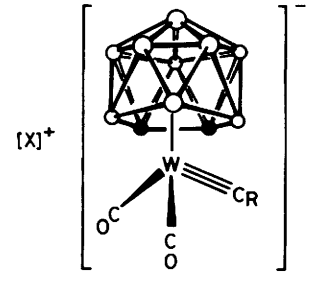
[*] 2,2-Dicarbonyl-2-[7′—11′-η-nonahydro-7′,8′-dimethyl-7′,8′-dicarba-*nido*-undecaborato(2−)]-μ-*p*-tolylmethylidyne-1-(triphenylphosphine)goldtungsten (*Au–W*), μ-carbonyl-2-carbonyl-2-[7′—11′-η-nonahydro-7′,8′-dimethyl-7′,8′-dicarba-*nido*-undecaborato(2−)]-μ-*p*-tolylmethylidyne-1,1-bis(triphenylphosphine)rhodiumtungsten (*Rh=W*), and μ-carbonyl-2-carbonyl-2{7′—11′-η-nonahydro-7′,8′-dimethyl-10′-tricyclo[2.2.1.$0^{2'',6''}$]hept-3″-yl-7′,8′-dicarba-*nido*-undecaborato(2−)}-μ-*p*-tolylmethylidyne-1,1-bis(triphenylphosphine)rhodiumtungsten (*Rh=W*) respectively.

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

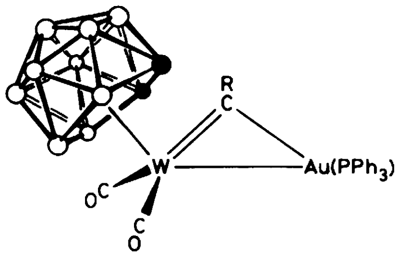
[†] In this paper, and in others to follow in this series, a tungsten atom forms with a $[nido\text{-}7,8\text{-}C_2B_9H_9R'_2]^{2-}$ anion a *closo*-1,2-dicarba-3-tungstadodecaborane structure. However, in the formulae the carbaborane group is designated as $\eta^5\text{-}C_2B_9H_9R'_2$ in order to emphasise its pentahapto ligand properties in which it formally acts as a four-electron donor.

There is evidence to suggest that the electron-donor ability and steric requirements of the *nido*-carbaborane di-anions $[C_2B_9H_9R'_2]^{2-}$ are similar to those of the pentamethylcyclopentadienyl anion.[8] Moreover, replacement of the η-C_5H_5 group in $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ by the carbaborane ligand[9] places a negative charge on the resultant species. There is thus an isolobal relationship between the groups $W(CO)_2(\eta\text{-}C_5R'_5)$ and $[W(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]^-$ ($R' = H$ or Me) so that synthesis of salts containing the anions $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]^-$ might be possible, thereby providing valuable reagents for further preparative work. Herein we describe the preparation of such salts and their use in the synthesis of compounds containing bonds between tungsten and gold or rhodium.[10]



○ BH

	X	●	R
(1a)	$N(PPh_3)_2$	CMe	C_6H_4Me-4
(1b)	$N(PPh_3)_2$	CH	C_6H_4Me-4
(1c)	NEt_4	CMe	Me



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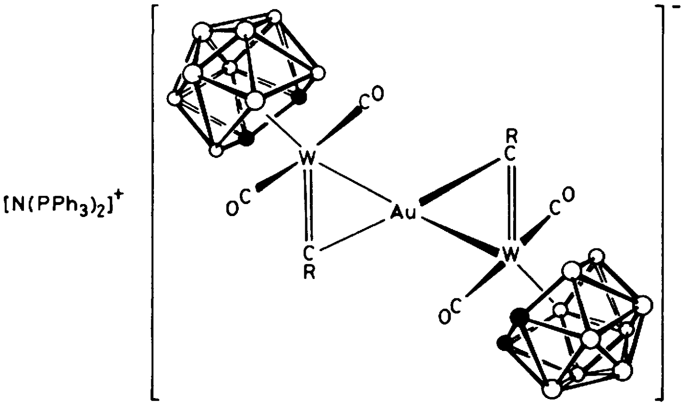
	●	R
(2a)	CMe	C_6H_4Me-4
(2b)	CH	C_6H_4Me-4
(2c)	CMe	Me



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	●	R
(3)	CMe	C_6H_4Me-4

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

Compound[b]	Colour	Yield (%)	$\nu_{max.}$[c]/cm^{-1} BH	CO		Analysis (%) C	H
(1a) $[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$[d]	Orange	82	2 516m	1 956s	1 874s	57.4 (57.8)	5.4 (5.1)
(1b) $[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_{11})]$[e]	Orange	71	2 525m	1 965s	1 880s	55.2 (56.8)	5.0 (4.7)
(1c) $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$[f]	Yellow	67	2 554m	1 955s	1 871s	34.4 (34.5)	7.9 (6.8)
(2a) $[AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Orange	62	2 554m	2 002s	1 993s	40.0 (39.9)	3.9 (3.8)
(2b) $[AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_{11})]$	Orange	51	2 557m	2 009s	1 941s	38.9 (38.5)	3.8 (3.5)
(2c) $[AuW(\mu\text{-}CMe)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Orange	45	2 564m	2 004s	1 934s	35.1 (34.9)	4.2 (3.7)
(3) $[N(PPh_3)_2][AuW_2(\mu\text{-}CR)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$[g]	Yellow	81	2 531m	1 989s	1 920s	44.1 (44.0)	5.1 (4.2)
(4a) $[RhW(\mu\text{-}CR)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$	Black	67	2 553m	1 961s	1 767s	52.3 (52.5)	4.8 (4.6)
(4b) $[RhW(\mu\text{-}CR)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})]$	Black	57	2 564m	1 974s	1 773s	51.7 (52.1)	4.1 (4.3)
(4c) $[RhW(\mu\text{-}CR)(CO)_2(dppe)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Orange	59	2 552m	1 970s	1 898m	47.5 (47.7)	4.5 (4.6)
(4d) $[RhW(\mu\text{-}CR)(CO)_2(PEt_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$	Green-black	95	2 551m	1 955s	1 761s	36.2 (36.8)	6.2 (6.1)
(5a) $[RhW(\mu\text{-}CR)(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9(C_7H_9)H_8Me_2\}]$	Black	65	2 553m	1 961s	1 756s	56.1 (55.9)	5.2 (4.9)
(5b) $[RhW(\mu\text{-}CR)(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9(C_7H_9)H_{10}\}]$	Black	60	2 555m	1 968s	1 767s	54.8 (55.2)	5.0 (4.7)
(6b) $[Rh(dppe)_2][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$	Orange	95	2 517m	1 956s	1 874s	57.5 (56.4)	4.9 (5.0)

[a] Calculated values are given in parentheses. [b] $R = C_6H_4Me$-4. [c] In CH_2Cl_2. [d] N, 1.3 (1.3%). [e] N, 1.6 (1.4%). [f] N, 2.8 (2.5%). [g] N, 0.8 (0.8%).

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the complexes

Compound	$^1H(\delta)^{b,c}$	$^{13}C(\delta)^d$
(1a)	2.07 (s, 6 H, Me), 2.18 (s, 3 H, Me-4), 7.25—7.70 (m, 34 H, C_6H_4 and Ph)	298.3 [*C*≡W, *J*(WC) 198], 226.8 [CO, *J*(WC) 182], 147.9 [$C^1(C_6H_4)$], 135.1—125.0 (C_6H_4 and Ph), 29.9 (Me), 21.4 (Me-4)
(1b)	2.20 (s, 3 H, Me-4), 7.21—7.54 (m, 34 H, C_6H_4 and Ph)	293.9 [*C*≡W, *J*(WC) 200], 225.0 [CO, *J*(WC) 184], 148.3 [$C^1(C_6H_4)$], 133.4—125.5 (C_6H_4 and Ph), 21.4 (Me-4)
(1c)	1.23 [t, 12 H, N–CH_2CH_3, *J*(HH) 8], 1.93 (s, 6 H, Me), 2.04 (s, 3 H, ≡CMe), 3.37 [q, 8 H, N–CH_2CH_3, *J*(HH) 8]	309.7 (*C*≡W), 225.8 (CO), 51.8 (NCH_2CH_3), 44.9 (Me), 21.0 (≡C*Me*), 7.6 (NCH_2CH_3)
(2a)	2.15 (s, 6 H, Me), 2.37 (s, 3 H, Me-4), 7.11, 7.28 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.50—7.75 (m, 15 H, Ph)	292.9 [d, μ-C, *J*(PC) 28], 220.0 [CO, *J*(WC) 162], 149.0 [$C^1(C_6H_4)$], 141.1—127.3 (C_6H_4 and Ph), 31.2 (Me), 22.1 (Me-4)
(2b)	2.36 (s, 3 H, Me-4), 7.07, 7.21 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.48—7.60 (m, 15 H, Ph)	286.7 [d, μ-C, *J*(PC) 31], 218.0 [CO, *J*(WC) 167], 141.1 [$C^1(C_6H_4)$], 133.2—128.1 (C_6H_4 and Ph), 21.4 (Me-4)
(2c)	1.99 (s, 6 H, Me), 2.55 (s, 3 H, μ-CMe), 7.07—7.41 (m, 15 H, Ph)	301.9 [d, μ-C, *J*(PC) 29], 218.8 [CO, *J*(WC) 167], 133.5—127.3 (Ph), 40.8 (Me), 29.5 (μ-C*Me*)
(3)	2.29 (s, 6 H, Me-4), 2.34 (s, 12 H, Me), 7.01—7.11 (m, 8 H, C_6H_4), 7.31—7.52 (m, 30 H, Ph)	283.6 (μ-C), 221.5 [CO, *J*(WC) 156], 145.7 [$C^1(C_6H_4)$], 140.1—126.1 (C_6H_4 and Ph), 21.6 (Me), 20.7 (Me-4)
(4a)	1.90 (s, 6 H, Me), 2.44 (s, 3 H, Me-4), 7.12—7.35 (m, 34 H, C_6H_4 and Ph)	343.1 [d, μ-C, *J*(RhC) 30], 236.1 [d, CO, *J*(RhC) 17], 151.2 [$C^1(C_6H_4)$], 139.2—124.3 (C_6H_4 and Ph), 27.7 (Me), 20.7 (Me-4)
(4b)	2.36 (s, 3 H, Me-4), 7.07—7.31 (m, 34 H, C_6H_4 and Ph)	
(4c)	2.10 (s, 6 H, Me), 2.16 (s, 3 H, Me-4), 2.40 [d, 4 H, PCH_2, *J*(PH) 20], 6.49 [d, 2 H, C_6H_4, *J*(HH) 7], 7.32—7.46 (m, 32 H, C_6H_4 and Ph)	300.1 [d, μ-C, *J*(RhC) 24], 224.7 (CO), 154.6 [$C^1(C_6H_4)$], 137.9—126.5 (C_6H_4 and Ph), 29.7 (Me), 25.9 [d, PCH_2, *J*(PC) 24], 21.0 (Me-4)
(4d)	1.00 [d of t, 18 H, *Me*CH_2P, *J*(PH) 15, *J*(HH) 8], 1.69 (m, 12 H, MeCH_2P), 2.15 (s, 6 H, Me), 2.36 (s, 3 H, Me-4), 7.21, 7.42 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	335.4 [d, μ-C, *J*(RhC) 22], 236.8 [d, CO, *J*(RhC) 12], 134.1, 130.8 [C^1 and C^4 (C_6H_4)], 128.2, 126.2 (C_6H_4), 29.4 (Me), 21.6 (Me-4), 19.6 [d, MeCH_2P, *J*(PC) 27], 7.8 (*Me*CH_2P)
(5a)[e]	0.54—1.79 (m, 9 H, C_7H_9), 1.87 (s, 3 H, Me), 2.09 (s, 3 H, Me), 2.35 (s, 3 H, Me-4), 6.76, 6.98 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.00—7.32 (m, 30 H, Ph)	338.2 [d, μ-C, *J*(RhC) 28], 256.2 (br, CO) 222.5 (br, CO), 152.0 [$C^1(C_6H_4)$], 138.4—126.7 (C_6H_4 and Ph), 37.7, 36.8 [C^1 and C^5 (C_7H_9)], 30.2 [$C^6(C_7H_9)$], 29.3, 28.9 (Me), 21.6 (Me-4), 19.1 [$C^3(C_7H_9)$], 11.5, 11.3 [C^2 and C^4 (C_7H_9)]
(5b)[e]	0.51—1.50 (m, 9 H, C_7H_9), 2.38, 2.40 (2 s, 3 H, Me-4), 6.98—7.00 (m, 4 H, C_6H_4), 7.05—7.32 (m, 30 H, Ph)	341.7 (br, μ-C), 251.1 (br, CO), 223.1 (br, CO), 152.2, 151.4 [$C^1(C_6H_4)$], 139.6—125.9 (C_6H_4 and Ph), 43.7, 41.4, 37.8, 36.7 [C^1 and C^5 (C_7H_9)], 29.7, 29.3 [$C^6(C_7H_9)$], 21.1 (Me-4), 19.7, 19.0 [$C^3(C_7H_9)$], 11.4, 11.1, 10.8, 10.5 [C^2 and C^4 (C_7H_9)]
(6b)	2.08 (s, 6 H, Me), 2.13 (m, 8 H, CH_2P), 2.23 (s, 3 H, Me-4), 7.03—7.38 (m, 44 H, C_6H_4 and Ph)	297.9 (*C*≡W), 227.5 (CO), 149.0 [$C^1(C_6H_4)$], 137.1—128.0 (C_6H_4 and Ph), 29.8 (Me), 28.7 [t, CH_2P, *J*(PC) 24], 21.6 (Me-4)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures. [b] Measured in CD_2Cl_2. [c] Proton resonances for B–H groups occur as broad unresolved signals in the range δ 0—3. [d] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$, with measurements in CD_2Cl_2–CH_2Cl_2. [e] For numbering of C_7H_9 groups see structure of (**5a**). Signal for C^7 of C_7 ring not observed.

Results and Discussion

Addition of a tetrahydrofuran (thf) solution of the salt $Na_2[7,8\text{-}C_2B_9H_9Me_2]$ to a solution of $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$ in the same solvent at −40 °C, followed by treatment of the mixture with $[N(PPh_3)_2]Cl$, afforded the orange compound $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1a**). A similar synthesis employing $Na_2[7,8\text{-}C_2B_9H_{11}]$ gave $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_{11})]$ (**1b**). The salt $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1c**) was prepared by adding $Tl_2[7,8\text{-}C_2B_9H_9Me_2]$ to a thf solution of $[W(\equiv CMe)Br(CO)_4]$ at −40 °C, with subsequent addition of $[NEt_4]Cl$. The compounds (**1**) were characterised by microanalysis and by their spectroscopic properties (Tables 1 and 2).

The presence of the alkylidyne ligand was established by the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra which showed characteristic signals for the ligating carbon nuclei at δ 298.3 (**1a**), 293.9 (**1b**), and 309.7 p.p.m. (**1c**). The chemical shifts of these signals are very similar to those observed for the alkylidyne carbon nuclei in the compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4, δ 300.1; R = Me, δ 311.4 p.p.m.).[11] The i.r. spectra of (**1**) show broad bands at *ca.* 2 525 cm^{-1}, characteristic of B–H stretching frequencies, and two bands in the CO stretching region. The latter occur at *ca.* 30 cm^{-1} to low frequency of the corresponding bands in the spectra of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = Me or C_6H_4Me-4). This presumably results from the presence of the negative charge on tungsten in the anionic complexes, and the increased electron-donor properties of the carbaborane ligands.[8]

Having characterised the salts (**1**) they were used to prepare dimetal complexes with heteronuclear metal–metal bonds. Thus the gold–tungsten compounds [$AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9R'_2)$] (**2a**, R = C_6H_4Me-4, R′ = Me; **2b**, R = C_6H_4-Me-4, R′ = H; **2c**, R = R′ = Me) were synthesised by treating [$AuCl(PPh_3)$] with the appropriate salt (**1**) in thf, and in the presence of $TlPF_6$ to remove chloride as insoluble TlCl. The compounds (**2**) are less labile than their cyclopentadienyl analogues [$AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)$][$PF_6$] (R = C_6H_4Me-4 or Me).[12] The latter dissociate in solution, affording equilibrium mixtures containing the species [$Au\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2$]$^+$ and [$Au(PPh_3)_2$]$^+$. Interestingly, the synthesis of (**2a**) was sometimes accompanied by formation of traces of the salt [$N(PPh_3)_2$][$Au\{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)\}_2$] (**3**), discussed further below.

The compounds (**2**) were characterised in the usual manner (Tables 1—3). In particular, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra showed resonances for the μ-C groups at δ 292.9 (**2a**), 286.7 (**2b**), and 301.9 p.p.m. (**2c**). Each signal was a doublet, as expected, due to $^{31}P\text{-}^{13}C$ coupling (Table 2). The corresponding resonances in the spectra of the salts [$AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)$]-[$PF_6$] occur at δ 292.6 (R = C_6H_4Me-4) and 304.7 p.p.m. (R = Me).[12]

In order to establish firmly the structure of the new complexes, an *X*-ray diffraction study was carried out on (**2a**). The results are summarised in Table 4, and the molecule is shown in Figure 1. Poor crystal quality, and the presence in the lattice of a disordered molecule of CH_2Cl_2, prevented a precise determination. However, the salient features of the molecular structure are readily apparent. The gold–tungsten bond is spanned by the *p*-tolylmethylidyne group with Au–W 2.780(8), Au–C(41) 2.19(3), and W–C(41) 1.88(3) Å. These distances may be compared with those found[12] in the alkylidene complex [$AuW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)$] [Au–W 2.729(1), μ-C–Au 2.27(1), and μ-C–W 2.06(1) Å]. The tungsten atom in (**2a**) carries the $\eta^5\text{-}C_2B_9H_9Me_2$ cage and two CO groups, the latter are essentially linear and orthogonal. The gold atom is co-ordinated by the PPh_3 group [Au–P 2.27(1) Å] which lies transoid to the μ-CC_6H_4Me-4 ligand [P–Au–C(41) 163(1)°]. This is consistent with the above mentioned $^{31}P\text{-}^{13}C$ coupling (28 Hz) associated with the μ-C resonance in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**2a**) (Table 2).

Both in (**2a**) and in [$AuW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)$] relatively short μ-C–W separations are accompanied by relatively long μ-C–Au distances, so that the μ-$CH(C_6H_4Me\text{-}4)$ and μ-CC_6H_4Me-4 ligands asymmetrically bridge their respective metal–metal bonds. In several complexes containing dimetallacyclopropene rings the μ-C–W separations are in the range 1.91(1)—2.03(1) Å, corresponding to a C=W bond.[13] However, the μ-C–W distance in (**2a**) [1.88(3) Å] is only slightly longer than that found for the C≡W bond [1.82(2) Å] in [$W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)$].[11a] In contrast, the μ-C–Au separation [2.19(3) Å] is significantly longer than μ-C–W, being comparable with the carbon-to-gold σ bond distance [2.13(3) Å] in [$AuMe(PPh_3)$].[14] The dimensions of the $\overline{Au(\mu\text{-}C)W}$ ring in (**2a**) correlate with the $^{13}C\text{-}\{^1H\}$ chemical shift for the μ-C group (δ 292.9 p.p.m.). This resonance is close to that recorded (298.3 p.p.m.) for the terminally bound *p*-tolylmethylidyne ligand in (**1a**) the precursor to (**2a**). Generally signals for alkylidyne-carbon atoms bridging two metal centres[13] are appreciably more deshielded than those found in the spectra of compounds (**2**). The structural and n.m.r. data thus suggest that the bonding within the three-membered rings in (**2**) might be represented by (**A**) or (**B**), rather than (**C**). If convention is followed of treating the carbaborane ligand as a

Table 3. Phosphorus-31 n.m.r. data[a] for the tungsten–gold and -rhodium complexes

Compound	$^{31}P(\delta)^b$
(**2a**)	56.1 (AuP)
(**2b**)	56.8 (AuP)
(**2c**)	55.1 (AuP)
(**4a**)	32.2 [d, RhP, *J*(RhP) 166]
(**4b**)	34.5 [d, RhP, *J*(RhP) 164]
(**4c**)	70.6 [d, RhP, *J*(RhP) 166]
(**4d**)	31.4 [d, RhP, *J*(RhP) 159]
(**5a**)	33.9 [d, RhP, *J*(RhP) 166]
(**5b**)	34.6 [d, RhP, *J*(RhP) 164]
(**6b**)	57.6 [d, RhP, *J*(RhP) 131]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures in CD_2Cl_2. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H_3PO_4 (external).

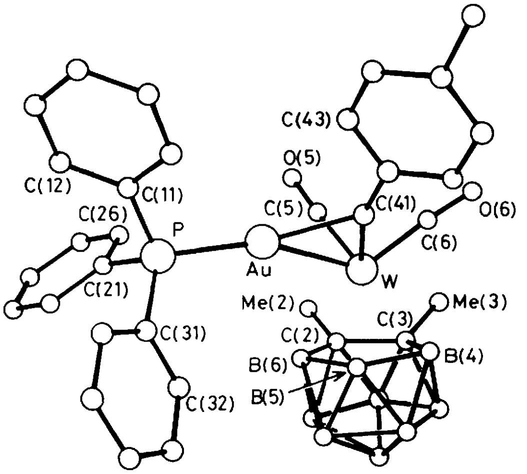


Figure 1. Molecular structure of [$AuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)$]·$CH_2Cl_2$ (**2a**) showing the atom-numbering scheme

Table 4. Selected internuclear distances (Å) and angles (°) for [$AuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)$]·$CH_2Cl_2$ (**2a**)

Au–W	2.780(8)	Au–C(41)	2.19(3)	W–C(41)	1.88(3)	Au–P	2.27(1)
W–C(5)	1.93(3)	W–C(6)	1.85(4)	C(5)–O(5)	1.19(4)	C(6)–O(6)	1.21(4)
W–C(2)	2.50(4)	W–C(3)	2.48(4)	W–B(4)	2.34(3)	W–B(5)	2.34(4)
W–B(6)	2.38(4)	C(41)–C(42)	1.44(3)	P–C(11)	1.81(2)	P–C(21)	1.79(2)
P–C(31)	1.80(2)						
W–Au–P	154.0(3)	W–Au–C(41)	42.4(7)	Au–W–C(41)	51.9(9)	P–Au–C(41)	163(1)
C(5)–W–C(6)	84(1)	C(5)–W–C(41)	92(1)	C(6)–W–C(41)	77(1)	Au–W–C(5)	81(1)
Au–W–C(6)	125.3(8)	Au–C(41)–W	86(1)	Au–C(41)–C(42)	111(2)	W–C(41)–C(42)	163(2)
Au–P–C(11)	112.4(8)	Au–P–C(21)	112.1(7)	Au–P–C(31)	113.0(6)	W–C(5)–O(5)	177(3)
W–C(6)–O(6)	174(2)						

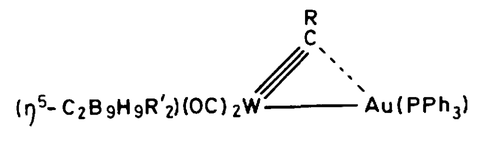
Table 5. Selected internuclear distances (Å) and angles (°) for $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4a**)

W-Rh	2.681(1)	Rh-C(a)	2.068(5)	W-C(a)	1.880(6)	Rh-P(1)	2.346(2)
Rh-P(2)	2.281(2)	W-C(01)	2.032(6)	W-C(02)	2.018(9)	Rh-C(01)	2.105(6)
C(01)-O(01)	1.186(8)	C(02)-O(02)	1.126(11)	W-C(2)	2.450(6)	W-C(3)	2.409(3)
W-B(4)	2.361(8)	W-B(5)	2.414(7)	W-B(6)	2.404(7)	C(a)-C(a1)	1.476(8)
C(2)-Me(2)	1.551(10)	C(3)-Me(3)	1.534(8)	P(1)-C(11)	1.827(6)	P(1)-C(21)	1.854(4)
P(1)-C(31)	1.839(4)	P(2)-C(41)	1.831(6)	P(2)-C(51)	1.837(5)	P(2)-C(61)	1.828(4)
W-Rh-P(1)	129.7(1)	W-Rh-P(2)	128.4(1)	W-Rh-C(a)	44.3(2)	Rh-W-C(a)	50.3(2)
W-C(a)-Rh	85.4(2)	W-Rh-C(01)	48.4(2)	Rh-W-C(01)	50.8(2)	W-C(01)-Rh	80.8(2)
P(1)-Rh-C(a)	129.6(2)	P(1)-Rh-C(01)	110.8(2)	P(2)-Rh-C(a)	119.0(2)	P(2)-Rh-C(01)	103.9(2)
P(1)-Rh-P(2)	98.8(1)	C(a)-W-C(01)	100.2(2)	C(a)-Rh-C(01)	92.0(2)	C(02)-W-C(01)	90.2(3)
C(02)-W-Rh	82.1(2)	C(02)-W-C(a)	89.6(3)	W-C(02)-O(02)	176.9(5)	W-C(01)-O(01)	160.2(5)
Rh-C(01)-O(01)	118.9(4)	W-C(a)-C(a1)	153.9(4)	Rh-C(a)-C(a1)	120.7(4)		

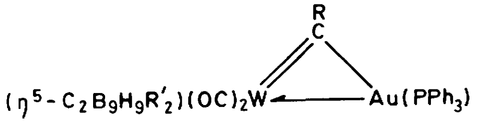
Table 6. Selected internuclear distances (Å) and angles (°) for $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9(C_7H_9)H_8Me_2\}]\cdot 0.5CH_2Cl_2$ (**5a**)

W-Rh	2.662(2)	Rh-C(71)	2.119(15)	W-C(71)	1.84(2)	Rh-P(1)	2.287(4)
Rh-P(2)	2.351(5)	W-C(4)	2.07(2)	W-C(5)	1.93(2)	Rh-C(4)	2.05(2)
C(4)-O(4)	1.17(3)	C(5)-O(5)	1.19(3)	W-C(2)	2.36(2)	W-C(3)	2.46(2)
W-B(4)	2.39(2)	W-B(5)	2.47(2)	W-B(6)	2.38(2)	C(71)-C(72)	1.49(3)
C(2)-Me(2)	1.53(3)	C(3)-Me(3)	1.52(3)	P(1)-C(11)	1.80(1)	P(1)-C(21)	1.81(1)
P(1)-C(31)	1.82(1)	P(2)-C(41)	1.82(1)	P(2)-C(51)	1.82(1)	P(2)-C(61)	1.80(2)
B(5)-C(n1)	1.64(4)						
W-Rh-P(1)	129.6(1)	W-Rh-P(2)	130.0(1)	W-Rh-C(71)	43.6(4)	Rh-W-C(71)	52.4(5)
W-C(71)-Rh	84.1(7)	W-Rh-C(4)	50.1(5)	Rh-W-C(4)	49.3(5)	W-C(4)-Rh	80.6(7)
P(1)-Rh-C(71)	109.2(4)	P(1)-Rh-C(4)	110.3(5)	P(2)-Rh-C(71)	138.5(5)	P(2)-Rh-C(4)	107.0(5)
P(1)-Rh-P(2)	98.7(2)	C(71)-W-C(4)	99.4(6)	C(71)-Rh-C(4)	91.7(7)	C(4)-W-C(5)	94.5(8)
C(5)-W-Rh	77.9(5)	C(5)-W-C(71)	85.5(8)	W-C(4)-O(4)	156(1)	W-C(5)-O(5)	175(2)
Rh-C(4)-O(4)	124(1)	W-C(71)-C(72)	160(1)	Rh-C(71)-C(72)	116.4(9)		

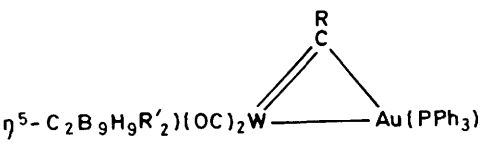
four-electron donor, (**C**) is unsatisfactory in implying 17 and 15 valence-electron counts, respectively, at the tungsten and gold atoms.



(**A**)



(**B**)



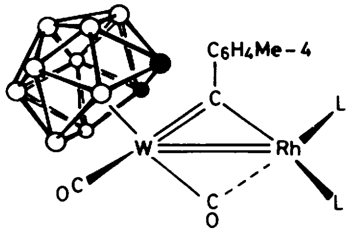
(**C**)

The 'semibridging' carbyne representation (**A**) would account for the short W–C(41) distance in (**2a**), and the chemical shifts for the μ-C resonances in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the three complexes (**2**) being similar to those in the spectra of their precursors (**1**). However, an attractive alternative is (**B**), involving a three-centre two-electron interaction, formed by a combination of the orbitals of Au(*sp*), C(*sp*^{2}), and W(d^2sp^3), and denoted by the half-arrow.[15] A similar representation has been proposed for $[AuW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$.[12]

As mentioned above, in the synthesis of (**2a**) formation of trace amounts of the salt (**3**) was sometimes observed. The latter may be prepared in good yield from the reaction between (**1a**) and [AuCl(tht)] (tht = tetrahydrothiophene) in CH_2Cl_2. Compound (**3**) was characterised by the data given in Tables 1 and 2. The resonance in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum at δ 283.6 p.p.m. for the μ-C nuclei compares with a similar resonance at δ 295.8 in the related cationic species $[Au\{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$. The latter has been structurally characterised[16] by *X*-ray diffraction, and (**3**) would be expected to have a similar structure in which two $[4\text{-}MeC_6H_4C\equiv W(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ fragments adopt a distorted tetrahedral arrangement around a central Au^+ cation. Compounds (**3**) and $[Au\{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)\}_2][PF_6]$ provide a good example of the isolobal model. Replacement of $C_5H_5^-$ in the latter by $C_2B_9H_9Me_2^{2-}$ in the former changes the complex from being cationic in nature to being anionic, with C≡W groups behaving formally as ligands in both species.

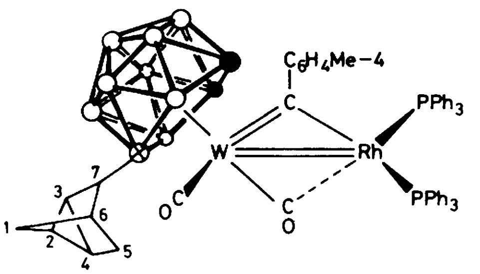
Reactions between the compounds (**1**) and various rhodium complexes were next investigated. Treatment of $[RhCl(PPh_3)_3]$ with (**1a**) in CH_2Cl_2 at room temperature affords the black crystalline complex $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4a**). The latter may also be prepared from $[Rh(PPh_3)_2(cod)][PF_6]$ (cod = cyclo-octa-1,5-diene) and (**1a**) in CH_2Cl_2. This route was also used to obtain $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})]$ (**4b**) using (**1b**) as the reagent. Data for (**4a**) and (**4b**) are given in Tables 1—3. Although it was not possible to obtain a $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**4b**), due to its low solubility, that of (**4a**) (Table 2) showed a characteristic resonance [δ 343.1 p.p.m., *J*(RhC) 30 Hz] for the μ-C group.

In contrast with the reactions between $[Rh(PPh_3)_2(cod)]$-



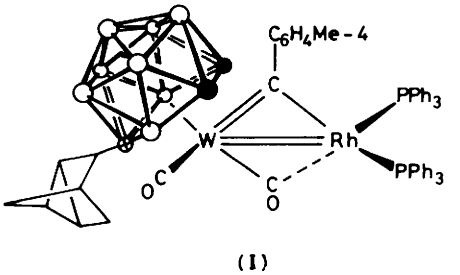
o BH

●	L	L–L
(4a) CMe	PPh_3	
(4b) CH	PPh_3	
(4c) CMe		dppe
(4d) CMe	PEt_3	

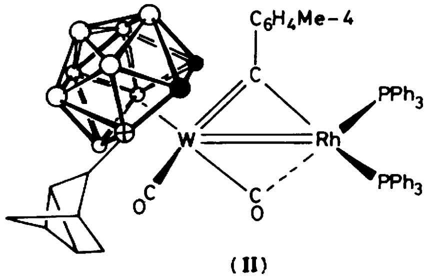


o BH ⊕ B ● CMe

(5a)



(I)



(II)

○ BH ⊕ B ● CH

(5b)

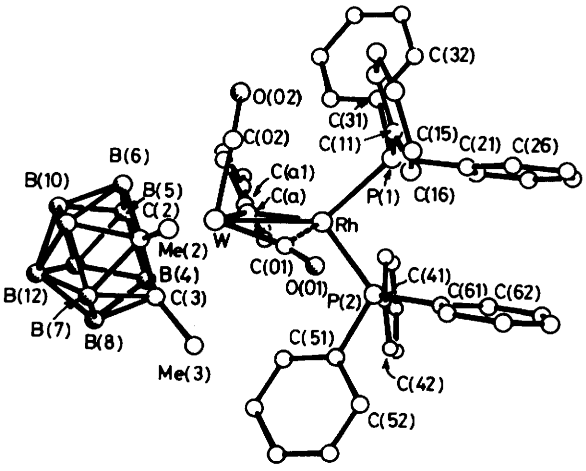


Figure 2. Molecular structure of $[RhW(\mu-CC_6H_4Me-4)(CO)_2(PPh_3)_2(\eta^5-C_2B_9H_9Me_2)]$ **(4a)** showing the atom-numbering scheme

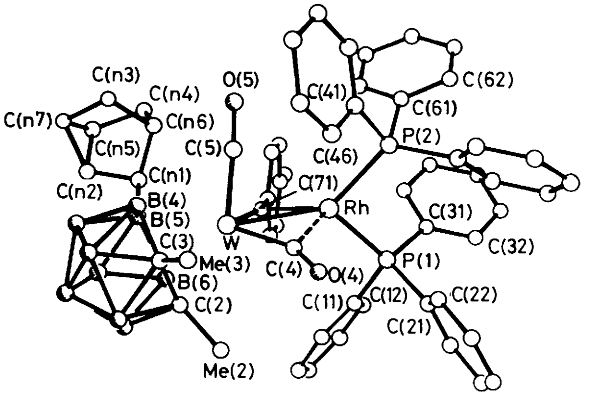


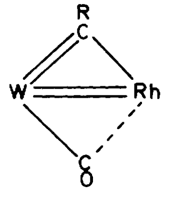
Figure 3. Molecular structure of $[RhW(\mu-CC_6H_4Me-4)(CO)_2(PPh_3)_2\{\eta^5-C_2B_9(C_7H_9)H_8Me_2\}]\cdot0.5CH_2Cl_2$ **(5a)** showing the atom-numbering scheme

$[PF_6]$ and **(1a)** or **(1b)**, those between the alkylidyne(carbaborane)tungsten salts and $[Rh(PPh_3)_2(nbd)][PF_6]$ [nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)] followed a different pathway, yielding the complexes $[RhW(\mu-CC_6H_4Me-4)(CO)_2(PPh_3)_2\{\eta^5-C_2B_9(C_7H_9)H_8R'_2\}]$ (**5a**, R′ = Me; **5b**, R′ = H). It was evident from the i.r. and n.m.r. data for the compounds **(5)** (Tables 1—3) that they had the same basic structural features as **(4a)** and **(4b)**, but that the nbd ligand had become attached to the carbaborane cage in some manner. In order to resolve the molecular structures of these two types of compound, *X*-ray diffraction studies were carried out on **(4a)** and **(5a)**. Selected bond distances and angles are given in Tables 5 and 6, and the structures are shown in Figures 2 and 3, respectively.

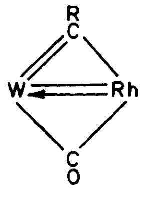
Compound **(4a)** has a Y-shaped $WRhP_2$ core bridged on the one side by the *p*-tolylmethylidyne group and semibridged on the other by a CO ligand [W–C(01)–O(01) 160.2(5)°]. The Rh–W separation [2.681(1) Å] lies between those found in $[RhW(\mu-CC_6H_4Me-4)(CO)_2(PMe_3)(\eta-C_5H_5)(\eta-C_9H_7)]$ [2.769(1) Å][17] and $[RhW(\mu-CO)_2(CO)(PPh_3)_2(\eta-C_5H_5)]$

[2.587(1) Å].[18] The latter, like **(4a)**, is a 30 valence-electron dimetal species, and in accord with the unsaturation it is reasonable to invoke the presence of rhodium–tungsten double bonds in both species. The W–C(a) [1.880(6) Å] separation in **(4a)** is shorter than the W–μ-C distance [1.913(14) Å] in the 34 valence-electron dimetal complex [RhW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)(η-C$_5$H$_5$)(η-C$_9$H$_7$)].[17] Moreover, in the latter the Rh–μ-C bond [2.048(14) Å] is somewhat shorter than Rh–C(a) [2.068(5) Å]. The data thus show that the μ-CC$_6$H$_4$Me-4 ligand is more displaced towards the tungsten in **(4a)** than in [RhW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)(η-C$_5$H$_5$)(η-C$_9$H$_7$)].

The dimensions of the μ-CRhW ring in **(4a)**, and the presence of the semibridging carbonyl group C(01)O(01), lead to representation **(D)** for the bridge system, giving 18 and 16 electron counts at the tungsten and rhodium centres, respectively. However, the i.r. spectrum of **(4a)** shows a carbonyl stretching band at 1 767 cm^{-1}, implying that in solution a more symmetrically bridging CO ligand might be present. This would lead to representation **(E)** for the bridge system, similar to that invoked to account for the metal–metal bonding in the compounds [MRh(μ-CO)$_2$(CO)(PPh$_3$)$_2$(η-C$_5$H$_5$)](M = Mo or W).[19] For the molecules **(4a)** and **(4b)** various electron distributions which differ little in energy are probably possible, leading to their dynamic behaviour, discussed below.



(D)

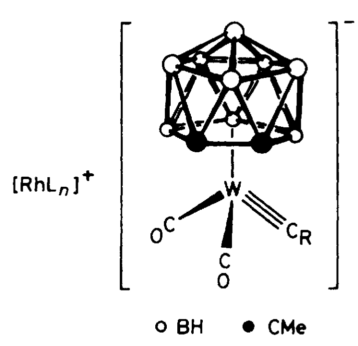


(E)

In **(4a)** the atoms C(a) and C(01) are not coplanar with the Rh and W atoms, the planes defined by RhC(a)W and RhC(01)W being inclined by 13° to one another. The tungsten carries the η^5-C$_2$B$_9$H$_9$Me$_2$ ligand and an essentially terminally bound CO group [W–C(02)–O(02) 176.9(5)°]. The rhodium atom is ligated by the two PPh$_3$ groups [P(1)–Rh–P(2) 98.8(1)°] but the P–Rh distances [2.346(2) and 2.281(2) Å] are appreciably different. The phosphorus P(1), more transoid to the μ-CC$_6$H$_4$Me-4 ligand, is associated with the longer P–Rh separation. This is a common feature of M(PR$_3$)$_2$ (R = alkyl or aryl) fragments ligated by C≡W or C=W bonds, and is evidently due to the transoid influence of the bridging μ-CR, μ-C(OMe)R, or μ-C=CH$_2$ groups.[20]

The geometry of the central core of **(5a)** (Figure 3) is very similar to that of **(4a)**. The Y-shaped WRhP$_2$ fragment is again bridged and semibridged by CC$_6$H$_4$Me-4 and CO groups, respectively. The angle between the planes WC(4)Rh and WC(71)Rh is 20°, compared with 13° for the corresponding angle in **(4a)**. The Rh–W distance [2.662(2) Å] is perceptively shorter than that in **(4a)**. However, the novel feature of the structure of **(5a)** is the attachment of the nortricyclene(tricyclo[2.2.1.0^{2,6}]heptane) fragment to the carbaborane cage at B(5).

In the formation of **(5a)** an unprecedented hydroboration of the C$_7$H$_8$ ligand has thus occurred, a cage B–H bond having added to the organic moiety. This is accompanied by C–C bond formation yielding the nortricyclene system. The reaction very probably proceeds with retention of the C$_7$H$_8$ ligand at the dimetal centre. Thus no reaction was observed on treatment of **(4a)** with nbd in CH$_2$Cl$_2$. It is likely that in the synthesis of **(5a)** a B–H group is activated at the Rh–W centre. This idea is supported by the existence in the molecular structures of [Rh$_2$(PPh$_3$)$_2$(η^5-C$_2$B$_9$H$_{11}$)$_2$][21] and [MoW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_9$H$_7$) (η^5-C$_2$B$_9$H$_9$Me$_2$)][22] of B–H ⇀ M (M = Rh or Mo) bonds. Moreover, it has recently been found that the molybdenum–tungsten species undergoes a reaction with hex-3-yne which results in hydroboration of the bridging *p*-tolylmethylidyne group. The CH(C$_6$H$_4$Me-4) fragment thus produced becomes attached in the final product to the central boron atom of the open pentagonal face of the carbaborane cage, *viz*. B(5) of Figure 3.

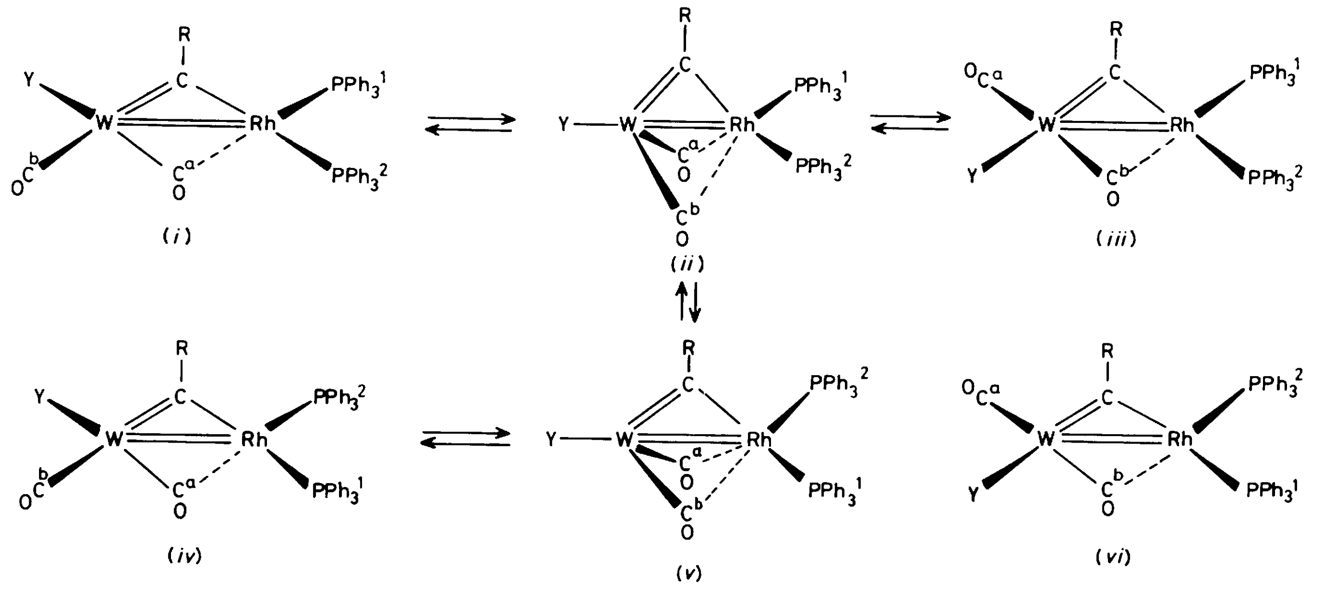


	RhL$_n$	R
(6a)	[Rh(PMe$_2$Ph)$_4$]	C$_6$H$_4$Me-4
(6b)	[Rh(dppe)$_2$]	C$_6$H$_4$Me-4
(6c)	[Rh(CO)$_3$(PPh$_3$)$_2$]	C$_6$H$_4$Me-4

Treatment of [Rh(PPh$_3$)$_2$(nbd)][PF$_6$] with **(1b)** afforded the black crystalline complex [RhW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)$_2${η^5-C$_2$B$_9$(C$_7$H$_9$)H$_{10}$}] **(5b)**, characterised by the data given in Tables 1—3. Examination of the ^{1}H and ^{13}C-{^{1}H} spectra of **(5b)** revealed that it was formed as a mixture of two isomers, which were produced in *ca.* equal amounts, based on peak intensities in the spectra. The ^{13}C-{^{1}H} n.m.r. spectrum is the most informative (Table 2), there being twelve peaks assignable to the C$_7$H$_9$ group. For two nortricyclene substituents in different environments fourteen resonances would be anticipated, however, we assume that the signal due to the C^7 nucleus in both isomers is not seen. Thus in the ^{13}C-{^{1}H} n.m.r. spectrum of **(5a)** the C$_7$H$_9$ fragment gives risk to six rather than seven peaks. It is also noticeable that in the spectrum of **(5b)** the resonance for the μ-*C*C$_6$H$_4$Me-4 ligand is very broad, suggestive of overlapping peaks. Moreover, the appearance of two signals in the spectrum for C^1 nuclei of C$_6$H$_4$Me-4 groups, also suggests the presence of the isomers. It seems probable that the two isomers of **(5b)**, **(I)** and **(II)** correspond to the C$_7$H$_9$ group being attached either to B(5) or to B(4) [B(6)] (see Figure 3) of the open face of the carbaborane ligand.

The complex [RhW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(dppe)(η^5-C$_2$B$_9$H$_9$Me$_2$)] **(4c**, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) was prepared by treating [Rh(dppe)(nbd)][PF$_6$] with **(1a)** in CH$_2$Cl$_2$. The compound was characterised in the usual manner (Tables 1—3), from which it was apparent that the nbd ligand present in the precursor [Rh(dppe)(nbd)][PF$_6$] had not become incorporated in the carbaborane cage of the product.

Reactions between **(4a)** and some donor molecules were also investigated as part of our studies. Treatment of **(4a)** with PEt$_3$ in excess afforded [RhW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PEt$_3$)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)] **(4d)**, quantitatively. The spectroscopic data for this species showed that it was structurally similar to **(4a)**. However, when **(4a)** was treated with PMe$_2$Ph, the product was the salt [Rh(PMe$_2$Ph)$_4$][W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)] **(6a)**. The ^{31}P-{^{1}H} n.m.r. spectrum showed a doublet resonance at δ −4.3 p.p.m. [*J*(RhP) 137 Hz], consistent with the presence of the [Rh(PMe$_2$Ph)$_4$]$^+$ cation. The i.r. spectrum had CO stretching bands at 1 956 and 1 874 cm^{-1}, characteristic of the anion of **(1a)** (Table 1). In a similar reaction, excess of dppe with **(4a)** affords the salt [Rh(dppe)$_2$][W(≡CC$_6$H$_4$Me-4)(CO)$_2$-



Scheme. R = C_6H_4Me-4; Y = η^5-$C_2B_9H_9R'_2$, R′ = Me (**4a**), R′ = H (**4b**); Y = η^5-$C_2B_9(C_7H_9)H_8R'_2$, R′ = Me (**5a**), R′ = H (**5b**)

(η^5-$C_2B_9H_9Me_2$)] (**6b**), data for which are given in Tables 1—3. Treatment of (**4a**) with one equivalent of dppe gives a mixture of (**4c**), (**6b**), and unreacted (**4a**). The stability of (**4d**) towards excess of PEt_3 must be associated with its greater basicity compared with PMe_2Ph or dppe. The $Rh(PEt_3)_2$ fragment evidently becomes more firmly attached to the C≡W group than is possible for the $Rh(PMe_2Ph)_2$ or Rh(dppe) moieties. Carbon monoxide reacts at 1 atm with (**4a**) in thf to give $[Rh(CO)_3(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6c**), characterised by its i.r. spectrum. Carbonyl stretching bands at 1 956 and 1 874 cm^{-1} identified the anion, while bands at 2 035 and 2 024 cm^{-1} were characteristic of the cation.[23]

It was evident from the ^{31}P-{^{1}H} n.m.r. spectra of the compounds (**4**) and (**5**) that at room temperature these species undergo dynamic behaviour, since only one phosphorus resonance is observed (Table 3). Although detailed variable-temperature n.m.r. studies (^{13}C-{^{1}H} and ^{31}P-{^{1}H}) on all the complexes were not possible, due to low solubility in some instances, sufficient data became available to delineate the dynamic process occurring. The ^{13}C-{^{1}H} n.m.r. spectrum of (**4a**) (Table 2) shows only one resonance for the CO ligands at δ 236.1 p.p.m., with *J*(RhC) 17 Hz. This can be explained by the exchange process (*i*) $\rightleftarrows$ (*ii*) $\rightleftarrows$ (*iii*) shown in the Scheme, which would make the CO ligands chemically equivalent on the n.m.r. time-scale. The PPh_3 groups would also become equivalent by this mechanism, leading to one ^{31}P signal as is observed in the spectra of (**4a**)—(**4d**).

Compound (**5a**) is asymmetric, due to the presence of the chiral atom C(n1) (Figure 3). This feature renders it impossible in this compound for CO^a and CO^b (Scheme) to become chemically equivalent, with the corollary that the two PPh_3 ligands also could not become equivalent by the exchange mechanism (*i*) $\rightleftarrows$ (*ii*) $\rightleftarrows$ (*iii*). Since only one signal is observed at room temperature in the ^{31}P-{^{1}H} n.m.r. spectrum, whereas two CO resonances occur in the ^{13}C-{^{1}H} n.m.r. spectrum, a different explanation is required. Site exchange of the PPh_3 ligands could be achieved in this complex, and in (**4**) also, *via* the process (*ii*) $\rightleftarrows$ (*v*) involving rotation of the RhP_2 fragments, and this coupled with the other transformations indicated in the Scheme would account for the data observed.

An interesting feature of the ^{13}C-{^{1}H} n.m.r. spectrum of (**5a**) is that the shifts for the CO groups vary with temperature. The signals at 256.2 and 222.5 p.p.m. in the room temperature spectrum become 258.8 and 219.2 p.p.m. at −20 °C, and 266.6 and 212.1 p.p.m. at −60 °C. This behaviour may be explained if the relative populations of the diastereoisomers (*i*) and (*iii*) (Scheme) are temperature dependent. However, exchange of CO ligands persists at −60 °C, otherwise four resonances rather than two would be observed. At −60 °C, rotation of the $Rh(PPh_3)_2$ group in (**5a**) ceases since the ^{31}P-{^{1}H} spectrum adopts an ABX pattern, with signals at δ 35.7 [d of d, *J*(PP) 32, *J*(RhP^1) 180 Hz] and 28.8 p.p.m. [d of d, *J*(PP) 32, *J*(RhP^2) 152 Hz].

The work described in this paper establishes the salts (**1**) as useful precursors in organometallic chemistry. It has also been shown that the carbaborane ligand is not innocent in all of the reactions; the formation of the compounds (**5**) representing a novel hydroboration of a co-ordinated nbd group. The gold–tungsten complexes (**2**) and (**3**) are analogues of the previously reported cationic species $[AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ and $[AuW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2]^+$ (R = C_6H_4-Me-4 or Me), and their synthesis correlates with the isolobal mapping of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R_2)]^-$ (R = Me or H).

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. All separations by chromatography were carried out on 2 × 20 cm columns, packed with Brockman activity II alumina. The compounds $[NHMe_3][7,8\text{-}C_2B_9H_{10}Me_2]$, $[NHMe_3][7,8\text{-}C_2B_9H_{12}]$,[24] $[W(\equiv CR)Br(CO)_4]$ (R = Me[25] or C_6H_4Me-4[26]), [AuCl(L)] (L = PPh_3[27] or tht[28]), $[RhCl(PPh_3)_3]$,[29] $[Rh(PPh_3)_2L_2][PF_6]$ (L_2 = cod or nbd), and $[Rh(dppe)(nbd)][PF_6]$[23] were prepared by literature methods. The i.r. spectra were measured with Nicolet MX-10 or MX-5 spectrophotometers, and n.m.r. spectra were recorded with JNM FX 90Q and FX 200 instruments. Analytical and other data for the new compounds are given in Table 1.

Synthesis of the Salts $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]$ (R = Me *or* H).—A solution of $Na_2[7,8\text{-}C_2B_9H_9Me_2]$ was prepared by refluxing $[NHMe_3][7,8\text{-}C_2B_9H_{10}Me_2]$ (1.1 g, 5.0 mmol) and NaH (2 g, from a 60% dispersion in mineral oil) in thf (40 cm^3) for 10 h. The resulting solution was decanted and added to $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$ (2.41 g, 5.0 mmol) in thf (10 cm^3) at −40 °C. After warming to room temperature, $[N(PPh_3)_2]Cl$ (2.87 g, 5.0 mmol) was added and the solution stirred for 15 min. Solvent was removed *in vacuo*, and the orange residue was extracted with CH_2Cl_2–Et_2O (1:1, 50 cm^3). The extract was evaporated *in vacuo*, and the residue was dissolved in CH_2Cl_2 (20 cm^3) and chromatographed, using the same solvent as eluate. Solvent was removed *in vacuo* from the solution, and the residue was crystallised from CH_2Cl_2–light petroleum (1:2, 30 cm^3) at −20 °C to give orange *microcrystals* of $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1a**) (4.28 g).

In a similar preparation, a solution of $Na_2[7,8\text{-}C_2B_9H_{11}]$, obtained from $[NHMe_3][7,8\text{-}C_2B_9H_{12}]$ (0.98 g, 5.0 mmol) and excess NaH (2 g) by refluxing in thf (50 cm^3) for 3 h, was added to a thf (10 cm^3) solution of $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$ (2.41 g, 5.0 mmol) at −40 °C. After adding $[N(PPh_3)_2]Cl$ (5 mmol) the salt $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_{11})]$ (**1b**) (3.61) was isolated as a finely divided orange *powder*.

Synthesis of the Salt $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$.—The compound $Tl_2[7,8\text{-}C_2B_9H_9Me_2]$ was prepared by treating $[NHMe_3][7,8\text{-}C_2B_9H_{10}Me_2]$ (1.0 g) with $Tl(O_2CMe)$ (3.0 g) and NaOH (3.2 g) in water (80 cm^3). The yellow precipitate thus obtained was washed with Et_2O (3 × 20 cm^3) and used without further purification.

Treatment of $[W(\equiv CMe)Br(CO)_4]$ (2.16 g, 5.0 mmol) with $Tl_2[7,8\text{-}C_2B_9H_9Me_2]$ (3.40 g, 6.0 mmol) in thf (20 cm^3) at −40 °C for 30 min afforded a yellow solution containing a small amount of solid. The mixture was filtered through a Celite pad (*ca.* 4 cm), and $[NEt_4]Cl$ (1.00 g, 6.0 mmol) was added to the resulting solution. After stirring at room temperature (10 min), solvent was removed *in vacuo* and the residue was extracted with CH_2Cl_2–light petroleum (1:1, 50 cm^3). Solvent was removed *in vacuo*, and the residue was washed with Et_2O (2 × 20 cm^3) affording $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1c**) (1.87 g) as a yellow *powder*.

Synthesis of the Gold–Tungsten Complexes.—(*i*) The compounds (**1a**) (1.04 g, 1.0 mmol), $[AuCl(PPh_3)]$ (0.49 g, 1.0 mmol), and $TlPF_6$ (0.52 g, 1.5 mmol) were stirred together in thf (15 cm^3) for 20 min. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (1:1, 20 cm^3) and chromatographed, eluting with the same solvent mixture. Solvent was removed *in vacuo* from an orange eluate and the residue was crystallised from CH_2Cl_2–light petroleum (1:4, 10 cm^3) at −20 °C, yielding orange *crystals* of $[AuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2a**) (0.60 g).

(*ii*) Similarly, (**1b**) (1.02 g, 1.0 mmol), $[AuCl(PPh_3)]$ (0.49 g, 1.0 mmol), and $TlPF_6$ (0.52 g, 1.5 mmol) were stirred together in thf (15 cm^3) for 20 min. Orange *crystals* of $[AuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_{11})]$ (**2b**) (0.48 g) were isolated, as described for (**2a**).

(*iii*)Treatment of (**1c**) (0.28 g, 0.50 mmol) with $[AuCl(PPh_3)]$ (0.25 g, 0.50 mmol) in the presence of $TlPF_6$ (0.26 g, 0.75 mmol) in thf (15 cm^3) for 20 min afforded an orange mixture. Solvent was removed *in vacuo*, and the residue was extracted with toluene (25 cm^3). Removal of the latter *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (1:4, 10 cm^3) at −20 °C, afforded orange *crystals* of $[AuW(\mu\text{-}CMe)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2c**) (0.20 g).

(*iv*) Compound (**1a**) (0.52 g, 0.50 mmol) and $[AuCl(tht)]$ (0.08 g, 0.25 mmol) were stirred in CH_2Cl_2 (10 cm^3) for 5 min. The mixture was filtered through a Celite pad (*ca.* 4 cm), and solvent was removed *in vacuo*. The residue was washed with Et_2O (2 × 10 cm^3), and dried *in vacuo* affording $[N(PPh_3)_2][AuW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ (**3**) (0.35 g) as a yellow *powder*.

Synthesis of the Rhodium–Tungsten Compounds.—(*i*) Compounds (**1a**) (0.52 g, 0.50 mmol) and $[RhCl(PPh_3)_3]$ (0.46 g, 0.50 mmol) were stirred together in CH_2Cl_2 (20 cm^3) for 4 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (1:1, 30 cm^3) and chromatographed. Elution with the same solvent mixture afforded a green eluate. Removal of solvent *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (1:2, 30 cm^3) at −20 °C gave black *crystals* of $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4a**) (0.30 g).

Compound (**4a**) may also be obtained by treating $[Rh(PPh_3)_2(cod)][PF_6]$ (0.44 g, 0.50 mmol) with (**1a**) (0.52 g, 0.50 mmol) in CH_2Cl_2 (15 cm^3) for 10 min. Black crystals of (**4a**) (0.38 g) may be isolated as described above.

(*ii*) In a similar synthesis, (**1b**) (0.51 g, 0.50 mmol) and $[Rh(PPh_3)_2(cod)][PF_6]$ (0.44 g, 0.50 mmol) were stirred in CH_2Cl_2 (15 cm^3) for 10 min. Black *crystals* of $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})]$ (**4b**) (0.31 g) were isolated, as described for (**4a**).

(*iii*) Treatment of compound (**1a**) (0.52 g, 0.50 mmol) with $[Rh(PPh_3)_2(nbd)][PF_6]$ (0.43 g, 0.50 mmol) in CH_2Cl_2 (15 cm^3) for 30 min afforded a green-brown solution. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (1:1, 30 cm^3) and chromatographed. Elution with the same solvent mixture gave a brown eluate. Removal of solvent *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (1:2, 30 cm^3) at −20 °C gave black *crystals* of $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9(C_7H_9)H_8Me_2\}]$ (**5a**) (0.39 g).

(*iv*) In a similar synthesis, (**1b**) (0.51 g, 0.50 mmol) and $[Rh(PPh_3)_2(nbd)][PF_6]$ (0.43 g, 0.50 mmol) were stirred in CH_2Cl_2 (15 cm^3) for 30 min. Black *crystals* of $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9(C_7H_9)H_{10}\}]$ (**5b**) (0.36 g) were isolated, as described for (**5a**).

(*v*) Treatment of compound (**1a**) (0.42 g, 0.40 mmol) with $[Rh(dppe)(nbd)][PF_6]$ (0.30 g, 0.40 mmol) in CH_2Cl_2 (10 cm^3) for 30 min afforded an orange solution. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (1:1, 30 cm^3) and chromatographed. Elution with the same solvent mixture gave an orange eluate. Removal of solvent *in vacuo* afforded orange *microcrystals* of $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(dppe)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4c**) (0.24 g).

(*vi*) Excess PEt_3 (0.2 cm^3) was added to a CH_2Cl_2 (10 cm^3) solution of (**4a**) (0.23 g, 0.20 mmol), and the mixture was stirred for 1 h. Volatile material was removed *in vacuo*, and the residue was washed with light petroleum (2 × 10 cm^3). Green-black *crystals* of $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PEt_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4d**) (0.16 g) were obtained, after crystallisation of the residue from CH_2Cl_2–light petroleum (1:2, 20 cm^3) at −20 °C.

(*vii*) A CH_2Cl_2 (10 cm^3) solution of (**4a**) (0.28 g, 0.25 mmol) was treated with dppe (0.20 g, 0.50 mmol), and the mixture was stirred for 1 h. Solvent was removed *in vacuo* and the residue was washed with Et_2O (10 cm^3). Orange *microcrystals* of $[Rh(dppe)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6b**) (0.33 g) were obtained from CH_2Cl_2–light petroleum (1:1, 10 cm^3) at −20 °C.

Crystal Structure Determinations.—(*a*) Orange crystals of (**2a**) were grown from CH_2Cl_2–light petroleum (1:2) at −20 °C, and that chosen for study was *ca.* 0.15 × 0.35 × 0.50 mm. Diffracted intensities were measured on a Nicolet

Table 7. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) for complex (**2a**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	64(1)	7 088(1)	6 636(1)	C(46)	1 026	2 103	5 874
Au	655(1)	5 111(1)	7 631(1)	C(47)	686	3 345	6 015
P	804(4)	4 177(8)	8 554(3)	C(42)	987	4 014	6 592
C(12)*	2 013(9)	2 951(18)	9 500(7)	C(48)	2 033(16)	216(35)	6 160(15)
C(13)	2 605	1 971	9 742	C(5)	882(17)	8 327(38)	7 136(15)
C(14)	2 751	933	9 365	O(5)	1 398(11)	9 083(26)	7 424(10)
C(15)	2 306	876	8 747	C(6)	401(15)	7 360(34)	6 047(13)
C(16)	1 714	1 856	8 506	O(6)	573(11)	7 443(25)	5 627(10)
C(11)	1 568	2 894	8 882	C(2)	−698(16)	9 262(41)	6 717(15)
C(22)*	1 267(8)	7 078(20)	9 050(7)	C(3)	−907(20)	8 896(49)	6 027(18)
C(23)	1 364	8 291	9 460	B(4)	−1 087(17)	6 905(42)	5 860(16)
C(24)	1 113	8 142	9 909	B(5)	−1 010(19)	6 008(45)	6 566(17)
C(25)	765	6 779	9 949	B(6)	−751(17)	7 579(40)	7 077(15)
C(26)	668	5 566	9 538	B(7)	−1 780(23)	8 324(52)	5 613(21)
C(21)	920	5 716	9 089	B(8)	−1 872(18)	6 637(43)	5 969(17)
C(32)*	−625(10)	3 624(17)	8 173(7)	B(9)	−1 662(22)	6 946(55)	6 755(20)
C(33)	−1 225	2 821	8 146	B(10)	−1 507(25)	8 815(59)	6 865(22)
C(34)	−1 146	1 438	8 472	B(11)	−1 527(29)	9 850(68)	6 164(26)
C(35)	−466	859	8 824	B(12)	−2 155(24)	8 346(56)	6 139(22)
C(36)	133	1 663	8 851	Me(2)	−620(22)	10 044(51)	5 731(19)
C(31)	54	3 046	8 525	Me(3)	−204(19)	10 718(45)	7 043(17)
C(41)	628(14)	5 306(31)	6 720(12)	Cl(1)	1 979(12)	2 833(30)	1 819(12)
C(43)*	1 629(9)	3 439(20)	7 027(6)	Cl(2)	1 269(12)	2 321(28)	595(11)
C(44)	1 969	2 197	6 885	Cl(3)	2 307(15)	1 908(35)	1 388(14)
C(45)	1 668	1 529	6 309	Cl(4)	1 071(16)	3 127(38)	996(15)

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

Table 8. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) for complex (**4a**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2 685(1)	2 670(1)	269(1)	C(62) *	6 498(4)	3 188(3)	4 984(3)
Rh	3 981(1)	2 298(1)	2 043(1)	C(63)	7 718	3 430	5 465
P(1)	5 431(2)	1 375(1)	2 576(1)	C(64)	8 508	3 908	4 985
P(2)	4 478(2)	3 122(1)	3 361(1)	C(65)	8 077	4 144	4 024
C(01)	4 392(6)	3 220(4)	992(4)	C(66)	6 857	3 902	3 543
O(01)	5 339(4)	3 701(3)	1 175(3)	C(61)	6 067	3 424	4 023
C(02)	3 296(7)	1 620(5)	−19(5)	C(2)	2 609(6)	3 564(4)	−1 204(4)
O(02)	3 594(6)	1 028(4)	−215(4)	C(3)	2 222(5)	4 076(4)	−459(4)
C(12)*	6 366(4)	958(2)	1 147(3)	Me(3)	3 111(7)	4 828(4)	128(5)
C(13)	7 103	1 152	547	H(3a)	3 110	4 699	777
C(14)	7 858	1 975	578	H(3b)	2 883	5 397	−73
C(15)	7 875	2 604	1 208	H(3c)	3 903	4 835	75
C(16)	7 137	2 409	1 808	Me(2)	3 905(6)	3 778(5)	−1 305(5)
C(11)	6 382	1 586	1 778	H(2a)	4 510	3 858	−702
C(22)*	5 991(3)	954(3)	4 518(3)	H(2b)	4 038	4 278	−1 724
C(23)	6 742	855	5 438	H(2c)	3 950	3 247	−1 578
C(24)	7 988	1 101	5 627	B(4)	1 025(7)	3 418(5)	−140(5)
C(25)	8 484	1 445	4 894	B(5)	647(7)	2 417(5)	−770(5)
C(26)	7 734	1 544	3 974	B(6)	1 756(7)	2 541(5)	−1 414(5)
C(21)	6 487	1 299	3 786	B(9)	−192(7)	3 289(6)	−1 192(5)
C(32)*	5 376(3)	−472(3)	2 728(4)	B(10)	245(7)	2 733(6)	−1 989(6)
C(33)	4 810	−1 356	2 615	B(12)	299(7)	3 900(6)	−2 129(5)
C(34)	3 566	−1 564	2 210	B(11)	1 499(7)	3 457(6)	−2 259(5)
C(35)	2 887	−887	1 919	B(7)	1 798(7)	4 408(5)	−1 653(5)
C(36)	3 453	−3	2 032	B(8)	797(7)	4 317(5)	−965(5)
C(31)	4 697	205	2 437	H(a2)	998(50)	477(37)	617(39)
C(42)*	3 466(4)	3 308(2)	4 801(3)	H(a3)	−433(72)	−572(51)	1 397(55)
C(43)	2 846	3 003	5 470	H(a5)	33(58)	1 213(42)	3 448(45)
C(44)	2 460	2 095	5 596	H(a6)	1 393(54)	2 325(39)	2 729(42)
C(45)	2 694	1 492	5 053	C(a)	2 192(5)	1 997(4)	1 256(4)
C(46)	3 314	1 797	4 384	C(a1)*	1 297(3)	1 433(3)	1 671(3)
C(41)	3 700	2 705	4 258	C(a2)	701	628	1 253
C(52)*	4 705(3)	4 999(3)	3 297(3)	C(a3)	−127	68	1 641
C(53)	4 239	5 784	3 068	C(a4)	−359	311	2 447
C(54)	3 032	5 759	2 552	C(a5)	237	1 115	2 865
C(55)	2 292	4 950	2 265	C(a6)	1 066	1 676	2 477
C(56)	2 757	4 165	2 494	C(a41)	−1 211(7)	−309(5)	2 903(6)
C(51)	3 964	4 189	3 010				

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

Table 9. Atomic positional parameters (fractional co-ordinates) for complex (**5a**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Rh	0.486 76(11)	0.195 53(9)	0.203 96(7)
W	0.649 53(7)	0.011 46(5)	0.206 58(4)
P(1)	0.296 4(4)	0.261 1(4)	0.264 8(3)
P(2)	0.473 8(4)	0.325 6(4)	0.118 0(3)
C(12)	0.247 3(12)	0.223 6(7)	0.417 4(8)
C(13)	0.233 3(12)	0.162 7(7)	0.477 4(8)
C(14)	0.253 5(12)	0.064 6(7)	0.465 4(8)
C(15)	0.287 6(12)	0.027 3(7)	0.393 6(8)
C(16)	0.301 6(12)	0.088 2(7)	0.333 6(8)
C(11)	0.281 4(12)	0.186 4(7)	0.345 5(8)
C(22)	0.181 5(10)	0.253 4(9)	0.139 4(7)
C(23)	0.084 4(10)	0.251 7(9)	0.104 6(7)
C(24)	−0.024 3(10)	0.261 7(9)	0.146 7(7)
C(25)	−0.036 0(10)	0.273 3(9)	0.223 7(7)
C(26)	0.061 0(10)	0.275 0(9)	0.258 6(7)
C(21)	0.169 8(10)	0.265 0(9)	0.216 5(7)
C(32)	0.143 5(10)	0.459 0(10)	0.299 0(7)
C(33)	0.123 4(10)	0.551 7(10)	0.325 5(7)
C(34)	0.216 6(10)	0.568 0(10)	0.354 9(7)
C(35)	0.329 8(10)	0.491 8(10)	0.357 6(7)
C(36)	0.349 9(10)	0.399 1(10)	0.331 1(7)
C(31)	0.256 7(10)	0.382 8(10)	0.301 8(7)
C(42)	0.679 7(11)	0.317 4(8)	0.022 7(7)
C(43)	0.772 0(11)	0.276 5(8)	−0.034 0(7)
C(44)	0.776 4(11)	0.195 4(8)	−0.072 2(7)
C(45)	0.688 5(11)	0.155 3(8)	−0.053 6(7)
C(46)	0.596 1(11)	0.196 2(8)	0.003 1(7)
C(41)	0.591 8(11)	0.277 3(8)	0.041 3(7)
C(52)	0.340 3(10)	0.399 7(8)	−0.007 6(6)
C(53)	0.235 7(10)	0.458 0(8)	−0.040 6(6)
C(54)	0.132 6(10)	0.515 9(8)	0.003 6(6)
C(55)	0.134 1(10)	0.515 4(8)	0.080 9(6)
C(56)	0.238 8(10)	0.457 1(8)	0.113 9(6)
C(51)	0.341 8(10)	0.399 2(8)	0.069 6(6)
C(62)	0.448 4(10)	0.518 6(10)	0.150 9(7)
C(63)	0.480 5(10)	0.584 2(10)	0.187 7(7)
C(64)	0.574 8(10)	0.548 5(10)	0.233 6(7)
C(65)	0.637 0(10)	0.447 1(10)	0.242 7(7)
C(66)	0.604 9(10)	0.381 5(10)	0.205 9(7)
C(61)	0.510 6(10)	0.417 2(10)	0.160 0(7)
C(71)	0.608 1(14)	0.104 4(12)	0.279 5(10)
C(73)	0.542 3(11)	0.132 0(9)	0.416 0(8)
C(74)	0.540 7(11)	0.175 7(9)	0.482 7(8)
C(75)	0.604 7(11)	0.237 1(9)	0.484 9(8)
C(76)	0.670 2(11)	0.254 7(9)	0.420 4(8)
C(77)	0.671 7(11)	0.211 0(9)	0.353 7(8)
C(72)	0.607 8(11)	0.149 6(9)	0.351 5(8)
C(78)	0.605(3)	0.280(3)	0.559(2)
C(4)	0.504(2)	0.076 7(11)	0.143 7(10)
O(4)	0.435 3(12)	0.078 5(9)	0.101 6(7)
C(5)	0.744(2)	0.082 3(14)	0.155 8(11)
O(5)	0.807 0(13)	0.124 0(11)	0.128 9(9)
C(2)	0.623(2)	−0.140 2(12)	0.214 1(11)
C(3)	0.715 3(15)	−0.143 6(12)	0.139 6(9)
B(4)	0.832(2)	−0.120 9(15)	0.163 5(12)
B(5)	0.824(2)	−0.112 0(14)	0.264 8(13)
B(6)	0.682(2)	−0.122 4(15)	0.294 3(11)
B(7)	0.708(3)	−0.254 0(15)	0.173 5(13)
B(8)	0.844(3)	−0.241(2)	0.144 7(13)
B(9)	0.916(3)	−0.223(2)	0.220 5(14)
B(10)	0.814(3)	−0.225 0(15)	0.302 3(13)
B(11)	0.690(3)	−0.240(2)	0.271 8(13)
B(12)	0.836(3)	−0.304(2)	0.225 9(13)
Me(2)	0.489(2)	−0.121 5(13)	0.210 6(13)
Me(3)	0.670(2)	−0.116 7(13)	0.062 5(10)
C(n1)	0.882(2)	−0.061 1(13)	0.319 8(11)
C(n2)	0.996(2)	−0.134(2)	0.355 1(14)
C(n3)	1.050(3)	−0.045(2)	0.248 3(14)
C(n4)	0.986(3)	0.033(2)	0.364 4(13)
C(n5)	1.057(3)	−0.075(2)	0.381(2)
C(n6)	0.934(3)	0.015(2)	0.293 7(13)
C(n7)	1.108(3)	−0.129(3)	0.306(2)
Cl(1)	0.922(3)	0.395(3)	0.450 2(14)
Cl(2)	0.716(4)	0.530(3)	0.430(2)
C(1)	0.838(7)	0.517(6)	0.446(4)

*P*3*m* automated diffractometer at 293 K using the θ—2θ scan mode (2.9 ⩽ 2θ ⩽ 50°). Of the 4 805 unique reflections, 2 783 had $I \geqslant 2.5\sigma(I)$, and only these were used in the solution and refinement of the structure. Intensity data were corrected for Lorentz polarisation and *X*-ray absorption effects, the latter by a semi-empirical method based on azimuthal scan data.[30]

Crystal data. $C_{32}H_{37}AuB_9O_2PW{\cdot}CH_2Cl_2$, *M* = 1 047.7, monoclinic, *a* = 20.655(7), *b* = 8.572(4), *c* = 24.256(12) Å, β = 114.62(3)°, *U* = 3 904(6) Å^3, *Z* = 4, D_c = 1.79 g cm^{-3}, *F*(000) = 1 999, space group $P2_1/n$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) 69.6 cm^{-1}.

The structure was solved by conventional heavy-atom and difference Fourier methods. Anisotropic thermal motion was allowed for the Au, P, and W atoms only, with all other non-hydrogen atoms isotropically refined. Hydrogen atoms were not located but those bonded to carbon were included in calculated positions (C–H 0.960 Å) and given fixed isotropic thermal parameters 1.2 times U_{equiv} of their parent carbon atoms. The lattice contained a disordered molecule of CH_2Cl_2 per molecule of (**2a**). Only the Cl atoms were located, each disordered over two sites (50% occupancy). Refinement by blocked-cascade least squares, with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.0007|F_o|^2]^{-1}$, converged at *R* = 0.072 (*R′* = 0.065). The final electron-density difference syntheses showed no peaks ⩾1.5 e Å^{-3}. Scattering factors with corrections for the effects of anomalous dispersion were from ref. 31. All calculations were carried out on a Data General 'Eclipse' computer with the SHELXTL system of programs.[30] Atomic co-ordinates are listed in Table 7.

(*b*) Crystals of (**4a**) grow as deep red prisms from CH_2Cl_2–Et_2O (1:2). That used for data collection had dimensions *ca.* 0.13 × 0.40 × 0.20 mm. Data were collected (2.9 ⩽ 2θ ⩽ 43°) as described above for (**2a**). Of the 5 797 unique reflections, 4 638 with $I \geqslant 1.5\sigma(I)$ were used for solution and refinement of the structure after correction for Lorentz, polarisation and *X*-ray absorption effects, the latter by a numerical method (faces ⟨0 1 1⟩, ⟨1 1 0⟩, ⟨1 $\bar{1}$ 0⟩).

Crystal data. $C_{50}H_{52}B_9O_2P_2RhW$, *M* = 1 130.8, triclinic, *a* = 11.814(3), *b* = 15.375(3), *c* = 14.756(3) Å, α = 84.74(2), β = 107.41(1), γ = 101.21(2)°, *U* = 2 506(1) Å^3, *Z* = 2, D_c = 1.50 g cm^{-3}, *F*(000) = 1 124, space group $P\bar{1}$ (no. 2), μ(Mo-K_α) = 27.7 cm^{-1}.

The solution and refinement of the structure was similar to that for (**2a**), except that all hydrogen atoms attached to the carbaborane ligand were located and refined freely. The phenyl and methyl hydrogens were refined as members of rigid groups. Refinement with the weighting scheme $w = [\sigma^2(F_o) + 0.000\,275|F_o|^2]^{-1}$ converged at *R* = 0.031 (*R′* = 0.030). The final electron-density difference synthesis showed no peaks ⩾1.3 e Å^{-3}. Atomic positional parameters are given in Table 8.

(*c*) Black crystals of (**5a**) were grown from CH_2Cl_2–light petroleum (1:2) at −20 °C, and that chosen for study had dimensions *ca.* 0.35 × 0.15 × 0.35 mm. Data were collected

$(2.9 \leqslant 2\theta \leqslant 40^\circ)$ as for (**2a**). Of 5 416 unique reflections, 3 889 met the criterion $I \geqslant 2\sigma(I)$ and only these were used for structure solution and refinement, after corrections for Lorentz polarisation and *X*-ray absorption effects. The latter was numerical (faces $\langle 1\,1\,1\rangle$, $\langle 0\,0\,1\rangle$, $\langle \bar{1}\,2\,0\rangle$, $\langle 1\,2\,1\rangle$).

Crystal data. $C_{57}H_{60}B_9O_2P_2RhW\cdot0.5CH_2Cl_2$, M = 1 262.5, triclinic, a = 12.006(4), b = 14.692(9), c = 18.033(7) Å, α = 86.28(4), β = 83.44(3), γ = 67.46(3)°, U = 2 918(3) Å^3, Z = 2, D_c = 1.44 g cm^{-3}, $F(000)$ = 1 266, space group $P\bar{1}$ (no. 2), μ(Mo-K_α) = 24.3 cm^{-1}.

Solution and refinement were as for (**2a**), except that the phenyl groups were refined as rigid groups (C–C 1.395 Å), the constituent atoms being given isotropic thermal parameters. Most hydrogen atoms were incorporated at calculated positions but some in the carbaborane cage were located and refined isotropically. The lattice contained 0.5 of a molecule of CH_2Cl_2 per molecule of (**5a**). A weighting scheme $w = [\sigma^2(F_o) + 0.0005|F_o|^2]^{-1}$ gave a satisfactory weight analysis, and refinement converged at R = 0.059 (R' = 0.056). The final electron density difference synthesis showed no peaks $\geqslant$0.98 e Å^{-3}. Scattering factors, corrections for anomalous dispersion, and calculations were as for (**2a**). The atom co-ordinates are given in Table 9.

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