Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 44.[1] Formation of Unsaturated Dimetal Compounds with Elimination of Alkylidyne Groups; *X*-Ray Crystal Structures of [FeW(μ-PPh$_2$)(CO)$_5${HB(pz)$_3$}] [HB(pz)$_3$ = Tris(pyrazol-1-yl)borate] and [RhW(μ-CO)$_2$(CO)(PPh$_3$)$_2$(η-C$_5$H$_5$)] *

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Treatment of the complexes [FeW(μ-CR)(CO)$_5${HB(pz)$_3$}] [R = C$_6$H$_4$Me-4 or Me; HB(pz)$_3$ = tris(pyrazol-1-yl)borate] with diphenylphosphine in dichloromethane at room temperature gives the compounds [FeW(μ-CR)(CO)$_4$(PHPh$_2$){HB(pz)$_3$}]. On heating in toluene, the *p*-tolylmethylidyne derivative affords the complex [FeW{μ-σ,η^3-CH(C$_6$H$_4$Me-4)}(μ-PPh$_2$)(μ-CO)(CO)$_3${HB(pz)$_3$}]. In contrast, the ethylidyne analogue under similar conditions yields the compound [FeW(μ-PPh$_2$)(CO)$_5${HB(pz)$_3$}]. The latter was structurally characterised by *X*-ray diffraction. A short Fe–W bond [2.658(2) Å] is spanned by a PPh$_2$ group [Fe–P 2.210(3), W–P 2.406(3) Å]. The iron atom is ligated by three CO groups and the tungsten atom by two such groups. One CO ligand on tungsten semi-bridges the Fe–W bond [W–C–O 168(1)°]. The tungsten atom carries the HB(pz)$_3$ ligand which functions as a tridentate group in the usual manner. The ethylidyne tungsten compound [W($\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)] reacts with the complexes [RhH(L)(PPh$_3$)$_3$] (L = CO or PPh$_3$) to give a mixture of the dimetal compounds [RhW(μ-CO)$_2$(CO)(PPh$_3$)$_2$(η-C$_5$H$_5$)] and [RhW(μ-CO)$_2$(PPh$_3$)$_2$(η-C$_2$H$_4$)(η-C$_5$H$_5$)]. The former species was identified by a single-crystal *X*-ray diffraction study [Rh–W 2.587(1) Å], the latter could only be identified by ^{1}H and ^{13}C-{^{1}H} n.m.r. spectroscopy. Spectroscopic data for all the new compounds are reported and discussed.

We have previously characterised[2] the complexes [W($\equiv$CR)(CO)$_2${HB(pz)$_3$}] [**1a**, R = C$_6$H$_4$Me-4; **1b**, R = Me; HB(pz)$_3$ = tris(pyrazol-1-yl)borate], and shown[1] that (**1a**) reacts with [Fe$_2$(CO)$_9$] in diethyl ether to give the 32 valence-electron dimetal compound [FeW(μ-CC$_6$H$_4$Me-4)(CO)$_5${HB(pz)$_3$}] (**2a**). In this paper we report the synthesis of (**2b**), the ethylidyne-bridged analogue of (**2a**), and describe reactions of both species with diphenylphosphine. As described below the reaction between PHPh$_2$ and (**2b**) occurred in a step-wise manner, and overall showed a similarity to reactions observed between [W($\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)] and the hydridorhodium complexes [RhH(L)(PPh$_3$)$_3$] (L = CO or PPh$_3$); hence these results are also reported herein.

Results and Discussion

The reaction between [Fe$_2$(CO)$_9$] and (**1b**) in diethyl ether at room temperature afforded the purple complex [FeW(μ-CMe)(CO)$_5${HB(pz)$_3$}] (**2b**) in *ca.* 80% yield. The ^{13}C-{^{1}H} n.m.r. spectrum of (**2b**) showed a characteristic resonance for the μ-C nucleus at δ 425.8 p.p.m. with ^{183}W–^{13}C coupling (128 Hz). The corresponding signal in the spectrum of (**2a**) is at δ 408.8 p.p.m. The very deshielded nature of these resonances, as compared with those in the spectra of other alkylidyne-bridged dimetal compounds, is apparently related to the unsaturated character of complexes (**2**), which are formally 32 rather than 34 valence electron species.[1]

The compounds (**2**) react with diphenylphosphine to give the complexes [FeW(μ-CR)(CO)$_4$(PHPh$_2$){HB(pz)$_3$}] (**3**), characterised by microanalysis, and by i.r. and n.m.r. spectroscopy. These compounds are related to the complexes [FeW(μ-CC$_6$H$_4$Me-4)(CO)$_4$(PR$_3$){HB(pz)$_3$}] (R = Me or Et),[1] and all four phosphine derivatives are electronically unsaturated like the precursors (**2**). For (**3a**) and (**3b**), the resonances for the μ-C nuclei in the ^{13}C-{^{1}H} n.m.r. spectra occur at δ 404.9 and 423.5 p.p.m., respectively. The ^{31}P-{^{1}H} spectra show signals for the PHPh$_2$ ligands at δ 73.1 (**3a**) and 64.8 p.p.m. (**3b**). In fully coupled ^{31}P spectra these resonances appear as doublets due to coupling with the proton attached to the phosphorus nucleus [(**3a**), *J*(PH) 369 Hz; (**3b**), *J*(PH) 361 Hz]. In the ^{1}H n.m.r. spectra characteristic signals for the PH group are seen as doublets at δ 6.54 (**3a**) and 6.85 (**3b**), with *J*(PH) 369 and 361 Hz, respectively.

When compound (**3a**) is heated in toluene it affords the brown crystalline complex [FeW{μ-σ,η^3-CH(C$_6$H$_4$Me-4)}(μ-PPh$_2$)(μ-CO)(CO)$_3${HB(pz)$_3$}] (**4**). The presence of the μ-PPh$_2$ ligand is clearly indicated by a singlet signal at δ 167.0 p.p.m. in the ^{31}P-{^{1}H} n.m.r. spectrum with strong ^{183}W–^{31}P coupling (361 Hz). The latter indicates the presence of a direct P–W bond, while the observed chemical shift is in the region commonly found for μ-phosphido groups.[3] The i.r. spectrum shows a band at 1 800 cm^{-1} in the carbonyl stretching region which may be ascribed to a μ-CO group, and this is confirmed by the ^{13}C-{^{1}H} n.m.r. spectrum with a resonance at δ 261.2 p.p.m.; signals for bridging carbonyls being more deshielded than those for terminally bound ligands.[4] The ^{13}C-{^{1}H} n.m.r. spectrum was especially informative. No resonance characteristic of the μ-CC$_6$H$_4$Me-4 group was observed. Instead signals occur at δ 190.8, 117.2, and 95.3 p.p.m. which may be assigned to the

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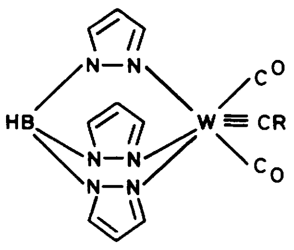
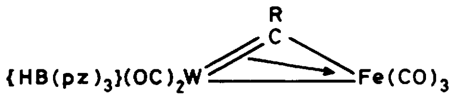
* 1,1,1,2,2-Pentacarbonyl-μ-diphenylphosphido-2-[tris(pyrazol-1-yl)borato]irontungsten (*Fe–W*) and di-μ-carbonyl-2-carbonyl-2-(η-cyclopentadienyl)-1,1-bis(triphenylphosphine)rhodiumtungsten (*Rh–W*) respectively.

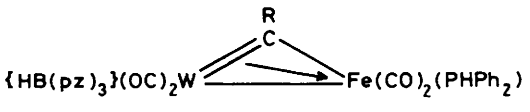
Supplementary data available (No. SUP 56524, 6 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.



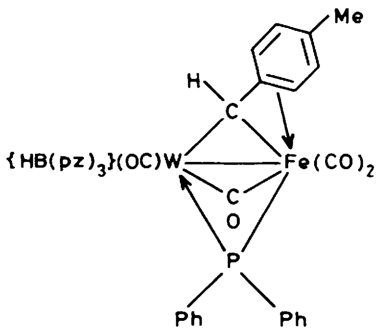
R
(**1a**) C_6H_4Me-4
(**1b**) Me



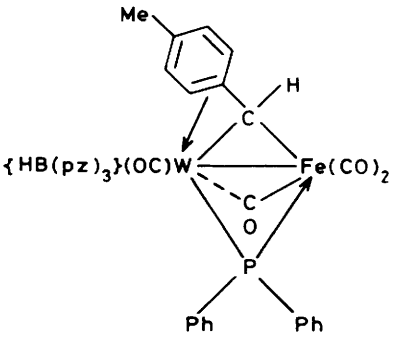
R
(**2a**) C_6H_4Me-4
(**2b**) Me



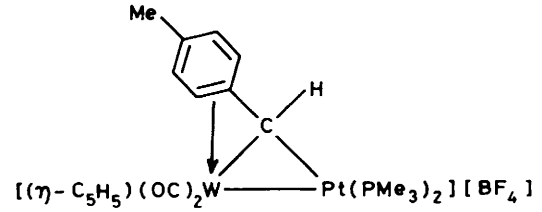
R
(**3a**) C_6H_4Me-4
(**3b**) Me



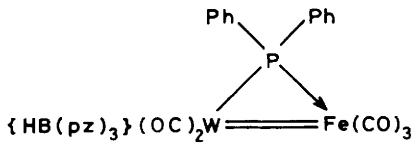
(**4a**)



(**4b**)



(**5**)



(**6**)

ligated carbon nuclei of a μ-σ,η^3-$CH(C_6H_4Me$-4) ligand, as previously found in compound (**5**), the structure of which has been established by *X*-ray diffraction.[5] Two alternative formulations for (**4**) are possible according to whether the $CH(C_6H_4Me$-4) group is σ bonded to tungsten, (**4a**), or to iron, (**4b**). On the basis of ^{13}C-{^1H} n.m.r. data, structure (**4a**) seems most probable since the signal at 190.8 p.p.m. for the μ-C nucleus shows strong ^{183}W–^{13}C coupling (107 Hz). In the spectrum of (**5**), and related complexes, the corresponding ^{183}W–^{13}C coupling is much smaller (20—30 Hz).[5] In a fully coupled ^{13}C n.m.r. spectrum of (**4a**), the resonance at 190.8 p.p.m. is a doublet [*J*(HC) 133 Hz], as expected for a μ-CH group. In the ^1H n.m.r. spectrum this moiety displays a peak at δ 13.26, much more deshielded than the corresponding signal in the spectrum of (**5**) which occurs at δ 6.71.

The μ-σ,η^3-bonding mode for the μ-$CH(C_6H_4Me$-4) group in (**4**) serves to provide an 18-electron configuration at the iron centre. It was therefore of interest to study the decomposition of (**3b**) in toluene, since if a μ-PPh_2 complex were formed a structure analogous to (**4a**) would not be possible. Heating (**3b**) in toluene for short periods afforded a green complex $[FeW(\mu\text{-}PPh_2)(CO)_5\{HB(pz)_3\}]$ (**6**), which was structurally characterised by a single-crystal *X*-ray diffraction study. The results are summarised in Table 1 and the molecule is shown in

Table 1. Selected internuclear distances (Å) and angles (°) for $[FeW(\mu\text{-}PPh_2)(CO)_5\{HB(pz)_3\}]$ **(6)**

W–Fe	2.658(2)	W–P	2.406(3)	W–N(11)	2.186(9)	W–N(21)	2.184(9)
W–N(31)	2.209(8)	W–C(1)	1.96(1)	W–C(2)	1.96(1)	Fe–P	2.210(3)
Fe–C(3)	1.80(2)	Fe–C(4)	1.74(2)	Fe–C(5)	1.76(2)	C(1)–O(1)	1.17(2)
C(2)–O(2)	1.17(2)	C(3)–O(3)	1.14(2)	C(4)–O(4)	1.16(2)	C(5)–O(5)	1.15(2)
B–N(12)	1.55(2)	B–N(22)	1.54(2)	B–N(32)	1.53(2)	N(11)–N(12)	1.40(2)
N(11)–C(11)	1.35(1)	N(12)–C(13)	1.34(2)	C(11)–C(12)	1.37(2)	C(12)–C(13)	1.39(2)
N(21)–N(22)	1.38(1)	N(21)–C(21)	1.36(1)	N(22)–C(23)	1.35(2)	C(21)–C(22)	1.43(2)
C(22)–C(23)	1.41(2)	N(31)–N(32)	1.36(1)	N(31)–C(31)	1.33(1)	N(32)–C(33)	1.34(2)
C(31)–C(32)	1.40(2)	C(32)–C(33)	1.39(2)				
Fe–W–P	51.5(1)	Fe–W–N(11)	143.3(2)	P–W–N(11)	164.8(3)	Fe–W–N(21)	134.8(3)
P–W–N(21)	87.0(3)	N(11)–W–N(21)	80.0(3)	Fe–W–N(31)	109.6(2)	P–W–N(31)	90.4(2)
N(11)–W–N(31)	80.6(3)	N(21)–W–N(31)	84.3(3)	Fe–W–C(1)	80.5(4)	P–W–C(1)	96.3(4)
N(11)–W–C(1)	91.2(4)	N(21)–W–C(1)	88.4(4)	N(31)–W–C(1)	169.9(4)	Fe–W–C(2)	64.5(3)
P–W–C(2)	113.4(4)	N(11)–W–C(2)	79.8(4)	N(21)–W–C(2)	159.6(4)	N(31)–W–C(2)	94.8(4)
C(1)–W–C(2)	89.5(5)	W–Fe–P	58.4(1)	W–Fe–C(3)	107.1(5)	P–Fe–C(5)	153.1(6)
W–Fe–C(4)	104.4(5)	P–Fe–C(4)	104.6(6)	C(3)–Fe–C(4)	100.9(8)	W–Fe–C(5)	143.1(6)
P–Fe–C(5)	89.6(6)	C(3)–Fe–C(5)	93.8(7)	C(4)–Fe–C(5)	101.0(9)	W–P–Fe	70.2(1)
W–P–C(46)	118.8(3)	Fe–P–C(46)	121.9(3)	W–P–C(56)	121.7(3)	Fe–P–C(56)	119.0(3)
W–C(1)–O(1)	178(1)	W–C(2)–O(2)	168(1)	Fe–C(3)–O(3)	174(2)	Fe–C(4)–O(4)	174(2)
Fe–C(5)–O(5)	174(2)						

Table 2. Selected bond lengths (Å) and angles (°) for $[RhW(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ **(7)**

W–Rh	2.587(1)	W–C(1)	2.009(7)	W–C(2)	1.990(9)	W–C(3)	1.94(1)
Rh–P(1)	2.315(2)	Rh–P(2)	2.263(2)	Rh–C(1)	2.116(8)	Rh–C(2)	2.158(8)
C(1)–O(1)	1.179(9)	C(2)–O(2)	1.18(1)	C(3)–O(3)	1.10(2)		
Rh–W–C(1)	53.0(2)	Rh–W–C(2)	54.4(2)	C(1)–W–C(2)	106.2(3)	Rh–W–C(3)	84.0(3)
C(1)–W–C(3)	95.4(4)	C(2)–W–C(3)	88.8(4)	W–Rh–P(1)	134.5(1)	W–Rh–P(2)	121.7(1)
P(1)–Rh–P(2)	103.8(1)	W–Rh–C(1)	49.3(2)	P(1)–Rh–C(1)	118.6(2)	P(2)–Rh–C(1)	108.8(2)
W–Rh–C(2)	48.6(2)	P(1)–Rh–C(2)	125.1(3)	P(2)–Rh–C(2)	102.2(2)	C(1)–Rh–C(2)	96.9(3)
W–C(1)–Rh	77.7(3)	W–C(1)–O(1)	162.0(6)	Rh–C(1)–O(1)	120.1(6)	W–C(2)–Rh	77.0(3)
W–C(2)–O(2)	164.0(7)	Rh–C(2)–O(2)	118.9(6)	W–C(3)–O(3)	176(1)		

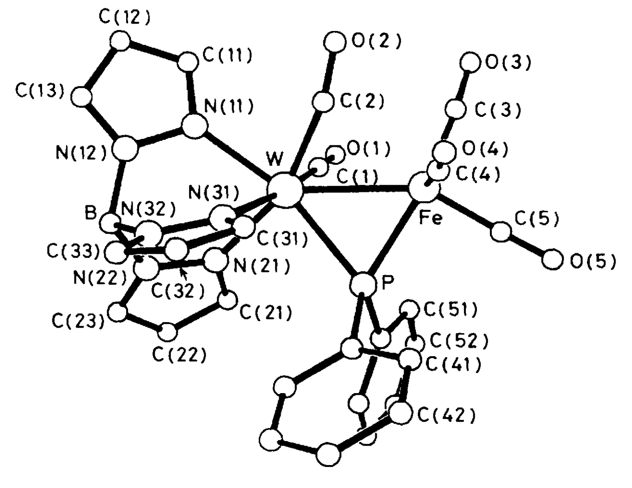
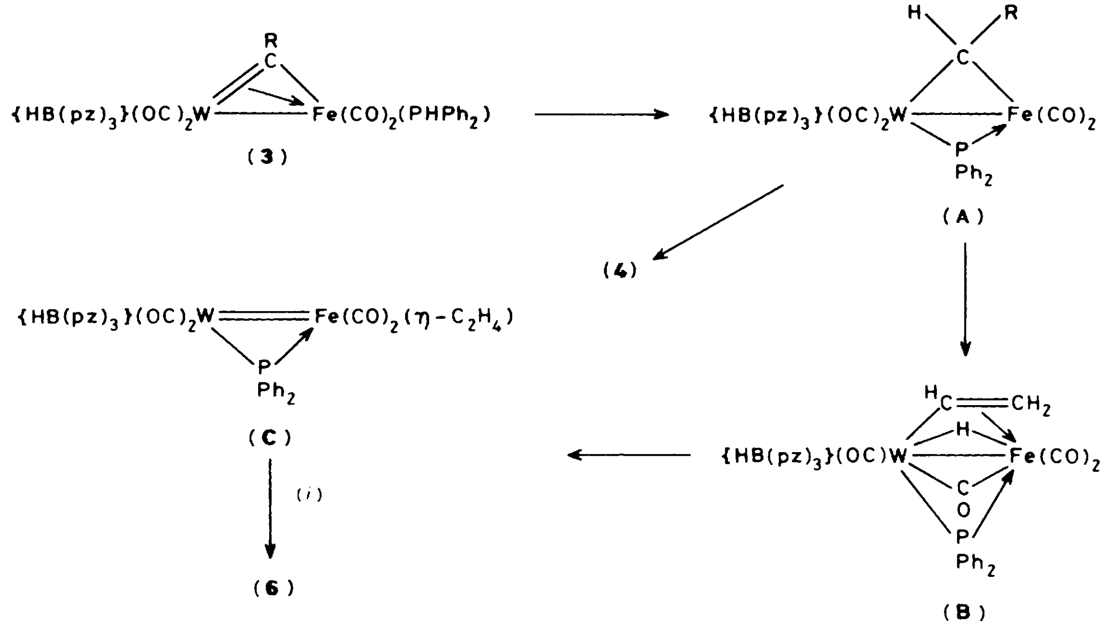


Figure 1. The molecular structure of $[FeW(\mu\text{-}PPh_2)(CO)_5\{HB(pz)_3\}]$ **(6)**, showing the atom-labelling scheme

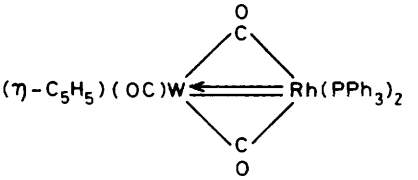
Figure 1. The structure confirms the presence of $\overline{W(\mu\text{-}PPh_2)Fe}$ core with the iron atom having three essentially orthogonal terminal carbonyl groups (mean Fe–C–O 174°). The tungsten atom is ligated by a tridentate $HB(pz)_3$ group and two CO ligands, one of which weakly semi-bridges the W–Fe bond [W–C(2)–O(2) 168(1)°]. The geometry of the $W(CO)_2\{HB(pz)_3\}$ fragment thus closely resembles that found in the related complex $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$.[1] Formation of **(6)** is non-stoicheiometric because it has five CO ligands whereas its precursor **(3b)** has only four. Presumably decomposition of an unstable μ-CHMe analogoue of **(4)** results in elimination of ethylene with concomitant scavenging of CO, as discussed below. The resulting complex, with 32 valence electrons, is unsaturated and the dimensions of the $\overline{W(\mu\text{-}PPh_2)Fe}$ core [W–Fe 2.658(2), W–P 2.406(3), and Fe–P 2.210(3) Å; W–P–Fe 70.2(1)°] are in good agreement with those found in the related co-ordinatively unsaturated complexes $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ [W–Fe 2.523(1), W–P 2.357(1), and Fe–P 2.219(1) Å; W–P–Fe 66.8(1)°], $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PHBu^t_2)(\eta\text{-}C_5H_5)]$ [W–Fe 2.614(1) Å],[6] and $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ [Fe–W 2.612(2) Å].[2] The short Fe–W separations in **(6)** and in the other complexes are consistent with the presence of appreciable Fe=W multiple bond character.[2]

A possible pathway for the formation of **(6)** is indicated in Scheme 1. The transformation **(A)** ⟶ **(B)** ⟶ **(C)** has precedent in the protonation and methylation of $[PtW(\mu\text{-}CMe)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ (R = Me or Et) which affords complexes structurally akin to intermediates **(A)**, **(B)**, and **(C)**, with bridging ethylidene, hydrido, and vinyl groups, or containing ligated ethylene.[7] The transformation of **(A)** into **(B)** corresponds to a β-hydrogen shift, and would be facilitated by electronic unsaturation at the iron centre in **(A)**, while step **(B)** to **(C)** has been invoked previously.

During the course of studies[8] on the addition of metal hydrides to alkylidynetungsten complexes we have observed reactions of the latter with hydridorhodium compounds $[RhH(L)(PPh_3)_3]$ (L = CO or PPh_3) which resemble the formation of **(6)**. Treatment of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ with



Scheme 1. R = C_6H_4Me-4 or Me; (*i*) + CO, $-C_2H_4$



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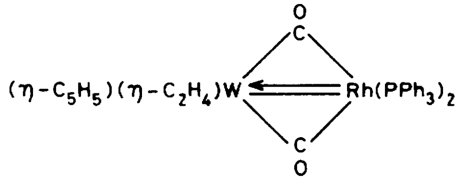

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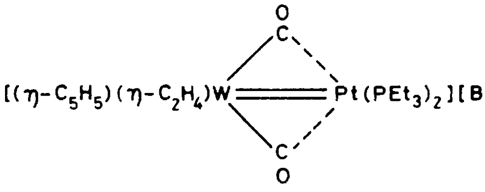


(9)

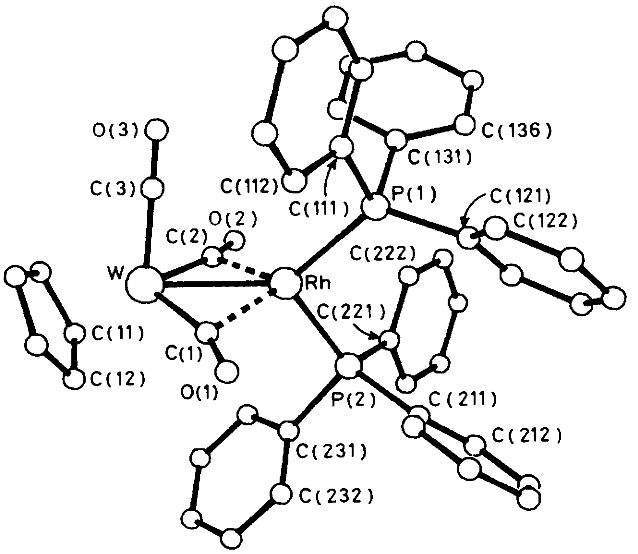
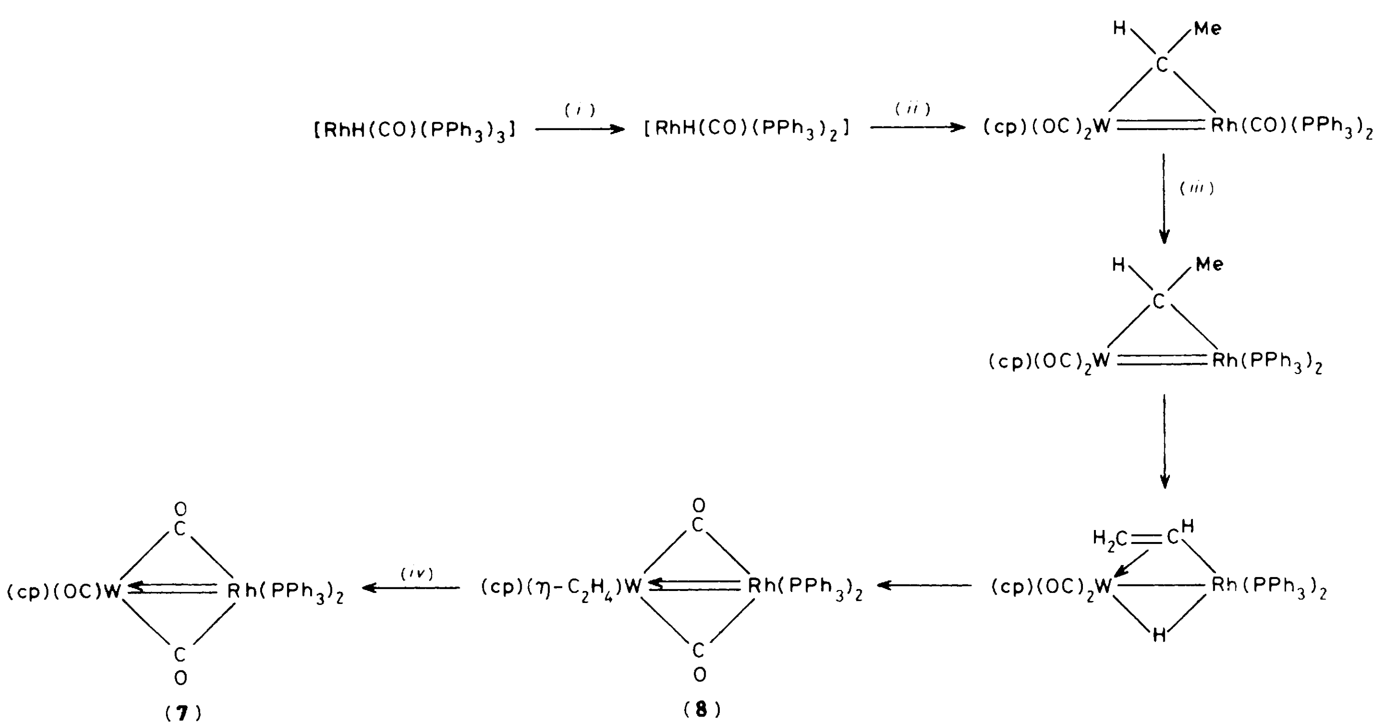


Figure 2. The molecular structure of $[RhW(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (7)

$[RhH(CO)(PPh_3)_3]$ in the expectation of obtaining a bridged alkylidene compound $[RhW(\mu\text{-}CHMe)(\mu\text{-}CO)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ resulted instead in the formation of a mixture of two rhodium–tungsten complexes, neither of which contained a μ-CHMe ligand as revealed by n.m.r. studies. It was possible to obtain crystals from the mixture, and an *X*-ray diffraction study enabled these to be identified as the known compound $[RhW(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (7), which has been prepared previously by another route.[9] The molecular structure is shown in Figure 2 and selected parameters are given in Table 2. However, since an *X*-ray crystal structure study has been carried out on the molybdenum-containing analogue $[MoRh(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$,[9] which is isomorphous with (7), the structure of the latter is not discussed herein.

Formation of (7) can be understood in terms of the reaction pathway depicted in Scheme 2, with intermediates having μ-CHMe, μ-H, or μ-CH=CH_2 groups, as postulated in Scheme 1. The complex $[RhW(\mu\text{-}CO)_2(PPh_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)]$ (**8**) is similar to the previously isolated compound $[PtW(\mu\text{-}CO)_2(PEt_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$ (**9**), which was structurally identified by *X*-ray diffraction.[7] It seemed likely that (**8**) is the precursor to (7), with the ethylene group in the former replaced by CO in the latter. In was hoped that by using $[RhH(PPh_3)_4]$



Scheme 2. cp = η-C_5H_5; (*i*) − PPh_3; (*ii*) + [W(≡CMe)$(CO)_2$(cp)]; (*iii*) − CO; (*iv*) + CO, −C_2H_4

instead of [RhH(CO)$(PPh_3)_3$] in the reaction with [W(≡CMe)$(CO)_2$(η-C_5H_5)] it might be possible to isolate and structurally identify (**8**). This expectation was based on the premise that [RhH(CO)$(PPh_3)_3$] releases CO in the reaction sequence, thereby providing a source of this reactant for the final step involving displacement of ethylene.

The reaction between [RhH$(PPh_3)_4$] and [W(≡CMe)$(CO)_2$(η-C_5H_5)] afforded a mixture of (**7**) and (**8**) in which the latter predominated, as deduced from the relevant intensity of peaks in the n.m.r. spectra. However, on standing (**8**) decomposed into (**7**). The presence of a co-ordinated C_2H_4 ligand in (**8**) was unambiguously established by the ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra. The ^1H spectrum showed peaks at δ −0.59 and 0.97, each corresponding to two protons, due to two inequivalent pairs of vicinal HC=CH groups in a static structure. The ^{13}C-$\{^1H\}$ n.m.r. spectrum showed a characteristic singlet peak for the ethylene ligand at δ 14.4 p.p.m.

Experimental

Reactions were carried out using Schlenk-tube techniques, under an atmosphere of oxygen-free nitrogen. Light petroleum refers to that fraction of b.p. 40—60 °C. The instrumentation used as been described in previous parts of this series.[1] Phosphorus-31 n.m.r. chemical shifts are relative to 85% H_3PO_4 (external), positive values representing shifts to high frequency of the reference. The compounds [W(≡CMe)$(CO)_2$$\{HB(pz)_3\}$],[2] [FeW($\mu$-$CC_6H_4$Me-4)$(CO)_5$$\{HB(pz)_3\}$],[1] [RhH$(PPh_3)_4$],[10] and [RhH(CO)$(PPh_3)_3$][10] were prepared by methods described previously. Alumina used for chromatography (3 × 20 cm columns) was Brockman Activity II, and Florisil used for this purpose was Aldrich, 100—200 mesh.

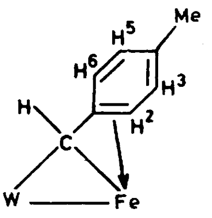
Synthesis of [FeW(μ-CMe)$(CO)_5$$\{HB(pz)_3\}$].—The compounds [$Fe_2(CO)_9$] (0.72 g, 2.0 mmol) and (**1b**) (0.48 g, 1.0 mmol) were stirred together in diethyl ether (20 cm^3) for 5 h. Solvent was removed *in vacuo* from the purple solution, and the residue dissolved in CH_2Cl_2–light petroleum (20 cm^3, 1:4) and chromatographed on Florisil. Elution with the same solvent mixture removed a trace of [$Fe_3(CO)_{12}$]. Elution with CH_2Cl_2–light petroleum (1:1) afforded a purple solution. Removal of solvent *in vacuo* gave purple *microcrystals* of [FeW(μ-CMe)$(CO)_5$$\{HB(pz)_3\}$] (**2b**) (0.48 g, 77%) (Found: C, 30.0; H, 2.1; N, 13.5. $C_{16}H_{13}BFeN_6O_5W$ requires C, 31.0; H, 2.8; N, 13.1%); $\nu_{max.}$(CO) at 2 046s, 1 980s, 1 959s, 1 923m, and 1 848m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H (CD_2Cl_2), δ 4.56 (s, 3 H, Me), 5.47—6.36 (m × 2, 3 H, $C_3H_3N_2$), and 6.60—8.26 (m × 4, 6 H, $C_3H_3N_2$); ^{13}C-$\{^1H\}$ (CD_2Cl_2–CH_2Cl_2), δ 425.8 [μ-*C*Me, *J*(WC) 128], 226.5 [WCO, *J*(WC) 153 Hz], 214.4 (FeCO), 147.6—105.7 ($C_3H_3N_2$), and 46.4 p.p.m. (μ-C*Me*).

Reactions with $PHPh_2$.—(*i*) The phosphine $PHPh_2$ (2 cm^3 of a 0.25 mol dm^{-3} solution in light petroleum) was added dropwise to a CH_2Cl_2 (10 cm^3) solution of (**2a**) (0.35 g, 0.50 mmol), and the mixture was stirred (0.5 h). Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:4) and chromatographed on alumina. Elution with CH_2Cl_2–light petroleum (1:1) gave a purple eluate. Removal of solvent *in vacuo* afforded purple *microcrystals* of [FeW(μ-CC_6H_4Me-4)$(CO)_4$($PHPh_2$)$\{HB(pz)_3\}$] (**3a**) (0.38 g, 90%) (Found: C, 46.3; H, 3.3; N, 8.8. $C_{33}H_{28}BFeN_6O_4PW$ requires C, 46.4; H, 3.3; N, 9.8%); $\nu_{max.}$(CO) at 1 984vs, 1 919s, 1 889m, and 1 819m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H ($CDCl_3$), δ 2.29 (s, 3 H, Me-4), 5.80 (m, 3 H, $C_3H_3N_2$), 6.31 (m, 1 H, $C_3H_3N_2$), 6.54 [d, 1 H, PH, *J*(PH) 369], 7.23—7.52 (m, 14 H, C_6H_4 and Ph), 7.62 [d, 2 H, $C_3H_3N_2$, *J*(HH) 2], 7.71 [d, 2 H, $C_3H_3N_2$, *J*(HH) 2], and 8.54 [d, 1 H, $C_3H_3N_2$, *J*(HH) 2 Hz]; ^{13}C-$\{^1H\}$ (CD_2Cl_2–CH_2Cl_2), δ 404.9 (μ-*C*C_6H_4Me-4), 229.4 [WCO, *J*(WC) 156], 220.8 [d, FeCO, *J*(PC) 18 Hz], 155.1 [C^1(C_6H_4)], 147.6—105.6 ($C_3H_3N_2$,

C_6H_4, and Ph), and 21.4 p.p.m. (Me-4); $^{31}P\text{-}\{^1H\}$ ($CDCl_3$), δ 73.1 p.p.m. (FeP); ^{31}P, δ 73.1 p.p.m. [d, *J*(PH) 369 Hz].

(*ii*) Similarly, $PHPh_2$ (2 cm^3 of a 0.25 mol dm^{-3} solution in light petroleum) was added dropwise to (**2b**) (0.31 g, 0.50 mmol), in CH_2Cl_2 (10 cm^3), and the mixture was stirred (0.5 h). After removal of solvent *in vacuo*, the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:4) and chromatographed on alumina. Elution with a mixture (1:1) of the same solvents gave, after removal of the volatile material *in vacuo*, purple *microcrystals* of $[FeW(\mu\text{-}CMe)(CO)_4(PHPh_2)\{HB(pz)_3\}]$ (**3b**) (0.35 g, 88%) (Found: C, 42.1; H, 3.3; N, 9.9. $C_{27}H_{24}BFeN_6O_4PW$ requires C, 41.6; H, 3.1; N, 10.8%); $\nu_{max.}$(CO) at 1 985vs, 1 920s, and 1 818m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H (CD_2Cl_2), δ 4.12 [d, 3 H, μ-CMe, *J*(PH) 3], 6.02 [t, 2 H, $C_3H_3N_2$, *J*(HH) 2], 6.08 (br, 2 H, $C_3H_3N_2$), 6.36 [t, 1 H, $C_3H_3N_2$, *J*(HH) 2], 6.85 [d, 1 H, PH, *J*(PH) 361], 7.34—7.53 (m, 10 H, Ph), 7.70 (m, 2 H, $C_3H_3N_2$), 7.80 [d, 1 H, $C_3H_3N_2$, *J*(HH) 2], and 8.49 [d, 1 H, $C_3H_3N_2$, *J*(HH) 2 Hz]; $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2–CH_2Cl_2), δ 423.5 (μ-*C*Me), 229.1 [WCO, *J*(WC) 156], 221.1 [d, FeCO, *J*(PC) 19 Hz], 148.1—105.8 (Ph and $C_3H_3N_2$), and 44.9 p.p.m. (μ-C*Me*); $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2), δ 64.8 p.p.m. (FeP); ^{31}P, δ 64.8 [d, *J*(PH) 361 Hz].

Synthesis of the Diphenylphosphido-bridged Iron–Tungsten Complexes.—(*i*) Compound (**3a**) (0.43 g, 0.50 mmol) in toluene (10 cm^3) in a Schlenk tube fitted with a high pressure stopcock was heated at 80 °C for 40 min. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:4) and chromatographed on alumina. Elution with CH_2Cl_2–light petroleum (3:7) afforded a brown eluate. Removal of solvent *in vacuo* gave brown *microcrystals* of $[FeW\{\mu\text{-}\sigma,\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_3\{HB(pz)_3\}]$ (**4**) (0.29 g, 67%) (Found: C, 46.7; H, 3.3; N, 9.1. $C_{33}H_{28}BFeN_6O_4PW$ requires C, 46.4; H, 3.3; N, 9.8%); $\nu_{max.}$(CO) at 1 983s, 1 933s, and 1 800m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H (CD_2Cl_2), δ 2.41 (s, 3 H, Me-4), 5.61 [d, 1 H, H^2, *J*(H^3H^2) 7 Hz], 5.88—7.88 (m, 22 H, C_6H_4, Ph, and $C_3H_3N_2$), and 13.26 (s, 1 H, μ-CH); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2–CH_2Cl_2), δ 261.2 (μ-CO), 211.4, 211.2, 211.0 (CO), 190.8 [μ-C, *J*(WC) 107 Hz], 148.8—126.8 (C_6H_4, Ph, and $C_3H_3N_2$), 117.2 [$C^1(C_6H_4)$], 106.4, 105.9, 105.5 ($C_3H_3N_2$), 95.3 [$C^2(C_6H_4)$], and 22.2 p.p.m. (Me-4); ^{13}C, 190.8 [d, μ-C, *J*(HC) 133 Hz]; $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2), δ 167.0 p.p.m. [μ-P, *J*(WP) 361 Hz].



(*ii*) Compound (**3b**) (0.39 g, 0.50 mmol) was heated at 90 °C in toluene (10 cm^3) in a Schlenk tube fitted with a high pressure stopcock for 30 min. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:4) and chromatographed on alumina. Elution with the same solvents (3:7) followed by evaporation of volatile material gave green *microcrystals* of $[FeW(\mu\text{-}PPh_2)(CO)_5\{HB(pz)_3\}]$ (**6**) (0.18 g, 45%) (Found: C, 40.4; H, 3.0; N, 10.2. $C_{26}H_{20}BFeN_6O_5PW$ requires C, 40.1; H, 2.6; N, 10.8%); $\nu_{max.}$(CO) at 2 033vs, 1 967s, 1 955s, 1 893m, and 1 825m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H (CD_2Cl_2), δ 5.83 [t, 2 H, $C_3H_3N_2$, *J*(HH) 2], 6.02 [d, 2 H, $C_3H_3N_2$, *J*(HH) 2], 6.39 [t, 1 H, $C_3H_3N_2$, *J*(HH) 2 Hz], 7.10—7.70 (m, 10 H, Ph), 7.71 (m, 3 H, $C_3H_3N_2$), and 8.48 (br s, 1 H, $C_3H_3N_2$); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2–CH_2Cl_2), δ 234.4 [WCO, *J*(WC) 157 Hz], 215.0 (FeCO), and 148.2—105.8 p.p.m. (Ph and $C_3H_3N_2$); $^{31}P\text{-}\{^1H\}$, δ 161.2 [μ-P, *J*(WC) 321 Hz].

Table 3. Atomic positional parameters (fractional co-ordinates × 10^4), with estimated standard deviations in parentheses, for (**6**)

Atom	*x*	*y*	*z*
W	8 042(1)	5 067(1)	2 666(1)
Fe	5 847(2)	4 442(1)	3 059(1)
P	7 176(2)	5 071(2)	3 784(1)
N(11)	9 272(10)	5 155(6)	1 797(4)
N(12)	10 546(10)	5 157(7)	1 876(5)
C(11)	9 079(13)	5 156(8)	1 125(5)
C(12)	10 147(13)	5 157(9)	764(6)
C(13)	11 053(15)	5 162(11)	1 258(7)
N(21)	9 337(9)	6 174(5)	3 032(5)
N(22)	10 588(8)	6 046(6)	2 972(5)
C(21)	9 153(13)	7 053(7)	3 345(6)
C(22)	10 323(13)	7 491(8)	3 478(6)
C(23)	11 199(12)	6 818(8)	3 236(7)
N(31)	9 452(8)	4 000(6)	2 992(4)
N(32)	10 666(8)	4 215(6)	2 945(5)
C(31)	9 365(12)	3 103(7)	3 264(6)
C(32)	10 537(13)	2 727(8)	3 392(7)
C(33)	11 341(12)	3 462(8)	3 176(7)
B	11 118(11)	5 149(10)	2 592(8)
C(41)	7 255(8)	3 545(7)	4 741(5)
C(42)	7 829	2 956	5 225
C(43)	9 042	3 141	5 406
C(44)	9 682	3 915	5 103
C(45)	9 108	4 504	4 619
C(46)	7 895	4 319	4 438
C(51)	5 917(8)	6 841(7)	3 935(4)
C(52)	5 692	7 767	4 218
C(53)	6 345	8 071	4 787
C(54)	7 223	7 450	5 073
C(55)	7 448	6 524	4 789
C(56)	6 795	6 220	4 220
C(1)	7 034(11)	6 142(8)	2 310(6)
O(1)	6 463(9)	6 795(7)	2 091(6)
C(2)	7 226(10)	4 151(8)	2 049(7)
O(2)	6 903(8)	3 643(6)	1 603(5)
C(3)	4 853(12)	4 514(13)	2 336(8)
O(3)	4 272(11)	4 645(12)	1 864(6)
C(4)	6 013(15)	3 168(11)	3 141(9)
O(4)	6 171(12)	2 319(8)	3 140(9)
C(5)	4 661(15)	4 670(16)	3 639(8)
O(5)	3 882(10)	4 728(12)	4 025(6)

Reactions between $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ *and* $[RhH(L)(PPh_3)_3]$ (L = CO *or* PPh_3).—(*i*) The compounds $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.20 g, 0.60 mmol) and $[RhH(CO)(PPh_3)_3]$ (0.55 g, 0.60 mmol) were stirred in CH_2Cl_2 (20 cm^3) for 2 h at room temperature. Solvent was removed *in vacuo* and the oily residue was dissolved in CH_2Cl_2–light petroleum (2 cm^3, 10:1) and chromatographed on alumina (10 × 1.25 cm column). Elution with the same solvent mixture afforded a brown eluate. The volume of solvent was reduced to *ca.* 2 cm^3 and light petroleum was added to precipitate the product. The latter was recrystallised from CH_2Cl_2–light petroleum giving a mixture (0.46 g) of spectroscopically identified (see Results and Discussion section) $[RhW(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (**7**)[9] (*ca.* 30%) and $[RhW(\mu\text{-}CO)_2(PPh_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)]$ (**8**) (*ca.* 25%). The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**7**) has not been previously reported: δ(CD_2Cl_2–CH_2Cl_2), 239.4 [d, 3 CO, *J*(RhC) 18 Hz], 136.1—127.4 (Ph), and 89.5 p.p.m. (C_5H_5).

(*ii*) The compounds $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.30 g, 0.90 mmol) and $[RhH(PPh_3)_4]$ (1.04 g, 0.90 mmol) were refluxed in benzene (20 cm^3) for 15 min. Solvent was removed *in vacuo* and the resultant oil dissolved in CH_2Cl_2 (20 cm^3). Light petroleum

Table 4. Atomic positional parameters (fractional co-ordinates × 10^4), with estimated standard deviations in parentheses, for (**7**)

Atom	*x*	*y*	*z*
W	1 092(1)	6 423(1)	5 975(1)
Rh	2 204(1)	4 922(1)	6 543(1)
P(1)	3 212(1)	3 957(2)	6 219(1)
P(2)	2 349(1)	4 248(2)	7 595(1)
C(1)	2 128(4)	6 948(7)	6 521(4)
O(1)	2 642(3)	7 573(5)	6 822(3)
C(2)	1 006(5)	4 545(9)	6 116(4)
O(2)	771(4)	3 488(6)	6 136(4)
C(3)	1 435(7)	6 047(11)	5 187(5)
O(3)	1 602(6)	5 782(10)	4 734(4)
C(111)	3 460(3)	4 848(4)	5 539(2)
C(112)	3 484	6 186	5 566
C(113)	3 697	6 881	5 069
C(114)	3 885	6 240	4 545
C(115)	3 861	4 902	4 518
C(116)	3 649	4 206	5 015
C(121)	4 159(2)	3 695(5)	6 781(2)
C(122)	4 809	4 324	6 690
C(123)	5 509	4 177	7 152
C(124)	5 559	3 401	7 704
C(125)	4 909	2 771	7 795
C(126)	4 209	2 918	7 334
C(131)	2 926(3)	2 376(4)	5 837(2)
C(132)	2 228	2 319	5 366
C(133)	1 962	1 149	5 074
C(134)	2 393	36	5 253
C(135)	3 091	93	5 724
C(136)	3 358	1 263	6 017
C(211)	3 273(2)	4 525(5)	8 195(2)
C(212)	3 534	3 765	8 753
C(213)	4 236	4 034	9 191
C(214)	4 678	5 062	9 069
C(215)	4 417	5 822	8 509
C(216)	3 715	5 553	8 072
C(221)	2 123(3)	2 562(3)	7 716(2)
C(222)	2 221	1 682	7 240
C(223)	2 143	371	7 341
C(224)	1 969	−61	7 919
C(225)	1 871	818	8 395
C(226)	1 949	2 130	8 293
C(231)	1 666(3)	5 109(5)	7 958(3)
C(232)	1 899	6 146	8 382
C(233)	1 357	6 863	8 604
C(234)	582	6 544	8 402
C(235)	349	5 507	7 978
C(236)	891	4 790	7 756
C(11)	−81(6)	6 760(11)	6 182(8)
C(12)	417	7 762	6 486
C(13)	613	8 498	5 979
C(14)	237	7 950	5 363
C(15)	−192	6 876	5 488

(20 cm^3) was added, and the mixture slowly evaporated to initiate precipitation of the product as brown *microcrystals* of $[RhW(\mu\text{-}CO)_2(PPh_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)]$ (**8**) (0.53 g, 61%) containing a small amount (*ca.* 10%) of (**7**), as deduced from peak intensities in the n.m.r. spectra. For (**8**) (Found: C, 55.5; H, 3.7. $C_{45}H_{39}O_2P_2RhW$ requires C, 56.3; H, 4.1%); $\nu_{max.}$(CO) at 1 737br cm^{-1} (CH_2Cl_2). N.m.r.: ^1H ($CDCl_3$), δ −0.59 (m, 2 H, C_2H_4), 0.97 (m, 2 H, C_2H_4), 4.46 (s, 5 H, C_5H_5), and 7.3 (br m, 30 H, Ph); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2–CH_2Cl_2), δ 264.3 [d of d, μ-CO, *J*(PC) 6, *J*(RhC) 32 Hz], 136.1—127.4 (Ph), 87.8 (C_5H_5), and 14.4 p.p.m. (C_2H_4); $^{31}P\text{-}\{^1H\}$ ($CDCl_3$), δ 33.3 [d of d, *J*(PP) 27, *J*(RhP) 172], and 31.3 [d of d, *J*(PP) 27, *J*(RhP) 168 Hz].

Crystal Structure Determination of $[FeW(\mu\text{-}PPh_2)(CO)_5\{HB(pz)_3\}]$ (**6**).—Crystals of (**6**) were grown from dichloromethane–light petroleum as dark prisms. Diffracted intensities were collected at 298 K from a crystal of dimensions *ca.* 0.5 × 0.4 × 0.3 mm. Data were collected on a Nicolet *P3m* four-circle diffractometer using θ—2θ scans. Of the total 3 796 intensities collected to $2\theta \leqslant 55°$, 3 302 had $F \geqslant 5.0\sigma(F)$, and these were used in the solution and refinement of the structure, after the data had been corrected for Lorentz, polarisation, and *X*-ray absorption effects. The last was by an empirical method based upon azimuthal scan data.[11]

Crystal data. $C_{26}H_{20}BFeN_6O_5PW$, *M* = 777.9, orthorhombic, *a* = 10.9185(8), *b* = 13.545(1), *c* = 19.788(3) Å, *U* = 2 926.4(5) $Å^3$, *Z* = 4, D_c = 1.77 g cm^{-3}, *F*(000) = 1 512, space group $P2_12_12_1$, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 46.1 cm^{-1}.

The structure was solved, and all non-hydrogen atoms were located by conventional heavy-atom and difference Fourier methods. Hydrogen atoms were not included in the refinement. All atoms were given anisotropic thermal parameters whilst the phenyl rings were treated as rigid groups [C–C(aryl) 1.395 Å]. Refinement by blocked-cascade least squares led to *R* 0.042 (*R'* 0.042) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$. A final electron-density difference synthesis showed no peaks > 1.2 e $Å^{-3}$. Scattering factors were from ref. 12. All computations were carried out on an Eclipse (Data General) computer with the SHELXTL system of programs.[11] Atomic co-ordinates are given in Table 3.

Crystal Structure Determination of $[RhW(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (**7**).—Dark red crystals of (**7**) were grown from dichloromethane–light petroleum. The data collection and the solution and refinement were the same as described above for (**6**) except in the following respects. Data were collected on a Nicolet $P2_1$ diffractometer with a crystal of dimensions *ca.* 0.50 × 0.15 × 0.15 mm [ω scans, $2\theta \leqslant 50°$, 4 740 intensities with $F \geqslant 5\sigma(F)$].

Crystal data. $C_{44}H_{35}O_3P_2RhW$, *M* = 960.4, monoclinic, *a* = 17.997(8), *b* = 10.420(3), *c* = 20.980(9) Å, β = 104.19(3)°, *U* = 3 801(3) $Å^3$, *Z* = 4, D_c = 1.68 g cm^{-3}, *F*(000) = 1 888, space group $P2_1/c$, μ(Mo-K_α) = 36.4 cm^{-1}.

Final *R* 0.043 (*R'* 0.048), with a final difference map showing no peaks $\geqslant 1$ e $Å^{-3}$, except in the vicinity of the tungsten atom where peaks of *ca.* 2 e $Å^{-3}$ were observed. Atomic co-ordinates are listed in Table 4.

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