Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 90.[1] Synthesis of the Complexes $[W_2M_2(\mu\text{-}CO)(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$ (M = Rh or Ir) and Related Tetra- and Penta-nuclear Metal Compounds; Interconversion of Ketenyl and λ^5-Phospha-alkyne Ligands bridging Tungsten–Rhodium Bonds

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The reaction between $[Ir_2(\mu\text{-}PPh_2)_2(cod)_2]$ (cod = cyclo-octa-1,5-diene) and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ in refluxing thf (tetrahydrofuran) affords the tetranuclear mixed-metal compound $[W_2Ir_2(\mu\text{-}CO)(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$. The pathway by which this complex is formed has been modelled by a series of reactions involving rhodium–tungsten species. Thus $[W_2Rh_2(\mu\text{-}CO)(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ reacts rapidly with CO to yield $[W_2Rh_2(\mu\text{-}CO)(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$. In refluxing thf the latter compound initially isomerises to give $[W_2Rh_2(\mu\text{-}CO)_2(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)PPh_2\}(\mu\text{-}PPh_2)(CO)_3(\eta\text{-}C_5H_5)_2]$, which on further heating loses CO and affords $[W_2Rh_2(\mu\text{-}CO)(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$. In an extension of these interconversions the pentanuclear metal cluster compound $[W_3Rh_2(\mu\text{-}CO)_3(\mu\text{-}CMe)(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)PPh_2\}(\mu\text{-}PPh_2)(CO)_2(\eta\text{-}C_5H_5)_3]$ on refluxing in thf for several hours also releases CO to give $[W_3Rh_2(\mu\text{-}CO)_2(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_3]$. The new compounds were characterised by their ^1H, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra.

In the previous paper[1] we reported the synthesis of some tetra- and penta-nuclear tungsten–rhodium cluster compounds in which the metal–metal bonds are bridged by carbonyl, ethylidyne, ketenyl, phosphido, or λ^5-phospha-alkyne groups. Thus treatment of $[Rh_2(\mu\text{-}PPh_2)_2(cod)_2]$ (cod = cyclo-octa-1,5-diene) with 2 equivalents of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ in thf (tetrahydrofuran) affords the tetranuclear complex $[W_2Rh_2(\mu\text{-}CMe)_2(\mu\text{-}PPh_2)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (1) (Scheme 1). The latter isomerises in solution to give $[W_2Rh_2(\mu\text{-}CO)(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ (2). In (2) the four-metal atom core is retained, but there is a different arrangement of diphenylphosphido and ethylidyne groups. Indeed one of the ethylidyne moieties has combined with a CO molecule to generate a ketenyl ligand. The terminal CO ligand in (2) may be replaced by another equivalent of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ to yield the pentanuclear metal compound $[W_3Rh_2(\mu\text{-}CO)_2(\mu\text{-}CMe)(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_3]$ (3). Under mild conditions complex (3) isomerises to give $[W_3Rh_2(\mu\text{-}CO)_3(\mu\text{-}CMe)(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)PPh_2\}(\mu\text{-}PPh_2)(CO)_2(\eta\text{-}C_5H_5)_3]$ (4). The conversion of (3) into (4) involves cleavage of a C–C bond in the former and formation of a C–P bond in the latter. Moreover, compound (4) has the interesting structural feature of having a λ^5-phospha-alkyne unit bridging one of the rhodium–tungsten bonds. The structures depicted for (3) and (4) (Scheme 1) are firmly based on *X*-ray diffraction studies.[1]

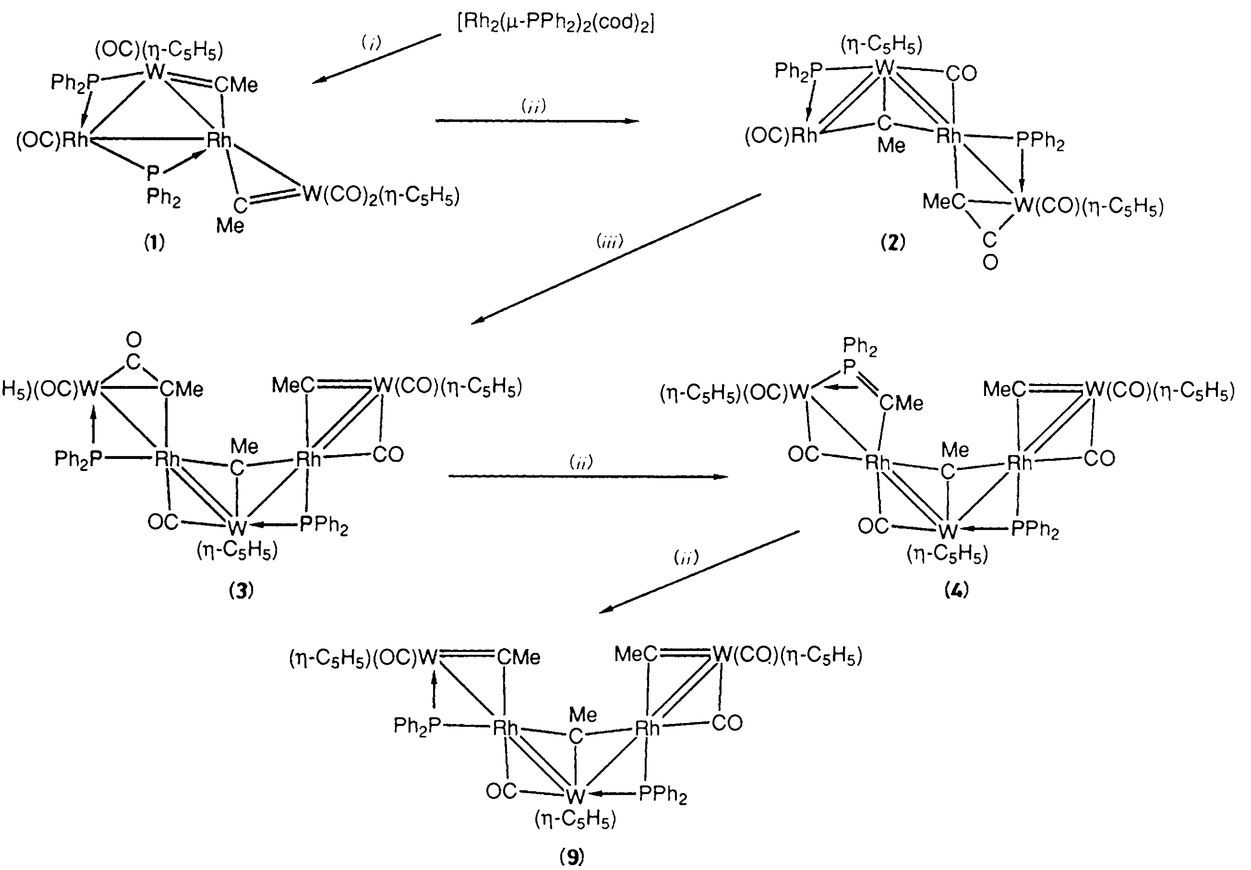
The reactions leading to the formation of the four compounds (1)—(4) are relevant to the current interest in facile C–C[2] and C–P[3] bond-making and -breaking processes occurring at di- or tri-metal centres. The work described in this paper extends that reported in the previous article.[1]

Results and Discussion

When the compound $[Ir_2(\mu\text{-}PPh_2)_2(cod)_2]$[4] is suspended in thf and treated with 3 equivalents of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ there is no reaction at room temperature. This is in contrast with the rapid reaction which occurs at ambient temperatures with the rhodium complex $[Rh_2(\mu\text{-}PPh_2)_2(cod)_2]$ which affords (1) (Scheme 1) in *ca.* 80% yield. However, if the iridium and tungsten reagents are refluxed in thf for 3 h, the red crystalline complex $[W_2Ir_2(\mu\text{-}CO)(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$ (5) is formed, but in relatively poor yield (Table 1).

The i.r. spectrum of complex (5) (Table 1) shows four bands in the CO region, including an absorption (1 715 cm^{-1}) indicating the presence of a bridging carbonyl ligand. The n.m.r data (Tables 2 and 3) agree with the formulation proposed. In the synthesis of (5) traces of another species were observed and discarded during separation of the product mixture by chromatography on alumina. This species was subsequently identified as a diastereoisomer as a result of $^{13}C\text{-}\{^1H\}$ n.m.r. studies. The long accumulation times required (*ca.* 12 h) to measure the spectrum resulted in the appearance of additional resonances due to the minor isomer. These signals are marked with an asterisk in Table 2. At equilibrium the isomer ratio is *ca.* 2:1. However, the ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of (5), when recorded on fresh samples obtained from the chromatography column, showed only peaks due to the major isomer, since only a short period of time was required to record the data. Two diastereoisomers of complex (5) probably exist as a consequence of the $Ir(CO)_2$ fragment being cisoid or transoid to the μ-CMe or $\mu\text{-}PPh_2$ groups attached to the tungsten atom at the end of the chain. Two diastereoisomers of (2) also exist, and it is suggested[1] that these differ according to whether the RhCO fragment has in closest proximity the ketenyl group or the $\mu\text{-}PPh_2$ ligand attached to the terminal $W(CO)(\eta\text{-}C_5H_5)$ fragment.

The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of complex (5) is diagnostically useful, but only peaks for the major isomer will be discussed. Resonances at δ 324.9 and 270.5 p.p.m. are clearly due to the μ-*C*Me and μ_3-*C*Me nuclei, respectively.[5] The signal at δ 258.5 p.p.m. may be assigned to the μ-CO ligand, and that at 224.7 p.p.m. to the WCO group. Peaks at δ 188.2 and 184.9 p.p.m. are attributable to the $Ir(CO)_2$ fragment. Both signals are doublets due to $^{31}P\text{–}^{13}C$ coupling. The more deshielded resonance has



Scheme 1. (*i*) $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (2 equivalents) in thf; (*ii*) isomerisation in thf (see text); (*iii*) $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ in thf

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

Compound	Colour	Yield (%)	$\nu(CO)^b/cm^{-1}$	Analysis (%) C	H
(**5**) $[W_2Ir_2(\mu\text{-}CO)(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$	Red	28	2 021vs, 1 970m, 1 883s, 1 715w	35.1(35.5)	2.9(2.5)
(**6**) $[W_2Rh_2(\mu\text{-}CO)(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$	Green	89	2 051vs, 2 039m, 1 994s, 1 904s, 1 884s, 1 750m	40.5(40.7)	3.4(2.4)
(**7**) $[W_2Rh_2(\mu\text{-}CO)_2(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)PPh_2\}(\mu\text{-}PPh_2)(CO)_3(\eta\text{-}C_5H_5)_2]$	Red	62	2 021m, 1 949m, 1 917vs, 1 742m, 1 717w	40.3(40.7)	2.9(2.4)
(**8**) $[W_2Rh_2(\mu\text{-}CO)(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$	[c]Green	58	2 037vs, 1 983m, 1 886m, 1 737m(br)	40.7(40.6)	2.6(2.4)
(**9**) $[W_3Rh_2(\mu\text{-}CO)_2(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_3]$	Brown	38	1 941s, 1 881m, 1 764m, 1 732m	38.2(38.8)	2.9(2.5)

[a] Calculated values are given in parentheses. [b] Measured in thf. [c] Other isomer is brown, see text.

the largest coupling (57 Hz), and this signal is therefore assigned to a carbonyl in a transoid $OClIrPPh_2$ arrangement. The other resonance at δ 184.9 p.p.m., with *J*(PC) 12 Hz, is attributed to the CO ligand in a cisoid $Ir(CO)(PPh_2)$ configuration.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (Table 3) shows two resonances in the chemical shift range for $\mu\text{-}PPh_2$ ligands.[6,7] The observation of one set of $^{183}W\text{-}^{31}P$ satellite peaks on each signal confirms that the $\mu\text{-}PPh_2$ groups are bridging Ir–W bonds.

Obviously compound (**5**) is related to the tetranuclear tungsten–rhodium complex (**2**) (Scheme 1), the only difference being that whereas the latter has RhCO and $\mu\text{-}C(Me)C(O)$ groups the former has $Ir(CO)_2$ and μ-CMe groups. Formally the structures differ by migration of the CO fragments of the ketenyl ligand to the metal atom at the other end of the chain. It is probable that an iridium analogue of (**2**) is an intermediate in the formation of (**5**), as discussed further below.

As described previously,[1] the CO ligand terminally bound to the rhodium in complex (**2**) is readily replaced by a molecule of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ to afford (**3**). In contrast, no pentanuclear metal compound was isolated when $[Ir_2(\mu\text{-}PPh_2)_2(cod)_2]$ was treated with a large excess of the ethylidynetungsten reagent. This result presumably reflects the

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

Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(**5**)	2.86, 3.93 (s × 2, 6 H, Me), 5.09, 5.25 (s × 2, 10 H, C_5H_5), 6.70—7.67 (m, 20 H, Ph)	*328.8, 324.9 (μ-C), 270.5 [d, μ_3-C, *J*(PC) 5], *267.4 (μ_3-C), 258.5, *250.8 (μ-CO), 224.7, *221.9 (WCO), 188.2 [d, IrCO, *J*(PC) 57], 184.9 [d, IrCO, *J*(PC) 12], 148.4—127.6 (Ph), *90.8, 90.7, 90.3, *89.9 (C_5H_5), *48.9, 47.7, *43.7, 41.1 (Me)
(**6**)	2.29 (s, 3 H, Me), *2.54, *3.33 (s × 2, 6 H, Me), 3.57 (s, 3 H, Me), *4.91 (s, 5 H, C_5H_5), 4.92, 5.06 (s × 2, 10 H, C_5H_5), *5.13 (s, 5 H, C_5H_5), 6.50—8.00 (m, 40 H, Ph)	*305.3 [d of d, μ_3-C, *J*(RhC) 29, 15], 301.6 [d of d, μ_3-C, *J*(RhC) 29, 16], *258.3 [d, μ-CO, *J*(RhC) 26], 253.8 [d, μ-CO, *J*(RhC) 23], *227.1 [d, WCO, *J*(PC) 6], 225.8 [d, WCO, *J*(PC) 6], *214.7, 211.2 [μ-C(Me)*C*(O)], *193.4 [d of d, RhCO, *J*(RhC) and *J*(PC) 86, 65], 193.3 [d of d, RhCO, *J*(RhC) and *J*(PC) 67, 59], *192.7 [d of d, RhCO, *J* (RhC) 71, *J*(PC) 11], 192.0 [d of d, RhCO, *J*(RhC) 66, *J*(PC) 11], 148.4—126.8 (Ph), 119.2 [d, μ-*C*(Me)C(O), *J*(RhC) 22], *100.9 [d, μ-*C*(Me)C(O), *J*(RhC) 30], *92.1, 91.1, *90.6, 90.2(C_5H_5), *46.3, 45.6, *25.4, 22.8 (Me)
(**7**)	1.69 [d, 3 H, Me, *J*(PH) 15], 3.52 (s, 3 H, Me), 4.96, 5.16 (s × 2, 10 H, C_5H_5), 7.17—7.90 (m, 20 H, Ph)	297.5 [d of d, μ_3-C, *J*(RhC) 28, 16], 257.0 [d, μ-CO, *J*(RhC) 29], 253.0 [d, μ-CO, *J*(RhC) 37], 223.1 [d, WCO, *J*(PC) 33], 197.0 [d of d, RhCO, *J*(RhC) and *J*(PC) 77, 56], 195.6 [d of d, RhCO, *J*(RhC) 63, *J*(PC) 11], 148.1—126.1 (Ph), 141.8 [d of d, μ-*C*(Me)PPh_2, *J*(RhC) and *J*(PC) 35, 30], 92.3, 89.9 (C_5H_5), 44.9 (Me), 28.0 [d, μ-C(*Me*)PPh_2, *J*(PC) 4]
(**8a**)	1.93, 2.53 (s × 2, 6 H, Me), 4.96, 5.23 (s × 2, 10 H, C_5H_5), 6.80—7.90 (m, 20 H, Ph)	332.7 [d, μ-C, *J*(RhC) 25], 292.9 [d of d, μ_3-C, *J*(RhC) 29, 15], 255.2 [d, μ-CO, *J*(RhC) 24], 227.0 (WCO), 194.9 [d of d, RhCO, *J*(RhC) and *J*(PC) 68, 57], 192.4 [d of d, RhCO, *J*(RhC) 66, *J*(PC) 12], 149.5—126.0 (Ph), 89.4, 88.9 (C_5H_5), 46.4, 44.1 (Me)
(**8b**)	2.72, 3.48 (s × 2, 6 H, Me), 5.03, 5.23 (s × 2, 10 H, C_5H_5), 6.80—7.90 (m, 20 H, Ph)	335.8 [d, μ-C, *J*(RhC) 36], 296.2 [d of d, μ_3-C, *J*(RhC) 28, 17], 260.1 [d, μ-CO, *J*(RhC) 29], 227.9 (WCO), 195.5 [d of d, RhCO, *J*(RhC) and *J*(PC) 62, 56], 194.6 [d of d, RhCO, *J*(RhC) 65, *J*(PC) 12], 150.7—127.6 (Ph), 91.7, 91.1 (C_5H_5), 50.1, 46.1 (Me)
(**9**)	1.06, 2.05, 2.61 (s × 3, 9 H, Me), 5.01, 5.14, 5.35 (s × 3, 15 H, C_5H_5), 6.60—7.80 (m, 20 H, Ph)	[d]354.4 [d, μ-C, *J*(RhC) 35], 338.4 (br, μ-C), 306.9 [d of d, μ_3-C, *J*(RhC) 29, 19], 260.8 [d, μ-CO, *J*(RhC) 25], 248.4 (br, μ-CO), 226.5 (br), 224.5 (WCO), 149.6—126.6 (Ph), 90.6, 90.0, 89.7 (C_5H_5), 46.9, 44.1,42.5 (Me)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures unless otherwise stated. [b] Measured in CD_2Cl_2. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. Measurements in CD_2Cl_2–CH_2Cl_2. Signals marked (*) correspond to a minor isomer (see text). [d] Measured at −40 °C.

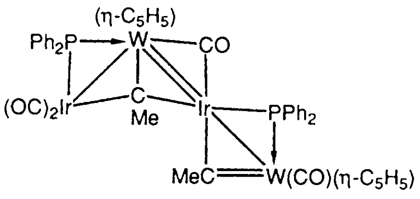
Table 3. Phosphorus-31 n.m.r. data* for the new complexes

Compound	
(**5**)	144.1 [d, *J*(PP) 5, *J*(WP) 364] 137.8 [d, *J*(PP) 5, *J*(WP) 393]
(**6**)	173.1 [d of d, *J*(RhP) 98, *J*(PP) 5, *J*(WP) 420] *164.9 [d, *J*(RhP) 137, *J*(WP) 405] 161.3 [d of d, *J*(RhP) 81, *J*(PP) 5, *J*(WP) 406] *160.0 [d, *J*(RhP) 73, *J*(WP) 396]
(**7**)	158.9 [d, PPh_2, *J*(RhP) 78] −50.6 [s, μ-C(Me)PPh_2]
(**8a**)	166.4 [d, *J*(RhP) 137, *J*(WP) 424] 161.6 [d, *J*(RhP) 72, *J*(WP) 403]
(**8b**)	172.4 [d, *J*(RhP) 98, *J*(WP) 439] 160.3 [d, *J*(RhP) 70, *J*(WP) 409]
(**9**)	174.3 [d, *J*(RhP) 129, *J*(WP) 430] 155.8 [d, *J*(RhP) 136, *J*(WP) 415]

* Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at room temperature. Hydrogen-1 decoupled, chemical shifts to high frequency of 85% H_3PO_4 (external) taken as positive. Measured in CD_2Cl_2. Peaks due to a minor isomer marked *, see text.

lower lability of CO groups when attached to iridium rather than rhodium.

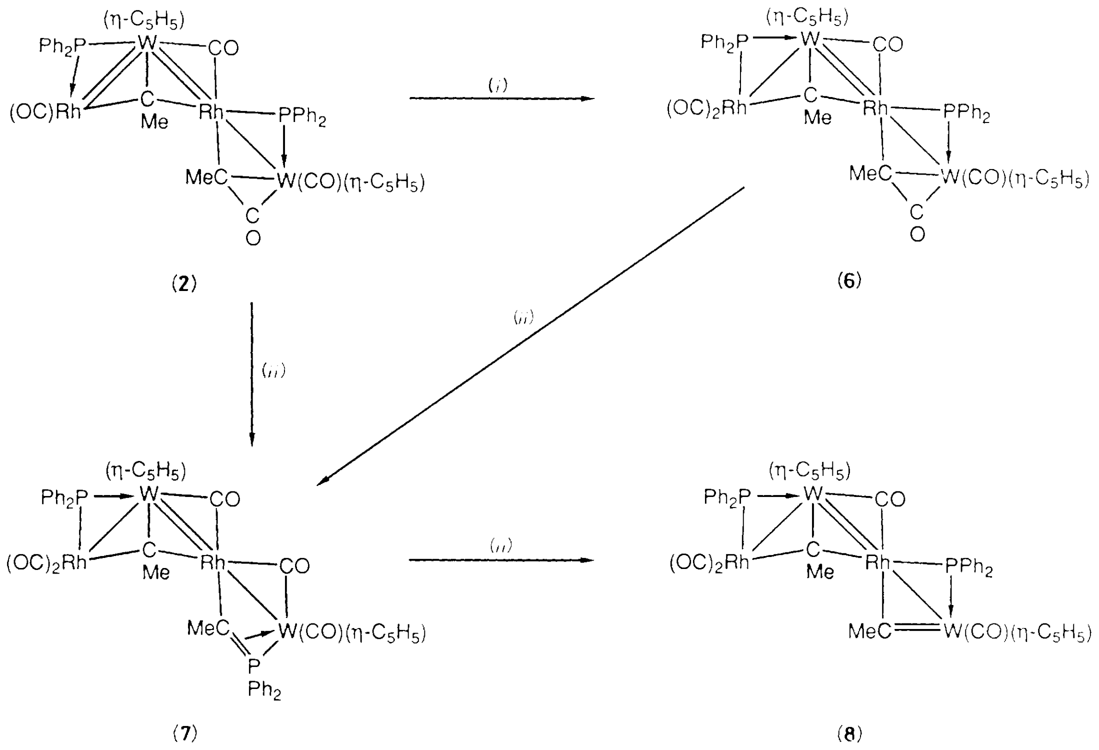
It had been previously observed[1] that solutions of complex (**2**) slowly decomposed after several days in solution affording other species. The nature of this process became apparent when it was found that treatment of CH_2Cl_2 solutions of (**2**) with CO afforded [W_2Rh_2(μ-CO)(μ_3-CMe){μ-C(Me)C(O)}(μ-PPh_2)$_2$(CO)$_3$(η-C_5H_5)$_2$] (**6**) in *ca.* 90% yield (Scheme 2). This



(**5**)

same species is formed slowly in the decompositon of (**2**), a process which involves scavenging of a molecule of CO in order to form a $Rh(CO)_2$ group at the end of the metal-atom chain. Compound (**6**) was fully characterised in the usual way (Tables 1—3). Not surprisingly the spectroscopic properties are very similar to those of (**2**),[1] except for the appearance of an extra terminal CO stretch in the i.r. spectrum, and the observation of two CO resonances for terminally bound carbonyls attached to rhodium, whereas only one such peak is seen in the spectrum of (**2**). The n.m.r. spectra of (**6**) revealed resonances due to the presence of a second isomer, and these signals are marked with an asterisk in Tables 2 and 3. As mentioned above, two diastereoisomers of the species (**2**) and (**5**) exist, and this property of the tetranuclear clusters is a common feature discussed further below.

When either of the compounds (**2**) or (**6**) is heated in thf the same products are formed (Scheme 2). After a short period (*ca.* 10 min) of reflux a chromatographically separable mixture of [W_2Rh_2(μ-CO)$_2$(μ_3-CMe){μ-C(Me)PPh_2}(μ-PPh_2)(CO)$_3$(η-C_5H_5)$_2$] (**7**) and [W_2Rh_2(μ-CO)(μ-CMe)(μ_3-CMe)(μ-PPh_2)$_2$-(CO)$_3$(η-C_5H_5)$_2$] (**8**) was obtained. With longer reflux times



Scheme 2. (*i*) +CO; (*ii*) thf reflux (see text)

(*ca.* 1 h) only compound (**8**) was isolated. The latter was formed as a mixture of two isomers.

The formulations for (**7**) and (**8**) are in agreement with the data listed in Tables 1—3. Compound (**7**) contains a bridging λ^5-phospha-alkyne fragment, as previously established in (**4**) by *X*-ray diffraction.[1] There are strong similarities in the n.m.r. spectra of the two compounds. As in the ^{1}H n.m.r. spectrum of (**4**), that of (**7**) (Table 2) shows a doublet signal [*J*(PH) 15 Hz] for the methyl protons of the μ-C(*Me*)PPh$_2$ group. In the ^{13}C-{^{1}H} n.m.r. spectrum this group gives rise to the resonances observed at δ 141.8 (μ-C) and 28.0 p.p.m. (Me). The former signal shows ^{103}Rh–^{13}C and ^{31}P–^{13}C coupling, and the latter ^{31}P–^{13}C coupling (Table 2). Characteristic peaks are also seen for the μ_3-*C*Me, Rh(μ-CO)W, WCO, and RhCO groups. The ^{31}P-{^{1}H} n.m.r. spectrum (Table 3) was especially diagnostic. A resonance at δ 158.9 p.p.m., a doublet with *J*(RhP) 78 Hz, may be ascribed to the μ-PPh$_2$ group, while a singlet at δ −50.6 p.p.m. is characteristic for the phosphorus nucleus of the λ^5-phospha-alkyne fragment μ-C(Me)PPh$_2$. The absence of ^{103}Rh–^{31}P coupling indicates that the phosphorus atom ligates the tungsten atom. In the ^{31}P-{^{1}H} n.m.r. spectrum of (**4**) the corresponding signal occurs at δ −29.6 p.p.m.[1]

The two isomers of complex (**8**) are readily separated by column chromatography and are formed in the ratio (**8a**):(**8b**) of 2:1, as deduced from the relative intensity of the peaks in the n.m.r. spectra (Tables 2 and 3). As mentioned above, two isomers of (**2**) and (**5**) also exist. It is likely that the isomerism for these compounds corresponds to different orientations of the two parts of the molecule about the central metal atom M (Rh or Ir), so that the μ-CMe and μ-PPh$_2$ groups attached to the W atom at the end of the chain are in greater or lesser proximity to the terminal RhCO group in (**2**), or the M(CO)$_2$ fragments in (**5**) and (**8**). We have chosen to depict one isomer of (**5**) and (**8**) with the μ-CMe ligand nearer the M(CO)$_2$ group. For (**8**) only the n.m.r. data for (**8a**) are discussed.

The ^{13}C-{^{1}H} n.m.r. spectrum reveals several diagnostically useful peaks (Table 2). The presence of ethylidyne ligands occupying edge-bridging and triply bridging sites is established by the signals observed at δ 332.7 and 292.9 p.p.m., respectively. In agreement with the structure proposed, the former signal is a doublet [*J*(RhC) 25 Hz], and the latter a doublet of doublets [*J*(RhC) 29 and 15 Hz]. The Rh(CO)$_2$ group gives rise to signals at δ 194.9 and 192.4 p.p.m. The former shows the larger ^{31}P–^{13}C coupling of 57 Hz, compared with 12 Hz for the latter. Again this is explained by transoid-OCRhPPh$_2$ and cisoid-Rh(CO)(PPh$_2$) arrangements for the respective CO ligands. The ^{31}P-{^{1}H} n.m.r. spectrum (Table 3) reveals that both μ-PPh$_2$ groups bridge Rh–W bonds, since large ^{183}W–^{31}P couplings are observed.

The formation of complex (**8**) from (**7**) involves cleavage of the C–P bond of the λ^5-phospha-alkyne ligand.[8] It was of interest to determine whether a similar process would take place with a pentanuclear rhodium–tungsten species. Accordingly compound (**4**) was refluxed in thf for 24 h, thereby affording the pentanuclear metal cluster [W$_3$Rh$_2$(μ-CO)$_2$(μ-CMe)$_2$(μ_3-CMe)(μ-PPh$_2$)$_2$(CO)$_2$(η-C$_5$H$_5$)$_3$] (**9**) (Scheme 1). Conversion of (**4**) into (**9**) required more vigorous conditions than those for (**7**) into (**8**). Compound (**9**) was characterised by the data listed in Tables 1—3. The n.m.r. spectra are again in agreement with the structure shown. However, it was necessary to measure the ^{13}C-{^{1}H} spectrum at −40 °C in order to observe peaks for the μ-*C*Me, μ-CO, and CO groups of the terminal Rh(μ-CMe)(μ-CO)W(CO)(η-C$_5$H$_5$) fragment. Presumably, at room temperature, rotation of the tungsten atom and its associated ligands about the Rh–W vector accounts for the dynamic behaviour, a feature observed previously with (**4**).[1] Confirmation that C–P bond cleavage had taken place in the formation of (**9**) came from the ^{31}P-{^{1}H} n.m.r. spectrum since there was no resonance for a μ-C(Me)PPh$_2$ ligand but there were two doublet signals for Rh(μ-PPh$_2$)W fragments (Table 3).

The reactions described herein and in the previous paper involving the rhodium–tungsten compounds (Schemes 1 and 2) provide strong evidence for the pathway by which the iridium–tungsten complex (**5**) is formed. In the previous paper[1] it was demonstrated that the first step in the reaction between $[Rh_2(\mu\text{-}PPh_2)_2(cod)_2]$ and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ was the formation of (**1**) and that the latter readily isomerised to (**2**). In the absence of an excess of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and assisted by the presence of CO, compound (**2**) affords (**6**). The latter undergoes a novel rearrangement of the type observed previously in the conversion of (**3**) into (**4**).[1] The ketenyl ligand in (**6**) is transformed into a μ-λ^5-phospha-alkyne group, while the PPh_2 group which bridged the Rh–W bond is replaced by a μ-CO ligand. In this manner (**7**) is formed. On heating, however, the latter is converted into (**8**), the rhodium analogue of the iridium–tungsten compound (**5**). The last step in the reaction sequence involves loss of a molecule of CO and cleavage of the C–P bond present in the μ-$C(Me)PPh_2$ moiety. This process is similar to that observed in the conversion of (**4**) into (**9**).

The lower reactivity of $[Ir_2(\mu\text{-}PPh_2)_2(cod)_2]$, compared with the rhodium reagent, towards $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$, necessitated more vigorous conditions for a reaction to occur. Evidently this is responsible for our failure to isolate the iridium analogues of compounds (**1**), (**2**), (**6**), and (**7**), since these analogues would sequentially give the thermodynamically most stable product (**5**).

The results described in this paper demonstrate the non-spectator role of bridging phosphido and bridging alkylidyne ligands in metal cluster chemistry involving the heteronuclear Rh–W system. Novel C–P bond-forming and bond-breaking processes occur under relatively mild conditions. Morever, it is to be anticipated that the tetra- and penta-nuclear rhodium complexes (**8**) and (**9**) will be useful starting points for the synthesis of other mixed-metal clusters of higher nuclearity.

Experimental

All experiments were carried out under nitrogen, using Schlenk-tube techniques. Light petroleum refers to that fraction of b.p. 40—60 °C. Chromatography columns (*ca.* 3 × 25 cm) were of alumina (Brockman activity II). The reagents $[Ir_2(\mu\text{-}PPh_2)_2(cod)_2]$[4] and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$[9] were prepared by methods previously reported. Analytical and other data for the new compounds are given in Table 1. The instrumentation used has been described in earlier papers in this series.

Reaction between $[Ir_2(\mu\text{-}PPh_2)_2(cod)_2]$ *and* $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$.—The compound $[Ir_2(\mu\text{-}PPh_2)_2(cod)_2]$ (0.20 g, 0.20 mmol), suspended in thf (25 cm^3), was treated with $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.20 g, 0.60 mmol), and the mixture was refluxed for 4 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (*ca.* 10 cm^3, 1 : 1) and chromatographed. Elution with the same solvent mixture removed initially unreacted $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$. Further elution removed a red fraction, from which solvent was removed *in vacuo*. Crystallisation of the residue from CH_2Cl_2–light petroleum (*ca.* 6 cm^3, 1 : 5) gave red *crystals* of $[W_2Ir_2(\mu\text{-}CO)(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$ (**5**) (0.08 g).

Synthesis of the Complex $[W_2Rh_2(\mu\text{-}CO)(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$.—Carbon monoxide was slowly bubbled (5 min) through a CH_2Cl_2 (20 cm^3) solution of complex (**2**) (0.20 g, 0.16 mmol). Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed. Elution with the same solvent gave a green-brown eluate. Removal of solvent *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (*ca.* 10 cm^3, 1 : 6), afforded dark green *crystals* of $[W_2Rh_2(\mu\text{-}CO)(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$ (**6**) (0.18 g).

Thermal Rearrangement of the Complex $[W_2Rh_2(\mu\text{-}CO)(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$.—(*i*) The complex (**6**) (0.20 g, 0.16 mmol) was refluxed in thf (20 cm^3) for 10 min. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 3 : 2) and chromatographed. Elution with the same solvent mixture removed a green eluate followed by a brown eluate. These two eluates preceded a third band. All three fractions were collected individually, solvent was removed *in vacuo*, and the residues were crystallised from CH_2Cl_2–light petroleum (*ca.* 5 cm^3, 1 : 4). This treatment gave dark green *crystals* of $[W_2Rh_2(\mu\text{-}CO)(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_3(\eta\text{-}C_5H_5)_2]$ (**8a**) (0.02 g), brown *crystals* of an isomer (**8b**) (0.01 g), and red *crystals* of $[W_2Rh_2(\mu\text{-}CO)_2(\mu_3\text{-}CMe)\{\mu\text{-}C(Me)PPh_2\}(\mu\text{-}PPh_2)(CO)_3(\eta\text{-}C_5H_5)_2]$ (**7**) (0.12 g).

(*ii*) Similarly, a sample of complex (**6**) (0.20 g, 0.16 mmol) was refluxed in thf (20 cm^3) for 1 h. Removal of solvent *in vacuo*, dissolving the residue in CH_2Cl_2–light petroleum (10 cm^3, 1 : 1) and column chromatography, eluting with the same solvent mixture gave initially a green eluate followed by a brown eluate. Removal of solvent *in vacuo*, and crystallisation of the residues from CH_2Cl_2–light petroleum (6 cm^3, 1 : 5), gave green *crystals* of (**8a**) (0.08 g) and brown *crystals* of the isomer (**8b**) (0.04 g).

Preparation of the Complex $[W_3Rh_2(\mu\text{-}CO)_2(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_3]$.—A thf (20 cm^3) solution of complex (**4**) (0.20 g, 0.13 mmol) was refluxed for 24 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (*ca.* 10 cm^3, 1 : 1) and chromatographed. Elution with the same solvent mixture gave a red-brown eluate. Removal of solvent *in vacuo* and crystallisation of the residue from CH_2Cl_2–light petroleum (6 cm^3, 1 : 5) gave brown *crystals* of $[W_3Rh_2(\mu\text{-}CO)_2(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_3]$ (**9**) (0.07 g).

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