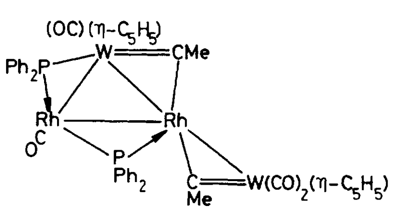
Facile Carbon–Carbon and Carbon–Phosphorus Bond-Forming and -Breaking Processes in Metal Chain Clusters: *X*-Ray Crystal Structures of $[W_3Rh_2(\mu\text{-}CO)_2(\mu\text{-}CMe)\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}PPh_2)_2(\mu_3\text{-}CMe)(CO)_2(\eta\text{-}C_5H_5)_3]$ and $[W_3Rh_2(\mu\text{-}CO)_3(\mu\text{-}CMe)\{\mu\text{-}C(Me)PPh_2\}(\mu\text{-}PPh_2)(\mu_3\text{-}CMe)(CO)_2(\eta\text{-}C_5H_5)_3]$

Simon J. Davies, Judith A. K. Howard, Massimino U. Pilotti, and F. Gordon A. Stone

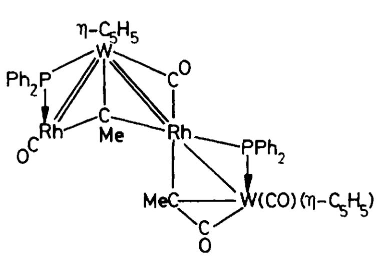
Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS, U.K.

Using the reagents $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Rh_2(\mu\text{-}PPh_2)_2(cod)_2]$ (cod = cyclo-octa-1,5-diene), tetra- and penta-nuclear tungsten-rhodium chain clusters have been prepared and the structures of $[W_3Rh_2(\mu\text{-}CO)_2(\mu\text{-}CMe)\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}PPh_2)_2(\mu_3\text{-}CMe)(CO)_2(\eta\text{-}C_5H_5)_3]$ and $[W_3Rh_2(\mu\text{-}CO)_3(\mu\text{-}CMe)\{\mu\text{-}C(Me)PPh_2\}(\mu\text{-}PPh_2)(\mu_3\text{-}CMe)(CO)_2(\eta\text{-}C_5H_5)_3]$ have been determined by *X*-ray diffraction; the latter contains a λ^5-phospha-alkyne ligand bridging a W–Rh bond.

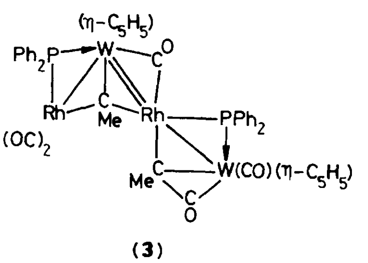
We have recently reported rational synthetic procedures for the step-wise synthesis of metal cluster complexes containing chains of metal atoms.[1] In these species bonds between molybdenum or tungsten and nickel or platinum are bridged by alkylidyne groups. In extending the methodology to tungsten–rhodium systems we have discovered new metal chain-type clusters, as well as facile migratory processes involving ethylidyne, diphenylphosphido, and carbonyl ligands. Carbon–carbon and carbon–phosphorus bond-making and -breaking reactions afford species in which ketenyl or



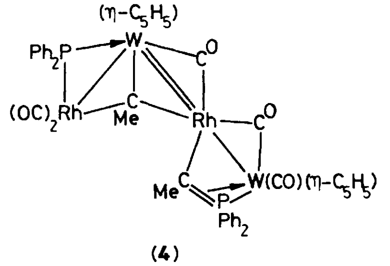
(1)



(2)



(3)



(4)

λ^5-phospha-alkyne fragments bridge tungsten–rhodium bonds.

Treatment of $[Rh_2(\mu\text{-}PPh_2)_2(cod)_2]$[2] (cod = cyclo-octa-1,5-diene) in thf (tetrahydrofuran) at room temperature with two equivalents of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ rapidly affords the tetranuclear metal complex (**1**).† The latter isomerises in solution to give (**2**), a process involving transfer of a μ-PPh_2 group from a Rh–Rh to a Rh–W bond, and attack of CO on a μ-CMe ligand to afford a ketenyl fragment. If CH_2Cl_2 solutions of (**2**) are treated with CO the compound (**3**) is formed quantitatively. The latter on refluxing in thf for *ca.* 10 mins affords a chromatographically separable mixture of compounds (**4**) and (**5**). With longer periods of reflux the sole product is (**5**) *via* the intermediacy of (**4**). The transformation of (**3**) into (**4**) involves an unprecedented conversion of μ-PPh_2 and μ-C(Me)C(O) groups into μ-CO and μ-$C(Me)PPh_2$ ligands at a dimetal centre.

These reactions have been extended to pentanuclear tungsten–rhodium compounds. Thus treatment of $[Rh_2(\mu\text{-}PPh_2)_2(cod)_2]$ with an excess of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ in thf affords, *via* (**2**), the complex (**6**). Formally the latter is produced by replacement of the CO group attached to the terminal Rh atom in (**2**) by a molecule of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ acting as pseudo-alkyne.[3] Compound (**6**) in thf rearranges after several hours to yield the isomer (**7**). The structures of (**6**) and (**7**) have been established by *X*-ray diffraction (Figures 1 and 2).‡ The presence of the μ-λ^5-phospha-alkyne fragment in (**7**) is confirmed, and as far as we are aware compounds (**4**) and (**7**) are the first examples of this ligand bridging a dimetal centre, although mononuclear metal complexes of λ^5-phospha-alkynes are known.[4] Just as

---

† All compounds have been fully characterised by analysis and by spectroscopy. Only selected spectroscopic data are given [i.r. measured in thf, n.m.r. measured in CD_2Cl_2 (^1H, $^{31}P\text{-}\{^1H\}$) or CD_2Cl_2–CH_2Cl_2 ($^{13}C\text{-}\{^1H\}$), coupling constants in Hz, chemical shifts are in p.p.m. and are relative to $SiMe_4$ ($^{13}C\text{-}\{^1H\}$) or 85% H_3PO_4 (external) for $^{31}P\text{-}\{^1H\}$]. Compond (**1**), dark green crystals, $\nu_{max}(CO)$ at 1962vs, 1931vs, 1872m(br), and 1838m(br) cm^{-1}; n.m.r.: $^{13}C\text{-}\{^1H\}$, δ 349.1 [dd, μ-C, J_{RhC} 37, J_{PC} 7], 346.5 [dd, μ-C, J_{RhC} 29, J_{PC} 14], 227.4, 218.5, 214.0 (WCO), and 199.5 [d, RhCO, J_{RhC} 81]; $^{31}P\text{-}\{^1H\}$, δ 271.2 [td, J_{RhP} 132, 103; J_{PP} 132] and 162.2 [dd, J_{RhP} 98, J_{PP} 132].

Compound (**2**), green crystals, n.m.r. (two separable diastereoisomers, *ca.* 1 : 1, data given for one species); $^{13}C\text{-}\{^1H\}$, δ 301.2 [dd, μ_3-C, J_{RhC} 19, 10], 253.5 [d, μ-CO, J_{RhC} 24], 225.5 (WCO), 211.0 [d, μ-C(Me)*C*(O), J_{PC} 6], 192.5 [dd, RhCO, J_{RhC} 67, J_{PC} 95] and 118.9 [d, μ-*C*(Me)C(O), J_{RhC} 18]; $^{31}P\text{-}\{^1H\}$, δ 164.7 [d, J_{RhP} 137] and 159.8 [d, J_{RhP} 76].

Compound (**4**), red crystals, n.m.r.: $^{13}C\text{-}\{^1H\}$, δ 297.5 [dd, 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 [dd, RhCO, J_{RhC} and J_{PC} 77, 56], 195.6 [dd, RhCO, J_{RhC} 63, J_{PC} 11], 141.8 [dd, μ-*C*(Me)PPh_2, J_{RhC} and J_{PC} 35, 30] and 28.0 [d, μ-C(*Me*)PPh_2, J_{PC} 4]; $^{31}P\text{-}\{^1H\}$, δ 158.9 [d, μ-PPh_2, J_{RhP} 78] and -50.6 [s, μ-C(Me)PPh_2].

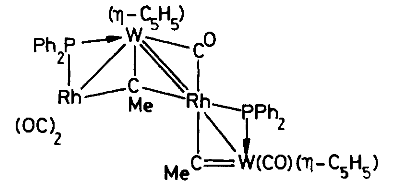
Compound (**5**), green or brown crystals, $\nu_{max}(CO)$ at 2037vs, 1983m, 1886m, and 1737m(br) cm^{-1}; n.m.r. (two diastereoisomers, *ca.* 2 : 1, data given for major isomer) $^{13}C\text{-}\{^1H\}$, δ 332.7 [d, μ-C, J_{RhC} 25], 292.9 [d of d, μ_3-C, J_{RhC} 29, 15], 255.2 [d, μ-CO, J_{PC} 24].

Compound (**7**), red crystals, $\nu_{max}(CO)$ at 1914vs, 1786m, 1737m, and 1715m cm^{-1}; $^{31}P\text{-}\{^1H\}$ n.m.r., δ 169.5 [d, μ-PPh_2, J_{RhP} 127] and -29.6 [s, μ-C(Me)PPh_2].

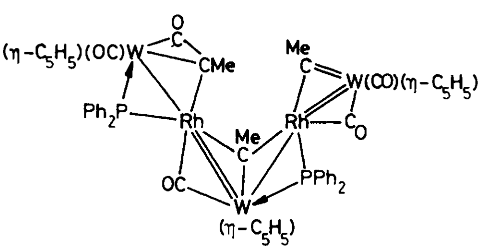
Compound (**8**), brown crystals, $\nu_{max}(CO)$ at 1941s, 1881m, 1764m and 1732m cm^{-1}; n.m.r.: $^{13}C\text{-}\{^1H\}$ (at −40 °C), δ 354.4 [d, μ-C, J_{RhC} 35], 338.4 (μ-C), and 306.9 [dd, μ_3-C, J_{RhC} 29, 19]; $^{31}P\text{-}\{^1H\}$, δ 174.3 [d, J_{RhP} 129, J_{WP} 430] and 155.8 [d, J_{RhP} 136, J_{WP} 415].

‡ *Crystal data* for (**6**): $C_{50}H_{44}O_5P_2Rh_2W_3\cdot 2CH_2Cl_2$, $M = 1714.1$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.523(2)$, $b = 14.066(5)$, $c = 25.144(9)$ Å, $\alpha = 109.54(3)$, $\beta = 105.46(2)$, $\gamma = 121.99(2)°$, $U = 2764(1)$ Å^3, $Z = 2$, $D_c = 2.06$ g cm^{-3}, $F(000) = 1620$, $\mu(Mo\text{-}K_\alpha) = 72.16$ cm^{-1}, $R = 0.106$ ($R_w = 0.105$) for 3283 unique absorption corrected intensities [298 K, θ-2θ scans, $2\theta \leqslant 50°$, $F \geqslant 8\sigma(F)$, Mo-K_α ($\bar{\lambda} = 0.710\,69$ Å)]. Data collected on a Nicolet *P3m* diffractometer and structure was solved by heavy-atom difference-Fourier methods with refinement by blocked-cascade least squares. Two solvent molecules co-crystallise in the lattice with positional disorder.

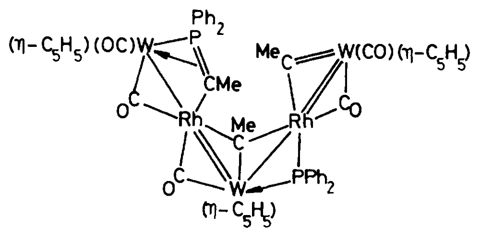
Crystal data for (**7**): $C_{50}H_{44}O_5P_2Rh_2W_3$, $M = 1543.6$, orthorhombic, space group *Pbca* (no. 61), $a = 19.091(5)$, $b = 22.245(5)$, $c = 21.804(5)$ Å, $U = 9335(2)$ Å^3, $Z = 8$, $D_c = 2.18$ g cm^{-3}, $F(000) = 5806$, $\mu(Mo\text{-}K_\alpha)$ 83.22 cm^{-1}, $R = 0.051$ ($R_w = 0.049$), for 3792 unique absorption corrected intensities [$F \geqslant 6\sigma(F)$, data collection as for (**6**)]. The structure was solved by direct methods. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



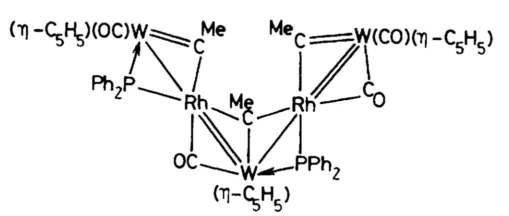
(5)



(6)



(7)



(8)

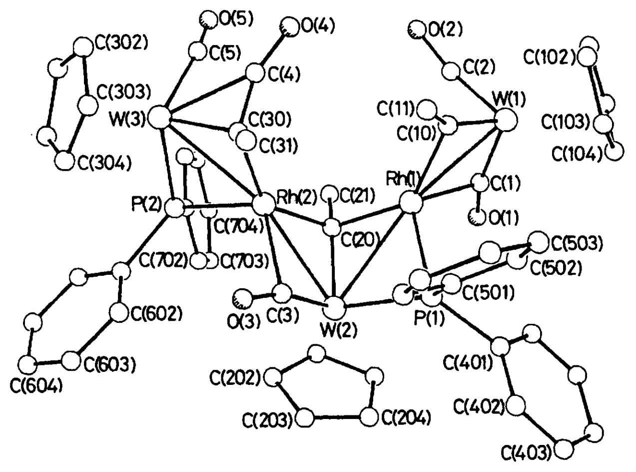


Figure 1. Molecular structure of $[W_3Rh_2(\mu\text{-}CO)_2(\mu\text{-}CMe)\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}PPh_2)_2(\mu_3\text{-}CMe)(CO)_2(\eta\text{-}C_5H_5)_3]$ (**6**). Bond lengths and angles: Rh(1)–W(2) 2.791(6), Rh(2)–W(3) 2.813(4), Rh(1)–W(1) 2.696(5), Rh(2)–W(2) 2.664(5), Rh(1) ··· Rh(2) 3.115(4), W(3)–C(4) 2.27(5), W(3)–C(30) 2.03(4), Rh(2)–C(30) 2.03(7), W(2)–P(1) 2.36(1), W(3)–P(2) 2.36(2), Rh(1)–P(1) 2.24(2), Rh(2)–P(2) 2.28(1) Å; W(1)–C(1)–O(1) 162(4), Rh(1)–C(1)–O(1) 115(4), W(2)–C(3)–O(3) 165(6), Rh(2)–C(3)–O(3) 110(4)°.

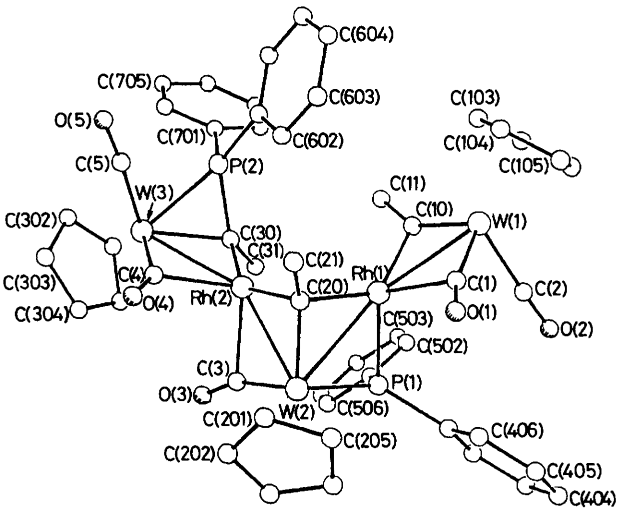


Figure 2. Molecular structure of $[W_3Rh_2(\mu\text{-}CO)_3(\mu\text{-}CMe)\{\mu\text{-}C(Me)PPh_2\}(\mu\text{-}PPh_2)(\mu_3\text{-}CMe)(CO)_2(\eta\text{-}C_5H_5)_3]$ (**7**). Bond lengths and angles: Rh(1)–W(1) 2.678(2), Rh(2)–W(2) 2.699(2), Rh(1)–W(2) 2.803(2), Rh(2)–W(3) 2.786(2), W(3)–P(2) 2.382(6), W(3)–C(30) 2.12(2), Rh(2)–C(30) 2.03(2), Rh(1)–P(1) 2.26(1), W(2)–P(1) 2.33(1) Å; W(1)–C(1)–O(1) 164(2), Rh(1)–C(1)–O(1) 117(2), W(2)–C(3)–O(3) 166(2), Rh(2)–C(3)–O(3) 118(1), W(3)–C(4)–O(4) 151(2), Rh(2)–C(4)–O(4) 123(2)°.

(**4**) readily releases CO to afford (**5**), with cleavage of the C–P bond in the μ-λ^5-C(Me)PPh$_2$ ligand, so (**7**) on prolonged refluxing (*ca.* 24 h) affords (**8**).

It is evident from these studies that unsaturated metal-chain clusters have a marked propensity to activate CO, CMe, and PPh$_2$ groups, and may well have the potential to promote reactions of other ligands as well.

We thank the S.E.R.C. for research studentships (to S. J. D. and M. U. P.)

Received, 27th September 1988; Com. 8/03833C

References

1 S. J. Davies, G. P. Elliott, J. A. K. Howard, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 2177; S. J. Davies and F. G. A. Stone, *ibid.* in the press.
2 P. E. Kreter and D. W. Meek, *Inorg. Chem.*, 1983, **22**, 319.
3 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.
4 V. C. Gibson, C. E. Graimann, P. M. Hare, M. L. H. Green, J. A. Bandy, P. D. Grebenik, and K. Prout, *J. Chem. Soc., Dalton Trans.*, 1985, 2025; T. P. Kee, V. C. Gibson, and W. Clegg, *J. Organomet. Chem.*, 1987, **325**, C14.