

**Polynuclear Tungsten-iron, -ruthenium and -osmium Carbonyl Complexes:
Crystal Structures of $[\text{FeW}_2(\mu_3\text{-C}_2\text{R}_2)(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$, $[\text{OsW}_2(\mu_3\text{-C}_2\text{R}_2)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_2]$ (two isomers), and $[\text{Os}_3\text{W}(\mu_3\text{-CR})(\text{CO})_{11}(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$)**

By LUIGI Busetto, MICHAEL GREEN, JUDITH A. K. HOWARD, BERND HESSNER, JOHN C. JEFFERY, RONA M. MILLS,
F. GORDON A. STONE, and PETER WOODWARD

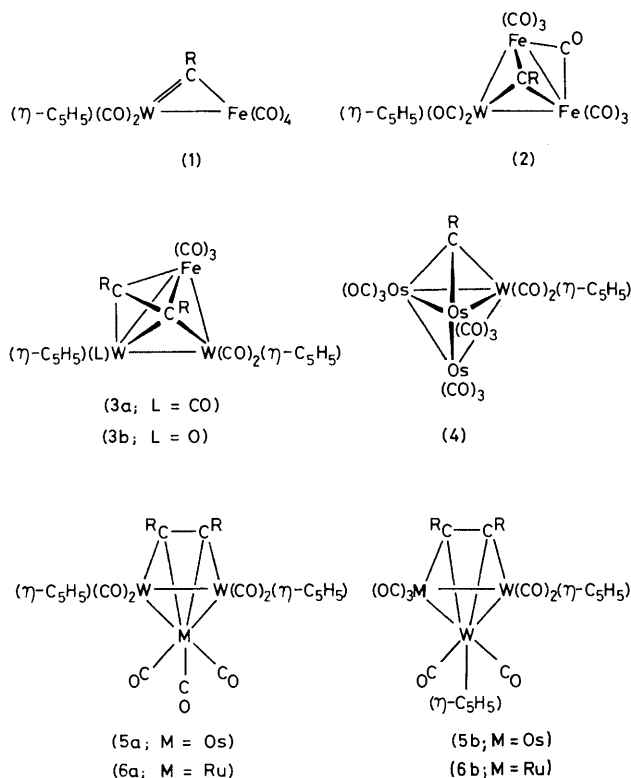
(Department of Inorganic Chemistry, The University, Bristol BS8 ITS)

Summary Reactions of polynuclear carbonyl complexes of iron, ruthenium, or osmium with $[\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) afford several heteronuclear metal cluster compounds, and the structures of $[\text{FeW}_2(\mu_3\text{-C}_2\text{R}_2)(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$, $[\text{Os}_3\text{W}(\mu_3\text{-CR})(\text{CO})_{11}(\eta\text{-C}_5\text{H}_5)]$, and $[\text{OsW}_2(\mu_3\text{-C}_2\text{R}_2)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_2]$ (two isomers) have been established by X-ray diffraction.

It is well known that reactions between alkynes and transition metal carbonyls afford a multitude of polynuclear metal species having the alkynes, their oligomers, or other organic moieties co-ordinated to the clusters.¹ Indeed from the standpoint of novel synthetic and structural results this field of study has been among the most productive in organometallic chemistry. The similarity between the co-ordinating abilities of $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{M}$ triple bonds towards low-valent metal species² suggests that

reactions of metal carbynes with polynuclear metal carbonyls should afford a plethora of new heteronuclear metal cluster complexes. The paradigm molecule for such a study is $[\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) because of the isobal relationship between the groups $\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ and CH . Illustrative of this approach to cluster species we report on products from reactions of the tungsten compound with $[\text{Fe}_2(\text{CO})_9]$, $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Fe}$ or Ru), $[\text{Os}_3(\text{CO})_{10}(\text{cyclo-C}_8\text{H}_{14})_2]$,³ and $[\text{Os}_3(\mu\text{-H})_2(\mu\text{-CH}_2)(\text{CO})_{10}]$.⁴

Reaction of $[\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ with $[\text{Fe}_2(\text{CO})_9]$ (1:1 mol ratio) in diethyl ether at 25 °C affords a chromatographically separable mixture of complexes **(1)**—**(3a)**. Compound **(1)** is very reactive towards addition of $\text{Fe}(\text{CO})_5$ or $\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ groups. By using an excess of $[\text{Fe}_2(\text{CO})_9]$, the di-iron compound **(2)** is obtained in 75% yield, whereas with an excess of $[\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$, the ditungsten species **(3a)** (>70%) is essentially the only reaction product. Complexes **(1)**—**(3a)** were characterised



R = $\text{C}_6\text{H}_4\text{Me-4}$, semi-bridging CO groups not depicted for the sake of clarity.

spectroscopically,[†] (2) and (3a) crystallographically. The structure of (2) involves no structural novelty and is not reported here; (3a) is, however, entirely new.[‡]

Crystal data for (3a): $\text{C}_{32}\text{H}_{24}\text{O}_6\text{FeW}_2$, M 927.6, triclinic, space group $P\bar{1}$, $a = 8.622(2)$, $b = 12.799(4)$, $c = 13.443(8)$ Å, $\alpha = 90.72(4)$, $\beta = 108.45(4)$, $\gamma = 93.34(2)^\circ$, $U = 1404(1)$ Å³, $Z = 2$, $D_c = 2.20$ g cm⁻³, $F(000) = 876$, $\mu(\text{Mo-K}\alpha) = 89.1$ cm⁻¹. Current R 0.037 (R' 0.039) for 4337 reflections [293 K, $2\theta \leq 50^\circ$, $I \geq 3\sigma(I)$, $\text{Mo-K}\alpha$ ($\lambda = 0.71069$ Å)]. From the molecular structure (Figure 1) it may be seen that coupling of two alkylidene ligands has occurred, generating a new species in which the alkyne $\text{C}_2(\text{C}_6\text{H}_4\text{Me-4})_2$ transversely bridges one Fe-W bond of an FeW_2 triangle. The C_2 moiety is σ -bonded to the second W atom, and one of the carbonyl ligands on this W atom is semi-bridging to the other W atom.

[†] Significant spectroscopic properties, compound (1): ν_{CO} (max) at 2073m, 2025m, 1993s, 1929s, and 1869w cm⁻¹ (in CH_2Cl_2). N.m.r. (CD_2Cl_2), ^1H δ 2.17 (s, 3 H, Me), 5.34 (s, 5 H, C_5H_5), and 7.19 (s, 4 H, C_6H_4); ^{13}C { ^1H }, δ 331.3 [$\mu\text{-C}$, $J(\text{WC})$ 137 Hz], 216.1 and 210.8 (CO) p.p.m. (2): ^{13}C { ^1H } n.m.r. ($\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$), δ 282.6 ($\mu\text{-C}$) and 212.9 (br, CO) p.p.m. (3a): ν_{CO} (max) 2024s, 1983s, 1962s, 1919s, and 1838br m cm⁻¹ (in cyclohexane). N.m.r.: ^1H (CD_2Cl_2) δ 2.19 (br, 6 H, Me), 5.09 (s, 10 H, C_5H_5), and 6.83 (br m, 8 H, C_6H_4); ^{13}C { ^1H } ($\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$), δ 225.6, 217.0, 215.0 (CO), 168.5 ($\text{CC}_6\text{H}_4\text{Me-4}$), 154.5 [C(1) of C_6H_4], 153.8 ($\text{CC}_6\text{H}_4\text{Me-4}$), 152.7 [C(1) of C_6H_4], 135.1, 133.8, 129.7, 128.3, 127.5 (C_6H_4), 92.0 (C_5H_5), and 21.0 (Me) p.p.m. (3b): ν_{CO} (max) at 2039s, 1979 m, 1954m, 1918w, and 1782 cm⁻¹ (CH_2Cl_2); ν_{WO} (max) 890s cm⁻¹ (Nujol). ^1H n.m.r.: δ 2.33 (s, 3 H, Me), 2.35 (s, 3 H, Me), 5.35 (s, 5 H, C_5H_5), 6.01 (s, 5 H, C_5H_5), and 6.5–7.1 (m, 8 H, C_6H_4). (4): ν_{CO} (max) at 2078s, 2040vs, 2033vs, 2009s, 1999w, 1980w, 1974w, and 1836w cm⁻¹ (methylcyclohexane). (5a) and (5b) mixture (see text): ν_{CO} (max) at 2062w, 2048vs, 2000w, 1980vs, 1977vs, 1916s, and 1835w cm⁻¹ (methylcyclohexane). (6): ν_{max} (CO) at 2046vs, 2010s, 1990vs, 1982vs, 1914s, and 1830 cm⁻¹ (methylcyclohexane). N.m.r.: ^1H (CDCl_3), δ 2.17 (s, 6 H, Me), 4.94 (s, 10 H, C_5H_5), and 6.71 (m, 8 H, C_6H_4); ^{13}C { ^1H } ($\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$), 221.1, 220.2 (WCO), 195.9 (RuCO), 153.1–128.0 (CC_6H_4), 92.8 (C_5H_5), and 20.5 (Me) p.p.m.

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

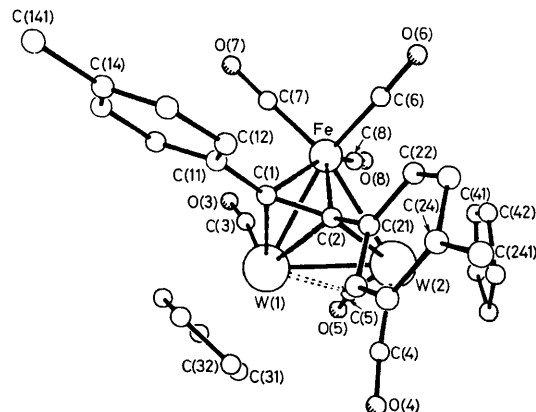


FIGURE 1. Molecular structure of $[\text{FeW}_2\{\mu_3\text{-C}_2(\text{C}_6\text{H}_4\text{Me-4})_2\}(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ (3a). W(1)–W(2), 2.747(1); Fe–W(1), 2.731(1); Fe–W(2), 2.745(1); C(1)–C(2), 1.399(9); C(2)–W(2), 2.264(7); C(1)–Fe, 2.052(5); C(2)–Fe, 2.011(5); C(1)–W(1), 2.040(6); C(2)–W(1), 2.289(5) Å; W(2)–C(5)–O(5), 165(1) $^\circ$.

Reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with $[\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ in THF (tetrahydrofuran) at 25 $^\circ\text{C}$ (2 d) affords a mixture of compounds (2) and (3a), together with a small amount of (3b).[†] The latter also forms by slow oxidation of (3a) in the solid state, and has been characterised by an X-ray diffraction study,⁵ not reported here.

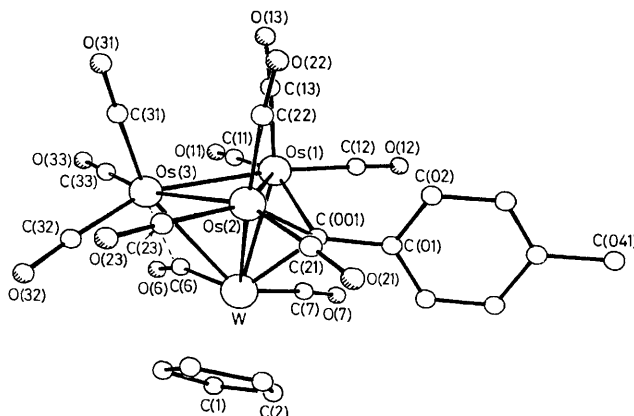


FIGURE 2. Molecular structure of $[\text{Os}_3\text{W}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_{11}(\eta\text{-C}_5\text{H}_5)]$ (4). Os–Os(mean), 2.793(2); W–Os(1), 2.874(1); W–Os(2), 2.867(1); W–Os(3), 2.915(1); C(001)–W, 2.138(15); C(001)–Os(1), 2.142(14); C(001)–Os(2), 2.048(15); Os(3) . . . C(6), 2.54(2) Å; W–C(6)–O(6), 159(2) $^\circ$.

The tetranuclear metal complex (4)[†] was isolated from the reaction of $[\text{Os}_3(\text{CO})_{10}(\text{cyclo-C}_8\text{H}_{14})_2]$ with $[\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (toluene, 5 d, 25 °C), and the structure established by X-ray diffraction.[†]

Crystal data for (4): $\text{C}_{24}\text{H}_{12}\text{O}_{11}\text{Os}_3\text{W}$, M 1 230, monoclinic, space group $P2_1/n$, $a = 14.508(6)$, $b = 13.793(4)$, $c = 13.440(6)$ Å, $\beta = 101.11(4)^\circ$, $U = 2 639(2)$ Å³, $Z = 4$, $D_c = 3.1$ g cm⁻³, $F(000) = 2 184$, $\mu(\text{Mo-K}\alpha) 189.2$ cm⁻¹. Current R 0.063 (R' 0.063) for 5 024 reflections [220 K, $2\theta \leq 55^\circ$, $I \geq 2\sigma(I)$].

The molecular structure (Figure 2) consists of an approximately tetrahedral arrangement of metal atoms with an Os_2W face capped by the triply-bridging tolylidyne ligand. Overall this *closo*-structure obeys skeletal electron pair theory with five core atoms and six electron pairs for cluster bonding.⁶ However, the tungsten atom and Os(3) have formally 19 and 17 electrons, respectively, which probably accounts for the presence of the semi-bridging carbonyl $\text{W}\cdot\text{C}(6)\cdot\text{O}(6)$ [$159(2)^\circ$].

Reaction of $[\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ with $[\text{Os}_3(\mu\text{-H})_2(\mu\text{-CH}_2)(\text{CO})_{10}]$ in THF at 60 °C affords red crystals (5) which were identified by X-ray diffraction.[†]

Crystal data for (5): $\text{C}_{33}\text{H}_{24}\text{O}_7\text{OsW}_2$, M 1 090, monoclinic, space group $P2_1$, $a = 10.248(11)$, $b = 18.168(25)$, $c = 16.637(16)$ Å, $\beta = 101.40(8)^\circ$, $U = 3 036(6)$ Å³, $Z = 4$, $D_c = 2.38$ g cm⁻³, $F(000) = 2 008$, $\mu(\text{Mo-K}\alpha) 119.5$ cm⁻¹. Current R 0.045 (R' 0.045) for 4 967 reflections [298 K, $2\theta \leq 55^\circ$, $I \geq 2\sigma(I)$].

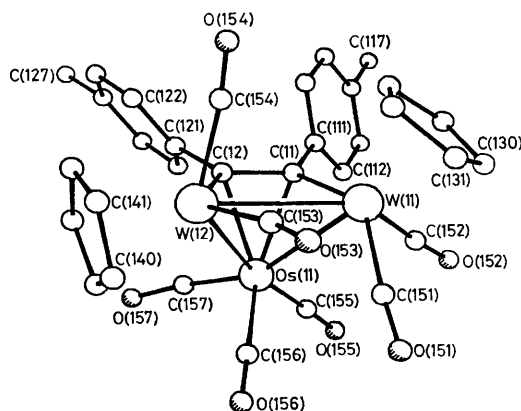


FIGURE 3. Molecular structure of $[\text{W}_2\text{Os}\{\mu_3\text{-C}_2(\text{C}_6\text{H}_4\text{Me-4})_2\}(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_2]$ (5a). W-W, 3.159(2); W(11)-Os(11), 2.863(2); W(12)-Os(11), 2.839(2); C(11)-W(11), 2.117(19); C(11)-Os(11), 2.320(20); C(12)-W(12), 2.111(24); C(12)-Os(12), 2.306(21); C(11)-C(12), 1.47(3).

The crystal structure shows, remarkably, that the asymmetric unit comprises two molecules, one of each isomer (5a) and (5b) (Figures 3 and 4). As in the formation of (3a), reaction has occurred with coupling of the alkylidyne ligands to generate the alkyne $\text{C}_2(\text{C}_6\text{H}_4\text{Me-4})_2$ but which here adopts a $\mu_3(\eta^2\text{-})$ mode⁷ of bonding to the metal triangles. Evidently methane is lost in the formation of

(5). Both (5a) and (5b) have the expected seven electron pairs for skeletal bonding of *nido*-structures based on octahedra with missing vertices. From the viewpoint of isolobal relationships the symmetrical molecule (5a), the ruthenium analogue of which, (6a),[†] is obtained by heating $[\text{Ru}_3(\text{CO})_{12}]$ with $[\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ in toluene, can be regarded as a dimetallacyclobutadiene to which an $\text{Os}(\text{CO})_3$ group is co-ordinated.

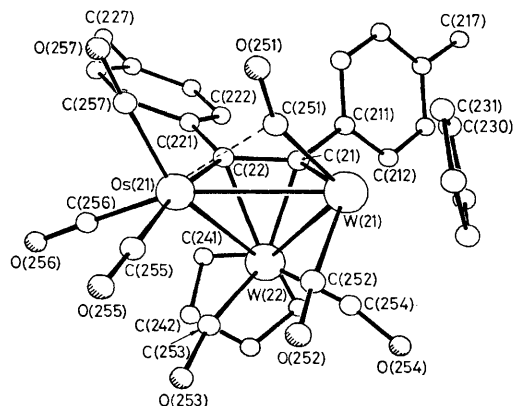
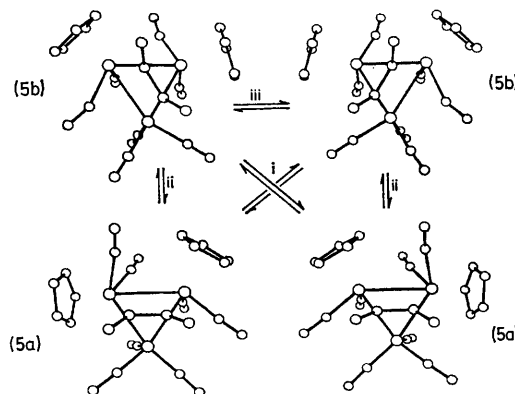


FIGURE 4. Molecular structure of $[\text{W}_2\text{Os}\{\mu_3\text{-C}_2(\text{C}_6\text{H}_4\text{Me-4})_2\}(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_2]$ (5b). W-W, 3.017(2); W(21)-Os(21), 2.981(2); W(22)-Os(21), 2.876(2); W(21)-C(21), 2.193(18); W(22)-C(21), 2.208(21); W(22)-C(22), 2.304(18); Os(21)-C(22), 2.052(20); C(21)-C(22), 1.43(3); Os(21) ... C(251), 2.51(3) Å; W(21)-C(251)-O(251), 156(2)°.

In solution, (5a) and (5b) [(6a) and (6b)] undergo dynamic behaviour consistent with the Scheme.



SCHEME. From variable temperature ¹H n.m.r. studies approximate coalescence temperatures for the processes shown are: i, 0 °C, site exchange of $\text{C}_6\text{H}_4\text{Me-4}$ groups; ii, -45 °C, interconversion of (5a) and (5b); iii, -75 °C, $\eta\text{-C}_5\text{H}_5$ exchange in (5b). For clarity, for the $\text{C}_6\text{H}_4\text{Me-4}$ groups only C(1) is shown.

We thank the S.E.R.C. for support, NATO for a Fellowship (B. H.), and the Italian CNR for a Visiting Fellowship (L. B.).

(Received, 20th July 1981; Com. 863.)

¹ W. Hübel, in 'Organic Syntheses via Metal Carbonyls,' Vol. 1, eds. I. Wender and P. Pino, Interscience-Wiley, 1968, ch. 3; F. L. Bowden and A. B. P. Lever, *Organomet. Chem. Rev.*, 1968, 3, 227.

² T. V. Ashworth, M. J. Chetcuti, J. A. K. Howard, F. G. A. Stone, S. J. Wisbey, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 763, and references cited therein.

³ M. Tachikawa and J. R. Shapley, *J. Organomet. Chem.*, 1977, 124, C19.

⁴ A. J. Schultz, J. M. Williams, R. B. Calvert, J. R. Shapley, and G. D. Stucky, *Inorg. Chem.*, 1979, 18, 319.

⁵ L. Busetto, J. C. Jeffery, and F. G. A. Stone, unpublished work.

⁶ K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, 18, 1.

⁷ M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *J. Am. Chem. Soc.*, 1976, 98, 4645.