Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 71.[1] Synthesis of Tungsten–Iridium Complexes. Crystal Structures of $[W_2Ir(\mu_3\text{-}RC_2R)Cl(CO)_4(\eta\text{-}C_5H_5)_2]\cdot CH_2Cl_2$ and $[W_2Ir(\mu\text{-}CR)(\mu_3\text{-}CR)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$ (R = C_6H_4Me-4) *

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In tetrahydrofuran at room temperature, the complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) and $[IrCl(CO)(\eta\text{-}C_8H_{14})_2]$ (C_8H_{14} = cyclo-octene) afford a chromatographically separable mixture of five cluster compounds $[W_2Ir(\mu_3\text{-}RC_2R)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$ (**1**), $[W_2Ir(\mu\text{-}CR)(\mu_3\text{-}CR)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**, **3**, and **4**, isomers), and $[W_2Ir_2(\mu_4\text{-}RC_2R)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (**5**). The reaction between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}4)]$ yields a similar mixture except that (**2**) is absent, and a possible reason for this is discussed. The molecular structures of compounds (**1**) and (**2**) have been established by single-crystal *X*-ray diffraction studies. That of (**1**) consists of a triangle of metal atoms [W–W 2.666(1), W–Ir 2.821(1) and 2.798(1) Å] with the W–W bond weakly semi-bridged by a CO ligand [W–C–O 169.1(9)°]. The alkyne RC_2R adopts a $\mu_3(\eta^2\text{-}\perp)$ bonding mode, transversely bridging a W–Ir bond, and tilted so that one of the ligated carbon atoms triply bridges the metal triangle [μ_3-C–Ir 2.05(1), μ_3-C–W 2.24(1) and 2.28(1) Å]. The tungsten and iridium atoms of the W–Ir bond transversely bridged by the alkyne are, respectively, co-ordinated by Cl and C_5H_5, and by two CO groups. The other tungsten atom, carrying the semi-bridging CO ligand, is ligated by a CO and a C_5H_5 group. Compound (**2**) also has a triangular core [W–W 2.951(1), W–Ir 2.867(1) and 2.698(1) Å]. One of the *p*-tolylmethylidyne ligands caps the metal triangle [μ_3-C–W 2.04(2) and 2.07(2), μ_3-C–Ir 2.19(2) Å] while the other bridges the shorter W–Ir edge [μ-C–W 1.90, μ-C–Ir 2.06(2) Å]. The tungsten atom of this edge carries a CO group and a C_5H_5 moiety. The other tungsten atom is ligated by Cl, CO, and C_5H_5 groups. Two CO ligands are co-ordinated to the iridium. The molecular structures of the isomers of (**2**), compounds (**3**) and (**4**), have been assigned from consideration of their n.m.r. spectra (^1H and $^{13}C\text{-}\{^1H\}$) and by comparison with those of complex (**2**) and a PPh_3 derivative $[W_2Ir(\mu\text{-}CR)(\mu_3\text{-}CR)Cl(CO)_3(PPh_3)(\eta\text{-}C_5H_5)_2]$ of (**4**) shown to contain an $Ir(CO)(PPh_3)$ group. Like (**2**), complexes (**3**) and (**4**) have μ-CR, μ_3-CR, and terminal W–Cl groups. However, in (**3**) the μ-CR ligand bridges a W–W bond and there is an $Ir(CO)_3$ group present, whereas (**4**) is structurally very similar to (**2**) differing only in the site of the terminal Cl atom and a CO group. The spectroscopic data (i.r. and ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r.) for the tetranuclear cluster (**5**) are discussed and its structure can be assigned on the basis of an earlier synthesis.

As a consequence of the ligating properties of their carbon–metal triple bonds, the tungsten compounds $[W(\equiv CR)(CO)_2L]$ {R = C_6H_4Me-4 or Me, L = $\eta\text{-}C_5H_5$ or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]; R = C_6H_4Me-4, L = $\eta\text{-}C_5Me_5$} and the related molybdenum species $[Mo(\equiv CR)(CO)_2L]$ [R = C_6H_4Me-4, L = $\eta\text{-}C_5H_5$; R = C_6H_4Me-4 or Me, L = $HB(pz)_3$] are versatile reagents for preparing complexes with metal–metal bonds bridged by alkylidyne groups.[1–6] The mononuclear tungsten and molybdenum compounds combine with co-ordinatively unsaturated metal–ligand fragments, derived from suitable precursors, to yield di-, tri-, or tetra-nuclear metal compounds, depending on the reagents employed.

Although this method for preparing polynuclear 'mixed-metal' complexes has been used extensively, only five species containing iridium have been reported. These are $[WIr(\mu\text{-}CC_6H_4Me\text{-}4)(acac)(CO)_3(\eta\text{-}C_5H_5)]$ (acac = acetylacetonate), $[MIr(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ [M = Mo or W, C_9H_7 = indenyl], $[WIr(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_9H_7)]$, and $[WRhIr(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2]$.[7] In this paper we describe further examples of 'mixed-metal' compounds containing tungsten and iridium, obtained from reactions between $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[IrCl(CO)(\eta\text{-}C_8H_{14})_2]$ ($\eta\text{-}C_8H_{14}$ = cyclo-octene) or $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}4)]$. It was anticipated that the iridium reagents would act as sources of the co-ordinatively unsaturated fragments IrCl(CO) and $IrCl(CO)_2$, respectively, and that these species would readily combine with the C≡W bond of the alkylidynetungsten compound. Moreover, since the iridium fragments contain only two or three ligands, it was expected that they would add more than one molecule of the tungsten complex in order to relieve the co-ordinative unsaturation at the iridium centres.

Results and Discussion

Essentially the same complex mixture of tungsten–iridium complexes is obtained by treating $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) in tetrahydrofuran (thf) with either $[IrCl(CO)(\eta\text{-}C_8H_{14})_2]$ or $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}4)]$. The reactions were carried out at room temperature, and although they

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* 1,1,2,2-Tetracarbonyl-3-chloro-2,3-di(η-cyclopentadienyl)-μ_3-[bis(*p*-tolylacetylene)-$C^1(Ir^1W^2W^3)C^2(Ir^1W^3)$]-*triangulo*-iridium-ditungsten–dichloromethane (1/1) and 1,1,2,3-tetracarbonyl-3-chloro-2,3-di(η-cyclopentadienyl)-1,2-μ-*p*-tolylmethylidyne-μ_3-*p*-tolylmethylidyne-*triangulo*-1-iridium-2,3-ditungsten.

Supplmentary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

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

Compound[b]	Colour	Yield (%)	$\tilde{\nu}(CO)$[c]/cm^{-1}	Analysis (%) C	Analysis (%) H
(**1**) $[W_2Ir(\mu_3\text{-}RC_2R)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$[d]	Dark red	15	1 996vs, 1 941s, 1 901vw(br), 1 823w(br)	32.9 (33.0)	2.3 (2.3)
(**2**) $[W_2Ir(\mu\text{-}CR)(\mu_3\text{-}CR)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$	Red	8	[e]2 041vs, 1 991s, 1 927m, 1 902m(br)	34.2 (34.5)	2.4 (2.3)
(**3**) $[W_2Ir(\mu\text{-}CR)(\mu_3\text{-}CR)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$	Green	12	2 052vs, 1 993s, 1 976s, 1 920w(br)	34.3 (34.5)	2.4 (2.3)
(**4**) $[W_2Ir(\mu\text{-}CR)(\mu_3\text{-}CR)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$[d]	Dark green	16	2 033vs, 1 977s, 1 964s (sh), 1 881m	33.4 (33.0)	2.6 (2.3)
(**5**) $[W_2Ir_2(\mu_4\text{-}RC_2R)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)_2]$	Green	4	[e]2 060vs, 2 033vs, 2 006w, 1 989w, 1 962vw, 1 814m, 1 766m	30.5 (31.1)	1.9 (1.8)
(**6**) $[W_2Ir(\mu\text{-}CR)(\mu_3\text{-}CR)Cl(CO)_3(PPh_3)(\eta\text{-}C_5H_5)_2]$	Black	87	[e]1 955m, 1 941s, 1 867m	43.8 (44.2)	3.2 (3.1)

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] In CH_2Cl_2, unless otherwise stated. [d] Crystallised with a molecule of CH_2Cl_2. [e] In thf.

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

Compd.	$^1H(\delta)$[b]	$^{13}C(\delta)$[c]
(**1**)	2.16 (s, 3 H, Me-4), 2.25 (s, 3 H, Me-4), 5.21 (s, 5 H, C_5H_5), 5.61 (s, 5 H, C_5H_5), 6.78—7.26 (m, 8 H, C_6H_4)	235.6, 216.2 (WCO), [d]206.2 (μ_3-*C*R), 199.2, 190.2 (IrCO), 143.4, 141.3 [$C^1(C_6H_4)$], 138.2, 135.7, 133.0, 131.6, 129.1, 128.9 (C_6H_4), [d]128.6 (μ-*C*R), 128.4, 128.1 (C_6H_4), 102.8, 93.1 (C_5H_5), 21.5, 21.1 (Me-4)
(**2**)	2.34 (s, 3 H, Me-4), 2.44 (s, 3 H, Me-4), 5.22 (s, 5 H, C_5H_5), 5.25 (s, 5 H, C_5H_5), 6.30 (br, 1 H, C_6H_4), 7.1—7.3 (m, 6 H, C_6H_4), 7.80 (br, 1 H, C_6H_4)	339.7 (μ-*C*R), 267.0 (μ_3-*C*R), 241.6, 235.6 (WCO), 190.4, 181.1 (IrCO), 165.6, 153.6 [$C^1(C_6H_4)$], 140.7, 134.5, 130.8, 128.9, 128.4, 127.4, 126.4, 126.0 (C_6H_4), 99.3, 98.7 (C_5H_5), 21.7, 21.4 (Me-4)
(**3**)	2.31 (s, 3 H, Me-4), 2.55 (s, 3 H, Me-4), 5.18 (s, 5 H, C_5H_5), 5.72 (s, 5 H, C_5H_5), 6.89—7.38 (m br, 8 H, C_6H_4)	370.7 [μ-*C*R, *J*(WC) 127], 253.7 (μ_3-*C*R), 220.5 (WCO), 175.0, 174.2, 172.3 (IrCO), 163.3, 159.9 [$C^1(C_6H_4)$], 136.4, 136.1, 130.4, 128.7, 128.5, 128.1, 122.6 (C_6H_4), 101.5, 98.2 (C_5H_5), 21.4, 20.7 (Me-4)
(**4**)	2.36 (s, 3 H, Me-4), 2.49 (s, 3 H, Me-4), 5.39 (s, 5 H, C_5H_5), 5.78 (s, 5 H, C_5H_5), 7.05—7.75 (m br, 8 H, C_6H_4)	349.3 (μ-*C*R), 275.1 (μ_3-*C*R), 220.1, 215.0 (WCO), 190.6, 181.6 (IrCO), 167.2, 154.0 [$C^1(C_6H_4)$], 141.0, 134.5, 132.3, 128.8, 128.2, 127.2, 126.5, 122.4 (C_6H_4), 104.0, 93.7 (C_5H_5), 21.7, 20.9 (Me-4)
(**5**)	2.28 (s, 3 H, Me-4), 4.80 (s, 5 H, C_5H_5), 6.90, 7.09 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 9]	[e]224.7 (WCO), 174.4, 174.3 (IrCO), 151.0 [$C^1(C_6H_4)$], 137.3, 129.6, 127.5 (C_6H_4), 110.0 (μ_4-C_2R_2), 96.9 (C_5H_5), 20.9 (Me-4)
(**6**)	2.20 (s, 3 H, Me-4), 2.34 (s, 3 H, Me-4), 5.30 (s, 5 H, C_5H_5), 5.60 (s, 5 H, C_5H_5), 6.50 (br, 1 H, C_6H_4), 7.03 (br, 1 H, C_6H_4), 7.10—7.35 (m, 17 H, C_6H_4, Ph)	[e]345.0 [d, μ-*C*R, *J*(PC) 6], 272.6 [d, μ_3-*C*R, *J*(PC) 20], 220.8, 217.1 (WCO), 185.4 [d, IrCO, *J*(PC) 15], 167.9 [$C^1(C_6H_4)$], 156.5 [d, $C^1(C_6H_4)$, *J*(PC) 7], 136.3—121.0 (C_6H_4, Ph), 104.8, 92.6 (C_5H_5), 21.1, 20.8 (Me-4)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in $CDCl_3$ at room temperature. [c] Hydrogen-1 decoupled, measured in CD_2Cl_2–CH_2Cl_2 at −60 °C unless otherwise stated. Chemical shifts are positive to high frequency of $SiMe_4$. [d] Tentative assignment. [e] Measured at room temperature.

Table 3. Selected internuclear distances (Å) and angles (°) for $[W_2Ir\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}Cl(CO)_4(\eta\text{-}C_5H_5)_2]\cdot CH_2Cl_2$ (**1**) with estimated standard deviations in parentheses

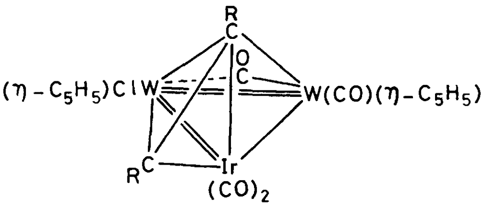
Ir–W(1)	2.821(1)	Ir–W(2)	2.798(1)	Ir–C(3)	1.87(1)	Ir–C(4)	1.88(1)
Ir–C(30)	2.15(1)	Ir–C(40)	2.05(1)	W(1)–W(2)	2.666(1)	W(1) · · · C(1)	2.55(1)
W(1)–Cl	2.379(3)	W(1)–C(30)	2.00(1)	W(1)–C(40)	2.24(1)	W(2)–C(1)	1.95(1)
W(2)–C(2)	1.98(1)	W(2)–C(40)	2.28(1)	C(1)–O(1)	1.15(2)	C(2)–O(2)	1.15(2)
C(3)–O(3)	1.14(2)	C(4)–O(4)	1.14(2)	C(30)–C(40)	1.46(1)		
W(2)–C(cp)* range		2.31(1)—2.34(1)		W(1)–C(cp) range		2.35(1)—2.38(1)	
W(1)–Ir–W(2)	56.6(1)	W(1)–Ir–C(3)	158.3(4)	W(2)–Ir–C(3)	114.1(4)	W(1)–Ir–C(4)	108.1(4)
W(2)–Ir–C(4)	128.9(4)	C(3)–Ir–C(4)	92.8(6)	W(1)–Ir–C(30)	44.9(3)	W(2)–Ir–C(30)	85.3(2)
C(3)–Ir–C(30)	119.6(5)	C(4)–Ir–C(30)	119.1(5)	W(1)–Ir–C(40)	51.8(3)	W(2)–Ir–C(40)	53.4(3)
C(3)–Ir–C(40)	106.6(5)	C(4)–Ir–C(40)	157.3(5)	C(30)–Ir–C(40)	40.4(4)	Ir–W(1)–W(2)	61.2(1)
Ir–W(1)–Cl	138.0(1)	W(2)–W(1)–Cl	104.3(1)	Ir–W(1)–C(30)	49.5(3)	W(2)–W(1)–C(30)	92.0(3)
Cl–W(1)–C(30)	96.1(3)	Ir–W(1)–C(40)	46.0(2)	W(2)–W(1)–C(40)	54.6(2)	Cl–W(1)–C(40)	92.6(3)
C(30)–W(1)–C(40)	39.7(4)	Ir–W(2)–W(1)	62.1(1)	Ir–W(2)–C(1)	123.1(3)	W(1)–W(2)–C(1)	64.7(3)
Ir–W(2)–C(2)	69.0(3)	W(1)–W(2)–C(2)	89.1(5)	Ir–W(2)–C(40)	46.2(2)	W(1)–W(2)–C(40)	53.1(2)
C(1)–W(2)–C(40)	110.4(4)	C(2)–W(2)–C(40)	113.0(4)	W(2)–C(1)–O(1)	169.1(9)	W(2)–C(2)–O(2)	172(1)
Ir–C(3)–O(3)	176(1)	Ir–C(4)–O(4)	176(1)	C(31)–C(30)–C(40)	134(1)	C(30)–C(40)–C(41)	117.4(8)

* cp = η-C_5H_5

proceeded slowly under these conditions thermal decomposition of some of the products was thereby avoided. Hence elevated temperatures in the syntheses were not employed. The tungsten–iridium complexes formed could be separated readily by column chromatography.

In a typical reaction, two equivalents of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and one equivalent of $[IrCl(CO)(\eta\text{-}C_8H_{14})_2]$ were stirred in thf for *ca.* 40 h, after which period i.r. measurements revealed that product formation had ceased. Following chromatography, the compounds $[W_2Ir(\mu_3\text{-}RC_2R)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$ (**1**), $[W_2Ir(\mu\text{-}CR)(\mu_3\text{-}CR)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**, **3**, and **4**, isomers), and $[W_2Ir_2(\mu_4\text{-}RC_2R)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (**5**) were isolated. Data for these species are given in Table 1, and although no one product was formed in high yield the overall yield of the mixture was *ca.* 40%.

The formulations of the complexes (**1**)—(**5**) were established



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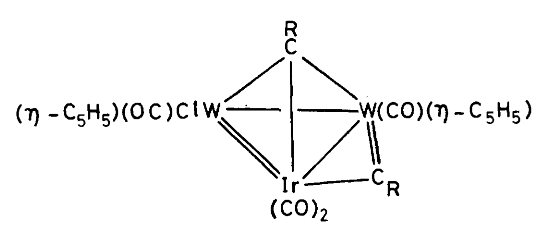

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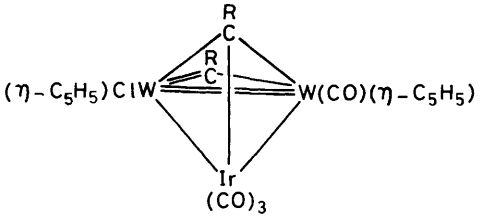

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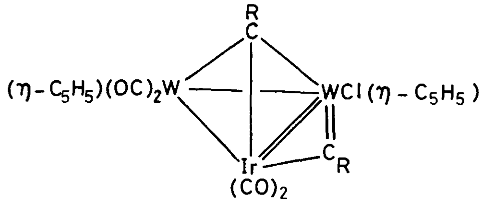

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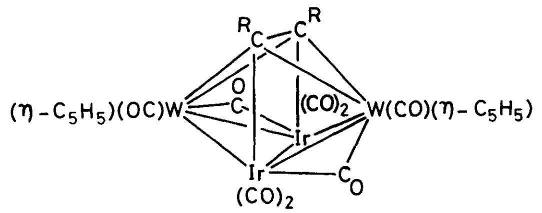

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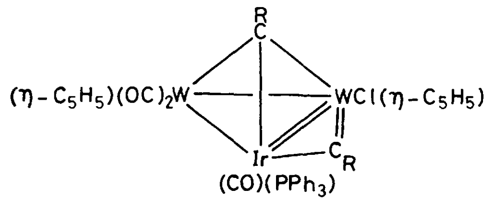

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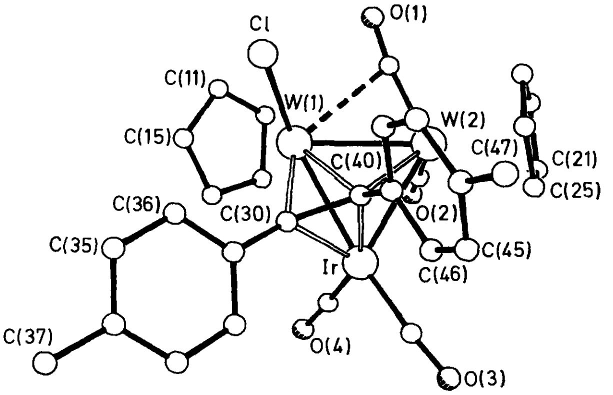

Figure 1. Molecular structure of $[W_2Ir\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}Cl(CO)_4(\eta\text{-}C_5H_5)_2]\cdot CH_2Cl_2$ (**1**) showing the atom numbering scheme

by a combination of *X*-ray diffraction and spectroscopic studies. The n.m.r. data (Table 2) were especially informative, but discussion is deferred until the results of *X*-ray diffraction studies on compounds (**1**) and (**2**) have been described. Crystals of (**2**) were only obtained after great difficulty, and suitable single crystals of (**3**) and (**4**) for *X*-ray diffraction work could not be obtained. Nevertheless, the formulations for these two products are firmly based on microanalytical and spectroscopic data, as is that of (**5**).

The results of the *X*-ray diffraction study on compound (**1**) are summarised in Table 3, and the molecular structure is shown in Figure 1. The compound is a trimetal species, the core of the molecule consisting of a triangle of metal atoms [W–W 2.666(1), W(1)–Ir 2.821(1), W(2)–Ir 2.798(1) Å]. The triangle is bridged by an alkyne ligand $C_2(C_6H_4Me\text{-}4)_2$ which adopts the bonding mode defined by the descriptor $\mu_3(\eta^2\text{-}\perp)$.[8] While the alkyne bridges the W(1)–Ir bond [W(1)–C(30) 2.00(1), W(1)–C(40) 2.24(1), Ir–C(30) 2.15(1), Ir–C(40) 2.05(1) Å], the atom C(40) is also within bonding distance [2.28(1) Å] of W(2). Similar bonding of the alkyne to a metal triangle occurs in the complex $[W_2Fe(\mu_3\text{-}RC_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$, a product of the reaction between $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Fe_2(CO)_9]$.[9] Formation of (**1**) evidently involves a coupling of two alkylidyne groups to give the alkyne, a common feature of reactions of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$,[2] as demonstrated also in the formation of $[W_2Fe(\mu_3\text{-}RC_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$.

The W(1)–W(2) bond in (**1**) is weakly semi-bridged by a CO group [W(2)–C(1)–O(1) 169.1(9)°, W(2)–C(1) 1.95(1), W(1) ··· C(1) 2.55(1) Å]. The atom W(2) also carries a second CO ligand which deviates from linearity [W(2)–C(2)–O(2) 172(1)°]. The iridium atom is co-ordinated by two terminal CO groups [Ir–C–O 176(1)°]. As expected, the tungsten atoms are each ligated by a C_5H_5 group, and in addition W(1) is bonded to a chlorine atom [W(1)–Cl 2.379(3) Å], which has migrated from iridium to tungsten during the reaction.

Compound (**1**) has 44 valence electrons and hence is electronically unsaturated for a trimetal compound, which would possess 48 valence electrons if three metal–metal single bonds were present and if each metal centre had an 18-electron valence shell. The unsaturation in (**1**) is probably delocalised within the cluster, but in the structural formula the species has been depicted with a W=W and a W=Ir bond in order to maintain an 18-electron formalism at each metal centre. Interestingly, the W(1)–W(2) bond [2.666(1) Å] is significantly shorter than that [2.731(1) Å] in $[\mathrm{W_2Fe}(\mu_3\text{-}\mathrm{RC_2R})(\mathrm{CO})_6(\eta\text{-}\mathrm{C_5H_5})_2]$ which is also unsaturated (46 valence electrons).[9] In the 48-valence-electron cluster $[\mathrm{W_2Fe}(\mu_3\text{-}\mathrm{MeC_2C_6H_4Me\text{-}4})(\mathrm{CO})_7(\eta\text{-}\mathrm{C_5H_5})_2]$[10] the W–W separation [2.949(1) Å] is significantly greater than that in (**1**). These data suggest a degree of tungsten–tungsten multiple bonding in the latter complex. Moreover, the W(1)–Cl separation in (**1**) [2.379(3) Å] is appreciably shorter than that found [2.505(4) Å] for the terminal W–Cl group in the compound $[\mathrm{WRu}(\mu\text{-}\mathrm{Cl})(\mu\text{-}\mathrm{CMe})\mathrm{Cl}(\mathrm{CO})_2(\mathrm{PPh_3})_2(\eta\text{-}\mathrm{C_5H_5})]$.[11] This may indicate the presence of a degree of $\mathrm{Cl} \rightleftharpoons \mathrm{W}$ bonding in (**1**) so as to relieve the electronic unsaturation of the cluster.

The spectroscopic data for compound (**1**) are in agreement with the results of the *X*-ray diffraction study. In the i.r. spectrum (Table 1) there are four bands in the CO stretching region, and that at 1 823 cm^{-1} may be assigned to the semi-bridging ligand C(1)O(1). The spectrum also shows a strong band at 297 cm^{-1} which may be attributed to the W–Cl group. The ^{1}H n.m.r. spectrum (Table 2) shows the expected resonances for two Me-4 and two $\mathrm{C_5H_5}$ groups in different environments. Correspondingly, in the $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum of (**1**) there are two Me-4 and two $\mathrm{C_5H_5}$ resonances. The $\mathrm{C_6H_4}$ moieties give rise to ten resonances between δ 143.4 and 128.1 p.p.m., a pattern suggesting that there is restricted rotation about one of the μ-C–$\mathrm{C_6H_4}$ bonds at the temperature of the measurement (−60 °C). Two chemically distinct $\mathrm{C_6H_4}$ groups with free rotation about the μ-C–$\mathrm{C_6H_4}$ bonds would give rise to eight resonances, and if both μ-C–$\mathrm{C_6H_4}$ bonds were restricted in rotation there would be twelve signals. Peaks at δ 206.2 and 128.6 p.p.m. are tentatively assigned to the ligated μ-C nuclei. The signals at δ 235.6 and 216.2 p.p.m. are due to the $\mathrm{W(CO)_2}$ group, and those at δ 199.2 and 190.2 p.p.m. to the $\mathrm{Ir(CO)_2}$ fragment, these assignments being based on chemical shift data reported previously.[7]

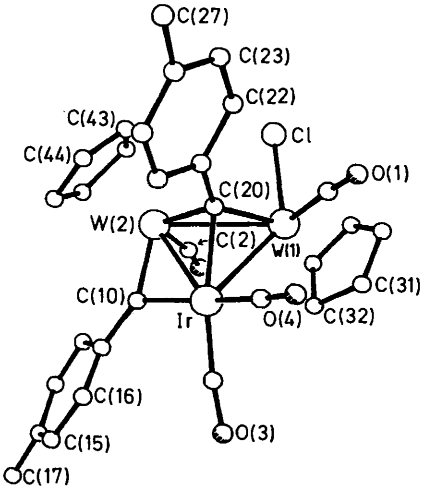

Figure 2. Molecular structure of $[\mathrm{W_2Ir}(\mu\text{-}\mathrm{CC_6H_4Me\text{-}4})(\mu_3\text{-}\mathrm{CC_6H_4Me\text{-}4})\mathrm{Cl}(\mathrm{CO})_4(\eta\text{-}\mathrm{C_5H_5})_2]$ (**2**) showing the atom numbering scheme

Selected parameters obtained from the *X*-ray diffraction study of compound (**2**) are listed in Table 4, and the structure is shown in Figure 2. A triangle of metal atoms [W(1)–W(2) 2.951(1), W(1)–Ir 2.867(1), W(2)–Ir 2.698(1) Å] is capped by a *p*-tolylmethylidyne group [W(1)–C(20) 2.04(2), W(2)–C(20) 2.07(2), Ir–C(20) 2.19(2) Å]. Another *p*-tolylmethylidyne ligand bridges the W(2)–Ir edge of the triangle [W(2)–C(10) 1.90(2), Ir–C(10) 2.06(2) Å]. The W(1) atom carries a terminal Cl ligand [W(1)–Cl 2.450(7) Å], a CO group deviating slightly from linearity [W(1)–C(1)–O(1) 174(2)°], and a $\mathrm{C_5H_5}$ moiety. A $\mathrm{C_5H_5}$ fragment and a CO ligand [W(2)–C(2)–O(2) 169(2)°] are co-ordinated to W(2). The two CO groups are essentially linearly bonded to the iridium atom.

Several aspects of the structure of (**2**) deserve comment. The presence in the molecule of alkylidyne ligands which both edge- and triply-bridged a closed metal triangle is of interest, since until recently such species were rare. The first examples of trimetal clusters with this structural feature were the ditungsten–rhenium compounds $[\mathrm{W_2Re}(\mu\text{-}\mathrm{Br})(\mu\text{-}\mathrm{L})(\mu\text{-}\mathrm{CR})(\mu_3\text{-}\mathrm{CR})(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})_2]$ (L = CO or O, R = $\mathrm{C_6H_4Me}$-4),[12] but subsequently the ditungsten–osmium complexes $[\mathrm{W_2Os}(\mu\text{-}\mathrm{CR})(\mu_3\text{-}\mathrm{CR})(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5H_5})_2]$, $[\mathrm{W_2Os}(\mu\text{-}\mathrm{H})(\mu\text{-}\mathrm{CR})(\mu_3\text{-}\mathrm{CR})\mathrm{H}(\mathrm{CO})_4(\eta\text{-}\mathrm{C_5H_5})_2]$ (R = $\mathrm{C_6H_4Me}$-4) were described.[13] Recently tetranuclear cluster compounds $[\mathrm{W_3Ru}(\mu\text{-}\mathrm{CR})_2(\mu_3\text{-}\mathrm{CR})(\mu\text{-}\mathrm{CO})(\mu_3\text{-}\eta\text{-}\mathrm{CO})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})_3]$ (R = Ph or $\mathrm{C_6H_4Me}$-4) with a tungsten-spiked $\mathrm{W_2Ru}$ core have been reported, with the $\mathrm{W_2Ru}$ triangle capped and edge-bridged by alkylidyne groups.[6]

Compound (**2**) has 46 valence electrons, and is therefore less unsaturated than compound (**1**). In accord with this property, the W–W separation in (**2**) [2.951(1) Å] is appreciably longer than that in (**1**) [2.666(1) Å]. Moreover, the W–Cl distances in the two species [(**1**) 2.379(3), (**2**) 2.450(7) Å] follow the same

Table 4. Selected internuclear distances (Å) and angles (°) for $[\mathrm{W_2Ir}(\mu\text{-}\mathrm{CC_6H_4Me\text{-}4})(\mu_3\text{-}\mathrm{CC_6H_4Me\text{-}4})\mathrm{Cl}(\mathrm{CO})_4(\eta\text{-}\mathrm{C_5H_5})_2]$ (**2**) with estimated standard deviations in parentheses

W(1)–W(2)	2.951(1)	W(1)–Ir	2.867(1)	W(1)–Cl	2.450(7)	W(1)–C(1)	1.98(3)
W(1)–C(20)	2.04(2)	W(2)–Ir	2.698(1)	W(2)–C(2)	2.20(2)	W(2)–C(10)	1.90(2)
W(2)–C(20)	2.07(2)	Ir–C(3)	1.88(3)	Ir–C(4)	1.87(3)	Ir–C(10)	2.06(2)
Ir–C(20)	2.19(2)	C(1)–O(1)	1.1(3)	C(2)–O(2)	1.1(3)	C(3)–O(3)	1.2(3)
C(4)–O(4)	1.1(3)	W(1)–C(cp) range	2.27(2)—2.42(2)			W(2)–C(cp) range	2.36(2)—2.37(2)
W(2)–W(1)–Ir	55.2(1)	W(2)–W(1)–Cl	83.2(2)	Ir–W(1)–Cl	135.7(2)	W(2)–W(1)–C(1)	119.9(7)
Ir–W(1)–C(1)	95.2(7)	Cl–W(1)–C(1)	93.1(7)	W(2)–W(1)–C(20)	44.4(5)	Ir–W(1)–C(20)	49.6(6)
Cl–W(1)–C(20)	91.2(6)	C(1)–W(1)–C(20)	76.0(8)	W(1)–W(2)–Ir	60.8(1)	W(1)–W(2)–C(2)	71.3(6)
Ir–W(2)–C(2)	97.8(6)	W(1)–W(2)–C(10)	100.9(6)	Ir–W(2)–C(10)	49.6(6)	C(2)–W(2)–C(10)	85(1)
W(1)–W(2)–C(20)	43.5(6)	Ir–W(2)–C(20)	52.7(5)	C(2)–W(2)–C(20)	114.7(8)	C(10)–W(2)–C(20)	101.6(8)
W(1)–Ir–W(2)	64.0(1)	W(1)–Ir–C(3)	122(1)	W(2)–Ir–C(3)	132.5(8)	W(1)–Ir–C(4)	88.5(9)
W(2)–Ir–C(4)	134.2(7)	C(3)–Ir–C(4)	93(1)	W(1)–Ir–C(10)	99.6(7)	W(2)–Ir–C(10)	44.5(6)
C(3)–Ir–C(10)	91.6(9)	C(4)–Ir–C(10)	167(1)	W(1)–Ir–C(20)	45.0(5)	W(2)–Ir–C(20)	48.6(5)
C(3)–Ir–C(20)	167(1)	C(4)–Ir–C(20)	85.8(9)	C(10)–Ir–C(20)	92.6(8)	W(1)–C(1)–O(1)	174(2)
W(2)–C(2)–O(2)	169(2)	Ir–C(3)–O(3)	175(2)	Ir–C(4)–O(4)	176(3)	W(2)–C(10)–Ir	85.9(9)
W(2)–C(10)–C(11)	142(1)	Ir–C(10)–C(11)	132(1)	W(1)–C(20)–W(2)	92.1(8)	W(1)–C(20)–Ir	85.4(6)
W(2)–C(20)–Ir	78.7(6)	W(1)–C(20)–C(21)	139(1)	W(2)–C(20)–C(21)	122(1)	Ir–C(20)–C(21)	120(1)

trend. As with (**1**), the structural formula of (**2**) has been depicted with a W=Ir bond, but this is merely a formalism to assign an 18-electron configuration at the two metal centres involved. Hence in (**2**), as in (**1**), it should be assumed that the electron deficiency is associated with the cluster as a whole, and not with particular metal centres.

Having established the structure of (**2**), the spectroscopic data can be readily interpreted. The i.r. spectrum shows (Table 1) four terminal CO stretching bands. There is also an absorption at 281 cm^{-1} assignable to a W–Cl stretch. The n.m.r. data (Table 2) are in agreement with the structure established by *X*-ray diffraction. The ^{1}H spectrum shows resonances due to two Me-4 and two C_5H_5 groups in different environments. The ^{13}C-{^{1}H} n.m.r. spectrum has resonances due to the ligated alkylidyne carbon nuclei at δ 339.7 and 267.0 p.p.m. The chemical shift of the former is in the range expected for an alkylidyne ligand edge-bridging a metal–metal bond, and the latter in the range anticipated for a triply bridging alkylidyne group. In general, μ-C resonances occur in the range 300—400 p.p.m., and μ_3-C signals in the range 250—300 p.p.m., depending on the metal atoms involved.[3–7]

In the ^{13}C-{^{1}H} n.m.r. spectrum of (**2**), resonances for CO ligands occur at δ 241.6 and 235.6 p.p.m., W(CO), and at 190.4 and 181.1 p.p.m., Ir(CO). The non-equivalent C_6H_4 fragments give rise to ten peaks in the range 165.6—126.0 p.p.m. Thus as with compound (**1**) (see above) there is restricted rotation about one of the μ-C–C_6H_4 bonds. As expected, the ^{13}C-{^{1}H} n.m.r. spectrum of (**2**) also shows two C_5H_5 and two Me-4 peaks (Table 2).

The formulation proposed for complex (**3**) is based on microanalysis, and the spectroscopic data. The ^{13}C-{^{1}H} n.m.r. spectrum (Table 2) was especially informative in the CO ligand region showing one resonance for the WCO group (δ 220.5 p.p.m.) and three peaks for the $Ir(CO)_3$ moiety (δ 175.0, 174.2, and 172.3 p.p.m.). This contrasts with the spectra of (**2**) and (**4**), both of which show two IrCO signals. The spectrum of (**3**) also reveals characteristic resonances for the μ-*C*R (δ 370.7 p.p.m.) and μ_3-*C*R (δ 253.7 p.p.m.) ligands. Interestingly, the resonance at δ 370.7 p.p.m. is more deshielded than the corresponding signals in the spectra of (**2**) (δ 339.7 p.p.m.) and (**4**) (349.3 p.p.m.), but is close to that observed for the bridging μ-tolylmethylidyne carbon nucleus in the structurally related compound $[W_2Re(\mu\text{-Br})(\mu\text{-CR})(\mu_3\text{-CR})(\mu\text{-CO})(CO)_3(\eta\text{-}C_5H_5)_2]$ in which the μ-*C*R group also bridges a formally unsaturated W=W bond.

As expected, both the ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra of complex (**3**) show peaks for two non-equivalent C_5H_5 and two non-equivalent Me-4 groups. In the i.r. spectrum (Table 1) there are four bands due to terminal CO ligands. A strong absorption at 309 cm^{-1} can be assigned to a W–Cl stretch, but the assignment is not unequivocal since there are other bands (weak) in this region. However, these are probably due to the organic groups present in the molecule.

Compound (**3**) readily decomposes on refluxing in thf. It had been thought that either complex (**2**) or (**3**) on heating might have afforded (**1**) *via* coupling of the alkylidyne ligands,[10,11,13] but this property was not observed. Solutions of (**2**) in CH_2Cl_2 at room temperature react reversibly with CO to give a product with $\nu_{max.}$(CO) at 2 056m, 2 003vs, 1 940w, and 1 880w br cm^{-1} (in CH_2Cl_2). However, this species was not isolated, and if the CO-saturated solutions of (**2**) are allowed to remain at room temperature for several days a slow conversion occurs to give compound (**4**), in $>80\%$ yield. This result may explain why compound (**2**) is not formed in the reaction between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}4)]$ but is formed in the reaction between the *p*-tolylmethylidyne tungsten compound and $[IrCl(CO)(\eta\text{-}C_8H_{14})_2]$. The latter is less rich in CO groups than $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}4)]$, and so CO released from the latter could promote the isomerisation. Moreover, once compound (**4**) is formed it does not react with CO even though it is formally unsaturated.

Compound (**4**) remains unchanged on refluxing in thf, and is also unaffected by u.v. irradiation, there being no evidence for conversion into (**1**) or other species. Complex (**4**) is characterised by the data given in Tables 1 and 2, and has been depicted with a W=Ir bond to emphasise the unsaturation of the cluster (46 valence electrons). The structure is very similar to that of (**2**), differing only in site exchange of the Cl and a CO group. The spectroscopic data are in agreement with the proposed structure. In particular, the ^{13}C-{^{1}H} n.m.r. spectrum (Table 2) shows resonances for μ-CR (δ 349.3), μ_3-CR (δ 275.1), W(CO) (δ 220.1 and 215.0), and Ir(CO) (δ 190.6 and 181.6 p.p.m.) fragments. The appearance of ten resonances for the C_6H_4 groups indicates that for one of these moieties there must be restricted rotation about one of the μ-C–C_6H_4 bonds as occurs also with compounds (**1**) and (**2**). The observation of nine rather than ten signals for the C_6H_4 groups in (**3**) evidently results from some overlap of peaks.

Evidence for the structure of (**4**) is further provided by the spectroscopic properties of its PPh_3 derivative $[W_2Ir(\mu\text{-CR})(\mu_3\text{-CR})Cl(CO)_3(PPh_3)(\eta\text{-}C_5H_5)_2]$ (**6**), data for which are given in Tables 1 and 2. In contrast with the ^{13}C-{^{1}H} n.m.r. spectrum of (**4**), which shows four CO resonances for the four non-equivalent carbonyl ligands on the tungsten and iridium centres, the spectrum of (**6**) shows three CO peaks. Moreover, on the basis of their chemical shifts these may be assigned to a $W(CO)_2$ and a $Ir(CO)(PPh_3)$ group, respectively. The ^{31}P-{^{1}H} n.m.r. spectrum of (**6**) (in $CDCl_3$, at room temperature) showed a singlet resonance at δ 29.3 p.p.m., [relative to 85% H_3PO_4 (external)], and the absence of $^{31}P\text{–}^{183}W$ satellite peaks establishes that the PPh_3 group ligates the Ir and not a W atom. The ^{31}P-{^{1}H} resonance for a $W(PPh_3)$ group is characterised by *J*(WP) values of *ca.* 200 Hz.[14]

The presence of the PPh_3 group in compound (**6**) results in ^{31}P–μ-*C*R coupling in the ^{13}C-{^{1}H} n.m.r. spectrum. Thus the resonance (δ 345.0 p.p.m.) for the ligating carbon nucleus of the *p*-tolylmethylidyne group edge-bridging the metal triangle appears as a doublet [*J*(PC) 6 Hz]. This observation strongly supports a formulation for (**6**), and by implication for (**4**) also, in which the μ-CR group bridges a W–Ir bond rather than the W–W bond.

The tetranuclear metal compound $[W_2Ir_2(\mu_4\text{-}RC_2R)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (**5**) also formed in the reactions between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[IrCl(CO)(\eta\text{-}C_8H_{14})_2]$ or $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}4)]$ has been reported previously,[15] having been prepared by refluxing mixtures of the cluster compound $[W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$ with RC≡CR in dichloromethane. Compound (**5**), and the analogue obtained from $[W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$ and PhC≡CPh,[15] have a 'butterfly' core of metal atoms with a μ_4-alkyne bridge. Two of the tungsten–iridium bonds are bridged by CO groups. The i.r. spectrum of (**5**) in the carbonyl stretching region shows seven bands (Table 1) two of which (1 814 and 1 766 cm^{-1}) are in the bridging region. Another species structurally similar to (**5**) is the tetracobalt cluster $[Co_4(\mu_4\text{-}HC_2H)(\mu\text{-}CO)_2(CO)_8]$, prepared by treating $[Co_4(CO)_{12}]$ with HC≡CH.[16]

The mechanisms by which the various compounds (**1**)—(**5**) are formed are evidently complex, and the different pathways are not evident at the present time. However, on the basis of the earlier work, leading to the synthesis of the dimetal tungsten–iridium compounds listed in the Introduction, it seems very likely that dimetal species are produced initially in the synthesis of (**1**)—(**5**). Depending on the iridium reagent used, these intermediates might be the dimetallacyclopropene complexes $[(\eta\text{-}C_5H_5)(OC)_2\overline{W(\mu\text{-CR})Ir}Cl(CO)_2]$ or $[(\eta\text{-}C_5H_5)\text{-}$

$(OC)_2\overline{W(\mu\text{-}CR)Ir}Cl(CO)(\eta\text{-}C_8H_{14})]$. Loss of the cyclo-octene ligand from the latter *via* its displacement by a molecule of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ would readily provide a route to one or other of the trimetal compounds (**1**)—(**4**), after release of a CO group at some stage. Similarly, $[(\eta\text{-}C_5H_5)(OC)_2\overline{W(\mu\text{-}CR)Ir}Cl(CO)_2]$ could also combine with additional $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$, and with release of CO afford (**1**), (**3**), or (**4**). As mentioned earlier, the absence of (**2**) in syntheses when the reagent $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}4)]$ is used is understandable since the former would release additional carbon monoxide, which facilitates isomerisation of (**2**) into (**4**).

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 atmosphere. The i.r. spectra were measured with Nicolet 10-MX and 5Z-DX spectrophotometers, and n.m.r. spectra with JNM FX 90Q, GX 270, and GX 400 instruments. Florisil used for column chromatography was Aldrich 100—200 mesh. The compounds $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$,[17] $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}4)]$,[18] and $[IrCl(CO)(\eta\text{-}C_8H_{14})_2]$[19] were prepared by methods previously described. Analytical and other data for the new compounds are listed in Table 1.

Reaction between $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ *and* $[IrCl(CO)(\eta\text{-}C_8H_{14})_2]$.—A mixture of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.41 g, 1 mmol) and $[IrCl(CO)(\eta\text{-}C_8H_{14})_2]$ (0.24 g, 0.50 mmol) was stirred in thf (40 cm^3) at room temperature for *ca.* 40 h, affording a dark brown-green solution. Solvent was removed *in vacuo*, and the residue was extracted with thf–light petroleum (15 × 5 cm^3, 1:9) and the extracts chromatographed (2 × 40 cm column) at −40 °C. Elution with the same solvent mixture separated four fractions which were orange, purple, orange, and grey-green in colour. Removal of solvent *in vacuo* from the first fraction yielded only a trace of unidentified material. The purple eluate afforded black *microcrystals* of $[W_2Ir\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}Cl(CO)_4(\eta\text{-}C_5H_5)_2]$ (**1**) (0.076 g), the third eluate gave red *microcrystals* of $[W_2Ir(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**) (0.04 g), and the grey-green fraction gave green *microcrystals* of $[W_2Ir(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$ (**3**) (0.065 g). Further elution of the chromatography column with thf–light petroleum, increasing the proportion of thf to 1:4 and finally to 1:1, led, respectively, to the recovery of two green fractions. Removal of solvent *in vacuo* from the first eluate afforded dark green *microcrystals* of $[W_2Ir(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)Cl(CO)_4(\eta\text{-}C_5H_5)_2]$ (**4**) (0.082 g), and from the second eluate green *microcrystals* of $[W_2Ir_2\{\mu_4\text{-}C_2(C_6H_4Me\text{-}4)_2\}(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (**5**) (0.014 g) were isolated. Crystals of (**5**) may be obtained from CH_2Cl_2–light petroleum (1:4).

Reaction between $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ *and* $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}4)]$.—A mixture of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.24 g, 0.60 mmol) and $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}4)]$ (0.12 g, 0.30 mmol) was stirred in thf (30 cm^3) for *ca.* 60 h at room temperature. Solvent was removed *in vacuo*, and the residue extracted with thf–light petroleum (10 × 5 cm^3, 1:9). The extracts were chromatographed (2 × 40 cm column) at −40 °C. Elution with thf–light petroleum (1:9) removed in sequence pink, orange, brown, and purple bands. The first three eluates each afforded less than 15 mg of product, and the purple fraction, after removal of solvent, gave 20 mg of a mixture of compound (**1**) and an unidentified species with $\nu_{max.}(CO)$ at 2 021s, 1 972vs, 1 946w, and 1 820w br cm^{-1} (in thf). The pink eluate yielded *ca.* 15 mg of a red powder with $\nu_{max.}(CO)$ at 2 049w, 2 004m, 1 986m, 1 950w, 1 926vs, and 1 841w cm^{-1} (in light petroleum). Further elution of the column with thf–light petroleum (1:4) led to grey-green and green eluates which, after removal of solvent *in vacuo*, gave green *microcrystals* of (**3**) (0.03 g) and green *microcrystals* of (**4**) (0.05 g). Final elution with thf–light petroleum (1:1) afforded green *microcrystals* of compound (**5**) (0.008 g).

Table 5. Atomic positional parameters (fractional co-ordinates × 10^4), for complex (**1**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ir	1 899(1)	9 044(1)	1 124(1)
W(1)	1 326(1)	7 064(1)	581(1)
W(2)	434(1)	7 634(1)	1 883(1)
C(1)	−318(8)	6 582(10)	1 439(6)
O(1)	−832(6)	5 917(7)	1 284(4)
C(2)	−211(9)	8 826(10)	1 453(6)
O(2)	−686(7)	9 462(7)	1 233(5)
C(3)	2 492(10)	9 974(11)	1 681(7)
O(3)	2 808(9)	10 542(8)	2 046(6)
C(4)	1 732(9)	10 170(10)	507(7)
O(4)	1 676(10)	10 817(8)	101(6)
Cl	1 668(2)	5 170(2)	660(1)
C(11)	696(10)	6 410(10)	−376(6)
C(12)	117(10)	7 317(11)	−123(6)
C(13)	724(10)	8 230(11)	−193(5)
C(14)	1 705(10)	7 899(12)	−529(6)
C(15)	1 681(11)	6 791(13)	−651(6)
C(21)	−364(12)	8 649(12)	2 859(7)
C(22)	−920(10)	7 683(14)	2 832(6)
C(23)	−339(10)	6 796(12)	2 925(6)
C(24)	625(11)	7 201(13)	3 006(6)
C(25)	593(14)	8 327(13)	2 969(6)
C(30)	2 684(7)	7 580(8)	709(5)
C(31)	3 752(7)	7 488(8)	363(5)
C(32)	4 435(8)	8 315(10)	365(6)
C(33)	5 430(9)	8 237(11)	−6(7)
C(34)	5 788(10)	7 323(10)	−409(7)
C(35)	5 084(9)	6 454(11)	−384(7)
C(36)	4 078(9)	6 555(10)	−18(7)
C(37)	6 824(11)	7 224(12)	−842(10)
C(40)	2 138(7)	7 485(8)	1 434(5)
C(41)	2 709(8)	6 964(9)	1 957(5)
C(42)	2 717(11)	5 854(10)	2 070(7)
C(43)	3 258(12)	5 442(11)	2 532(8)
C(44)	3 755(10)	6 045(11)	2 921(7)
C(45)	3 764(12)	7 157(13)	2 807(7)
C(46)	3 238(9)	7 618(10)	2 336(6)
C(47)	4 311(12)	5 548(16)	3 462(8)
C(9)	3 785(40)	3 513(24)	8 685(25)
Cl(1)	3 746(8)	4 627(8)	8 549(6)
Cl(2)	3 076(9)	2 439(7)	8 514(7)

Reaction between Compound (**4**) *and* PPh_3.—A mixture of complex (**4**) (0.084 g, 0.080 mmol) and PPh_3 (0.026 g, 0.10 mmol) was stirred in thf (15 cm^3) at room temperature for 20 min, affording a dark brown solution. Solvent was removed *in vacuo*, and the residue was suspended in thf–light petroleum (3 × 10 cm^3, 1:4) and chromatographed (1.5 × 15 cm column) at *ca.* 10 °C. Elution with the same solvent mixture removed traces of unidentified material. Elution with thf–light petroleum (3:1) gave a brown eluate which after removal of solvent *in vacuo* afforded black *microcrystals* of $[W_2Ir(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)Cl(CO)_3(PPh_3)(\eta\text{-}C_5H_5)_2]$ (**6**) (0.089 g).

Crystal Structure Determination of Complex (**1**).—Crystals of complex (**1**) were grown from CH_2Cl_2–light petroleum as dark red prisms. Diffracted intensities were collected at 293 K on a Nicolet $P2_1$ diffractometer from a crystal of dimensions *ca.* 0.45 × 0.44 × 0.30 mm. Of the 6 123 unique data collected

Table 6. Atomic positional parameters (fractional co-ordinates × 10^4) for complex (**2**), with estimated standard deviations in parentheses

Atom	x	y	z
W(1)	285(1)	7 440(1)	3 984(1)
W(2)	1 806(1)	8 686(1)	2 955(1)
Ir	2 465(1)	8 093(1)	4 269(1)
Cl	−677(6)	7 160(5)	2 876(4)
C(1)	569(21)	5 940(20)	4 111(12)
O(1)	712(19)	5 112(14)	4 247(10)
C(2)	531(21)	9 579(18)	3 349(11)
O(2)	−87(18)	10 205(15)	3 508(10)
C(3)	2 727(27)	8 837(19)	5 127(14)
O(3)	2 847(22)	9 244(16)	5 691(9)
C(4)	2 649(24)	6 810(20)	4 722(12)
O(4)	2 802(22)	6 066(16)	5 009(9)
C(10)	2 606(20)	9 423(16)	3 634(11)
C(11)	3 096(13)	10 490(8)	3 770(8)
C(12)	2 590	11 357	3 489
C(13)	2 950	12 353	3 650
C(14)	3 817	12 482	4 092
C(15)	4 324	11 615	4 373
C(16)	3 964	10 619	4 212
C(17)	4 144(29)	13 584(23)	4 303(16)
C(20)	1 786(18)	7 203(14)	3 391(10)
C(21)	2 454(12)	6 308(9)	3 004(7)
C(22)	1 878	5 507	2 694
C(23)	2 459	4 684	2 334
C(24)	3 617	4 661	2 284
C(25)	4 194	5 462	2 594
C(26)	3 612	6 285	2 954
C(27)	4 149(25)	3 715(20)	1 891(13)
C(31)	−363(18)	7 311(17)	5 204(12)
C(32)	−245	8 387	5 039
C(33)	−1 040	8 655	4 547
C(34)	−1 649	7 746	4 408
C(35)	−1 230	6 915	4 814
C(41)	1 840(18)	9 694(11)	1 867(11)
C(42)	1 117	8 841	1 788
C(43)	1 759	7 916	1 769
C(44)	2 879	8 197	1 836
C(45)	2 929	9 296	1 896

(ω–2θ scans, 2θ ⩽ 50°), 4 697 had $I \geqslant 2.5\sigma(I)$, and only these were used in the structure solution and refinement. The data were corrected for Lorentz, polarisation, and X-ray absorption effects, the latter by an empirical method based on azimuthal scan data.[20]

Crystal data. $C_{31}H_{26}Cl_3IrO_4W_2$, M = 1 128.8, monoclinic, a = 13.443(3), b = 12.261(2), c = 19.534(2) Å, β = 77.76(1)°, U = 3 146.6(9) Å^3, Z = 4, D_c = 2.38 g cm^{-3}, $F(000)$ = 2 080, space group $P2_1/c$, Mo-K_α X-radiation (graphite monochromator, λ = 0.710 69 Å), μ(Mo-K_α) = 119.5 cm^{-1}.

The structure was solved by conventional heavy-atom methods, and difference Fourier syntheses were used to locate all non-hydrogen atoms, which were refined with anisotropic thermal parameters. Aromatic hydrogen atoms were included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters *ca.* 1.2 $U_{\text{equiv.}}$ of the parent carbon atom. Refinement by blocked-cascade least squares, with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,4|F|^2]$, led to R = 0.041 (R' = 0.041). The final electron-density difference synthesis showed no peaks ⩾1.4 or ⩽ −1.4 e Å^{-3}.

Crystal Structure Determination of Complex (**2**).—Crystals of (**2**) were plate-like and of poor quality even after several attempts to grow suitable specimens form various proportions of CH_2Cl_2–light petroleum and other solvents. Moreover, the majority of the crystals examined were not single. That used for data collection may have had a small misaligned sub-crystal present, since a number of weak intensities were observed at low angle, which could not be reconciled with the main lattice. The structural analysis, whilst qualitatively correct, must therefore be treated with some caution. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.62 × 0.55 × 0.15 mm. Of the 4 072 unique data obtained (Wyckoff ω scans, 2θ ⩽ 45°), 2 584 had $I \geqslant 2.5\sigma(I)$, and only these were used in the structure solution and refinement. The data were corrected for Lorentz, polarisation, and X-ray absorption effects, the latter by an empirical method based on azimuthal scan data.[20]

Crystal data. $C_{30}H_{24}ClIrO_4W_2$, M = 1 043.9, monoclinic, a = 12.102(7), b = 12.870(8), c = 18.101(5) Å, β = 83.97(4)°, U = 2 804(3) Å^3, Z = 4, D_c = 2.47 g cm^{-3}, $F(000)$ = 1 912, space group $P2_1/c$, μ(Mo-K_α) = 132.1 cm^{-1}.

The structure was solved as for compound (**1**). Aromatic rings were included as rigid isotropic groups [C–C(tolyl) 1.395 and C–C(cyclopentadienyl) 1.42 Å] and hydrogen atoms were not included in the refinement. All remaining atoms were refined with anisotropic thermal parameters, Final R = 0.063 (R' = 0.063) with $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$. The comparatively poor level of refinement and large residuals (*ca.* 1.9 e Å^{-3}) reflect poor crystal quality and large X-ray absorption effects.

For both structure determinations, all calculations were carried out with an 'Eclipse' Data General computer, using the SHELXTL system of programs.[20] Scattering factors and corrections for anomalous dispersion are from ref. 21. Atomic co-ordinates for compounds (**1**) and (**2**) are given in Table 5 and 6, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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