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Mixed-metal cluster chemistry.[☆] Part 17. Syntheses of $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ and its reactivity towards diphenylacetylene

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Abstract

The X-ray structurally confirmed tetrahedral mixed-metal cluster $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (**1**) is prepared in 8% yield from reactions between $[W(CO)_3(\eta\text{-}C_5H_4Me)]^-$ and $IrCl(CO)_2$(*p*-toluidine) under an Ar atmosphere, and in 46% yield from reaction between $WH(CO)_3(\eta\text{-}C_5H_4Me)$ and $IrCl(CO)_2$(*p*-toluidine) under a CO atmosphere; both reactions also afford tetrahedral $W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_4Me)_2$ (**2**). Cluster **1** reacts with diphenylacetylene to afford three products, namely tetrahedral $WIr_3(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(CO)_7(\eta\text{-}C_5H_4Me)$ (**3**), butterfly $WIr_3\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5(\eta\text{-}C_5H_4Me)$ (**4**) and the binuclear product $Ir_2\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$ (**5**); X-ray studies of **4** and **5** reveal a common (iridacyclopentadienyl)iridium structural motif. © 2001 Published by Elsevier Science B.V.

Keywords: Tungsten; Iridium; Carbonyl; Cyclopentadienyl; Clusters; Alkyne

1. Introduction

Combining metals possessing widely differing electron counts to afford mixed-metal clusters, and studies of the structure, reactivity and properties of the resultant clusters, is a subject of significant current interest [2–8]. The tetrahedral mixed-metal clusters $MIr_3(CO)_{11}(\eta\text{-}C_5H_5)$ and $M_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2$ (M = Mo, W) are pivotal examples; originally prepared as precursors to supported bimetallic catalysts with well defined stoichiometries [9,10], they have been the subject of structure [11–14], reactivity [15–28], and fluxionality [29,30] studies. Replacing the cyclopentadienyl ring with a methylcyclopentadienyl ligand in these clusters may be expected to enhance solubility in organic solvents, provide alternative paths to crystallization (due to the decrease in symmetry), and possibly modify reactivity (due to the more electron-releasing $\eta\text{-}C_5H_4Me$ ligand). We present herein two synthetic procedures to afford $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$, and examination of its reactivity with diphenylacetylene, which affords inter alia the (iridacyclopentadienyl)iridium complex $Ir_2\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$ (**5**).

2. Results and discussion

2.1. Syntheses of $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (1)

The Group 6–Group 9 mixed-metal clusters $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (**1**) (8%) and the previously reported [31] $W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_4Me)_2$ (**2**) (81%) are formed when $IrCl(CO)_2$(*p*-toluidine) is reacted with an excess of $[W(CO)_3(\eta\text{-}C_5H_4Me)]^-$ (Scheme 1). Reacting $IrCl(CO)_2$(*p*-toluidine) with $WH(CO)_3(\eta\text{-}C_5H_4Me)$ provides **1** in greater yield (46%) (Scheme 1). Complex **1** was characterized by IR, ^{1}H-NMR spectroscopy, and secondary ion (SI) mass spectrometry. The solution IR spectrum for **1** in cyclohexane indicates the presence of terminal carbonyl ligands and shows no evidence for bridging carbonyl ligands. The ^{1}H-NMR spectrum con-

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[☆] For part 16 see Ref. [1].

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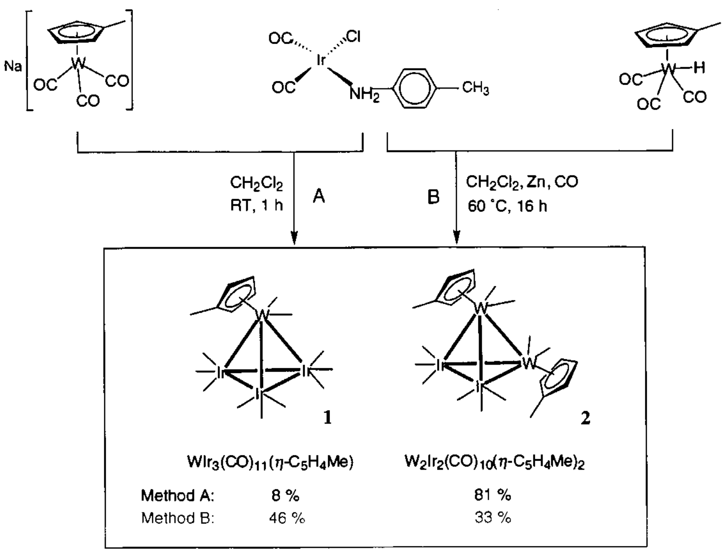


Scheme 1. Syntheses of $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (**1**) and $W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_4Me)_2$ (**2**).

tains two triplets of equal intensity at 5.06 and 5.45 ppm, indicative of a methylcyclopentadienyl group. The mass spectrum contains a molecular ion and consecutive loss of eleven carbonyl ligands. The identity of **1** was confirmed by a single-crystal X-ray study.

2.2. X-ray structural study of $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (1)

Fig. 1 shows an ORTEP plot of **1** indicating the molecular structure and the atomic labelling scheme, and Table 1 lists significant bond lengths and angles. Cluster **1** has a tetrahedral geometry, with the tungsten ligated by one methylcyclopentadienyl group and two carbonyl ligands, and each iridium possessing three terminal carbonyl ligands; it contains 60 cluster valence electrons, is electron precise for a tetrahedral geometry, and is one of the few tetrahedral cluster complexes held together solely by metal–metal bonds. The metal core bonding distances are similar to those of the cyclopentadienyl analogue [11].

2.3. Reaction of $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (1) with diphenylacetylene

Heating a mixture of $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (**1**) and excess diphenylacetylene in refluxing toluene affords three products identified as $WIr_3(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(CO)_7(\eta\text{-}C_5H_4Me)$ (**3**) (31%), $WIr_3(\mu_3\text{-}CPh)\{\mu_3\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(\mu\text{-}CPh)(CO)_5(\eta\text{-}C_5H_4Me)$ (**4**) (39%) and $Ir_2\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$ (**5**) (13%) (Scheme 2). Cluster **3** was characterized by IR and ^1H-NMR spectroscopy, and SI MS. The solution IR spectrum contains six $\nu(CO)$ bands, all in the terminal carbonyl region 2057–1967 cm^{-1}. The ^1H-NMR spectrum contains phenyl proton resonances at 7.23–6.92 ppm, two singlets for the cyclopentadienyl rings at 3.48 and 3.32 ppm, and a resonance for the methyl group of the cyclopentadienyl ligand located at 2.11 ppm. The mass spectrum is consistent with the molecular ion being $WIr_3(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(CO)_7(\eta\text{-}C_5H_4Me)$, and shows sequential loss of seven carbonyl ligands. The cyclopentadienyl analogue of this compound has been structurally characterized [16], showing the cluster to contain a WIr_3 tetrahedral framework with two intact diphenylacetylene ligands, a η^5-coordinated cy-

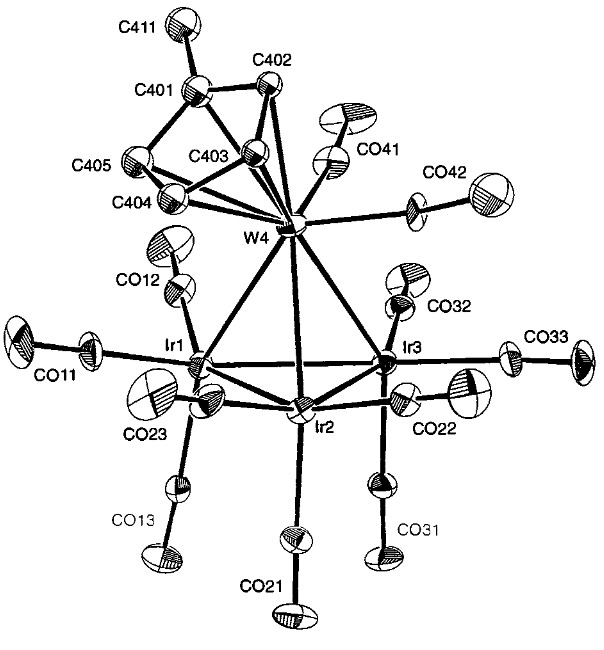
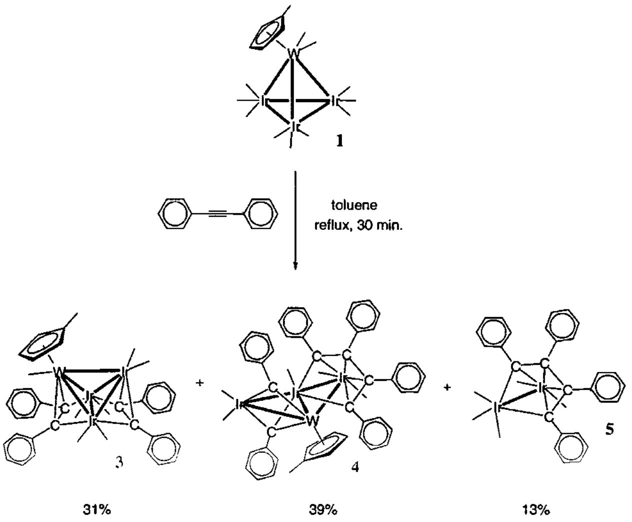


Fig. 1. ORTEP plot of $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (**1**) showing the molecular structure and atomic labelling scheme. Displacement ellipsoids are shown at the 30% probability level for the non-hydrogen atoms.

Table 1
Selected bond lengths (Å) and angles () for $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (**1**)

Bond lengths			
Ir1–Ir2	2.6973(7)	Ir3–C33	1.93(1)
Ir1–Ir3	2.7008(7)	W4–C41	2.00(1)
Ir1–W4	2.8028(7)	W4–C42	1.92(1)
Ir2–Ir3	2.7008(7)	O11–C11	1.18(2)
Ir2–W4	2.8089(7)	O12–C12	1.12(2)
Ir3–W4	2.8582(6)	C13–C13	1.11(2)
Ir1–C11	1.86(1)	O21–C21	1.13(1)
Ir1–C12	1.90(1)	O22–C22	1.13(2)
Ir1–C13	1.96(1)	O23–C23	1.14(2)
Ir2–C21	1.93(1)	O31–C31	1.15(1)
Ir2–C22	1.90(1)	C32–C32	1.12(1)
Ir2–C23	1.87(1)	C33–O33	1.10(1)
Ir3–C31	1.89(1)	O41–C41	1.12(2)
Ir3–C32	1.92(1)	O42–C42	1.17(2)
Bond angles			
Ir2–Ir1–Ir3	60.04(2)	Ir1–C11–O11	179(2)
Ir2–Ir1–W4	61.38(2)	Ir1–C12–O12	178(1)
Ir3–Ir1–W4	62.54(2)	Ir1–C13–O13	177(1)
Ir1–Ir2–Ir3	60.04(2)	Ir2–C21–O21	178(1)
Ir1–Ir2–W4	61.16(2)	Ir2–C22–O22	179(1)
Ir3–Ir2–W4	62.46(2)	Ir2–C23–O23	177(2)
Ir1–Ir3–Ir2	59.91(2)	Ir3–C31–O31	177(1)
Ir1–Ir3–W4	60.48(2)	Ir3–C32–O32	176(1)
Ir2–Ir3–W4	60.62(2)	Ir3–C33–O33	176(1)
Ir1–W4–Ir2	57.46(2)	W4–C41–O41	172(1)
Ir1–W4–Ir3	56.98(2)	W4–C42–O42	173(1)
Ir2–W4–Ir3	56.92(2)		



Scheme 2. Syntheses of $WIr_3(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(CO)_7(\eta\text{-}C_5H_4Me)$ (**3**), $WIr_3\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5(\eta\text{-}C_5H_4Me)$ (**4**) and $Ir_2\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$ (**5**).

clopentadienyl group and seven terminal carbonyls. The alkyne ligands are bonded with their C–C bonds parallel to a metal–metal vector, the most common bonding mode of alkynes in clusters [32].

Cluster **4** was characterized by IR spectroscopy, SI MS and a single-crystal X-ray structural study. The solution IR spectrum contains three ν(CO) bands, all in the terminal carbonyl region 2042–1979 cm^{-1}. The mass spectrum is consistent with the molecular ion being $WIr_3(\mu_3\text{-}CPh)\{\mu_3\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(\mu\text{-}CPh)(CO)_5(\eta\text{-}C_5H_4Me)$, and shows the sequential loss of five carbonyl ligands. A satisfactory ^{1}H-NMR spectrum could not be obtained due to the limited quantity of material available. The yellow coloured minor product **5** was characterized by IR spectroscopy, mass spectrometry and X-ray structural determination. It is unique, in that no related product has been identified in the cyclopentadienyl-containing system. The IR spectrum contains four ν(CO) bands all within the terminal bridging region, 2097–1969 cm^{-1}. The mass spectrum is consistent with the molecular ion being $Ir_2\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$ (as revealed by the structural study below), and shows the expected carbonyl loss fragmentation.

2.4. X-ray structural studies of *$WIr_3(\mu_3\text{-}CPh)\{\mu_3\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(\mu\text{-}CPh)(CO)_5(\eta\text{-}C_5H_4Me)$* (**4**) and *$Ir_2\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$* (**5**)

The molecular structure of **4** (Fig. 2) has a 'butterfly' cluster core framework, with the η^5-methylcyclopentadienyl-ligated tungsten at the 'hinge' position and a large hinge angle of 118.19°. A C_4 fragment, most likely formed from the coupling of two diphenylacetylene molecules, forms an iridacyclopentadienyl moiety in conjunction with the hinge iridium Ir2. One phenyl-

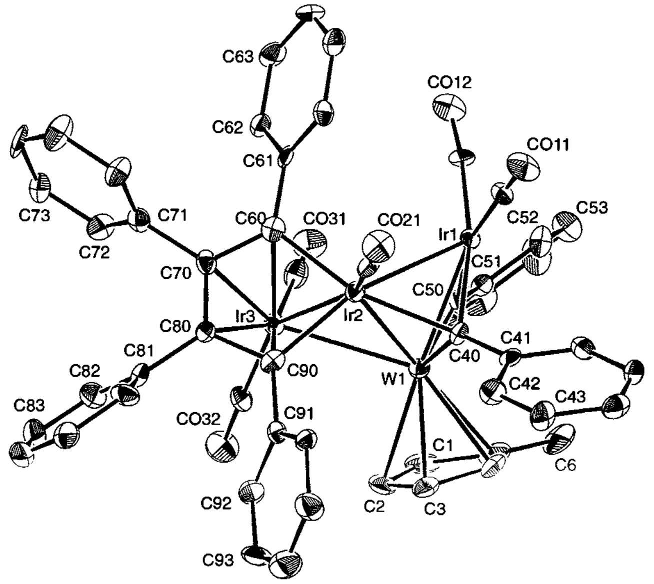


Fig. 2. ORTEP plot of $WIr_3(\mu_3\text{-}CPh)\{\mu_3\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(\mu\text{-}CPh)(CO)_5(\eta\text{-}C_5H_4Me)$ (**4**) showing the molecular structure and atomic labelling scheme. Displacement ellipsoids are shown at the 30% probability level for the non-hydrogen atoms.

Table 2
Selected bond lengths (Å) for $WIr_3(\mu_3\text{-}CPh)\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(\mu\text{-}CPh)(CO)_5(\eta\text{-}C_5H_5)$, $WIr_3(\mu_3\text{-}CPh)\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(\mu\text{-}CPh)(CO)_5(\eta\text{-}C_5H_4Me)$ (**4**) and $Ir_2\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$ (**5**)

Bond	$WIr_3(\mu_3\text{-}CPh)\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(\mu\text{-}CPh)(CO)_5(\eta\text{-}C_5H_4R)$		$Ir_2\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$ (**5**)
	R = H [16]	R = Me (**4**)	
Ir1–Ir2	2.814(3)	2.7952(6)	
Ir2–Ir3	2.644(3)	2.6525(7)	2.7199(3)
Ir1–W1	2.698(3)	2.7025(8)	
Ir2–W1	2.711(3)	2.7112(7)	
Ir3–W1	2.896(3)	2.8963(7)	
Ir1–C40	2.19(5)	2.15(1)	
Ir2–C40	2.08(4)	2.15(1)	
W1–C40	2.07(5)	1.96(1)	
Ir1–C50	2.11(5)	2.14(2)	
W1–C50	1.90(5)	1.89(1)	
Ir2–C60	2.14(5)	2.07(1)	2.084(5)
Ir3–C60	2.33(5)	2.29(2)	2.255(4)
Ir3–C70	2.31(4)	2.24(1)	2.293(4)
Ir3–C80	2.35(4)	2.27(1)	2.293(4)
Ir2–C90	2.05(4)	2.06(1)	2.097(5)
Ir3–C90	2.19(4)	2.25(1)	2.216(5)
C60–C70	1.44(6)	1.43(2)	1.417(7)
C70–C80	1.47(6)	1.40(2)	1.439(6)
C80–C90	1.40(6)	1.43(2)	1.422(7)

methylidyne group spans a W–Ir bond, while the second caps a WIr_2 face; these fragments are most likely generated by the cleavage of the C≡C bond in a diphenylacetylene molecule.

Comparison with the cyclopentadienyl-containing analogue [16] reveals the opposite absolute configuration for cluster **4**; bond lengths for both structures are listed in Table 2. The Ir1–Ir2 distance in the methylcyclopentadienyl-containing cluster is slightly shorter but other metal–metal distances are equivalent within 3σ. The better defined Ir–C bond distances for the C_4 fragment in **4** reveal lack of appreciable asymmetry in the iridacyclopentadienyl system, the Ir3–C_4 bond lengths, and the Ir2–C_4 bond lengths, being equal within 3σ error. As was seen in the cyclopentadienyl example, the μ_3-phenylmethylidyne ligand capping the W1–Ir1–Ir2 face is displaced markedly towards the W1 atom. Likewise, the μ_2-phenylmethylidyne fragment spans the W1–Ir1 vector asymmetrically with the W–C50 bond [1.89(1) Å] significantly shorter than the Ir1–C50 bond [2.14(2) Å].

Fig. 3 shows the ORTEP plot of **5**, indicating the molecular structure and atomic labelling scheme. A C_4 fragment is formed by alkyne dimerization and, in conjunction with the tricarbonyl-ligated iridium, affords an iridacyclopentadienyl system. This moiety coordinates to the second iridium in a η^5-manner, similar to the (iridacyclopentadienyl)iridium unit seen in **4**. The Ir–Ir bond distance [2.7199(3) Å] is significantly longer than the comparable Ir2–Ir3 bond in **4** [2.6524(7) Å]; this is the principle metrical difference between **5** and the corresponding sub-unit of **4** (Table 2). Bonds from Ir3 to the C_4 termini C60 and C90 are shorter in **5** than are the comparable bonds in **4**, but differences as such are within 3σ. The variation in the Ir2–C_4 bond lengths is not significant.

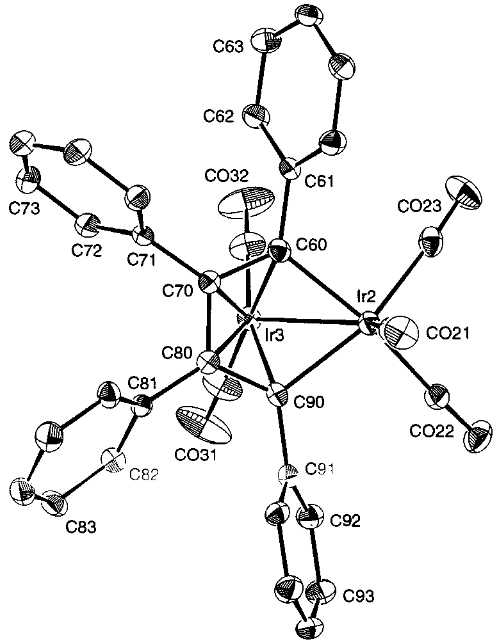


Fig. 3. ORTEP plot of $Ir_2\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$ (**5**) showing the molecular structure and atomic labelling scheme. Displacement ellipsoids are shown at the 30% probability level for the non-hydrogen atoms.

Complex **5** is of interest as an organometallic isolobal analogue of prototypical mononuclear complexes such as $Co(CO)_2(\eta\text{-}C_5H_5)$ for which the isolobal replacements $Co(CO)_2 \leftrightarrow Ir(CO)_2$, $CPh \leftrightarrow CH$, and $Ir \leftrightarrow (CO)_3CH$ have conceptually been made. The common (iridacyclopentadienyl)iridium unit in **4** and **5** suggests that the former may be a reaction intermediate en route to the latter. Difficulties attendant with obtaining sufficient pure **4** (it is separable from **3** with extreme difficulty) have thus far precluded an examination of this possibility.

2.5. Conclusions

The new tetrahedral cluster $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (**1**) is a methylcyclopentadienyl-containing analogue of a previously reported cyclopentadienyl-containing cluster. Reaction of **1** with diphenylacetylene affords a mixture of three products. Two of the products, separable with difficulty, were identified as $WIr_3(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(CO)_7(\eta\text{-}C_5H_4Me)$ (**3**) and $WIr_3\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5(\eta\text{-}C_5H_4Me)$ (**4**), methylcyclopentadienyl-containing analogues of clusters previously identified in the cyclopentadienyl system. The third product, $Ir_2\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$ (**5**), has not been observed in the cyclopentadienyl system, and is of interest as a binuclear isolobally related analogue of the classic two-legged ‘piano stool’ complex $Co(CO)_2(\eta\text{-}C_5H_5)$.

3. Experimental

Reactions were performed under an atmosphere of argon (high-purity, CIG) using standard Schlenk techniques [33]. All cluster complexes proved to be indefinitely stable in air as solids and for at least short periods of time in solution, and thus no precautions were taken to exclude air in their manipulation. All reaction solvents used were analytical reagent (AR) grade. The reaction solvents were dried and distilled under argon using standard methods: CH_2Cl_2 over CaH_2; toluene over sodium benzophenone ketyl. Petroleum spirit refers to a petroleum fraction of boiling range 60–80°C. Methylcyclopentadiene was cracked from methylcyclopentadiene dimer (Aldrich) immediately prior to use. Glacial acetic acid was purified by distillation under nitrogen from a solution containing some acetic anhydride and $KMnO_4$. The diphenylacetylene was purchased commercially from Aldrich and used as received. Literature procedures (or minor modifications thereof) were used to synthesize $IrCl(CO)_2(p\text{-toluidine})$ [34], and $Na[W(CO)_3(\eta\text{-}C_5H_4Me)]$ [35].

The products were purified by thin-layer chromatography (TLC) on 20 × 20 cm glass plates coated with Merck GF_{254} silica gel (0.5 mm). Analytical TLC, used for monitoring the extent of reaction, was carried out on aluminium sheets coated with 0.25 mm silica gel. Column chromatography was performed using Merck silica of particle size 0.063–0.200 mm.

Infrared spectra were recorded on a Perkin–Elmer system 2000 FT-IR with CaF_2 solution cells; spectral frequencies are recorded in cm^{-1}. All analytical spectra were recorded as solutions in cyclohexane (AR grade). ^1H spectra were recorded in $CDCl_3$ (Cambridge Isotope Laboratories) using a Varian Gemini-300 spectrometer (at 300 MHz) and are referenced to residual $CHCl_3$ at 7.24 ppm. Secondary ion mass spectra (SI MS) were recorded using a VG ZAB 2SEQ instrument (30 kV Cs^+ ions, current 1 mA, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix) at the Research School of Chemistry, Australian National University. All SI MS were calculated with m/z based on ^{183}W and ^{192}Ir assignments, and are reported in the form: m/z (assignment, relative intensity). Elemental microanalyses were carried out by the Microanalysis Service Unit in the Research School of Chemistry, Australian National University.

3.1. Syntheses of $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (1)

3.1.1. Method A

$Na[W(CO)_3(\eta\text{-}C_5H_4Me)]$ was prepared from Na (46.8 mg, 2.03 mmol), methylcyclopentadiene (410 mg, 5.11 mmol), and $W(CO)_6$ (543 mg, 5.10 mmol). $IrCl(CO)_2(p\text{-toluidine})$ (598 mg, 1.53 mmol) was added to the crude solid $Na[W(CO)_3(\eta\text{-}C_5H_4Me)]$ in CH_2Cl_2 (20 ml) and the mixture stirred at room temperature for 2 h. The solvent was removed in vacuo, and the resulting red–brown residue dissolved in CH_2Cl_2 (ca. 3 ml) and applied to preparative TLC plates. Elution with CH_2Cl_2–petroleum spirit (2:3) gave two major bands: orange ($R_f = 0.68$) and red ($R_f = 0.52$).

Crystallization of the contents of the first band from CH_2Cl_2–MeOH by liquid diffusion at 3°C over 24 h afforded an orange crystalline product identified as $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (**1**) (43.0 mg, 0.037 mmol, 8%). Anal. Found: C, 17.70; H, 0.65. Calc. for $C_{17}H_7Ir_3O_{11}W$: C, 17.79; H, 0.61%. IR ($c\text{-}C_6H_{12}$): ν(CO) 2091m, 2053s, 2046vs, 2028m, 1994m, 1967w cm^{-1}. ^1H-NMR: δ 5.45 (t, $J_{HH} = 2$ Hz, 2H, C_5H_4Me), 5.06 (t, $J_{HH} = 2$ Hz, 2H, C_5H_4Me), 2.25 (s, 3H, C_5H_4Me) ppm. MS (SI): 1148 ($[M]^+$, 15), 1120 ($[M-CO]^+$, 23), 1092 ($[M-2CO]^+$, 33), 1064 ($[M-3CO]^+$, 100), 1036 ($[M-4CO]^+$, 64), 1008 ($[M-5CO]^+$, 40), 980 ($[M-6CO]^+$, 39), 952 ($[M-7CO]^+$, 45), 924 ($[M-8CO]^+$, 35), 896 ($[M-9CO]^+$, 19), 868 ($[M-10CO]^+$, 13), 840 ($[M-11CO]^+$, 10).

Crystallization of the contents of the second band from CH_2Cl_2–MeOH by liquid diffusion at 3°C over 24 h afforded a deep red crystalline product that was identified as $W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_4Me)_2$ (**2**) (733 mg, 0.616 mmol, 81%). [31].

3.1.2. Method B

Excess methylcyclopentadiene (800 mg, 10 mmol) in THF (75 ml) was reacted with sodium hydride (60% in oil, 120 mg, 3.0 mmol) for 16 h with stirring. To the resulting pale orange solution was added $W(CO)_6$ (1.05 g, 3.0 mmol) and the mixture was heated at reflux for 16 h. After cooling to room temperature, glacial acetic acid (0.5 ml, 8.8 mmol) was added and the solution stirred for 1 h to form $WH(CO)_3(\eta\text{-}C_5H_4Me)$. Volatile materials were removed from the reaction mixture in vacuo, and CH_2Cl_2 (25 ml) was added to the residue. The resulting solution was transferred to a pressure bottle (glass, 250 ml) with the exclusion of oxygen, followed by addition of $IrCl(CO)_2(p\text{-toluidine})$ (430 mg, 1.1 mmol) and granular zinc (ca. 3 g). The bottle was charged with 40 psig of carbon monoxide, valved off, then heated at 60°C for 16 h. The bottle was cooled and carefully vented. The resulting solution was filtered through a small plug of cotton wool, and taken to dryness on a rotary evaporator. The red residue was transferred to a 30 × 3 cm silica column with a small quantity of CH_2Cl_2, and elution with CH_2Cl_2–petroleum spirit (1:1) gave two major bands (orange, red).

Crystallization of the contents of the first band from CH_2Cl_2–MeOH by liquid diffusion at 3°C over 72 h afforded an orange crystalline product identified as $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (**1**) (194 mg, 0.169 mmol, 46%).

Crystallization of the contents of the second band from CH_2Cl_2–MeOH by liquid diffusion at 3°C over 72 h afforded a deep red crystalline product that was identified as $W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_4Me)_2$ (**2**) (222 mg, 0.186 mmol, 33%) [31].

3.2. Reaction of $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (1) with diphenylacetylene

Diphenylacetylene (21.1 mg, 0.118 mmol) was added to an orange solution of $WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)$ (**1**) (26.2 mg, 0.023 mmol) in toluene (25 ml) and the mixture was refluxed for 40 min. The resulting red–brown solution was taken to dryness on a rotary evaporator, and the residue dissolved in a minimum of CH_2Cl_2 (ca. 3 ml) and applied to preparative TLC plates. Elution with CH_2Cl_2–petroleum spirit (3:7) gave three major bands.

The contents of the first band ($R_f = 0.59$) were crystallized from CH_2Cl_2–MeOH at −18°C to afford yellow microcrystals, which were identified as $Ir_2\{\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$ (**5**) (3.1 mg, 0.0048 mmol, 13%). IR ($c\text{-}C_6H_{12}$): ν(CO) 2097s, 2045m, 2027vs, 1969m cm^{-1}. MS (SI): 882 ($[M]^+$, 62), 854 ($[M-CO]^+$, 100), 826 ($[M-2CO]^+$, 80), 798 ($[M-3CO]^+$, 30).

The remaining bands ($R_f = 0.42$) were collected together and redeveloped a further five times on preparative TLC plates eluting with toluene–petroleum spirit (1:4), to give two separate bands.

The contents of the first band ($R_f = 0.43$) were crystallized from CH_2Cl_2–MeOH at −3°C to afford dark brown microcrystals, which were identified as $WIr_3(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(CO)_7(\eta\text{-}C_5H_4Me)$ (**3**) (9.8 mg, 0.0070 mmol, 31%). IR ($c\text{-}C_6H_{12}$): ν(CO) 2057m, 2051w, 2024vs, 2016s, 1978m, 1967w cm^{-1}. ^{1}H-NMR: δ 7.23–6.92 (m, 20H, Ph), 3.48, 3.32 (2 × s, 2 × 2H, C_5H_4Me), 2.11 (s, 3H, C_5H_4Me) ppm. MS (SI): 1394 ($[M]^+$, 20), 1366 ($[M-CO]^+$, 55), 1338 ($[M-2CO]^+$, 85), 1310 ($[M-3CO]^+$, 100), 1282 ($[M-4CO]^+$, 66), 1254 ($[M-5CO]^+$, 65), 1226 ($[M-6CO]^+$, 54), 1198 ($[M-7CO]^+$, 66).

The contents of the second band ($R_f = 0.40$) were crystallized from CH_2Cl_2–MeOH at −3°C to afford dark red microcrystals, which were identified as $WIr_3(\mu_3\text{-}CPh)\{\mu_3\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph)\}(\mu\text{-}CPh)(CO)_5(\eta\text{-}C_5H_4Me)$ (**4**) (10.6 mg, 0.0070 mmol, 39%). Anal. Found: C, 40.71; H, 2.59. Calc. for $C_{53}H_{37}Ir_3O_5W\cdot CH_2Cl_2$: C, 40.55; H, 2.48%. IR ($c\text{-}C_6H_{12}$): ν(CO) 2042s, 1997m, 1979s cm^{-1}. MS (SI): 1514 ($[M]^+$, 22), 1458 ($[M-2CO]^+$, 55), 1430 ($[M-3CO]^+$, 85), 1402 ($[M-4CO]^+$, 100), 1374 ($[M-5CO]^+$, 66).

3.3. X-ray crystallographic studies

The crystal and refinement data for compounds **1**, **4** and **5** are summarized in Table 3. Crystals suitable for X-ray structural analyses were grown by liquid diffusion techniques from CH_2Cl_2–MeOH at 276 K. For each study a single crystal was mounted on a fine glass capillary, and data were collected at 296 K (**1**) or 200 K (**4**, **5**) on a Nonius KappaCCD diffractometer using graphite-monochromated Mo–K$_\alpha$ ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by least-squares refinement [36] of N_{cell} reflections with $3.4 \leq \theta \leq 27.5°$. The reduced data [36] were corrected for absorption using numerical [37] (**1**, **5**) or multi-scan Sortav [38,39] (**4**) methods, implemented from within MAXUS [40]; equivalent reflections were merged. The structures were solved by heavy-atom Patterson methods [41] and expanded using Fourier techniques [42] within the software package TEXSAN [43]. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in idealized positions which were frequently recalculated (see variation to procedure for **1** below). The final cycle of full-matrix least-squares refinement was based on N_{obs} reflections ($I > 2\sigma(I)$) and converged to R and

Table 3
Crystallographic data and structure refinement details for **1**, **4** and **5**

	1	**4**	**5**
Empirical formula	$C_{17}H_7Ir_3O_{11}W$	$C_{53}H_{37}Ir_3O_5W \cdot CH_2Cl_2$	$C_{33}H_{20}Ir_2O_5$
M_r	1147.75	1599.32	880.96
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$ (#14)	$Pca2_1$ (#29)	$P2_1/n$ (#14)
Unit cell dimensions			
a (Å)	9.2709(1)	21.5485(4)	8.6911(2)
b (Å)	14.5699(3)	12.7462(2)	20.1638(4)
c (Å)	16.6489(4)	17.1849(3)	16.1949(3)
α (°)	90	90	90
β (°)	105.633(1)	90	97.165(1)
γ (°)	90	90	90
V (Å^3)	2165.67(7)	4720.0(1)	2815.92(9)
D_{calc} (g cm^{-3})	3.520	2.25	2.078
Crystal size (mm)	$0.20 \times 0.20 \times 0.15$	$0.30 \times 0.15 \times 0.06$	$0.47 \times 0.33 \times 0.09$
μ (mm^{-1})	23.784	11.049	9.509
θ_{max} (°)	27.49	27.51	27.46
T (K)	296	200	200
N_{cell}	25331	136989	62769
$N_{collected}$	43315	90924	12275
N_{unique}	4965	5602	6430
N_{obs}	3272	5172	4962
Absorption correction	Integration	Multi-scan	Integration
T_{min}, T_{max}	0.020, 0.087	0.150, 0.515	0.032, 0.482
No. parameters	269	585	361
R ($I>2\sigma(I)$) [a]	0.0401	0.0412	0.0316
R_w ($I>2\sigma(I)$) [b]	0.0439	0.0430	0.0345
Weighting scheme, w	$[\sigma^2(F_o)+0.0001\lvert F_o\rvert^2]^{-1}$	$[\sigma^2(F_o)+0.0004\lvert F_o\rvert^2]^{-1}$	$[\sigma^2(F_o)]^{-1}$
$(\Delta/\rho)_{min}$ (e Å^{-3})	−2.61	−2.62	−1.58
$(\Delta/\rho)_{max}$ (e Å^{-3})	1.71	2.15	1.10

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{1/2}$.

R_w. The absolute configuration for **4** was determined by comparison of the R factors for each of the two configurations when refined to convergence.

The methylcyclopentadienyl group of **1** was initially refined anisotropically, and showed elongation of the ellipsoids suggesting a disordering of the ring over two positions. This was supported by a Fourier electron density map in the plane of the ring. Atoms C402–405 and C411 were split appropriately allowing the group to be refined isotropically as two rings (rotated approximately 25° about C401). All intra-ring and ring–Me bond lengths and angles were restrained to geometrically sensible values. Each pair of carbon atoms was constrained to have equal B_{iso} values, and the populations of the two rings were set to p and $1-p$; the parameter p was refined to a final value of 0.58(1). Hydrogen atoms could not be located and were not included. The oxygen O42 would not refine anisotropically (mostly likely related to the disorder in the adjacent methylcyclopentadienyl ring) and was modelled isotropically.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 158997 (**1**), 158998 (**4**) and 158999 (**5**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1E2, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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