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Mixed-Metal Cluster Chemistry. 28. Core Enlargement of Tungsten–Iridium Clusters with Alkynyl, Ethyndiyl, and Butadiyndiyl Reagents

Gulliver T. Dalton,[†] Lydie Viau,[†] Susan M. Waterman,[†] Mark G. Humphrey,*[,†] Michael I. Bruce,[‡]
Paul J. Low,[‡,§] Rachel L. Roberts,[§] Anthony C. Willis,[||] George A. Koutsantonis,[⊥]
Brian W. Skelton,[⊥] and Allan H. White[⊥]

Department of Chemistry and Research School of Chemistry, Australian National University,
Canberra ACT 0200, Australia, Department of Chemistry, University of Adelaide,
Adelaide SA 5005, Australia, Department of Chemistry, University of Durham,
South Road, Durham DH1 3LE, U.K., and Chemistry M313, University of Western Australia,
Crawley WA 6009, Australia

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Reaction of $[WIr_3(\mu\text{-CO})_3(CO)_8(\eta\text{-}C_5Me_5)]$ (**1c**) with $[W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)]$ afforded the edge-bridged tetrahedral cluster $[W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-CO})(CO)_9(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (**3**) and the edge-bridged trigonal-bipyramidal cluster $[W_3Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}\eta^2\text{-}C{=}CHPh)(Cl)(CO)_8(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)_2]$ (**4**) in poor to fair yield. Cluster **3** forms by insertion of $[W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)]$ into Ir—Ir and W—Ir bonds, accompanied by a change in coordination mode from a terminally bonded alkynyl to a $\mu_4\text{-}\eta^2$ alkynyl ligand. Cluster **4** contains an alkynyl ligand interacting with two iridium atoms and two tungsten atoms in a $\mu_4\text{-}\eta^2$ fashion, as well as a vinylidene ligand bridging a W—W bond. Reaction of $[WIr_3(CO)_{11}(\eta\text{-}C_5H_5)]$ (**1a**) or **1c** with $[(\eta\text{-}C_5H_5)(CO)_2Ru(C{\equiv}C)Ru(CO)_2(\eta\text{-}C_5H_5)]$ afforded $[Ru_2WIr_3(\mu_5\text{-}\eta^2\text{-}C_2)(\mu\text{-CO})_3(CO)_7(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5R_5)]$ [R = H (**5a**), Me (**5c**)] in low yield, a structural study of **5a** revealing a WIr_3 butterfly core capped and spiked by Ru atoms; the diruthenium ethyndiyl precursor has undergone Ru—C scission, with insertion of the C_2 unit into a W—Ir bond of the cluster precursor. Reaction of $[W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$ with the diruthenium ethyndiyl reagent gave $[RuW_2Ir_2\{\mu_4\text{-}\eta^2\text{-}(C_2C{\equiv}C)Ru(CO)_2(\eta\text{-}C_5H_5)\}(\mu\text{-CO})_2(CO)_6(\eta\text{-}C_5H_5)_3]$ (**6**) in low yield, a structural study of **6** revealing a butterfly W_2Ir_2 unit capped by a $Ru(\eta\text{-}C_5H_5)$ group resulting from Ru—C scission; the terminal C_2 of a new ruthenium-bound butadiyndiyl ligand has been inserted into the W—Ir bond. Reaction between **1a**, $[WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)]$ (**1b**), or **1c** and $[(\eta\text{-}C_5H_5)(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3(\eta\text{-}C_5H_5)]$ afforded $[W_2Ir_3\{\mu_4\text{-}\eta^2\text{-}(C_2C{\equiv}C)W(CO)_3(\eta\text{-}C_5H_5)\}(\mu\text{-CO})_2(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5R_5)]$ [R = H (**7a**), Me (**7c**); R_5 = H_4Me (**7b**)] in good yield, a structural study of **7c** revealing it to be a metallaethynyl analogue of **3**.

Introduction

The cluster chemistry of alkynes has been of long-standing interest and is well-developed.[1] Conceptually, replacing one of the alkyne substituents with a ligated metal center affords metal alkynyl complexes; not surprisingly, the reactions of transition metal clusters with transition metal alkynyl complexes have been the subject of many studies, proving a fertile procedure for cluster-core expansion and thereby synthesis of higher-nuclearity clusters.[1] Ethyndiyl complexes are the third member of the series in the (conceptual) progression RC≡CR → [M]C≡CR → [M]C≡C[M] (for ligated metal fragments [M]). Their utility in cluster synthesis is comparatively little explored (indeed, reliable synthetic procedures for these complexes have become available only in the past few years), but they might be advantageous in that they can, in principle, deliver two metal atoms to the cluster per reagent molecule, facilitating core nuclearity increase.[2]

Clusters incorporating disparate metals are of interest for a number of reasons: Coupling of an electropositive metal

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* To whom correspondence should be addressed. Tel.: +61 2 6125 2927. Fax: +61 2 6125 0760. E-mail: Mark.Humphrey@anu.edu.au.
[†] Department of Chemistry, Australian National University.
[‡] University of Adelaide.
[§] University of Durham.
[||] Research School of Chemistry, Australian National University.
[⊥] University of Western Australia.

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and an electronegative metal to give a polar metal–metal bond might enhance organic substrate activation and facilitate discrimination of fluxional processes; combinations of such metals might afford active catalysts for several important catalytic transformations.[3] Our particular focus has been on molybdenum/tungsten–iridium clusters, reactions with alkynes having afforded products involving alkyne coordination, dimerization, or $C\equiv C$ scission, generally in good to excellent yields,[4] although there are no reports of reactions between these "very mixed" metal clusters and ethyndiyl or butadiyndiyl reagents, and only one study of metal alkynyl complex reactivity toward tungsten–iridium clusters.[4a] (Note, however, that reactions of metal alkynyl complexes with metal clusters have afforded many examples of cluster expansion.[5]) We report herein studies exploring the utility of selected metal alkynyl, ethyndiyl, and butadiyndiyl complexes in expanding the core nuclearity of tetranuclear tungsten–iridium clusters.

Experimental Section

General Conditions. Reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques. All cluster complexes appear 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. The reaction solvents were dried and distilled under nitrogen using standard methods: THF [tetrahydrofuran (laboratory reagent, LR grade)] and toluene [analytical reagent (AR) grade] over sodium benzophenone, and dichloromethane (LR grade) over calcium hydride. Petrol refers to a fraction of boiling range 60–80 °C. 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 extents of reaction, was carried out on aluminum sheets coated with 0.25-mm silica gel. Column chromatography was performed using Merck silica.

Infrared spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer with CaF_2 solution cells; spectral frequencies are reported in wavenumbers. All analytical spectra were recorded as solutions in either cyclohexane or CH_2Cl_2 (both AR grade). ^1H NMR 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. Unit-resolution SI mass spectra were recorded using a VG Autospec instrument at the Research School of Chemistry, Australian National University (ANU). Unit-resolution FAB mass spectra were recorded on an AutoSpecE instrument at the University of Western Australia. Elemental microanalyses were carried out by the Microanalysis Service Unit in the Research School of Chemistry, ANU.

Literature procedures (or minor modifications thereof) were used to synthesize $[WIr_3(CO)_{11}(\eta\text{-}C_5H_5)]$ (**1a**),[6] $[WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)]$ (**1b**),[7] $[WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5Me_5)]$ (**1c**),[8] $[W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$ (**2**),[6] $[(\eta\text{-}C_5R_5)(CO)_3W(C\equiv CC\equiv C)W(CO)_3(\eta\text{-}C_5R_5)]$ (R = H, Me),[9] $[W(C\equiv CPh)(CO)_3(\eta\text{-}C_5H_5)]$,[10] $[(\eta\text{-}C_5H_5)(CO)_2Ru(C\equiv C)Ru(CO)_2(\eta\text{-}C_5H_5)]$.[11]

Reaction of $[WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5Me_5)]$ with $[W(C\equiv CPh)(CO)_3(\eta\text{-}C_5H_5)]$. An orange solution of $[WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5Me_5)]$ (**1c**) (19.0 mg, 0.0158 mmol) and $[W(C\equiv CPh)(CO)_3(\eta\text{-}C_5H_5)]$ (7.2 mg, 0.017 mmol) in CH_2Cl_2 (20 mL) was heated at reflux for 60 h in the absence of light. The brown solution was evaporated to dryness in vacuo. The resulting brown residue was dissolved in a minimum of CH_2Cl_2 (ca. 2 mL) and applied to preparative TLC plates. Elution with CH_2Cl_2/petrol (1:1) gave five bands: Band 1 was yellow ($R_f = 0.85$), band 2 was light brown ($R_f = 0.61$), band 3 was brown ($R_f = 0.52$), band 4 was purple ($R_f = 0.47$), and band 5 was gray ($R_f = 0.38$). Bands 3 and 5 were in trace amounts and could not be identified. Band 1 was identified by solution IR spectroscopy and MS as the starting cluster $[WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5Me_5)]$ (**1c**) (8.0 mg, 0.007 mmol). The contents of band 2 were crystallized from CH_2Cl_2/MeOH at −3 °C to afford brown crystals identified as $[W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)]$ (**3**) (5.0 mg, 21%). Anal. Found: C, 25.96; H, 1.57%. Calcd for $C_{33}H_{25}Ir_3O_{10}W_2$: C, 25.98; H, 1.65%. IR ($c\text{-}C_6H_{12}$): ν(CO) 2077 vs, 2030 s, 2020 vs, 2001 m, 1991 vw, 1963 w, 1951 w, 1938 w, 1761 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.90–7.10 (m, 5H, Ph), 4.56 (s, 5H, C_5H_5), 2.26 (s, 15H, C_5Me_5) ppm. MS (SI): 1526 ($[M]^+$, 14), 1498 ($[M - CO]^+$, 27), 1442 ($[M - 3CO]^+$, 50), 1414 ($[M - 4CO]^+$, 59), 1386 ($[M - 5CO]^+$, 100), 1330 ($[M - 7CO]^+$, 34). The contents of band 4 were crystallized from CH_2Cl_2/MeOH at −3 °C to afford dark purple crystals identified as $[W_3Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}\eta^2\text{-}C{=}CHPh)(Cl)(CO)_8(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)_2]\cdot 0.5CH_2Cl_2$ (**4**) (2.0 mg, 7%). IR (CH_2Cl_2): ν(CO) 2022 s, 1992 s, 1981 sh, 1962 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.21–7.20 (m, 10H, Ph), 6.90 (s, 1H, CCH), 6.01 (s, 5H, C_5H_5), 5.28 (s, 1H, CH_2Cl_2), 4.78 (s, 5H, C_5H_5), 1.99 (s, 15H, C_5Me_5) ppm. MS (FAB): 1856 ($[M]^+$, 100), 1744 ($[M - 4CO]^+$, 17). Insufficient material precluded microanalysis.

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Reaction of $[\mathrm{WIr_3(CO)_{11}}(\eta\text{-}\mathrm{C_5H_5})]$ with $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2Ru(C{\equiv}C)Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$. A yellow solution of $[\mathrm{WIr_3(CO)_{11}}(\eta\text{-}\mathrm{C_5H_5})]$ (**1a**) (20.5 mg, 0.0181 mmol) and $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2Ru(C{\equiv}C)Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ (8.5 mg, 0.018 mmol) in THF (20 mL) was refluxed for 45 min in the absence of light, after which time the resulting green-brown solution was allowed to cool to room temperature, and the solvent was removed in vacuo. The resulting black residue was dissolved in $\mathrm{CH_2Cl_2}$ (ca. 2 mL) and subjected to TLC (5:2 $\mathrm{CH_2Cl_2}$/petrol eluant), affording six bands: Band 1 was yellow ($R_f = 0.80$), band 2 was brown ($R_f = 0.73$), band 3 was green ($R_f = 0.36$), band 4 was green ($R_f = 0.22$), band 5 was brown ($R_f = 0.08$), and band 6 was orange ($R_f = 0.04$). Bands 1−3, 5, and 6 were in trace amounts and could not be identified. The contents of the fourth band were crystallized from $\mathrm{CH_2Cl_2}$/MeOH at 3 °C to afford dark green crystals of $[\mathrm{Ru_2WIr_3}(\mu_5\text{-}\eta^2\text{-}\mathrm{C_2})(\mu\text{-}\mathrm{CO})_3\mathrm{(CO)_7}(\eta\text{-}\mathrm{C_5H_5})_3]$ (**5a**) (5.0 mg, 19%). Analytical data for **5a** are as follows. IR ($\mathrm{CH_2Cl_2}$): 2049 m, 2018 s, 1959 m. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 5.88 (s, 5H, η-$\mathrm{C_5H_5}$), 5.60 (s, 5H, η-$\mathrm{C_5H_5}$), 5.44 (s, 5H, η-$\mathrm{C_5H_5}$). MS (FAB): 1351 ($[\mathrm{M} - 4\mathrm{CO}]^+$, 63), 1323 ($[\mathrm{M} - 5\mathrm{CO}]^+$, 55), 1211 ($[\mathrm{M} - 9\mathrm{CO}]^+$, 100). Anal. Calcd for $\mathrm{C_{27}H_{15}Ir_3O_{10}Ru_2W}$: C, 22.18; H, 1.03. Found: C, 22.60; H, 0.94.

Reaction of $[\mathrm{WIr_3}(\mu\text{-}\mathrm{CO})_3\mathrm{(CO)_8}(\eta\text{-}\mathrm{C_5Me_5})]$ with $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2Ru(C{\equiv}C)Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$. An orange solution of $[\mathrm{WIr_3}(\mu\text{-}\mathrm{CO})_3\mathrm{(CO)_8}(\eta\text{-}\mathrm{C_5Me_5})]$ (**1c**) (21.7 mg, 0.0180 mmol) and $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2Ru(C{\equiv}C)Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ (8.5 mg, 0.018 mmol) in THF (20 mL) was heated at reflux for 100 min in the absence of light. The green-brown solution was then evaporated to dryness under a vacuum. The resulting black residue was dissolved in a minimum of $\mathrm{CH_2Cl_2}$ (ca. 2 mL) and applied to preparative TLC plates. Elution with $\mathrm{CH_2Cl_2}$/petrol (3:2) gave four bands: Band 1 was yellow ($R_f = 0.79$), band 2 was green ($R_f = 0.26$), band 3 was brown ($R_f = 0.15$), and band 4 was orange ($R_f = 0.02$). Band 1 was identified from IR spectroscopy and the R_f value as the starting cluster $[\mathrm{WIr_3}(\mu\text{-}\mathrm{CO})_3\mathrm{(CO)_8}(\eta\text{-}\mathrm{C_5Me_5})]$ (6 mg, 0.0050 mmol). Bands 3 and 4 were in trace amounts and could not be identified. The contents of band 2 were crystallized from $\mathrm{CH_2Cl_2}$/EtOH at 3 °C to afford dark green crystals of $[\mathrm{Ru_2WIr_3}(\mu_5\text{-}\eta^2\text{-}\mathrm{C_2})(\mu\text{-}\mathrm{CO})_3\mathrm{(CO)_7}(\eta\text{-}\mathrm{C_5H_5})_2(\eta\text{-}\mathrm{C_5Me_5})]$ (**5c**) (4.0 mg, 14%). Analytical data for **5c** are as follows. IR ($\mathrm{CH_2Cl_2}$): 2048 m, 2018 s, 2002 m. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 5.42 (s, 5H, η-$\mathrm{C_5H_5}$), 5.34 (s, 5H, η-$\mathrm{C_5H_5}$), 2.26 (s, 15H, η-$\mathrm{C_5Me_5}$). MS (FAB): 1533 ($[\mathrm{M}]^+$, 100). Anal. Calcd for $\mathrm{C_{32}H_{35}Ir_3O_{10}Ru_2W}$: C, 25.09; H, 1.64. Found: C, 24.91; H, 1.38.

Reaction of $[\mathrm{W_2Ir_2(CO)_{10}}(\eta\text{-}\mathrm{C_5H_5})_2]$ with $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2Ru(C{\equiv}C)Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$. A yellow solution of $[\mathrm{W_2Ir_2(CO)_{10}}(\eta\text{-}\mathrm{C_5H_5})_2]$ (**2**) (34.1 mg, 0.0293 mmol) and $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2Ru(C{\equiv}C)Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ (35.4 mg, 0.0755 mmol) in THF (20 mL) was heated at reflux for 2 h in the absence of light, after which time the resulting red-brown solution was allowed to cool to room temperature, and the solvent was removed in vacuo. The resulting black residue was dissolved in $\mathrm{CH_2Cl_2}$ (ca. 2 mL) and subjected to TLC ($\mathrm{CH_2Cl_2}$ eluant) affording five bands: Band 1 was yellow ($R_f = 0.88$), band 2 was yellow ($R_f = 0.78$), band 3 was yellow ($R_f = 0.24$), band 4 was brown ($R_f = 0.20$), and band 5 was green-brown ($R_f = 0.09$). Bands 1, 3, and 4 were in trace amounts and could not be identified. The contents of the second band were collected as a yellow solid (2 mg). Analytical data are as follows. IR (c-$\mathrm{C_6H_{12}}$): 2055 w, 2018 w, 2009 m, 1973 s, 1964 m, 1943 vs, 1793 m. The compound could not be crystallized and is therefore of unknown composition. The contents of the fifth band were dissolved in $\mathrm{CH_2Cl_2}$ (ca. 2 mL) and subjected to TLC. Three elutions (1:2 acetone/petrol eluant) afforded four bands: Band 1 was gray ($R_f = 0.68$), band 2 was green ($R_f = 0.55$), band 3 was purple ($R_f = 0.50$), and band 4 was orange ($R_f = 0.36$). Bands 1, 3, and 4 were in trace amounts and could not be identified. The contents of band 2 were crystallized from $\mathrm{CH_2Cl_2}$/EtOH at 3 °C to afford dark green crystals of $[\mathrm{RuW_2Ir_2}\{\mu_4\text{-}\eta^2\text{-}\mathrm{C_2(C{\equiv}C)Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})\}(\mu\text{-}\mathrm{CO})_2\mathrm{(CO)_6}(\eta\text{-}\mathrm{C_5H_5})_3]$ (**6**) (3.0 mg, 7%). Analytical data for **6** are as follows. IR ($\mathrm{CH_2Cl_2}$): 2071 s, 2044 m, 2014 vs, 1996 m, 1961 w, 1818 br. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 5.70 (s, 5H, η-$\mathrm{C_5H_5}$), 5.46 (s, 5H, η-$\mathrm{C_5H_5}$), 5.14 (s, 5H, η-$\mathrm{C_5H_5}$), 4.65 (s, 5H, η-$\mathrm{C_5H_5}$). MS (FAB): 1543 ($[\mathrm{M}]^+$, 62), 1459 ($[\mathrm{M} - 3\mathrm{CO}]^+$, 54). Anal. Calcd for $\mathrm{C_{34}H_{20}Ir_2O_{10}Ru_2W_2}$: C, 26.47; H, 1.39. Found: C, 26.46; H, 1.07.

Reaction of $[\mathrm{WIr_3(CO)_{11}}(\eta\text{-}\mathrm{C_5H_5})]$ with $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2Ru(C{\equiv}CC{\equiv}C)Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$. A yellow solution of $[\mathrm{WIr_3(CO)_{11}}(\eta\text{-}\mathrm{C_5H_5})]$ (21.5 mg, 0.0190 mmol) and $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2Ru(C{\equiv}CC{\equiv}C)Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ (12.6 mg, 0.0183 mmol) in toluene (15 mL) was stirred for 72 h in the absence of light, after which time the carbonyl absorptions of $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2Ru(C{\equiv}CC{\equiv}C)Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ in the IR spectrum were no longer present. The dark brown solution was then transferred to a round-bottomed flask and evaporated to dryness in vacuo. The resulting black residue was dissolved in a minimum of $\mathrm{CH_2Cl_2}$ (ca. 2 mL) and applied to preparative TLC plates. Elution with $\mathrm{CH_2Cl_2}$/petrol (4:3) gave one major band ($R_f = 0.93$) and many trace bands that could not be separated. The major band was dissolved in a minimum of $\mathrm{CH_2Cl_2}$ (ca. 2 mL) and applied to preparative TLC plates. Elution six times with $\mathrm{CH_2Cl_2}$/petrol (3:4) gave three trace bands.

Reaction of $[\mathrm{WIr_3(CO)_{11}}(\eta\text{-}\mathrm{C_5H_5})]$ with $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})]$ (Method A). An orange suspension of $[\mathrm{WIr_3(CO)_{11}}(\eta\text{-}\mathrm{C_5H_5})]$ (**1a**) (20.0 mg, 0.0176 mmol) and $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})]$ (12.6 mg, 0.0176 mmol) in toluene (20 mL) was slowly heated to 110 °C, and the resulting solution was refluxed for 15 min, after which time the dark brown solution was allowed to cool to room temperature, and the solvent was removed in vacuo. The deep brown residue was dissolved in $\mathrm{CH_2Cl_2}$ (ca. 1 mL) and subjected to TLC (2:1 $\mathrm{CH_2Cl_2}$/petrol eluant), affording one band. The contents of the band ($R_f = 0.30$) were crystallized from $\mathrm{CH_2Cl_2}$/c-$\mathrm{C_6H_{12}}$ to afford brown crystals of $[\mathrm{W_2Ir_3}\{\mu_4\text{-}\eta^2\text{-}(\mathrm{C_2C{\equiv}C)W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})\}(\mu\text{-}\mathrm{CO})_2\mathrm{(CO)_8}(\eta\text{-}\mathrm{C_5H_5})_2]$ (**7a**) (12.2 mg, 40%). Analytical data for **7a** are as follows. IR (c-$\mathrm{C_6H_{12}}$): 2079 s, 2033 vs, 2011 m, 1976 m, 1972 w, 1962 w, 1952 w. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 5.75 (s, 5H, η-$\mathrm{C_5H_5}$), 5.69 (s, 5H, η-$\mathrm{C_5H_5}$), 4.70 (s, 5H, η-$\mathrm{C_5H_5}$). MS (FAB) 1735 ($[\mathrm{M}]^+$, 21), 1707 ($[\mathrm{M} - \mathrm{CO}]^+$, 45), 1679 ($[\mathrm{M} - 2\mathrm{CO}]^+$, 40), 1651 ($[\mathrm{M} - 3\mathrm{CO}]^+$, 95), 1623 ($[\mathrm{M} - 4\mathrm{CO}]^+$, 97), 1595 ($[\mathrm{M} - 5\mathrm{CO}]^+$, 100), 1567 ($[\mathrm{M} - 6\mathrm{CO}]^+$, 29), 1539 ($[\mathrm{M} - 7\mathrm{CO}]^+$, 28), 1511 ($[\mathrm{M} - 8\mathrm{CO}]^+$, 54), 1483 ($[\mathrm{M} - 9\mathrm{CO}]^+$, 59), 1455 ($[\mathrm{M} - 10\mathrm{CO}]^+$, 38), 1427 ($[\mathrm{M} - 11\mathrm{CO}]^+$, 58), 1399 ($[\mathrm{M} - 12\mathrm{CO}]^+$, 55), 1371 ($[\mathrm{M} - 13\mathrm{CO}]^+$, 65). Anal. Calcd for $\mathrm{C_{32}H_{15}Ir_3O_{13}W_3}$: C, 22.14; H 0.87. Found: C, 22.05; H 1.16.

Reaction of $[\mathrm{WIr_3}(\mu\text{-}\mathrm{CO})_3\mathrm{(CO)_8}(\eta\text{-}\mathrm{C_5Me_5})]$ with $[(\eta\text{-}\mathrm{C_5Me_5})\mathrm{(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3}(\eta\text{-}\mathrm{C_5Me_5})]$. Following method A, reaction of $[\mathrm{WIr_3}(\mu\text{-}\mathrm{CO})_3\mathrm{(CO)_8}(\eta\text{-}\mathrm{C_5Me_5})]$ (**1c**) (20.7 mg, 0.0172 mmol) and $[(\eta\text{-}\mathrm{C_5Me_5})\mathrm{(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3}(\eta\text{-}\mathrm{C_5Me_5})]$ (14.2 mg, 0.0166 mmol) in refluxing toluene (20 mL) for 15 min afforded two bands after TLC (2:1 $\mathrm{CH_2Cl_2}$/petrol eluant). The first yellow band was identified from IR spectroscopy and TLC ($R_f = 0.85$) as the starting cluster $[\mathrm{WIr_3}(\mu\text{-}\mathrm{CO})_3\mathrm{(CO)_8}(\eta\text{-}\mathrm{C_5Me_5})]$ (10.0 mg, 0.0083 mmol). The contents of the second band were in trace amounts and were not identified.

Reaction of $[\mathrm{WIr_3(CO)_{11}}(\eta\text{-}\mathrm{C_5H_4Me})]$ with $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})]$. Following method A, reaction of $[\mathrm{WIr_3(CO)_{11}}(\eta\text{-}\mathrm{C_5H_4Me})]$ (**1b**) (21.2 mg, 0.0185 mmol) and $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})]$ (13.8 mg, 0.0193 mmol) in refluxing toluene (20 mL) for 15 min afforded four bands after

TLC (2:1 CH_2Cl_2/petrol eluant): Band 1 was yellow ($R_f = 0.81$), band 2 was orange ($R_f = 0.51$), band 3 was brown ($R_f = 0.43$), and band 4 was gray ($R_f = 0.16$). The contents of band 1 were identified as the starting cluster $[WIr_3(CO)_{11}(\eta\text{-}C_5H_4Me)]$ (3.0 mg, 0.0026 mmol). Bands 2 and 4 were in trace amounts and could not be identified. The contents of the third band were crystallized from CH_2Cl_2/MeOH at 3 °C to afford dark purple crystals of $[W_2Ir_3\{\mu_4\text{-}\eta^2\text{-}(C_2C{\equiv}C)W(CO)_3(\eta\text{-}C_5H_5)\}(\mu\text{-}CO)_2(CO)_8(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (**7b**) (16.1 mg, 50%). Analytical data for **7b** are as follows. IR (CH_2Cl_2): 2081 m, 2028 s, 1995 w, 1959 m, 1943 sh, 1867 br, 1743 w. ^1H NMR ($CDCl_3$): δ 6.12−5.38 (m, 4H, $\eta\text{-}C_5H_4CH_3$), 5.68 (s, 5H, $\eta\text{-}C_5H_5$), 4.71 (s, 5H, $\eta\text{-}C_5H_5$), 2.33 (s, 3H, $\eta\text{-}C_5H_4CH_3$). MS (SI): 1749 ($[M]^+$, 12), 1721 ($[M - CO]^+$, 14), 1693 ($[M - 2CO]^+$, 8), 1665 ($[M - 3CO]^+$, 55), 1637 ($[M - 4CO]^+$, 28), 1609 ($[M - 5CO]^+$, 100). Anal. Calcd for $C_{33}H_{17}Ir_3O_{13}W_3$: C, 22.65; H, 0.98. Found: C, 22.83; H, 0.91.

Reaction of $[WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5Me_5)]$ with $[(\eta\text{-}C_5H_5)(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3(\eta\text{-}C_5H_5)]$. Following method A, reaction of $[WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5Me_5)]$ (**1c**) (19.3 mg, 0.0160 mmol) and $[(\eta\text{-}C_5H_5)(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3(\eta\text{-}C_5H_5)]$ (11.8 mg, 0.0165 mmol) in refluxing toluene (20 mL) for 15 min afforded two bands after TLC (2:1 CH_2Cl_2/petrol eluant). The first yellow band was identified from IR spectroscopy and the R_f value ($R_f = 0.85$) as the starting cluster $[WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5Me_5)]$ (5.0 mg, 0.0041 mmol). The contents of the second brown band ($R_f = 0.62$) were crystallized from CH_2Cl_2/MeOH at 3 °C to afford brown crystals of $[W_2Ir_3\{\mu_4\text{-}\eta^2\text{-}(C_2C{\equiv}C)W(CO)_3(\eta\text{-}C_5H_5)\}(\mu\text{-}CO)_2(CO)_8(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (**7c**) (10.4 mg, 36%). Analytical data for **7c** are as follows. IR (CH_2Cl_2): 2078 m, 2025 s, 1992 w, 1957 m, 1744 w. ^1H NMR ($CDCl_3$): δ 6.78 (s, 5H, $\eta\text{-}C_5H_5$), 5.65 (s, 5H, $\eta\text{-}C_5H_5$), 5.28 (s, 2H, CH_2Cl_2), 2.15 (s, 15H, $\eta\text{-}C_5Me_5$). MS (SI): 1805 ($[M]^+$, 100), 1777 ($[M - CO]^+$, 73), 1749 ($[M - 2CO]^+$, 62). Anal. Calcd for $C_{37}H_{25}Ir_3O_{13}W_3{\cdot}CH_2Cl_2$: C, 24.14; H, 1.44. Found: C, 24.13; H, 1.50.

Reaction of $[W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$ with $[(\eta\text{-}C_5H_5)(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3(\eta\text{-}C_5H_5)]$. Following method A, reaction of $[W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$ (**2**) (20.0 mg, 0.0172 mmol) and $[(\eta\text{-}C_5H_5)(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3(\eta\text{-}C_5H_5)]$ (12.3 mg, 0.0172 mmol) in refluxing toluene (20 mL) for 15 min afforded a brown residue. No tractable products were obtained, decomposition of the cluster having occurred.

Crystallographic Studies. Suitable crystals for structural studies were obtained by slow diffusion of MeOH (**3**, **4**, **5a**, **7c**) or EtOH (**6**) into a solution of the cluster in CH_2Cl_2 at 3 °C. Crystal/refinement data for these complexes follow.

3. $C_{33}H_{25}Ir_3O_{10}W_2$, $M = 1525.9$. Triclinic, $P\bar{1}$, $a = 9.5204(1)$ Å, $b = 10.8559(1)$ Å, $c = 17.9731(3)$ Å, $\alpha = 95.2323(6)°$, $\beta = 99.5846(6)°$, $\gamma = 100.5873(5)°$, $V = 1786$ Å^3. D_c ($Z = 2$) = 2.83_7 g cm^{-3}. μMo = 17.6 mm^{-1}; specimen 0.34 × 0.22 × 0.13 mm; $T_{min/max} = 0.17$. $2\theta_{max} = 60°$; $N_{t(otal)} = 40961$ (full sphere; CCD diffractometer, monochromatic Mo Kα radiation, $\lambda = 0.71073$ Å; $T \approx 200$ K) merging to $N = 10500$ unique ($R_{int} = 0.080$), $N_o = 7207$ [$I > 3\sigma(I)$] refining to $R = 0.030$, $R_w = 0.035$. **Variata.** The largest difference map residues are located near the Ir and W atoms. A void about the origin, identified by the program SQUEEZE within PLATON, potentially could contain disordered solvent (estimated at 18 electrons per unit cell). As a trial to see whether the structure could be improved, SQUEEZE was used to remove all electron density from this region of the cell.[12] A slightly lower residual was obtained, but the resulting substrate structure was not nontrivially different from the original. The structure reported here uses the unmodified data.

4. $C_{44}H_{36}ClIr_3O_8W_3{\cdot}0.5CH_2Cl_2$, $M = 1898.9$. Triclinic, $P\bar{1}$, $a = 12.6651(9)$ Å, $b = 16.120(1)$ Å, $c = 22.176(2)$ Å, $\alpha = 85.326(2)°$, $\beta = 76.885(2)°$, $\gamma = 85.912(3)°$, $V = 4388$ Å^3. D_c ($Z = 4$) = 2.87_4 g cm^{-3}. μMo = 17.1 mm^{-1}; specimen 0.16 × 0.13 × 0.06 mm; $T_{min/max} = 0.48$. $2\theta_{max} = 75°$; $N_t = 90820$, $N = 45267$ ($R_{int} = 0.080$), N_o [$F > 4\sigma(F)$] = 30550; $R = 0.053$, $R_w = 0.061$. $T \approx 150$ K. **Variata.** Displacement parameters on the CH_2Cl_2 molecule in this structure were high, and the geometry was constrained in the refinement.

5a. $C_{27}H_{15}Ir_3O_{10}Ru_2W$, $M = 1463.0$. Orthorhombic, $Pca2_1$, $a = 14.919(1)$ Å, $b = 11.864(1)$ Å, $c = 16.223(1)$ Å, $V = 2871$ Å^3. D_c ($Z = 4$) = 3.38_1 g cm^{-3}. μMo = 18.9 mm^{-1}; specimen 0.16 × 0.10 × 0.06 mm; $T_{min/max} = 0.48$. $2\theta_{max} = 75°$; $N_t = 59481$, $N = 7745$ ($R_{int} = 0.076$), N_o [$F > 4\sigma(F)$] = 6425; $R = 0.037$, $R_w = 0.044$; $x_{abs} = 0.005(8)$. $T \approx 150$ K.

6. $C_{34}H_{20}Ir_2O_{10}Ru_2W_2$, $M = 1542.8$. Monoclinic, $P2_1/n$, $a = 10.1190(1)$ Å, $b = 15.0991(1)$ Å, $c = 22.4328(2)$ Å, $\beta = 101.7764(5)°$, $V = 3355$ Å^3. D_c ($Z = 4$) = 3.05_4 g cm^{-3}. μMo = 15.7 mm^{-1}; specimen 0.29 × 0.22 × 0.05 mm; $T_{min/max} = 0.12$. $2\theta_{max} = 60°$; $N_t = 80141$, $N = 9803$ ($R_{int} = 0.080$), N_o [$I > 3\sigma(I)$] = 4502; $R = 0.021$, $R_w = 0.023$. $T \approx 200$ K.

7c. $C_{37}H_{25}Ir_3O_{13}W_3{\cdot}CH_2Cl_2$, $M = 1890.7$. Triclinic, $P\bar{1}$, $a = 10.3264(1)$ Å, $b = 13.5767(2)$ Å, $c = 15.6551(3)$ Å, $\alpha = 103.8998(8)°$, $\beta = 93.3532(10)°$, $\gamma = 95.1018(10)°$, $V = 2115$ Å^3. D_c ($Z = 2$) = 2.96_9 g cm^{-3}. μMo = 17.7 mm^{-1}; specimen 0.22 × 0.07 × 0.04 mm; $T_{min/max} = 0.24$. $2\theta_{max} = 54°$; $N_t = 52181$, $N = 9708$ ($R_{int} = 0.090$), N_o [$I > 3\sigma(I)$] = 7834; $R = 0.033$, $R_w = 0.039$. $T \approx 200$ K. **Variata.** The dichloromethane molecule is disordered such that there is one site for one Cl atom but two sites each for the C and other Cl atom. The relative populations were refined, with constraints imposed on geometrical and displacement parameters.

In all structures, assignments of Ir vs W were made on the basis of the chemistry and refinement behavior statistics. Non-hydrogen displacement ellipsoid amplitudes in the figures are at the 50% probability level; hydrogen atoms have arbitrary radii of 0.1 Å. Full details of the five determinations are available in the Supporting Information.

Results and Discussion

Core Expansion Using Ethynyltungsten Reagents. Several years ago, we reported reactions of the tetranuclear cluster $[WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5H_5)]$ (**1a**) with $[W(C{\equiv}CR)(CO)_3(\eta\text{-}C_5H_5)]$, which afforded the pentanuclear clusters $[W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2R)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)_2]$ in excellent yields; an X-ray structural study of $[W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)_2]$ suggested that these products form by insertion of a $[W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)]$ unit into an Ir−Ir bond of the tetrahedral precursor, with concomitant elimination of carbonyl.[4a] Since this report, we have synthesized $[WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5Me_5)]$ (**1c**), the pentamethylcyclopentadienyl-containing analogue of the starting cluster,[8] and we have now examined its corresponding reaction with $[W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)]$. Reaction proceeded in refluxing CH_2Cl_2 to afford a pentanuclear cluster as the major product in 21% yield, structurally characterized as $[W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (**3**), and a hexanuclear cluster in 7% yield, structurally characterized as $[W_3Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}\eta^2\text{-}C{=}CHPh)(Cl)(CO)_8(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)_2]$ (**4**) (Scheme 1).

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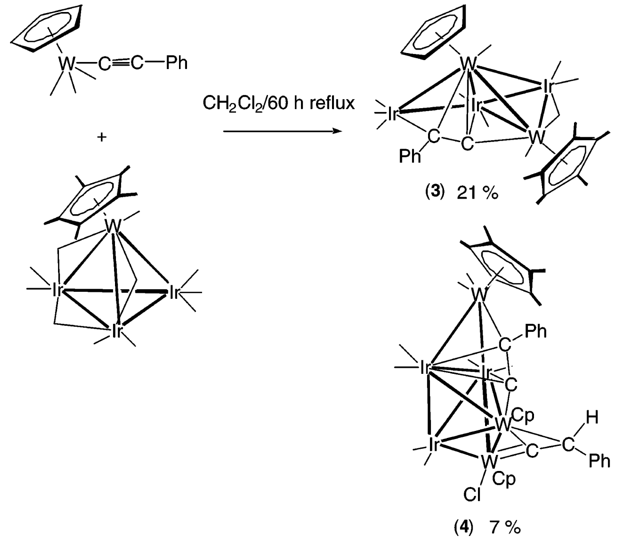
(12) van der Sluis, P.; Spek, A. L. *Acta Crystallogr. A* **1990**, *46*, 194.

Scheme 1. Reaction of [$WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5Me_5)$] with [$W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$]



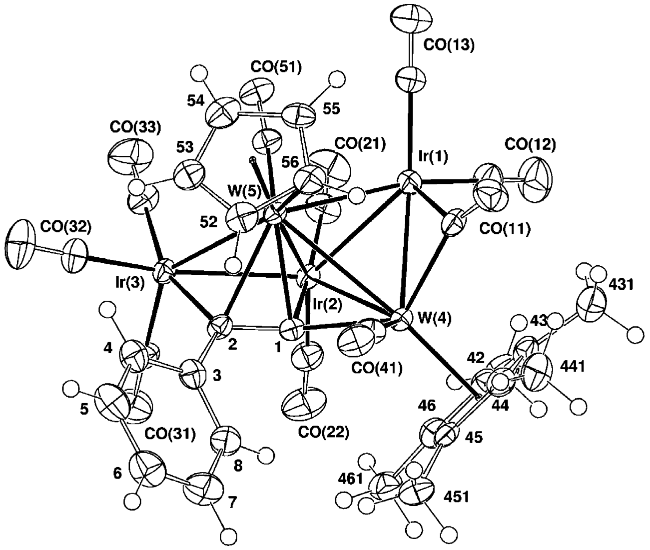


Figure 1. ORTEP plot of [$W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)$] (**3**). Selected bond distances: Ir(1)−Ir(2) 2.7870(4), Ir(1)−W(4) 2.7481(4), Ir(1)−W(5) 2.8339(4), Ir(2)−Ir(3) 2.7497(4), Ir(2)−W(4) 2.9195(4), Ir(2)−W(5) 2.7448(4), Ir(3)−W(5) 2.8199(4), W(4)−W(5) 3.0336(4) Å.

Cluster **3** was characterized by IR and ^{1}H NMR spectroscopies, FAB MS, and a single-crystal X-ray diffraction study. The solution IR spectrum of **3** shows the presence of terminal and edge-bridging carbonyl ligands. The ^{1}H NMR spectrum contains a multiplet in the phenyl region, a singlet at 2.26 ppm indicative of a pentamethylcyclopentadienyl group, and a singlet at 4.56 ppm indicative of a cyclopentadienyl group. The mass spectrum exhibits a molecular ion peak followed by consecutive losses of eight carbonyl groups. Figure 1, from the structural study, shows the molecular structure and atomic labeling scheme.

The cluster core consists of a tetrahedron of two tungsten and two iridium atoms with an iridium atom bridging the Ir(2)−W(5) bond and the C_2 unit of a phenylethynyl ligand interacting with two iridiums and two tungsten atoms. There is a single bridging carbonyl ligand between W(4) and Ir(1), the other nine carbonyls being terminally coordinated. W(5) is ligated by a cyclopentadienyl group. and W(4) is ligated by a pentamethylcyclopentadienyl group. The cluster is electron-precise with 74 cluster valence electrons (CVEs). The Ir−Ir distances [2.7497(4)−2.7870(4) (**3**); cf. previously reported 2.598(1)[4b]−2.814(3)[4b] Å], W−Ir vectors [2.7448-(4)−2.9195(4) (**3**); cf. previously reported 2.665(2)[13]−2.9023(9)[14] Å] and W(4)−W(5) bond [3.0336(4) Å (**3**); cf. previously reported W−W distances 2.9057(9)[4c]−3.080(1)[13] Å] are not unprecedented. The different cyclopentadienyl ligands in the starting materials have labeled the tungsten atoms, and the reaction can now be seen to proceed by an unusual and unanticipated insertion of a [$W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$] unit into Ir−Ir and W−Ir bonds, accompanied by a change in coordination mode from a terminally bonded alkynyl to a μ_4-η^2 alkynyl ligand.

Cluster **4** was characterized by IR and ^{1}H NMR spectroscopies, SI MS, and a single-crystal X-ray diffraction study. The solution IR spectrum of compound **4** shows the presence of terminal carbonyl ligands. The ^{1}H NMR spectrum contains a multiplet in the phenyl region, a singlet at 6.90 ppm consistent with a hydrogen of a vinylidene ligand, singlets at 6.01 and 4.78 ppm indicative of cyclopentadienyl groups, and a singlet at 1.99 ppm indicative of a pentamethylcyclopentadienyl group. The mass spectrum contains a molecular ion peak, followed by a loss of four carbonyl groups. Figure 2, from the structural study, shows the molecular structure and atomic labeling scheme.

The cluster consists of a trigonal-bipyramidal core of three iridium atoms and two adjacent tungsten atoms with a tungsten bridging the Ir(11)−Ir(12) bond and eight carbonyl groups terminally coordinated. There is an alkynyl ligand interacting with two iridium atoms and two tungsten atoms in a μ_4-η^2 fashion and a μ-η^2-bound vinylidene ligand bridging the W(15)−W(16) bond. W(15) is ligated by a chlorine atom and a cyclopentadienyl group, W(16) is ligated by a cyclopentadienyl group, and W(14) is ligated by a pentamethylcyclopentadienyl group. The cluster is electron-precise with 86 CVEs. The structural study shows that hydrogen has been incorporated to form the vinylidene ligand and chlorine has bonded to W(15). This suggests that either the solvent has been activated in this reaction or traces of HCl (possibly present in the dichloromethane solvent) might be responsible. (Note that, in contrast, previous examples of halogen incorporation in mixed-metal clusters have involved halide coordination to the later transition metal).[3] In related studies, dichloromethane was activated upon reaction with [$Mo_2Co_2(\mu_3\text{-}CO)(\mu_3\text{-}S)_3(dmpe)_2(\eta\text{-}C_5H_4Me)_2$], but instead gave the dichloromethane-derived methylidyne-containing cluster cation [$Mo_2Co_2(\mu_3\text{-}CH)(\mu_3\text{-}S)_3(dmpe)_2(\eta\text{-}C_5H_4Me)_2$]$^+$ with chloride counterion.[15] If the dichloromethane has been activated, the residue of the solvent

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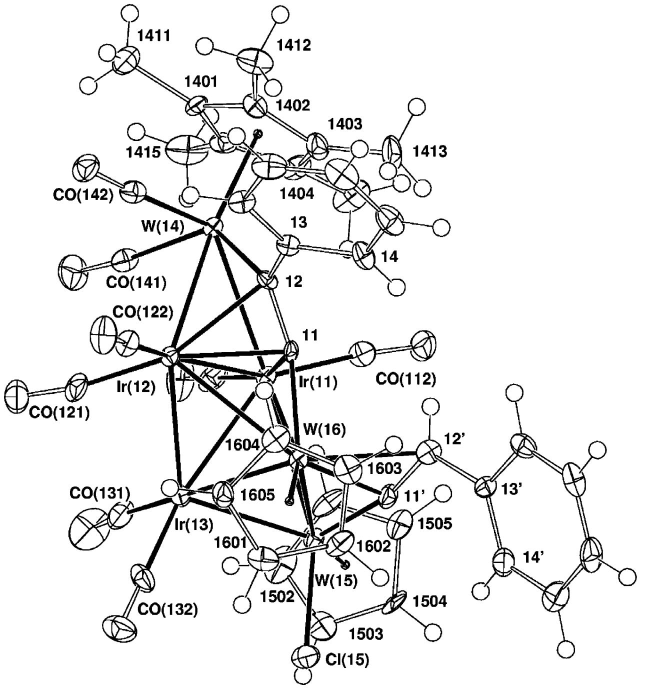
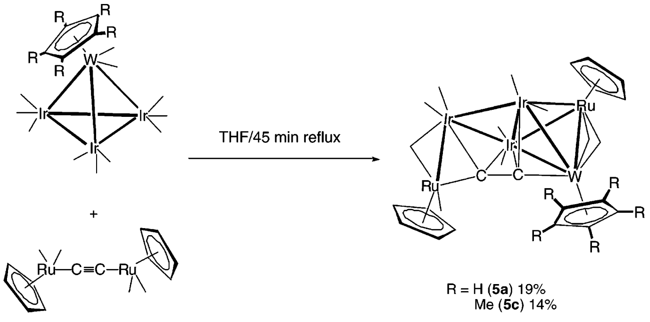


Figure 2. ORTEP plot of $[W_3Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}\eta^2\text{-}C{=}CHPh)(Cl)(CO)_8(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)_2]$ (**4**; molecule 1). Selected bond distances (two values each, corresponding to the two molecules in the asymmetric unit): Ir(n1)—Ir(n2) 2.6811(5), 2.6997(5); Ir(n1)—Ir(n3) 2.7359(4), 2.7099(4); Ir(n2)—Ir(n3) 2.8134(5), 2.8203(5); Ir(n1)—W(n4) 2.9208(5), 2.9284(5); Ir(n1)—W(n5) 3.0234(5), 3.0779(5); Ir(n1)—W(n6) 2.8615(5), 2.8563(5); Ir(n2)—W(n4) 2.7837(4), 2.7836(5); Ir(n2)—W(n6) 2.9720(5), 2.9535(5); Ir(n3)—W(n5) 2.6383(5), 2.6544(5); Ir(n3)—W(n6) 2.7477(5), 2.7506(5); W(n5)—W(n6) 2.8528(5), 2.8440(5) Å.

molecules from the formation of **4** might be present in some of the other products not characterized in this reaction. The Ir—Ir bond lengths in **4** are within the range of those previously reported (see above). In contrast, the bond lengths Ir(n3)—W(n5) [2.6383(5), 2.6544(5) Å], Ir(n2)—W(n6) [2.9720(5), 2.9535(5) Å], Ir(n1)—W(n5) [3.0234(5), 3.0779(5) Å], Ir(n1)—W(n4) [2.9208(5), 2.9284(5) Å], and W(n5)—W(n6) [2.8528(5), 2.8440(5) Å] are unusually short or long compared to literature precedents. Adjacent tungsten atoms in a trigonal bipyramid have only been seen in two other tungsten−iridium clusters,[4c,13] presumably a result of the steric effect of adjacent cyclopentadienyl groups disfavoring this disposition. Few examples of transition metal clusters with edge-bridged trigonal-bipyramidal core geometries have been crystallographically authenticated: the only precedents are the 84-CVE $[Ru_4Cu_2(\mu_3\text{-}H)_2(CO)_{12}\{P(c\text{-}C_6H_{11})_3\}_2]$[16] and $[Ru_4Cu_2(\mu_3\text{-}H)_2(CO)_{12}\{P(CH_2Ph)_3\}_2]$,[17] and the 86-CVE $[Ru_6(\mu_3\text{-}H)(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}\eta^7\text{-}C_6H_3Me_2CH_2)(CO)_{13}]$,[18] $[WRu_5(\mu\text{-}H)_4(\mu_4\text{-}C)(\mu_3\text{-}CCH_2Ph)(CO)_{12}]$[19] and $[W_3Ir_3(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}CO)_{10}(\eta\text{-}C_5H_4Me)]$,[4c] and, as such, **4** provides a rare example of an 86-CVE cluster adopting an edge-bridged trigonal-bipyramidal geometry rather than the "conventional" octahedral core geometry.

Scheme 2. Synthesis of $[Ru_2WIr_3(\mu_5\text{-}\eta^2\text{-}C_2)(\mu\text{-}CO)_3(CO)_7(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5R_5)]$ [R = H (**5a**), Me (**5c**)]



Core Expansion Using Ethyndiyl Reagents. In our aforementioned report,[4a] we described the insertion of alkynes into the W—W bond of $[W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$ (**2**) to afford complexes of composition $[W_2Ir_2(\mu_4\text{-}\eta^2\text{-}RC_2R)(\mu\text{-}CO)_4(CO)_4(\eta\text{-}C_5H_5)_2]$. Extension to ethyndiyl reagents is clearly of interest. A number of ethyndiyl complexes are extant, ruthenium examples of which have been reported by one of us.[11] Pursuing this idea, an equimolar mixture of $[WIr_3(CO)_{11}(\eta\text{-}C_5H_5)]$ (**1a**) or $[WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5Me_5)]$ (**1c**) and $[(\eta\text{-}C_5H_5)(CO)_2Ru(C{\equiv}C)Ru(CO)_2(\eta\text{-}C_5H_5)]$ was heated in refluxing THF, affording many minor products and one major product identified as $[Ru_2WIr_3(\mu_5\text{-}\eta^2\text{-}C_2)(\mu\text{-}CO)_3(CO)_7(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5R_5)]$ [R = H, 19% (**5a**); Me, 14% (**5c**)] (Scheme 2).

Compounds **5a** and **5c** were characterized by IR and ^1H NMR spectroscopies, FAB MS, and, in the case of **5a**, a single-crystal X-ray structural analysis (the structure of compound **5c** is assumed to be the same, from comparison of their IR and ^1H NMR spectra). For both compounds, the solution IR spectrum shows the presence of terminal and bridging carbonyl groups. The ^1H NMR spectrum for compound **5a** contains singlets at 5.88, 5.60, and 5.44 ppm, indicative of cyclopentadienyl groups, whereas that of compound **5c** shows singlets at 5.42 and 5.34 ppm, indicative of cyclopentadienyl groups, and a singlet at 2.26 ppm indicative of a pentamethylcyclopentadienyl group. The mass spectrum for compound **5a** contains a characteristic carbonyl loss pattern, namely, $[M - n\mathrm{CO}]^+$ ($n = 4-9$), but no molecular ion; in contrast, the mass spectrum for compound **5c** shows a molecular ion, suggesting that additional stability has been conferred on the molecular ion by permethylating the cyclopentadienyl ring. Figure 3 shows an ORTEP plot from the single-crystal X-ray diffraction study of compound **5a** with the molecular structure and atomic labeling scheme.

The structural study reveals that the WIr_3 tetrahedral unit of the precursor cluster has undergone W(4)—Ir(3) bond cleavage to form a butterfly unit. The Ru(5)—C(1) bond of the $[(\eta\text{-}C_5H_5)(CO)_2Ru(C{\equiv}C)Ru(CO)_2(\eta\text{-}C_5H_5)]$ precursor has also undergone cleavage, with Ru(5) capping a WIr_2 face

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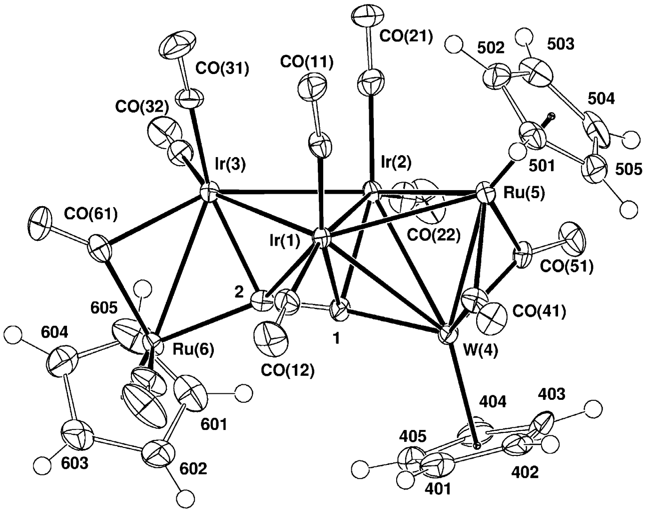

Figure 3. ORTEP plot of $[\mathrm{Ru_2WIr_3}(\mu_5\text{-}\eta^2\text{-}\mathrm{C_2})(\mu\text{-}\mathrm{CO})_3(\mathrm{CO})_7(\eta\text{-}\mathrm{C_5H_5})_3]$ (**5a**). Selected bond distances: Ir(1)—Ir(2) 2.6073(6), Ir(1)—Ir(3) 2.7701(6), Ir(1)—W(4) 2.9741(6), Ir(1)—Ru(5) 2.9178(10), Ir(2)—Ir(3) 2.8204(7), Ir(2)—W(4) 2.9589(7), Ir(2)—Ru(5) 2.7941(10), Ir(3)—Ru(6) 2.7939(12), W(4)—Ru(5) 2.6402(11) Å.

and Ru(6) becoming a spike on the butterfly-wing-tip atom Ir(3). This affords a spiked edge-bridged tetrahedron or, perhaps more usefully given the reagents, a capped and spiked butterfly. The C(1)—C(2) unit interacts with three iridium atoms, a tungsten atom, and a ruthenium atom. There are two carbonyls bridging W(4)—Ru(5) and one bridging the Ir(3)—Ru(6) bond, all other carbonyl groups being terminally ligated; all three of the bridging carbonyls are unsymmetrically disposed, although none correspond to a semibridging interaction defined by the Curtis asymmetry parameter[20]. The atoms W(4), Ru(5), and Ru(6) are each ligated by a cyclopentadienyl group. The cluster is electron-precise with 90 cluster valence electrons. The C(1)—C(2) bond length, a triple bond in the precursor, is now 1.34(2) Å, close to the distance of a formal double bond. The Ir—Ir and Ru—Ir bond lengths of this cluster are not unusual, but the W—Ru distance is surprisingly short [2.6402(11) Å], and the W—Ir bonds are both longer than literature precedents [2.9589(7), 2.9741(6) Å].

With the same goal of cluster core expansion in mind, a mixture of **2** and $[(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\mathrm{Ru}(\mathrm{C{\equiv}C})\mathrm{Ru}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]$ was heated to 60 °C in toluene, affording no tractable products. The reaction was then repeated in refluxing THF; subsequent TLC afforded many minor products, the major product being identified as $[\mathrm{RuW_2Ir_2}\{\mu_4\text{-}\eta^2\text{-}(\mathrm{C_2C{\equiv}C})\mathrm{Ru}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})\}(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})_6(\eta\text{-}\mathrm{C_5H_5})_3]$ (**6**) in 7% yield (Scheme 3). Compound **6** was characterized by IR and ^{1}H NMR spectroscopies, FAB MS, and a single-crystal X-ray diffraction analysis. The solution IR spectrum shows the presence of bridging and terminal carbonyl ligands. The ^{1}H NMR spectrum contains singlets at 5.70, 5.46, 5.14, and 4.65 ppm, indicative of four nonequivalent cyclopentadienyl groups. The mass spectrum shows a molecular ion followed by a loss of three carbonyl groups. Figure 4 shows an ORTEP plot with the molecular structure and atomic labeling scheme from the single-crystal X-ray diffraction study of compound **6**.

In all previous reports of reactions of **2** or its methylcyclopentadienyl-containing analogue with organic alkynes, the alkyne C≡C inserts into the W—W bond in high yield.[4a,d−f] In contrast, the present reaction results in a product corresponding to formal insertion of the terminal $\mathrm{C_2}$ of an $(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\mathrm{RuC_4}$ fragment into the Ir(3)—W(4) bond and capping of the $\mathrm{W_2Ir}$ face by Ru(1), forming an edge-bridged tetrahedron or, perhaps more usefully given the reagents, a face-capped butterfly. There are two carbonyls bridging the W(4)—Ru(1) bond, all other carbonyl groups being terminally coordinated. The atoms W(4), W(5), Ru(1), and Ru(6) are each ligated by a cyclopentadienyl group. The cluster is electron-precise with 74 cluster valence electrons. The $[(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\mathrm{Ru}(\mathrm{C{\equiv}C})\mathrm{Ru}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]$ reagent has undergone Ru—C bond cleavage to form a cap on the $\mathrm{W_2Ir}$ face and has combined with another $\mathrm{C_2}$ fragment to form an $(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\mathrm{RuC_4}$ unit. The Ir(2)—W(4) distance is slightly longer than literature precedents, the doubly bridged W(4)—Ru(1) vector is short for a linkage of this type (see above), and the W(5)—Ru(1) distance [2.9811(6) Å] is longer than the other W—Ru vectors across this series of clusters. CO(11) and CO(41) bridge unsymmetrically, with shorter W—CO bond lengths [2.050(7), 2.047(7) Å, respectively] than Ru—CO vectors [2.107(8), 2.159(8) Å]. Bond lengths and angles in the pendant ruthenium ethynyl unit are not unexpected.

Core Expansion Using Butadiyndiyl Reagents. The diruthenium ethyndiyl reagent has been shown to deliver two ruthenium atoms to the mixed tungsten−iridium cluster cores, albeit with core rearrangement and low yields of identified products. Related dimetal reagents with butadiyndiyl linkages were therefore investigated. Heating an equimolar mixture of **1a**, **1b**, or **1c** and $[(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3\mathrm{W}(\mathrm{C{\equiv}CC{\equiv}C})\mathrm{W}(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})]$ in refluxing toluene afforded one major product in each case, identified as $[\mathrm{W_2Ir_3}\{\mu_4\text{-}\eta^2\text{-}(\mathrm{C_2C{\equiv}C})\mathrm{W}(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})\}(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})_8(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5R_5})]$ [R = H (**7a**) or Me (**7c**); $\mathrm{R_5} = \mathrm{H_4Me}$ (**7b**)], in addition to some trace products (Scheme 4). In contrast, stirring an equimolar mixture of $[\mathrm{WIr_3}(\mathrm{CO})_{11}(\eta\text{-}\mathrm{C_5H_5})]$ (**1a**) and $[(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{CO})_2\mathrm{Ru}(\mathrm{C{\equiv}CC{\equiv}C})\mathrm{Ru}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5Me_5})]$ in toluene or heating a mixture of $[\mathrm{W_2Ir_2}(\mathrm{CO})_{10}(\eta\text{-}\mathrm{C_5H_5})_2]$ and $[(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3\mathrm{W}(\mathrm{C{\equiv}CC{\equiv}C})\mathrm{W}(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})]$ in refluxing toluene failed to give identifiable products.

Products **7a**−**7c** were characterized by IR and ^{1}H NMR spectroscopies, mass spectrometry, satisfactory microanalysis, and, in the case of **7c**, a single-crystal X-ray diffraction study. The solution IR spectra for **7b** and **7c** show the presence of terminal and bridging carbonyl groups, whereas that of **7a** is consistent with an all-terminal CO disposition. The ^{1}H NMR spectra contain three (**7a**) or two (**7b**, **7c**) singlets indicative of cyclopentadienyl groups, while the spectrum of **7b** contains a multiplet and a singlet at 2.33 ppm indicative of a methylcyclopentadienyl group and that of **7c** contains a singlet at 2.15 ppm consistent with a pentamethylcyclopentadienyl ligand. The mass spectra show molecular ion signals followed by consecutive losses of 13

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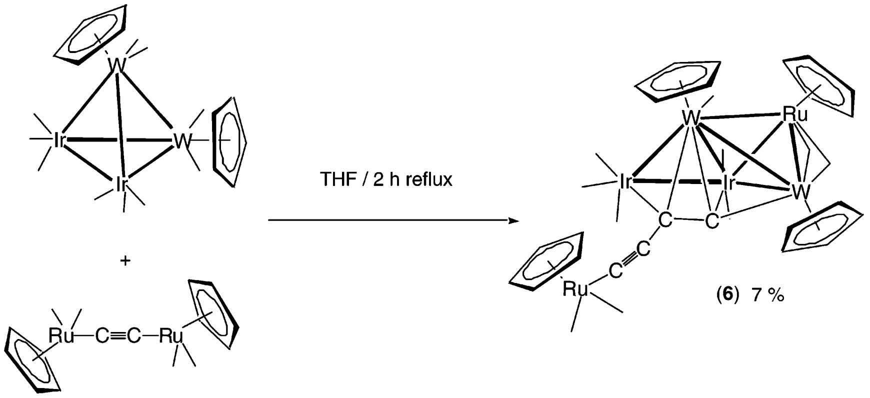
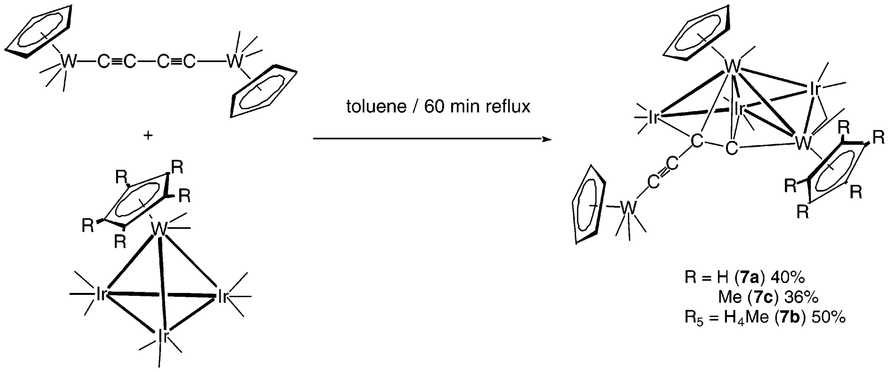
Scheme 3. Synthesis of $[\mathrm{RuW_2Ir_2}\{\mu_4\text{-}\eta^2\text{-}(\mathrm{C_2C{\equiv}C})\mathrm{Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})\}(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})_6(\eta\text{-}\mathrm{C_5H_5})_3]$ (**6**).



Scheme 4. Synthesis of $[\mathrm{W_2Ir_3}\{\mu_4\text{-}\eta^2\text{-}(\mathrm{C_2C{\equiv}C})\mathrm{W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})\}(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})_8(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5R_5})]$ [R = H (**7a**), Me (**7c**), $\mathrm{R_5}$ = $\mathrm{H_4Me}$ (**7b**)]



(**7a**), 5 (**7b**), or 2 (**7c**) carbonyl groups. Figure 5 shows an ORTEP plot of **7c** with the molecular structure and atomic labeling scheme.

The cluster core of **7c** consists of a tetrahedron of two tungsten and two iridium atoms with an iridium atom bridging the Ir(2)—W(5) bond and the $\mathrm{C_2}$ unit of a tungstenabutadiyndiyl "ligand" interacting with two iridiums and two tungsten atoms. W(5) and W(6) are ligated by cyclopentadienyl groups, and W(4) is ligated by a pentamethylcyclopentadienyl group. The cluster is electron-precise with 74 cluster valence electrons. As with the synthesis of **3**, the different cyclopentadienyl ligands in the starting materials for the preparation of **7c** have labeled the tungsten atoms,

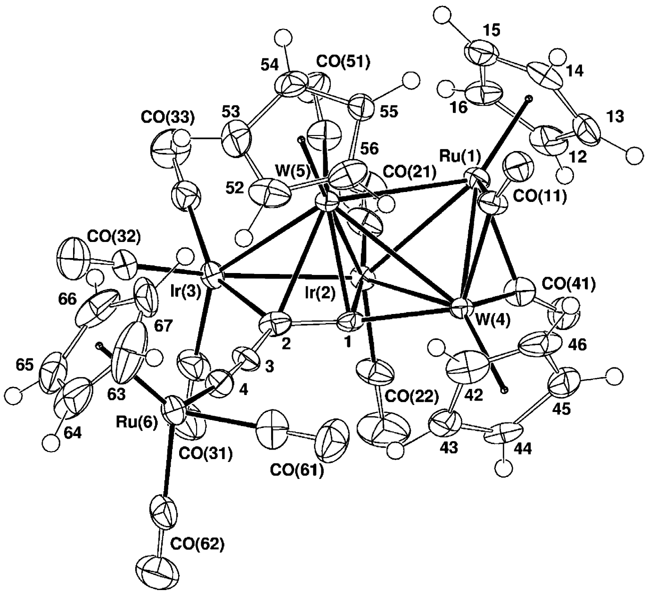


Figure 4. ORTEP plot of $[\mathrm{RuW_2Ir_2}\{\mu_4\text{-}\eta^2\text{-}(\mathrm{C_2C{\equiv}C})\mathrm{Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})\}(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})_6(\eta\text{-}\mathrm{C_5H_5})_3]$ (**6**). Selected bond distances: Ir(2)—Ir(3) 2.7565(4), Ir(2)—W(4) 2.9266(4), Ir(2)—W(5) 2.7223(4), Ir(2)—Ru(1) 2.8202(6), Ir(3)—W(5) 2.8198(4), W(4)—Ru(1) 2.6598(6), W(5)—Ru(1) 2.9811(6), W(4)—W(5) 3.0207(4) Å.

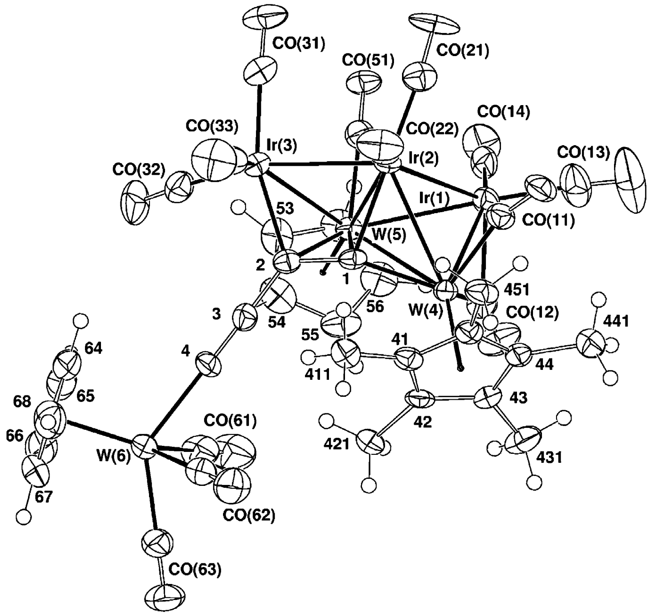


Figure 5. ORTEP plot of $[\mathrm{W_2Ir_3}\{\mu_4\text{-}\eta^2\text{-}(\mathrm{C_2C{\equiv}C})\mathrm{W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})\}(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})_8(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5Me_5})]$ (**7c**). Selected bond distances: Ir(1)—Ir(2) 2.9830(4), Ir(1)—W(4) 2.7278(4), Ir(1)—W(5) 2.8783(4), Ir(2)—Ir(3) 2.7525(4), Ir(2)—W(4) 2.8858(4), Ir(2)—W(5) 2.7540(4), Ir(3)—W(5) 2.8339(4), W(4)—W(5) 3.1117(4) Å.

the product corresponding to insertion of the ditungsten butadiyndiyl reagent into Ir−Ir and W−Ir bonds and a coordination mode change of one ethynyl group from η^1- to μ_4-η^1:η^1:η^1:η^2-bound. The Ir(1)−Ir(2) and W(4)−W(5) bonds are exceptionally long compared to previously reported values (see above), other metal−metal vectors being within the literature ranges. CO(12) symmetrically bridges W(4) and Ir(1), CO(11) formally semibridges the same bond (Curtis asymmetry parameter $\alpha = 0.24^{20}$), and the other eight carbonyls are terminally coordinated.

Discussion

The present studies have highlighted the utility of employing differing cyclopentadienyl ligands in the starting materials; the labeled tungsten atoms permit identification of the mononuclear-complex-derived tungsten atom that is inserted into the frameworks of **3** and **7c**. The cluster expansion reaction reported in ref 4a, and presumed to result from insertion of a tungsten alkynyl complex into the Ir−Ir bond of the tetrahedral tungsten-triiridium starting material, is now seen to proceed by the unusual insertion of a [W(C≡CPh)(CO)$_x$(η-C$_5$H$_5$)] unit into Ir−Ir and W−Ir bonds, accompanied by a change in coordination mode from a terminally bonded alkynyl to a μ_4-η^2 alkynyl, to afford **3**. Unlike in our earlier study, a second product (**4**) has been identified and structurally characterized; it contains an unusual edge-bridged trigonal-bipyramidal core, an alkynyl ligand interacting with two iridium atoms and two tungsten atoms in a μ_4-η^2 fashion, and a vinylidene ligand bridging a W−W bond, solvent activation or reaction with adventitious HCl having presumably resulted in hydrogen incorporation to afford the vinylidene ligand, and chlorine bonding to a tungsten atom. The pentamethylcyclopentadienyl ligand-labeling of the precursor cluster tungsten atom also permits comment on the formation of **4**, which, in contrast to that of **3**, seems to proceed by insertion of [W(C≡CPh)(CO)$_x$(η-C$_5$H$_5$)] into a W−Ir bond, accompanied by a change in mode of coordination from a terminally bonded alkynyl to a μ_4-η^2 alkynyl ligand and formation of new W−Ir bonds. This is then followed by capping this new WIr$_2$ face by an additional [W(C≡CPh)(CO)$_x$(η-C$_5$H$_5$)] unit to afford W-bound chloro and vinylidene and μ-η^1 ligation of the vinylidene. Judging from the foregoing discussion, we do not anticipate that **3** is an intermediate en route to **4**, but the low yields have precluded examination of this possibility.

Cluster **5a** contains the edge-bridged tetrahedral core motif observed for **3**, but in this case with an additional “spike”. Reactions of tungsten-triiridium clusters with internal alkynes proceed with alkyne dimerization and/or C≡C scission,[4b,c] and reactions with tungsten alkynyl complexes afford products with intact tungsten alkynyl linkages;[4a] in contrast, **5a** results from Ru−C cleavage. Clusters **6** and **7** also contain edge-bridged tetrahedral cores. Reactions of ditungsten−diiridium clusters with internal alkynes proceed by insertion of the C$_2$ unit into the W−W bond to afford pseudooctahedral cores or, in one case, dimerization and C≡C scission to give C$_3$ and C$_1$ ligands.[4d] In contrast, **6** corresponds to Ru−C cleavage, formal insertion of the C$_2$ into a W−Ir bond, and dimerization to give a C$_4$ ligand. C$_4$ chains have been prepared by several procedures,[2j] but to the best of our knowledge, this is the first synthesis using a dimetalated C$_2$ precursor. The presence of the ditungsten−diiridium cluster is critical; heating [(η-C$_5$H$_5$)(CO)$_2$Ru(C≡C)Ru(CO)$_2$(η-C$_5$H$_5$)] in solvents of progressively increasing boiling point up to and including refluxing toluene resulted in no reaction.[21] The formation of **7** proceeds in a fashion similar to that of **3**, the ditungsten butadiyndiyl reacting as a tungsten alkynyl complex.

Thus far, few medium- or high-nuclearity clusters incorporating disparate metals have been reported,[3] and only one structurally authenticated example each of penta-,[4a] hexa-,[4c] or heptametallic[13] tungsten−iridium clusters are extant. Although yields of all clusters other than **7a**−**c** mitigate against subsequent studies, the present study expands this class to include further examples of pentametallic (**3**, **7c**) and hexametallic (**4**) tungsten−iridium clusters, together with the first examples of penta- and hexametallic mixed tungsten−ruthenium−iridium clusters (**5a**, **6**).

Acknowledgment. We thank the Australian Research Council (ARC) for financial support and Johnson-Matthey Technology Centre for the generous loan of iridium salts. M.G.H. holds an ARC Australian Professorial Fellowship.

Supporting Information Available: Tables giving atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **3**, **4**, **5a**, **6**, and **7c** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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