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Mixed-Metal Cluster Chemistry. 11.[1] Reactions of Tungsten−Iridium Clusters with Terminal Alkynes and Tungsten Acetylides: X-ray Crystal Structures of $Cp_2W_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu\text{-}CO)_4(CO)_4$ and $Cp_2W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2C_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9$

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Reactions of $Cp_2W_2Ir_2(CO)_{10}$ (**1**) with terminal arylalkynes HC≡CR afford the complexes $Cp_2W_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2R)(\mu\text{-}CO)_4(CO)_4$ [R = Ph (**3**), C_6H_4Me-4 (**4**), $C_6H_4NO_2$-4 (**5**)] in excellent yields (56−70%). The analogous adduct with the terminal alkylalkyne $HC{\equiv}CBu^t$ is obtained in much lower yield (20%). An X-ray structural study of **3** reveals that the alkynes have formally inserted into the W−W bond of **1**, affording clusters with a pseudooctahedral geometry. The site of reactivity in **1** is consistent with the lack of reactivity towards terminal alkynes of the isostructural and isolobally related $CpWIr_3(CO)_{11}$ (**2**). Reaction of **1** with the buta-1,3-diynyl complex $CpW(CO)_3(C{\equiv}CC{\equiv}CH)$ (**8**) affords the analogous adduct $Cp_2W_2Ir_2\{\mu_4\text{-}\eta^2\text{-}HC_2C{\equiv}CW(CO)_3Cp\}(\mu\text{-}CO)_4(CO)_4$ (**9**), shown spectroscopically to be attached via the C≡CH unit rather than the WC≡C group. Attempts at condensing the pendant $CpW(CO)_3C{\equiv}C$ unit with the W_2Ir_2 core in **9** have proven unsuccessful. Reactions of $CpWIr_3(CO)_{11}$ (**2**) with equimolar amounts of the tungsten acetylides $CpW(CO)_3(C{\equiv}CR)$ (R = Ph, C_6H_4Me-4, $C_6H_4NO_2$-4, C≡CPh) afford the products $Cp_2W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2R)(\mu\text{-}CO)(CO)_9$ [R = Ph (**11**), C_6H_4-Me-4 (**12**), $C_6H_4NO_2$-4 (**13**), C≡CPh (**14**)] in fair yields (23−45%). Product **12** has been structurally characterized, with the structural study revealing an edge-bridged tetrahedral metal core geometry and an unusual $\mu_4\text{-}\eta^2$ $(3\sigma + \pi)$-coordinated alkynyl ligand. The reaction corresponds to formal insertion of the alkynyltungsten reagent into an Ir−Ir linkage of **2**. Reactions of **1** with these tungsten acetylides were not successful under the experimental conditions attempted, a result ascribed to steric constraints.

Introduction

The chemistry of mixed-metal clusters has been of enduring interest.[2−12] Mixed-metal clusters are potential precursors to supported bimetallic catalysts, the differing metals provide effective labels for ligand fluxionality studies, and the varying metals of the cluster core afford the possibility of metallo- and bond-selectivity and thus directing reactivity for a range of reagents. We have probed the last-mentioned feature utilizing phosphines and the systematically varied series of tetrahedral clusters $Cp_xM_xIr_{4-x}(CO)_{12-x}$ (x = 0−2, M = W, Mo)[13−21] noting enhanced reactivity and

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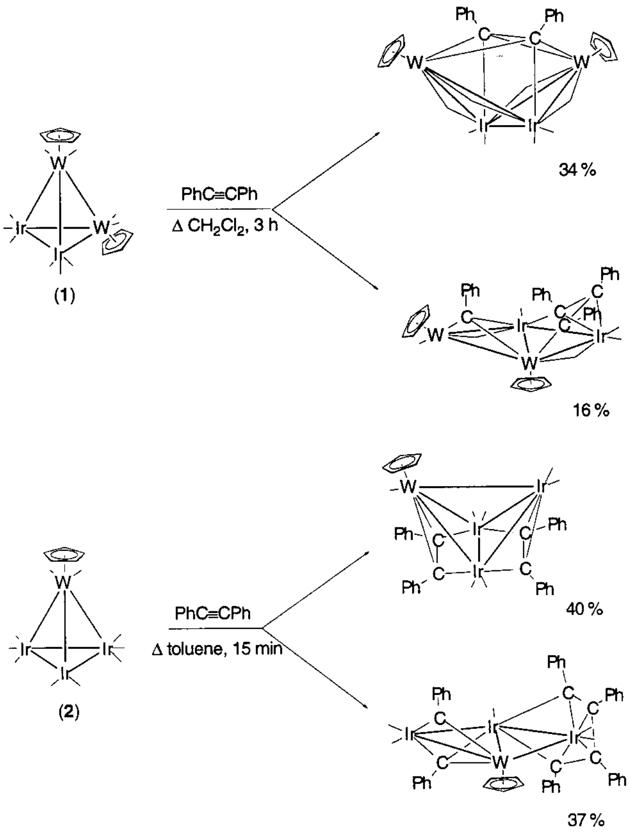
differing site-selectivity and carbonyl fluxionality upon heterometal incorporation into the "parent" cluster $Ir_4(CO)_{12}$.

Our studies have, however, thus far focused largely on P-donor ligands. Acetylenes are the prototypical C_x ligands; their cluster chemistry is of interest, not only in its own right but also in modeling Fischer–Tropsch and other catalyzed processes.[9,22–24] The acetylene chemistry of $Ir_4(CO)_{12}$ has been summarized;[25] excluding phosphinoalkynes which initially react by way of P-coordination, the only tetranuclear product isolated thus far is the rectangular $[Ir_4\{\mu\text{-}\eta^4\text{-Me(O)OCC}_2\text{C(O)OMe}\}_2\{\mu\text{-Me(O)OCC}_2\text{C(O)OMe}\}_2(CO)_8]$.[26] The mixed-metal system shows significantly enhanced reactivity. Shapley and co-workers have reported the reactions of $Cp_xW_xIr_{4-x}(CO)_{12-x}$ ($x = 1, 2$) with internal acetylenes. The addition of diphenylacetylene to $Cp_2W_2Ir_2(CO)_{10}$ (**1**) affords $Cp_2W_2Ir_2(CO)_8(PhC_2Ph)$ (34%) and the structurally verified $Cp_2W_2Ir_2(\mu_3\text{-CPh})\{\mu_3\text{-}\eta^3\text{-C(Ph)C(Ph)C(Ph)}\}(CO)_6$ (16%).[27] In contrast, diphenylacetylene reacts with $CpWIr_3(CO)_{11}$ (**2**) to give the crystallographically confirmed clusters $CpWIr_3(\mu_3\text{-}\eta^2\text{-PhC}_2\text{Ph})_2(CO)_7$ (40%) and $CpWIr_3(\mu_3\text{-CPh})(\mu\text{-CPh})\{\mu\text{-}\eta^4\text{-C(Ph)C(Ph)C(Ph)C(Ph)}\}(CO)_5$ (37%)[28] (Scheme 1).

The reactions of these mixed tungsten–iridium clusters with terminal alkynes have not thus far been investigated. We have therefore extended our ongoing research of the reactions of tungsten–iridium clusters to embrace a range of terminal alkynes, and we report herein the results of reacting **1** and **2** with $HC{\equiv}CR$ [R = Ph, $C_6H_4Me\text{-}4$, $C_6H_4NO_2\text{-}4$, Bu^t, and $C{\equiv}CW(CO)_3Cp$], and the results of a single-crystal X-ray study of a representative adduct $Cp_2W_2Ir_2(\mu_4\text{-}\eta^2\text{-HC}_2\text{Ph})(\mu\text{-CO})_4(CO)_4$ (**3**). Extension of the earlier studies to include "inorganic acetylenes" such as alkynylmetal complexes is also logical. Reaction of **1** and **2** with tungsten acetylide complexes potentially affords a method of expanding the metal core nuclearity under controlled conditions. With this idea in mind, we report herein the results of treating **1** and **2** with tungsten acetylides and characterization by single-crystal X-ray study of the reaction product $Cp_2W_2Ir_3(\mu_4\text{-}\eta^2\text{-C}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(CO)_9$ (**12**).

Scheme 1. Reactions of $Cp_2W_2Ir_2(CO)_{10}$ (1) and $CpWIr_3(CO)_{11}$ (2) with Diphenylacetylene



Experimental Section

General Information. All reactions were performed under an atmosphere of dry nitrogen (high-purity grade, BOC), although no special precautions were taken to exclude air during workup. The reaction solvents were dried and distilled under nitrogen using standard methods: CH_2Cl_2 over CaH_2, and toluene from sodium/benzophenone. All other solvents were reagent grade and used as received. Petroleum ether refers to a fraction of boiling point range 60–80 °C. The products of thin-layer chromatography were separated on 20 × 20 cm glass plates coated with Merck GF_{254} silica gel (0.5 mm). The complexes $Cp_2W_2Ir_2(CO)_{10}$,[29] $CpW(CO)_3(C{\equiv}CR)$ (R = Ph, $C_6H_4Me\text{-}4$, $C_6H_4NO_2\text{-}4$, $C{\equiv}CH$, $C{\equiv}CPh$),[30] and 4-nitrophenylacetylene[31] were prepared by the literature procedures. Phenylacetylene, 4-ethynyltoluene, and 3,3-dimethyl-1-butyne were purchased commercially and used as received.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer system 2000 Fourier transform spectrophotometer with NaCl optics. ^1H NMR spectra were recorded on a Varian Gemini 300 spectrometer (300 MHz). ^{13}C NMR and INEPT spectra were recorded on a Varian VXR300S spectrometer (75 MHz) and are proton decoupled. Spectra were run in $CDCl_3$ (Aldrich), acetone-d_6 (Aldrich), or CD_2Cl_2 (Fluorochem); chemical shifts in ppm are referenced to internal

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residual solvent (^{1}H, $CHCl_3$ = 7.24 ppm, acetone-d_5 = 2.04 ppm;^{13}C, CD_2Cl_2 = 53.8 ppm). The ^{13}C NMR spectra were proton decoupled and recorded using ca. 0.02 M Cr(acac)$_3$ as a relaxation agaent. The INEPT experiments were run with a multiplicity of 2, selecting methine carbons only. Mass spectra were obtained at the Australian National University on a VG ZAB 2SEQ instrument (30 kV Cs^+ ions, current 1 mA, accelerating potential 8 kV, matrix 3-nitrobenzyl alcohol). Peaks are reported in the form: *m*/*z* (assignment, relative intensity). Elemental microanalyses were performed by the Microanalysis Service Unit in the Research School of Chemistry, Australian National University.

Reaction of $Cp_2W_2Ir_2(CO)_{10}$ with HC≡CPh (Method A). A deep red solution of $Cp_2W_2Ir_2(CO)_{10}$ (20.0 mg, 0.0172 mmol) and HC≡CPh (3.2 μL, 0.03 mmol) in toluene (20 mL) was stirred at 50 °C for 1 h, after which time the reaction solution was allowed to cool to room temperature and the solvent was removed in vacuo. Alternatively, the solution was stirred at room temperature for 16 h (the result and yield of product were approximately the same). The resultant brown residue was dissolved in CH_2Cl_2 (ca. 1 mL) and chromatographed (3:1 CH_2Cl_2:petroleum ether eluant) to afford one product. The band at R_f 0.30 was crystallized from CH_2Cl_2/*n*-C_6H_{14} to afford dark green crystals of $Cp_2W_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu\text{-}CO)_4(CO)_4$, **3** (14.5 mg, 70%). Analytical data for **3**: IR (CH_2Cl_2) 2061vs, 2032vs, 2008m, 1986m, 1821br m; ^{1}H NMR (acetone-d_6) δ 9.77 (s, 1H, ≡CH), 7.32−7.00 (m, 5H, Ph), 5.28 (s, 1H, CH_2Cl_2), 5.14 (s, 10H, C_5H_5); ^{13}C NMR (CD_2Cl_2) δ 222.0 (CO), 220.9 (CO), 177.9 (CO), 177.7 (CO), 175.7 (CO), 173.1 (CO), 152.8 (*C*Ph), 128.9−118.9 (Ph), 99.2 (≡CH), 93.5 (C_5H_5); FAB MS 1208 ([M]$^+$, 58), 1152 ([M − 2CO]$^+$, 29), 1124 ([M − 3CO]$^+$, 100), 1096 ([M − 4CO]$^+$, 47), 1068 ([M − 5CO]$^+$, 12), 1040 ([M − 6CO]$^+$, 98), 1012 ([M − 7CO]$^+$, 39). Anal. Calcd: C, 25.84; H, 1.33. Found: C, 25.50; H, 1.26.

Reaction of $Cp_2W_2Ir_2(CO)_{10}$ with HC≡CC$_6$H$_4$Me-4. Following method A, $Cp_2W_2Ir_2(CO)_{10}$ (20.0 mg, 0.0172 mmol) and HC≡CC$_6$H$_4$Me-4 (3.5 mg, 0.03 mmol) in toluene (20 mL) afforded one product after chromatography (3:1 CH_2Cl_2: petroleum ether eluant). The band at R_f 0.32 was crystallized from CH_2Cl_2/c-C_6H_{12} to afford purple/green crystals of $Cp_2W_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2C_6H_4Me\text{-}4)(\mu\text{-}CO)_4(CO)_4$, **4** (12.5 mg, 59%). Analytical data for **4**: IR (CH_2Cl_2) 2060vs, 2031vs, 2006m, 1986m, 1825br m; ^{1}H NMR (acetone-d_6) δ 9.12 (s, 1H, ≡CH), 7.00−6.45 (m, 4H, C_6H_4), 4.90 (s, 10H, C_5H_5), 2.22 (s, 3H, Me); FAB MS 1222 ([M]$^+$, 57), 1166 ([M − 2CO]$^+$, 30), 1138 ([M − 3CO]$^+$, 98), 1110 ([M − 4CO]$^+$, 37), 1082 ([M − 5CO]$^+$, 10), 1054 ([M − 6CO]$^+$, 100), 1026 ([M − 7CO]$^+$, 42). Anal. Calcd: C, 26.53; H, 1.70. Found: C, 26.82; H, 1.90.

Reaction of $Cp_2W_2Ir_2(CO)_{10}$ with HC≡CC$_6$H$_4$NO$_2$-4. Following method A, $Cp_2W_2Ir_2(CO)_{10}$ (20.0 mg, 0.0172 mmol) and HC≡CC$_6$H$_4$NO$_2$-4 (4.4 mg, 0.03 mmol) in toluene (20 mL) afforded two products after chromatography (3:1 CH_2Cl_2: petroleum ether eluant), one of which was in trace quantities. Crystallization of the contents of the second band at R_f 0.40 from CH_2Cl_2/c-C_6H_{12} afforded brown crystals of $Cp_2W_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2C_6H_4NO_2\text{-}4)(\mu\text{-}CO)_4(CO)_4$, **5** (12.0 mg, 56%). Analytical date for **5**: IR (CH_2Cl_2) 2064vs, 2036vs, 2006w, 1991m, 1829br m; ^{1}H NMR ($CDCl_3$) δ 8.95 (s, 1H, ≡CH), 8.10−7.02 (m, 4H, C_6H_4), 4.95 (s, 10H, C_5H_5); FAB MS 1253 ([M]$^+$, 37), 1197 ([M − 2CO]$^+$, 26), 1169 ([M − 3CO]$^+$, 100), 1141 ([M − 4CO]$^+$, 80), 1113 ([M − 5CO]$^+$, 61), 1085 ([M − 6CO]$^+$, 88), 1057 ([M − 7CO]$^+$, 47). Satisfactory microanalyses could not be obtained due to sample decomposition in solution over days.

Reaction of $Cp_2W_2Ir_2(CO)_{10}$ with HC≡CBu^t. A deep red solution of $Cp_2W_2Ir_2(CO)_{10}$ (20.0 mg, 0.0172 mmol) and HC≡CBu^t (4 μL, 0.03 mmol) in toluene (20 mL) was refluxed for 1 h, after which time the reaction solution was allowed to cool to room temperature and the solvent was removed in vacuo. The resultant brown residue was dissolved in CH_2Cl_2 (ca. 1 mL) and chromatographed (3:1 CH_2Cl_2:petroleum ether eluant) to afford five bands, four of which were in minor amounts and not isolated. Band 3 at R_f at 0.30 was crystallized from CH_2Cl_2/c-C_6H_{12} to afford brown crystals of $Cp_2W_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2Bu^t)(\mu\text{-}CO)_4(CO)_4$, **6** (4.0 mg, 20%). Analytical data for **6**: IR (CH_2Cl_2) 2065vs, 2036vs, 2010m, 1990m, 1835br m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.64 (s, 1H, ≡CH), 4.73 (s, 10H, C_5H_5), 2.12 (s, 9H, Me); FAB MS 1192 ([M]$^+$, 35), 1164 ([M − CO]$^+$, 6), 1136 ([M − 2CO]$^+$, 14), 1108 ([M − 3CO]$^+$, 100), 1080 ([M − 4CO]$^+$, 80), 1052 ([M − 5CO]$^+$, 58). Anal. Calcd: C, 24.25; H, 1.70. Found: C, 23.86; H, 1.90.

Reaction of $Cp_2W_2Ir_2(CO)_{10}$ with CpW(CO)$_3$(C≡CC≡CH). A deep red solution of $Cp_2W_2Ir_2(CO)_{10}$ (20.0 mg, 0.0172 mmol) and CpW(CO)$_3$(C≡CC≡CH) (6.6 mg, 0.0172 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 16 h. The brown solution was evaporated to dryness. The resultant brown residue was redissolved in CH_2Cl_2 (ca. 1 mL) and chromatographed (3:1 CH_2Cl_2:petroleum ether eluant) to afford one product. The band at R_f 0.28 was crystallized from CH_2Cl_2/c-C_6H_{12} to afford dark green crystals of $Cp_2W_2Ir_2\{\mu_4\text{-}\eta^2\text{-}HC_2C{\equiv}CW(CO)_3Cp\}(\mu\text{-}CO)_4(CO)_4$, **9** (15.3 mg, 62%). Analytical data for **9**: IR (CH_2Cl_2) ν(C≡C) 2155w, ν(C≡O) 2058s, 2055sh, 2033vs, 2003m, 1984w, 1945br s, 1823 br m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.40 (s, 1H, ≡CH), 5.54 (s, 5H, C_5H_5), 5.29 (s, 10H, C_5H_5); ^{13}C NMR (CD_2Cl_2) δ 227.6 (CO), 222.3 (CO), 221.7 (CO), 212.9 (CO), 177.9 (CO), 177.7 (CO), 173.5 (CO), 172.3 (CO), 146.8 (*C*≡CH), 109.6 (≡CH), 106.2 (W*C*≡), 94.2 (C_5H_5), 92.3 (C_5H_5), 78.0 (s, WC≡*C*); FAB MS 1488 ([M]$^+$, 10), 1460 ([M − CO]$^+$, 4), 1432 ([M − 2CO]$^+$, 6), 1404 ([M − 3CO]$^+$, 13), 1376 ([M − 4CO]$^+$, 3), 1348 ([M − 5CO]$^+$, 7), 1320 ([M − 6CO]$^+$, 17), 1292 ([M − 7CO]$^+$, 65), 1264 ([M − 8CO]$^+$, 37), 1236 ([M − 9CO]$^+$, 42), 1208 ([M − 10CO]$^+$, 35), 1180 ([M − 11CO]$^+$, 100). Anal. Calcd: C, 24.21; H, 1.08. Found: C, 24.31; H, 0.84.

Reaction of CpWIr$_3$(CO)$_{11}$ with HC≡CR [R = Ph, C$_6$H$_4$NO$_2$-4, C≡CW(CO)$_3$Cp]. An orange solution of CpWIr$_3$(CO)$_{11}$ (20.0 mg, 0.0176 mmol) and HC≡CR (0.0176−0.03 mmol) in toluene (20 mL) was slowly heated to 110 °C and refluxed for 15 min. No reaction was apparent by IR monitoring of the reaction mixture. The solution was allowed to reflux for a further 45 min, and the resultant brown solution was then evaporated to dryness. The brown residue was dissolved in CH_2Cl_2 (ca. 1 mL). Purification by thin-layer chromatography (3:1 CH_2Cl_2:petroleum ether) eluted one to three bands in trace amounts.

Reaction of $Cp_2W_2Ir_2(CO)_{10}$ with CpW(CO)$_3$(C≡CPh). An orange-red solution of $Cp_2W_2Ir_2(CO)_{10}$ (**1**) (20.0 mg, 0.0172 mmol) and CpW(CO)$_3$(C≡CPh) (7.6 mg, 0.0176 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 60 h in the absence of light. No reaction was apparent by IR monitoring of the reaction mixture. The solution was slowly heated to 40 °C and refluxed 15 min. No reaction was apparent by IR monitoring. The solvent was then removed in vacuo and replaced with toluene (20 mL). The solution was slowly heated to 110 °C and finally refluxed for 15 min. The resultant dark brown solution was then evaporated to dryness. The brown residue obtained was dissolved in CH_2Cl_2 (ca. 1 mL). Purification by thin-layer chromatography (1:1 CH_2Cl_2:petroleum ether) eluted five bands in trace amounts. Related reactions of **1** with CpW(CO)$_3$(C≡CR) (R = C$_6$H$_4$Me-4, C$_6$H$_4$NO$_2$-4, or C≡CPh) afforded similar results.

Reaction of CpWIr$_3$(CO)$_{11}$ with CpW(CO)$_3$(C≡CPh) (Method B). An orange solution of CpWIr$_3$(CO)$_{11}$ (20.0 mg, 0.0176 mmol) and CpW(CO)$_3$(C≡CPh) (7.6 mg, 0.0176 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 60 h in the absence of light. The brown solution was then evaporated to dryness. The resultant brown residue was dissolved in CH_2Cl_2 (ca 1 mL) and chromatographed (3:2 CH_2Cl_2: petroleum ether eluant) to afford three bands. The contents of the first two bands were identified as starting materials by IR spectroscopy. The third band at R_f 0.43 was crystallized from CH_2Cl_2/*n*-C_8H_{18} to afford brown crystals of $Cp_2W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}CO)(CO)_9$, **11** (11.5 mg, 45%). Analytical data for **11**: IR (c-C_6H_{12}) 2080vs, 2037s, 2032vs, 2024s, 2017m, 2004s, 1996w, 1982w, 1968m, 1958br m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.69−7.34 (m, 5H, Ph), 5.59 (s, 5H, C_5H_5), 4.64 (s, 5H, C_5H_5); FAB MS 1456 ([M]$^+$, 15), 1428 ([M − CO]$^+$, 34), 1400 ([M − 2CO]$^+$, 22), 1372 ([M − 3CO]$^+$, 84), 1344 ([M − 4CO]$^+$, 75), 1316 ([M − 5CO]$^+$, 100), 1288 ([M − 6CO]$^+$, 60), 1260 ([M − 7CO]$^+$, 59), 1232 ([M − 8CO]$^+$, 60), 1204 ([M − 9CO]$^+$, 39), 1176 ([M − 10CO]$^+$, 740). Anal. Calcd: C, 23.21; H, 1.04. Found: C, 23.64; H, 1.25.

Reaction of $CpWIr_3(CO)_{11}$ with $CpW(CO)_3(C{\equiv}CC_6H_4Me$-4). Following method B, $CpWIr_3(CO)_{11}$ (20.0 mg, 0.0176 mmol) and $CpW(CO)_3(C{\equiv}CC_6H_4Me$-4) (7.9 mg, 0.0176 mmol) in CH_2Cl_2 (20 mL) afforded one product after purification by preparative thin-layer chromatography (1:1 CH_2Cl_2:petroleum ether eluant). The contents of the band at R_f 0.41 were crystallized from CH_2Cl_2/c-C_6H_{12} to afford brown crystals of $Cp_2W_2Ir_3(\mu_4$-η^2-$C_2C_6H_4Me$-4)(μ-CO)$(CO)_9$, **12** (10.3 mg, 40%). Analytical data for **12**: IR (c-C_6H_{12}) 2079vs, 2036s, 2031vs, 2024s, 2016m, 2003s, 1995w, 1981w, 1967m, 1958br m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.73−7.42 (m, 4H, C_6H_4), 5.58 (s, 5H, C_5H_5), 4.63 (s, 5H, C_5H_5), 2.40 (s, 3H, Me); FAB MS 1470 ([M]$^+$, 27), 1442 ([M − CO]$^+$, 34), 1414 ([M − 2CO]$^+$, 3), 1386 ([M − 3CO]$^+$, 90), 1358 ([M − 4CO]$^+$, 66), 1330 ([M − 5CO]$^+$, 100), 1302 ([M − 6CO]$^+$, 95), 1274 ([M − 7CO]$^+$, 90), 1246 ([M − 8CO]$^+$, 60). Anal. Calcd: C, 23.70; H, 1.17. Found: C, 24.14; H, 0.73.

Reaction of $CpWIr_3(CO)_{11}$ with $CpW(CO)_3(C{\equiv}CC_6H_4$-$NO_2$-4). Following method B, $CpWIr_3(CO)_{11}$ (20.0 mg, 0.0176 mmol) and $CpW(CO)_3(C{\equiv}CC_6H_4NO_2$-4) (8.4 mg, 0.0176 mmol) in CH_2Cl_2 (20 mL) afforded three products after purification by preparative thin-layer chromatography (1:1 CH_2Cl_2:petroleum ether eluant). Crystallization of the contents of the third band at R_f 0.38 from CH_2Cl_2/c-C_6H_{12} afforded brown crystals of $Cp_2W_2Ir_3(\mu_4$-η^2-$C_2C_6H_4NO_2$-4)(μ-CO)$(CO)_9{\cdot}CH_2Cl_2$, **13** (11.6 mg, 44%). Analytical data for **13**: IR (c-C_6H_{12}) 2082vs, 2040s, 2035vs, 2029s, 2019m, 2007s, 1972w, 1961m, 1955br m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.36 (d, 2H, C_6H_4), 7.75 (d, 2H, C_6H_4), 5.57 (s, 5H, C_5H_5), 5.28 (s, 2H, CH_2Cl_2), 4.66 (s, 5H, C_5H_5); FAB MS 1501 ([M]$^+$, 10), 1473 ([M − CO]$^+$, 25), 1445 ([M − 2CO]$^+$, 26), 1417 ([M − 3CO]$^+$, 71), 1389 ([M − 4CO]$^+$, 67), 1361 ([M − 5CO]$^+$, 100), 1333 ([M − 6CO]$^+$, 59), 1305 ([M − 7CO]$^+$, 51), 1277 ([M − 8CO]$^+$, 48). Anal. Calcd: C, 21.97; H, 1.02; N, 0.88. Found: C, 21.50; H, 0.89; N, 1.02.

Reaction of $CpWIr_3(CO)_{11}$ with $CpW(CO)_3(C{\equiv}CC{\equiv}CPh)$. Following method B, $CpWIr_3(CO)_{11}$ (20.0 mg, 0.0176 mmol) and $CpW(CO)_3(C{\equiv}CC{\equiv}CPh)$ (8.0 mg, 0.0176 mmol) in CH_2Cl_2 (20 mL) afforded four bands after purification by preparative thin-layer chromatography (1:1 CH_2Cl_2:petroleum ether eluant). The contents of the first two bands were identified as starting material by IR spectroscopy. The third band was in trace amounts. The contents of the fourth band at R_f 0.29 were crystallized from CH_2Cl_2/c-C_6H_{12} to afford brown crystals of $Cp_2W_2Ir_3(\mu_4$-η^2-$C_2C{\equiv}CPh)(\mu$-CO)$(CO)_9$, **14** (6.1 mg, 23%). Analytical data for **14**: IR (c-C_6H_{12}) 2085s, 2053w, 2037vs, 2019vs, 1980m, 1975w, 1967br w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.47−7.36 (m, 5H, Ph), 5.80 (s, 5H, C_5H_5), 4.80 (s, 5H, C_5H_5); FAB MS 1423 ([M − 2CO]$^+$, 20), 1395 ([M − 3CO]$^+$, 40), 1367 ([M − 4CO]$^+$, 61), 1339 ([M − 5CO]$^+$, 100), 1311 ([M − 6CO]$^+$, 86), 1283 ([M − 7CO]$^+$, 50), 1255 ([M − 8CO]$^+$, 63). Anal. Calcd: C, 24.35; H, 1.02. Found: C, 24.64; H, 1.00.

Structure Determinations. Crystals of compound **3** and **12** suitable for diffraction analysis were grown by slow diffusion of *n*-hexane into dichloromethane at −5 °C (**3**) or slow evaporation of dichloromethane from a dichloromethane/octane solution of (**12**). Unique diffractometer data sets were measured at ~295 K within the specified $2\theta_{max}$ limit ($2\theta/\theta$ scan mode; monochromatic Mo $K\alpha$ radiation (λ = 0.7107$_3$ Å)), yielding N independent reflections. N_o of these with $I > 3\sigma(I)$ were considered "observed" and used in the full matrix/large block least-squares refinements after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included, constrained at estimated values. Conventional residuals R, R_w on $|F|$ at convergence are given. Neutral atom complex scattering factors were used, computation using teXsan.[32] Pertinent results are given in the figure and tables. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Structural Database.

Table 1. Crystallographic Data for $Cp_2W_2Ir_2(\mu_4$-η^2-$HC_2Ph)(\mu$-$CO)_4(CO)_4$ (3) and $Cp_2W_2Ir_3(\mu_4$-η^2-$C_2C_6H_4Me$-4)(μ-CO)$(CO)_9$ (12)

formula	$C_{26}H_{17}Ir_2O_8W_2{\cdot}0.5CH_2Cl_2$	$C_{29}H_{17}Ir_3O_{10}W_2$
fw	1252.02	1469.81
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
cryst syst	monoclinic	monoclinic
a (Å)	15.253(4)	29.570(3)
b (Å)	10.343(5)	9.607(4)
c (Å)	17.637(3)	21.333(3)
β (deg)	106.12(2)	99.72(1)
V (Å$^{3)}$	2673(2)	5973(3)
ρ_{calcd} (g cm^{-3})	3.121	3.269
Z	4	8
μ (mm$^{-1)}$	35.3	21.1
cryst size (mm^3)	0.12 × 0.08 × 0.04	0.32 × 0.16 × 0.12
A (min, max)	0.63, 1.00	0.43, 1.00
$2\theta_{max}$ (deg)	120.3	50.1
N	4247	5646
N_o	3007	3996
R	0.043	0.028
R_w	0.058	0.027

Results and Discussion

Syntheses and Characterization of $Cp_2W_2Ir_2(\mu_4$-η^2-$HC_2R)(\mu$-$CO)_4(CO)_4$ [R = Ph (3), C_6H_4Me-4 (4), $C_6H_4NO_2$-4 (5), Bu^t (6)]. The reactions of $Cp_2W_2Ir_2(CO)_{10}$ (**1**) with the terminal alkynes HC≡CR (R = Ph, C_6H_4Me-4, $C_6H_4NO_2$-4) proceed either in CH_2Cl_2 at room temperature overnight or in toluene for 1 h at 50 °C. Purification by preparative thin-layer chromatography affords clusters with the composition $Cp_2W_2Ir_2(HC_2R)(CO)_8$ [R = Ph (**3**), C_6H_4Me-4 (**4**), $C_6H_4NO_2$-4 (**5**)] in excellent yields (56−70%). The comparatively more sterically encumbered 3,3-dimethyl-1-butyne requires significantly more forcing conditions (refluxing toluene, 1 h) for reaction to proceed, and the analogous product $Cp_2W_2Ir_2(HC_2Bu^t)(CO)_8$ (**6**) is isolated in much lower yield (20%). The products have been characterized by a combination of IR and ^{1}H NMR spectroscopies, FAB MS, satisfactory microanalyses, and, in the case of **3**, a single-crystal X-ray diffraction study. The infrared spectra are consistent with the presence of edge-bridging carbonyl ligands in all complexes [ν(CO) 1835−1821 cm^{-1}], which contrasts with the all-terminal precursor **1**. The ^{1}H NMR spectra contain characteristic resonances at 9.77−8.95 ppm corresponding to the acetylenic protons (≡CH) and signals assigned to Cp (**3**−**6**), Ph (**3**−**5**), and Me (**4** and **6**) groups in the appropriate ratios. The mass spectra of all complexes (**3**−**6**) show molecular ions, followed by stepwise loss of carbonyls, and particularly intense fragment ions [M − 3CO]$^+$ and [M − 6CO]$^+$; isotope patterns are consistent with the presence of two iridium atoms and two tungsten atoms. A single-crystal X-ray diffraction study of **3** was undertaken to confirm the acetylene coordination mode and carbonyl disposition in these complexes.

X-ray Structural Study of 3. A summary of crystal and refinement data for **3** is found in Table 1, and

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(32) teXsan: Single Crystal Structure Analysis Software, Version 1.7−3; Molecular Structure Corporation: The Woodlands, TX, 1995.

Table 2. Important Bond Lengths (Å) and Angles (°) for $Cp_2M_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu\text{-}CO)_4(CO)_4$ [M = W (3), Mo (7)]

	3	**7**[19]
Ir(1)−Ir(2)	2.688(1)	2.6982(6)
Ir(1)−M(1)	2.813(1)	2.8199(9)
Ir(1)−M(2)	2.802(1)	2.8146(9)
Ir(2)−M(1)	2.812(1)	2.8209(9)
Ir(2)−M(2)	2.813(1)	2.8222(9)
Ir(1)−C(19)	2.07(2)	2.074(8)
Ir(2)−C(20)	2.09(2)	2.107(9)
M(1)−C(19)	2.25(2)	2.299(8)
M(1)−C(20)	2.34(2)	2.298(8)
M(2)−C(19)	2.29(2)	2.290(8)
M(2)−C(20)	2.28(2)	2.340(8)
Ir(1)−C(1)	1.97(3)	1.91(1)
Ir(1)−C(2)	1.90(3)	1.91(1)
Ir(1)−C(5)	2.33(2)	2.333(9)
Ir(1)−C(6)	2.33(2)	2.314(9)
Ir(2)−C(3)	1.88(3)	1.92(1)
Ir(2)−C(4)	1.93(2)	1.93(1)
Ir(2)−C(7)	2.38(2)	2.35(1)
Ir(2)−C(8)	2.42(2)	2.37(1)
M(1)−C(5)	1.95(2)	1.98(1)
M(1)−C(7)	1.97(2)	1.98(1)
M(2)−C(6)	1.97(2)	2.00(1)
M(2)−C(8)	2.03(3)	1.99(1)
M(1)−C(9)	2.27(2)	2.28(1)
M(1)−C(10)	2.30(2)	2.28(1)
M(1)−C(11)	2.32(2)	2.32(1)
M(1)−C(12)	2.34(2)	2.334(10)
M(1)−C(13)	2.29(2)	2.313(10)
M(2)−C(14)	2.28(2)	2.29(1)
M(2)−C(15)	2.36(2)	2.32(1)
M(2)−C(16)	2.35(3)	2.35(1)
M(2)−C(17)	2.34(2)	2.33(1)
M(2)−C(18)	2.28(2)	2.284(9)
M(1)−Ir(1)−M(2)	94.83(4)	95.69(3)
M(1)−Ir(2)−M(2)	94.59(4)	95.50(3)
Ir(1)−M(1)−Ir(2)	57.10(3)	57.15(2)
Ir(1)−M(2)−Ir(2)	57.20(4)	57.20(2)

selected bond distances and angles are listed in Table 2, together with those of the isostructural molybdenum analogue $Cp_2Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu\text{-}CO)_4(CO)_4$ (**7**).[19] An ORTEP plot showing the molecular geometry and atomic numbering scheme is shown in Figure 1.

Complex **3** possesses a W_2Ir_2 core in which the metals adopt a butterfly geometry; the iridium atoms form the hinge and the tungsten atoms occupy the wing-tip sites. Each iridium atom is ligated by two terminal carbonyls, and each tungsten atom is coordinated by an η^5-cyclopentadienyl ligand. The four remaining carbonyl ligands bridge the W−Ir bonds. The spectroscopically identified acetylenic proton could not be located crystallographically. The phenylacetylene ligand bridges all four metals in a μ_4-η^2-fashion, lying parallel to the Ir(1)−Ir(2) vector. This arrangement completes a *closo*-octahedral core consisting of the four metals and the two "acetylenic" carbon atoms. The Ir−Ir bond length [2.688(1) Å], and the W−Ir distances [2.802(1)−2.813(1) Å] are "normal" and consistent with a marginal contraction of M_2Ir_2 butterfly core compared to the analogous distances in **7**. As with **7**, the core carbons C(19) and C(20) in **3** interact more closely with the iridium atoms [C−Ir 2.07(2)−2.09(2) Å] than with the group 6 metal [C−W 2.25(2)−2.34(2) Å]. All tungsten−iridium bonds are spanned by an asymmetrically disposed bridging carbonyl ligand [W−C 1.95(2)−2.03(3) Å compared to Ir−C 2.33(2)−2.42(2) Å]; the asymmetry of the bridging carbonyl ligands increases slightly in proceeding from the molybdenum containing cluster **7** (W−C_{av} 1.99 Å; Ir−C_{av} 2.34 Å) to its tungsten analogue **3** (W−C_{av} 1.98 Å; Ir−C_{av} 2.37 Å). Cluster **3** has seven bonding pairs by the polyhedral skeletal electron pair theory, electron precise for a *closo*-octahedron.

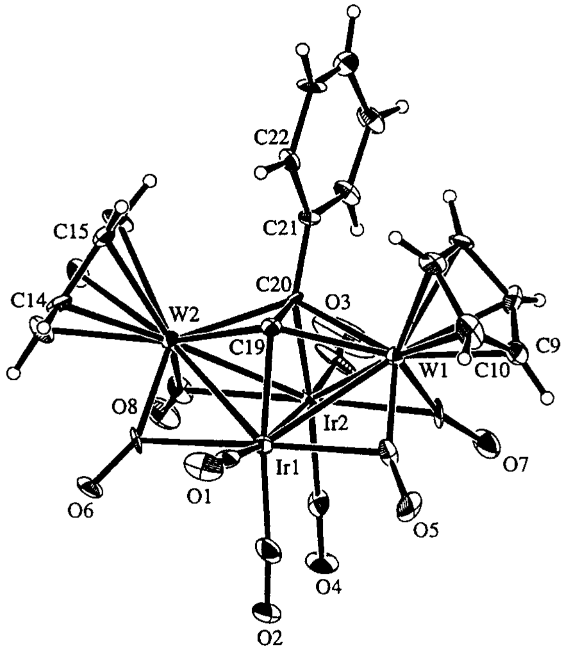

Figure 1. Molecular structure and atomic labeling scheme for $Cp_2W_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu\text{-}CO)_4(CO)_4$ (**3**). Thermal envelopes (20%) are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

Syntheses and Characterization of $Cp_2W_2Ir_2\{\mu_4\text{-}\eta^2\text{-}HC_2C{\equiv}CW(CO)_3Cp\}(\mu\text{-}CO)_4(CO)_4$ (9). $Cp_2W_2Ir_2(CO)_{10}$ (**1**) reacts with the buta-1,3-diynyl complex $CpW(CO)_3(C{\equiv}CC{\equiv}CH)$ (**8**) in CH_2Cl_2 at room temperature to afford $Cp_2W_2Ir_2\{\mu_4\text{-}\eta^2\text{-}HC_2C{\equiv}CW(CO)_3Cp\}(\mu\text{-}CO)_4(CO)_4$ (**9**), characterized by a combination of IR, ^1H and ^{13}C NMR spectroscopies, FAB MS, and satisfactory microanalyses. Spectroscopic evidence is consistent with the least hindered C≡C triple bond (that remote from the tungsten atom) being coordinated to the cluster. The IR spectrum for **9** is suggestive of a superposition of the characteristic carbonyl absorption pattern of **3**−**6**, two carbonyl absorptions for the pendant $W(CO)_3Cp$ moiety, and a weak absorption assigned to the uncomplexed alkynyl linkage (2155w cm^{-1}). Replacing the organic substituents (R = Ph, C_6H_4Me-4, $C_6H_4NO_2$-4, Bu^t) by the organometallic substituent [R = $CpW(CO)_3C{\equiv}C$] leads to a decrease in the weighted ν(CO) average for the W_2Ir_2 core. Coordinating $CpW(CO)_3(C{\equiv}CC{\equiv}CH)$ to the ditungsten−diiridium cluster leads to a similar decrease in weighted ν(CO) average for the pendant group. The shift in both IR parameters indicates enhanced π back-donation to carbonyl ligands upon formation of the cluster−butadiynyl complex adduct. The ^1H NMR contains resonances assigned to ≡CH (8.40 ppm) and Cp (5.54 and 5.29 ppm), ratio 1:5:10; the chemical shift of the acetylenic proton is similar to that in **3**−**6** and thus consistent with coordination of the buta-1,3-diynyl complex to the cluster via the C≡CH unit. To facilitate assignment of the ^{13}C NMR spectrum of cluster **9**, the ^{13}C NMR spectrum of the X-ray crystallographically characterized cluster **3** has also been obtained. Some carbonyl resonances in the ^{13}C NMR spectrum of

9 (222.3, 221.7 ppm, ratio 2:2, W−Ir μ-CO; 177.9, 177.7, 173.5, 172.3 ppm, ratio 1:1:1:1, Ir−CO) are analogous to those of complex **3** (222.0, 220.9 ppm, ratio 2:2, W−Ir μ-CO; 177.9, 177.7, 175.7, 173.1 ppm, ratio 1:1:1:1, Ir−CO). The chemical shifts of the remaining two signals in the carbonyl region of the ^{13}C NMR spectrum of **9** (227.6, 212.9 ppm, ratio 1:2) are similar to those of the carbonyl ligands in **8** (227.4, 210.9 ppm, ratio 1:2 in $CDCl_3$[30b]) and are thus assigned to carbonyls of the pendant $CpW(CO)_3$ group. The signals at 99.2 ppm (**3**) and 109.6 ppm (**9**) are assigned to ≡CH with the aid of INEPT spectra. The signals at 78.0 ppm (WC≡*C*) and 106.2 ppm (W*C*≡C) are assigned by comparison to the equivalent carbons in **8** (71.6 and 110.5 ppm in $CDCl_3$, respectively[30]). The remaining signal at 146.8 ppm (**9**) is assigned to *C*≡CH by comparison to the analogous resonance in **3** (152.8 ppm). These similar NMR shifts are a further indication that the $CpW(CO)_3C{\equiv}C$ linkage is a pendant group. The FAB mass spectrum of **9** contains a parent ion and stepwise loss of eleven carbonyl groups; the isotope patterns are consistent with the presence of two iridium atoms and three tungsten atoms. Attempts to coordinate the pendant group or activate the ≡C−H bond (thermolysis, prior activation with Me_3NO) have thus far resulted in decomposition of the cluster. The buta-1,3-diynyl complex coordination mode in **9** is the same as that of the product from the reaction between **8** and $Ru_3(CO)_{10}(NCMe)_2$,[33] namely $Ru_3\{\mu_3\text{-}\eta^2\text{-}HC_2C{\equiv}CW(CO)_3Cp\}(\mu\text{-}CO)(CO)_9$ (**10**). In contrast to **9**, thermolysis of **10** results in ≡C−H activation to afford $Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}C_2C{\equiv}CW(CO)_3Cp\}(CO)_9$.

Syntheses and Characterization of $Cp_2W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2R)(\mu\text{-}CO)(CO)_9$ [R = Ph (11), C_6H_4Me-4 (12), $C_6H_4NO_2$-4 (13), C≡CPh (14)]. The reactions of **2** with $CpW(CO)_3(C{\equiv}CR)$ (R = Ph, C_6H_4Me-4, $C_6H_4NO_2$-4, C≡CPh) proceed slowly in dichloromethane at room temperature to afford clusters of composition $Cp_2W_2Ir_3(CO)_{10}(C_2R)$ [R = Ph (**11**), C_6H_4Me-4 (**12**), $C_6H_4NO_2$-4 (**13**), C≡CPh (**14**)] as the major reaction product in fair to reasonable yield (23−45%). The products are characterized by a combination of IR and ^1H NMR spectroscopies, FAB MS, and satisfactory microanalyses. Infrared spectra indicate the presence of edge-bridging carbonyl ligands in all complexes. The ^1H NMR spectra contain signals assigned to cyclopentadienyl and phenyl groups for all complexes and a methyl group for **12**. The mass spectra of **11**−**13** contain molecular ions, and all complexes show sequential loss of carbonyl ligands; isotope patterns are consistent with the presence of three iridium atoms and two tungsten atoms.

Table 3. Important Bond Lengths (Å) and Angles (°) for $Cp_2W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2C_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9$ (12)

Ir(1)−Ir(2)	2.7934(7)	Ir(1)−W(4)	2.7251(8)
Ir(1)−W(5)	2.8253(7)	Ir(2)−lr(3)	2.7422(7)
Ir(2)−W(4)	2.8811(7)	Ir(2)−W(5)	2.7281(8)
Ir(3)−W(5)	2.8347(7)	W(4)−W(5)	3.0245(8)
Ir(1)−C(11)	2.05(1)	Ir(1)−C(12)	1.84(2)
Ir(1)−C(13)	1.86(1)	Ir(2)−C(1)	2.08(1)
Ir(2)−C(21)	1.89(1)	Ir(2)−C(22)	1.85(1)
Ir(3)−C(2)	2.07(1)	lr(3)−C(31)	1.93(1)
Ir(3)−C(32)	1.89(1)	Ir(3)−C(33)	1.94(1)
W(4)−C(1)	2.00(1)	W(4)−C(11)	2.06(1)
W(4)−C(41)	1.97(1)	W(4)−C(42)	2.30(1)
W(4)−C(43)	2.34(1)	W(4)−C(44)	2.30(1)
W(4)−C(45)	2.25(2)	W(4)−C(46)	2.31(1)
W(5)−C(1)	2.22(1)	W(5)−C(2)	2.29(1)
W(5)−C(51)	1.96(1)	W(5)−C(52)	2.35(1)
W(5)−C(53)	2.35(1)	W(5)−C(54)	2.37(2)
W(5)−C(55)	2.32(1)	W(5)−C(56)	2.37(1)
Ir(2)−Ir(l)−W(4)	62.93(2)	Ir(2)−Ir(l)−W(5)	58.09(2)
W(4)−lr(l)−W(5)	66.01(2)	Ir(l)−Ir(2)−Ir(3)	121.12(3)
Ir(l)−Ir(2)−W(4)	57.38(2)	lr(l)−Ir(2)−W(5)	61.54(2)
Ir(3)−lr(2)−W(4)	111.38(2)	Ir(3)−lr(2)−W(5)	62.42(2)
W(4)−Ir(2)−W(5)	65.19(2)	Ir(2)−Ir(3)−W(5)	58.54(2)
Ir(l)−W(4)−Ir(2)	59.69(2)	Ir(l)−W(4)−W(5)	58.59(2)
Ir(2)−W(4)−W(5)	54.96(2)		
Ir(1)−Ir(2)−C(1)	90.3(3)	Ir(3)−Ir(2)−C(1)	69.5(3)
W(4)−Ir(2)−C(1)	43.9(3)	W(5)−Ir(2)−C(1)	53.0(3)
Ir(2)−Ir(3)−C(2)	72.5(4)	W(5)−lr(3)−C(2)	52.8(3)
Ir(l)−W(4)−C(1)	94.0(3)	Ir(2)−W(4)−C(1)	46.1(3)
W(5)−W(4)−C(1)	47.3(3)		

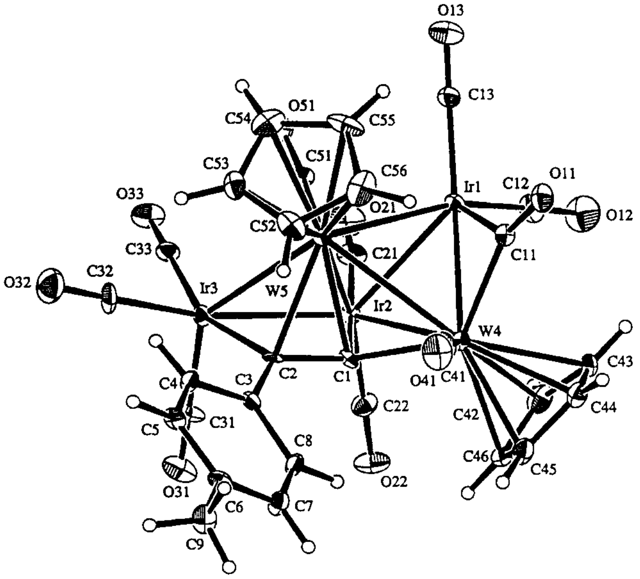

Figure 2. Molecular structure and atomic labeling scheme for $Cp_2W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2C_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9$ (**12**). Thermal envelopes (20%) are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

X-ray Structural Study of 12. A single-crystal X-ray diffraction study of $Cp_2W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2C_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9$ (**12**) was undertaken to ascertain the molecular geometry. Crystallographic data are summarized in Table 1, and significant bond lengths and angles are collected in Table 3. An ORTEP plot showing the molecular geometry is shown in Figure 2. The pentanuclear cluster **12** is comprised of three iridium atoms and two tungsten atoms arranged as an edge-bridged tetrahedron. The two tungsten atoms and two of the iridium atoms define the core tetrahedral unit; the remaining iridium atom [Ir(3)] bridges the Ir(2)−W(5) vector. Terminal carbonyl ligands are coordinated to Ir(1) (two), Ir(2) (two), Ir(3) (three), W(4) (one), and W(5) (one), a carbonyl symmetrically bridges the Ir(1)−W(4) linkage [Ir(1)−C(11) 2.05(1), W(4)−C(11) 2.06(1) Å], and each tungsten atom is ligated by an η^5-cyclopentadienyl group. Core bond distances in **12** [W−Ir 2.7251(8)−2.8811(7) Å; Ir−Ir 2.7422(7)−2.7934(7) Å] fall within the range of those previously reported [W−Ir 2.665(2)[27]−2.9023(9)[13] Å; Ir−Ir 2.598(1)[28]−2.814(3)[28] Å] in mixed-metal tungsten−iridium clusters. The alkynyl ligand is coordinated in a μ_4-η^2 ($3\sigma + \pi$)-fashion, capping the Ir(2)Ir(3)W(4)W(5) butterfly cleft. This unusual coordination mode, with the alkynyl ligand π-bonded to a hinge

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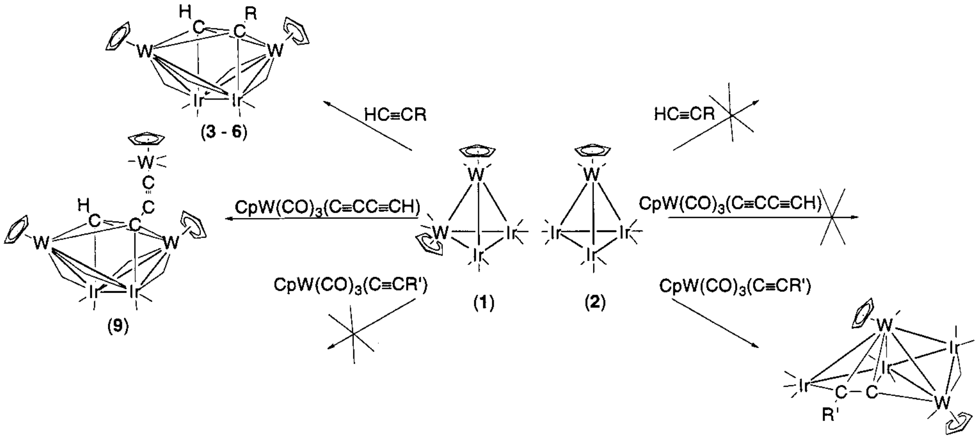
[33] Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Chem. Soc., Dalton Trans* **1996**, 3151.

Scheme 2. Reactivity of $Cp_2W_2Ir_2(CO)_{10}$ (1) and $CpWIr_3(CO)_{11}$ (2) with Terminal Alkynes and Alkynyltungsten Complexes [R = Ph (3), C_6H_4Me-4 (4), $C_6H_4NO_2$ (5), Bu^t (6); R′ = Ph (11), C_6H_4Me-4 (12), $C_6H_4NO_2$ (13), C≡CPh (14)]



rather than a wing-tip metal, has been observed previously only in $Cp^*WOs_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu_3\text{-}\eta^2\text{-}MeC_2Me)(CO)_9$ ($Cp^* = \eta^5\text{-}C_5Me_5$),[34] although a similar coordination mode for benzonitrile was found in $Fe_4(\mu_4\text{-}\eta^2\text{-}NCPh)(\mu\text{-}CO)(CO)_{11}$.[35] The geometry of **12** is consistent with formal insertion of $CpW(CO)_3(C{\equiv}CC_6H_4Me\text{-}4)$ into an Ir−Ir bond in **2**, with concomitant elimination of CO ligands.

Discussion. A summary of the results is given in Scheme 2. In contrast to the facile reactivity of **1** toward terminal alkynes, all attempts at reacting $CpWIr_3(CO)_{11}$ (**2**) with HC≡CR [R = Ph, $C_6H_4NO_2$-4, $C{\equiv}CW(CO)_3Cp$] have thus far proven unsuccessful. Terminal alkyne reactions at **1** occur with bond selectivity; in addition to clusters **3**−**6** and **9** arising from formal insertion into the W−W linkage, only trace quantities of thus-far-uncharacterized byproducts were obtained. Conceptual heterometal replacement in proceeding from **1** to **2** removes the preferred site of reactivity for terminal alkynes. Conversely, reactions of **2** with the alkynyltungsten complexes $CpW(CO)_3(C{\equiv}CR)$ (R = Ph, C_6H_4-Me-4, $C_6H_4NO_2$-4, C≡CPh) proceed smoothly to afford the adducts $Cp_2W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2R)(\mu\text{-}CO)(CO)_9$ [R = Ph (**11**), C_6H_4Me-4 (**12**), $C_6H_4NO_2$-4 (**13**), C≡CPh (**14**)], whereas attempted reactions with **1** were all unsuccessful. Reactions of alkynyltungsten complexes with **2** afford major products corresponding to bond-selective formal insertion into an Ir−Ir linkage (minor amounts of thus-far-uncharacterized products are also obtained in some cases). Although an analogous insertion is possible with **1**, it may be disfavored sterically by the necessity to place bulky CpW(CO) units at the hinge position of the putative product. It is perhaps significant that **1** reacts with internal acetylenes by way of W−W and W−Ir cleavage, but not via formal Ir−Ir insertion (Scheme 1). It is not clear at present why **2** does not react with $CpW(CO)_3(C{\equiv}CC{\equiv}CH)$ at the W−C≡C unit.

Other tetrahedral group 6−group 9 mixed-metal clusters have been reacted with terminal acetylenes. $Cp'WCo_3(\mu\text{-}CO)_3(CO)_8$ ($Cp' = \eta^5\text{-}C_5H_4Me$) reacts with phenylacetylene with cluster fragmentation and acetylene oligomerization to afford the binuclear derivative $Cp'WCo\{\mu\text{-}\eta^2,\eta^4\text{-}CPhCHCHCPh\}_2(CO)_4$.[36] In contrast to the $[WCo_3]$ cluster, and to the $[WIr_3]$ cluster of the current studies, introduction of a 4d metal in proceeding to $Cp'MoCo_3(\mu\text{-}CO)_3(CO)_8$ results in phenylacetylene reaction with retention of nuclearity, to afford $Cp'MoCo_3(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu\text{-}CO)_2(CO)_6$, with formal insertion of acetylene into a Mo−Co bond.[36] Weakening the M−M′ bond in proceeding to a 4d−3d linkage enables control over reactivity. $Cp'_2W_2Co_2(\mu\text{-}CO)_3(CO)_7$ reacts with phenylacetylene to afford $Cp'_2W_2Co_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu\text{-}CO)_4(CO)_4$ in very low yield,[36] in contrast to $Cp_2Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7$ [19] and $Cp_2W_2Ir_2(CO)_{10}$ in the present work which afford analogous acetylene adducts in good to excellent yields. Across this series of $[M_2M'_2]$ clusters, insertion into the group 6 M−M bond is facile, and the stability conferred by the heavier group 9 metal is the most important consideration.

The nature of the acetylene significantly affects the product distribution; whereas cluster **1** reacts with internal acetylenes to afford inter alia a product involving C≡C cleavage and C−C formation (Scheme 1), only products of general formula $Cp_2W_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2R)(\mu\text{-}CO)_4(CO)_4$ are observed with terminal acetylenes. In combination with the above-mentioned studies, the present work provides an interesting comparison of the effect of heterometal vertex replacement on the reactivity of a tetrahedral cluster, and the possibility of directing the chemistry of alkyne- or alkynyl-containing reagents toward specific sites by varying heterometal introduction and M−M′ bond weakening. This differing alkyne reactivity of **1** and **2** does not extend to differing P-ligand substitution chemistry, although differences in thermolytic ligand transformations have been noted.[15,37]

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Supporting Information Available: Tables of X-ray crystallographic data for **3** and **12** (26 pages). See any current masthead page for ordering information.

OM980692O

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