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Mixed-Metal Cluster Chemistry. 21. Synthesis and Crystallographic and Electrochemical Studies of Alkyne-Coordinated Group 6−Iridium Clusters Linked by Phenylenevinylene Groups

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The pseudooctahedral monocluster compounds $M_2Ir_2(\mu_4\text{-}\eta^2\text{-}R^1C_2R^2)(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4\text{-}Me)_2$ ($M = Mo$, $R^2 = Ph$, $R^1 = H$ (**12**), Ph (**13**), Me (**14**); $M = W$, $R^2 = Ph$, $R^1 = Me$ (**15**); $M = Mo$, $R^1 = n$-hexyl, $R^2 = C_6H_4\text{-}4\text{-}CHO$ (**16**), $C_6H_4\text{-}4\text{-}CH_2P(O)(OEt)_2$ (**17**)) have been prepared from reactions between the tetrahedral cluster compounds $M_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4\text{-}Me)_2$ and the alkynes $R^1C_2R^2$. Similar reactions between tetrahedral cluster precursors and di- or triynes have afforded the related compounds $[M_2Ir_2(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4R)_2]_2(\mu_8\text{-}\eta^4\text{-}R^1C_2BC_2R^1)$ ($R = H$, $R^1 = H$, $B = 4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CH\text{-}4\text{-}C_6H_4$, $M = Mo$ (**18**); $R = Me$, $R^1 = n$-hexyl, $B = 4\text{-}C_6H_4$, $M = Mo$ (**19**), W (**20**); $R = Me$, $R^1 = n$-hexyl, $B = 4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CH\text{-}4\text{-}C_6H_4$, $M = Mo$ (**22**), W (**23**); $R = Me$, $R^1 = n$-hexyl, $B = 4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CH\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CH\text{-}4\text{-}C_6H_4$, $M = Mo$ (**24**); $R = Me$, $R^1 = H$, $B = (CH_2)_2$, $M = W$ (**27**)), $[Mo_2Ir_2(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4Me)_2]_3\{\mu_{12}\text{-}\eta^6\text{-}1,3,5\text{-}C_6H_3[(E)\text{-}CH{=}CHC_6H_4\text{-}4'\text{-}C_2(CH_2)_5Me]_3\}$ (**25**), and $W_2Ir_2(\mu_4\text{-}\eta^2\text{-}R^1C_2R^2)(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4Me)_2$ ($R^1 = n$-hexyl, $R^2 = 4\text{-}C_6H_4C{\equiv}C(CH_2)_5Me$ (**21**); $R^1 = H$, $R^2 = (CH_2)_2C{\equiv}CH$ (**26**)). Compounds **18**−**20** and **22**−**25** contain two or three cluster units linked by unsaturated bridges, while **27** contains two cluster units linked by a saturated bridge. Compound **22** was prepared in lower yield by coupling **16** and **17** under Emmons−Horner conditions. Structural studies of examples of mono- (**15**), di- (**22**), and tricluster (**25**) compounds have been undertaken. Cyclic voltammetric scans for **12**−**15**, **19**, **20**, **22**−**24**, **27** and the related cluster $W_2Ir_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4Me)_2$ (**4**) have been collected. All compounds show a reversible/partially reversible oxidation, followed by an irreversible oxidation process; potentials for the former increase on replacement of tungsten by molybdenum and alkyne substituent variation $Me < H < Ph$. UV−vis−near-IR spectroelectrochemical studies of the first oxidation process for **12**, **15**, and **20** show similar spectral progressions for these mono- and dicluster compounds. The reductive cyclic voltammetric scans for **4**, **12**−**15**, **22**−**24**, and **27** all show one irreversible reduction process; compounds **19** and **20**, distinguished by possessing the shortest unsaturated bridge, show two reduction processes.

Introduction

Linking electroactive modules by π-delocalizable and potentially conducting bridging units is a topic of significant interest.[1] Electrochemical studies of transition-metal carbonyl clusters have shown that they can be structurally flexible electron reservoirs with "tunable" redox properties dependent on the coordination sphere of the metal core.[2−6] Not surprisingly, clusters linked through π-delocalizable backbones have come under considerable scrutiny, with the vast majority of such studies involving the linking of identical homometallic cores.[7−19] Introduction of a heterometal into the cluster core can further modify the electronic environ-

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ment, in addition to conferring benefits upon other aspects of its chemistry (e.g. substrate activation by the polar metal−metal bonds, the possibility of clusters as precursors to bimetallic particles with well-defined metal−metal stoichiometry, the heterometal providing a label for ligand fluxionality studies, etc.).[20] Few examples of heterometallic clusters linked by unsaturated bridges exist,[21−23] and thus far none have been probed utilizing electrochemical techniques. We have been studying group 6−iridium clusters[24−43] and have recently reported cluster-containing oligourethanes in which the cluster units are linked via saturated bridges.[39] We report herein synthetic procedures to and structural confirmation of the first group 6−iridium mixed-metal clusters linked by unsaturated bridging groups and their examination by cyclic voltammetry and UV−vis−near-IR spectroelectrochemistry; this is the first electrochemical study of linked heterometallic clusters.

Experimental Section

General Conditions. Reactions were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques.[44] Glassware used in reactions involving sodium hydride was flame-dried under vacuum before use. All cluster complexes proved to be indefinitely stable in air as solids and for at least short periods of time in solution, and thus no precautions were taken to exclude air in their manipulation. Tetrahydrofuran was laboratory reagent (LR) grade. All other solvents used were analytical reagent (AR) grade. Unless stated otherwise, the following reaction solvents were dried and distilled under argon using standard methods: CH_2Cl_2, dimethoxyethane, and acetonitrile over CaH_2; THF and diethyl ether over sodium benzophenone ketyl. Triethylamine was used without drying but was purged with nitrogen prior to use. Solvents used in the workup (including chromatography and crystallizations) were used as received. Petroleum spirit refers to a petroleum fraction of boiling range 60−80 °C. Column chromatography was performed using Merck silica gel 60 of particle size 0.040−0.063 mm (230−400 mesh ASTM). The cluster products were purified by thin-layer chromatography (TLC) on 20 × 20 cm glass plates coated with Merck silica gel 60 PF_{254} (0.5 mm). Analytical TLC, used for monitoring the extent of reactions, was carried out on Merck aluminum sheets coated with 0.25 mm silica gel 60 PF_{254} and visualized under UV light (for colorless compounds).

Starting Materials and Reagents. The following reagents were purchased commercially and used as received: 1-octyne, 4-bromo-1-iodobenzene, 4-bromobenzaldehyde, phenylacetylene, diphenylacetylene, (trimethylsilyl)acetylene, sodium hydride (60% dispersion in oil), triphenylphosphine, triethyl phosphite, and *tert*-butyllithium solution (Aldrich); copper(I) iodide (Unilab); bromine and potassium carbonate (BDH); iodine (M&B). Sodium methoxide solution was prepared by addition of sodium to dried methanol. Literature procedures (or minor variations thereof) were used to synthesize dichlorobis(triphenylphosphine)palladium(II),[45] 4-(oct-1′-ynyl)benzyl alcohol,[46] 4,4′-(*E*)-dibromostilbene,[47] 1,4-bis(diethyl methylphosphonate)benzene,[48] 1,4-bis(oct-1′-ynyl)benzene,[49] 1,3,5-tris(diethyl methylphosphonate)benzene,[50,51] $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (**1**),[42] $W_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (**2**),[52] $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_5)_2$ (**3**),[28] and $W_2Ir_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**4**).[53] Hexa-1,5-diyne was provided by Mr. J. H. Chaplin, Department of Chemistry, Australian National University.

Instruments. Infrared spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer in a solution cell with CaF_2 windows; spectral frequencies are recorded in cm^{-1}. All analytical spectra were recorded as solutions in either cyclohexane or CH_2Cl_2 (both AR grade). UV−vis spectra were recorded using a Cary 5G spectrophotometer as solutions in THF in 1 cm quartz cells, recorded over the range 240−1000 nm, and are reported in the form λ_{max} (ϵ). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ (Cambridge Isotope Laboratories) using a Varian Gemini-300 spectrometer (^1H at 300 MHz; ^{13}C at 75 MHz, broadband proton decoupled; ^{31}P at 121 MHz, broadband proton decoupled). Spectra are referenced to residual $CHCl_3$ at 7.24 ppm (^1H), $CDCl_3$ at 77.0 ppm (^{13}C), or external 85% H_3PO_4 at 0.0 ppm (^{31}P). The assignments of the

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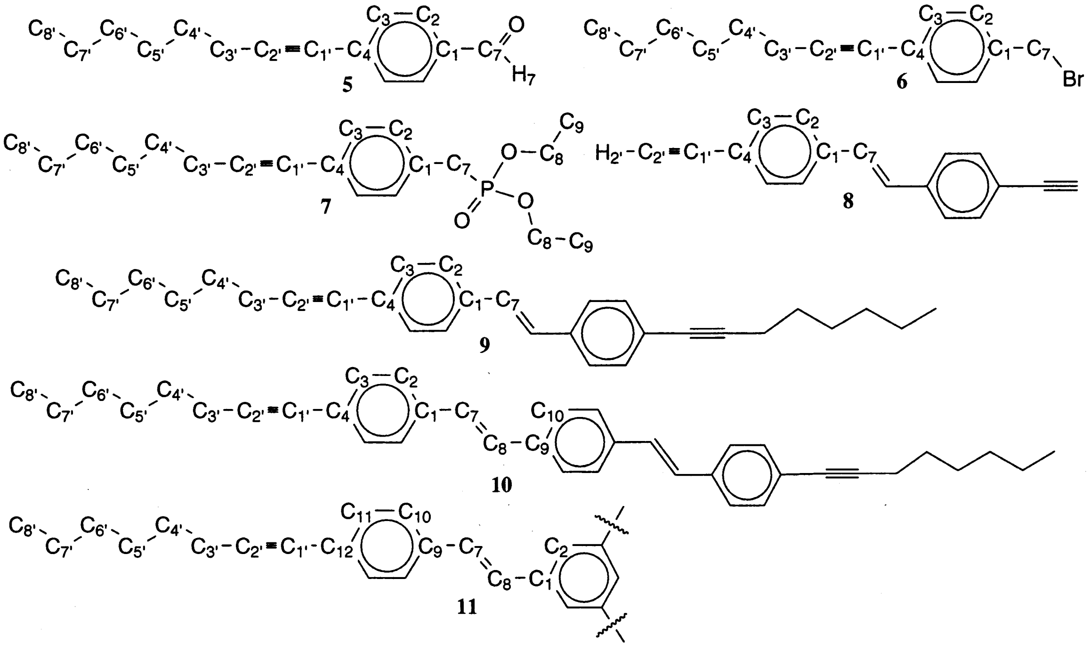

Figure 1. ^{1}H and ^{13}C NMR numbering schemes.

organic compounds follow the numbering schemes shown in Figure 1. Electron impact (EI) mass spectra (unit resolution and high resolution (HR)) were recorded using a VG Autospec instrument (70 eV electron energy, 8 kV accelerating potential) at the Research School of Chemistry, Australian National University. Secondary ion mass spectrometry (SIMS) spectra were recorded using a VG ZAB 2SEQ instrument (30 kV Cs^+ ions, current 1 mA, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix, solutions in CH_2Cl_2) at the Research School of Chemistry, Australian National University, or the Department of Chemistry, University of Western Australia. Fast-atom bombardment (FAB) spectra were recorded at the University of Bristol, Bristol, U.K., using a VG Autospec mass spectrometer (Ar source with accelerating potential of 6−8 kV, 3-nitrobenzyl alcohol matrix, solutions in CH_2Cl_2). All mass spectra were calculated with the *m*/*z* based on ^{79}Br, ^{96}Mo, ^{183}W, and ^{192}Ir assignments and are reported in the form *m*/*z* (assignment, relative intensity). Elemental microanalyses were carried out by the Microanalysis Service Unit in the Research School of Chemistry, Australian National University. Melting points were determined in unsealed capillaries in the presence of air.

Synthesis of 4-(Oct-1′-ynyl)benzaldehyde (5). Dichlorobis(triphenylphosphine)palladium(II) (71 mg, 0.10 mmol) and copper(I) iodide (21 mg, 0.11 mmol) were added to a solution of 4-bromobenzaldehyde (2.02 g, 10.9 mmol) and 1-octyne (1.80 mL, 12.2 mmol) in triethylamine (70 mL). The mixture was stirred at 60 °C for 1.5 h and then cooled to room temperature before the triethylammonium bromide precipitate was removed by filtration through a sintered-glass funnel. The filtrate was reduced to dryness in vacuo and the residue transferred to a silica column using a small quantity of petroleum spirit. The major product was eluted from the column with dichloromethane/petroleum spirit mixtures (up to 1/2). The solvent was removed from the eluate using a rotary evaporator to afford a viscous pale yellow oil, which was identified as 4-(oct-1′-ynyl)benzaldehyde (**5**; 2.12 g, 9.89 mmol, 91%). IR (cyclohexane): ν(C≡C) 2228 w; ν(C=O) 1710 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.96 (s, 1H, H_7), 7.77 (d, J_{HH} = 8 Hz, 2H, H_2), 7.50 (d, J_{HH} = 8 Hz, 2H, H_3), 2.42 (t, J_{HH} = 7 Hz, 2H, $H_{3'}$), 1.60−1.30 (m, 8H, $H_{4'}$−$H_{7'}$), 0.89 (t, J_{HH} = 7 Hz, 3H, $H_{8'}$). ^{13}C NMR ($CDCl_3$): δ 191.5 (C_7), 132.2, 132.1, 130.6, 129.5 (C_1, C_2, C_3, C_4), 95.4 ($C_{1'}$), 80.1 ($C_{2'}$), 31.3 ($C_{3'}$), 28.6 ($C_{4'}$), 28.5 ($C_{5'}$), 22.5 ($C_{6'}$), 19.6 ($C_{7'}$), 14.0 ($C_{8'}$). MS (EI): 214 ([M$^+$, 49), 213 ([M − H]$^+$, 10), 199 ([M − Me]$^+$, 18), 185 ([M−C_2H_5]$^+$ or [M-CHO]$^+$, 29), 171 ([M − CO − Me]$^+$, 47), 157 ([M − CO − C_2H_5]$^+$, 26), 143 ([M − CO − C_3H_7]$^+$, 80), 129 ([M − CO − C_4H_9]$^+$, 100), 115 ([M − CO − C_5H_{11}]$^+$, 92), 91 ([C_7H_7]$^+$, 42). HR-MS (EI): calcd for $C_{15}H_{18}O$, 214.1358; found, 214.1354.

Synthesis of 4-(Oct-1′-ynyl)benzyl Bromide (6). Bromine (ca. 590 mg, 3.69 mmol) was added dropwise to a suspension of triphenylphosphine (961 mg, 3.66 mmol) in acetonitrile (10 mL) at 0 °C until a pale orange color persisted and no solid remained. If the coloration becomes too intense, triphenylphosphine may be added in small amounts until the solution is again colorless. A solution of 4-(oct-1′-ynyl)benzyl alcohol (720 mg, 3.33 mmol) in acetonitrile (5 mL) was added dropwise to the triphenylphosphine dibromide solution over 2 min. The reaction mixture was stirred at room temperature for 16 h. The volume of acetonitrile was reduced to half in vacuo and then dichloromethane (40 mL) was added and the mixture transferred to a separating funnel. The organic phase was extracted twice with water and then dried with magnesium sulfate, filtered through a sintered-glass funnel, and taken to dryness on a rotary evaporator. Purification by column chromatography on silica with elution by dichloromethane/petroleum (3/1), followed by removal of solvent on a rotary evaporator, afforded 4-(oct-1′-ynyl)benzyl bromide (**6**; 520 mg, 1.86 mmol, 56%) as a colorless liquid. IR (cyclohexane): ν(C≡C) 2229 w; ν(C−Br) 608 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.35 (d, J_{HH} = 8 Hz, 2H, H_2 or H_3), 7.29 (d, J_{HH} = 8 Hz, 2H, H_2 or H_3), 4.45 (s, 2H, H_7), 2.40 (t, J_{HH} = 7 Hz, 2H, $H_{3'}$), 1.60−1.30 (m, 8H, $H_{4'}$−$H_{7'}$), 0.88 (t, J_{HH} = 7 Hz, 3H, $H_{8'}$). ^{13}C NMR ($CDCl_3$): δ 136.9 (C_1), 131.9 (C_3), 128.9 (C_2), 124.4 (C_4), 91.5 ($C_{1'}$), 80.1 ($C_{2'}$), 33.1 (C_7), 31.3 ($C_{3'}$), 28.7 ($C_{4'}$), 28.6 ($C_{5'}$), 22.6 ($C_{6'}$), 19.4 ($C_{7'}$), 14.1 ($C_{8'}$). MS (EI): 278 ([M]$^+$, 29), 199 ([M − Br]$^+$, 100), 141 ([M − Br − C_4H_{10}]$^+$, 17), 128 ([M − Br − C_5H_{11}]$^+$, 54), 115 ([M − Br − C_6H_{12}]$^+$, 30), 91 ([C_7H_7]$^+$, 14). HR-MS (EI): calcd for $C_{15}H_{19}Br$, 278.0670; found, 278.0668.

Synthesis of Diethyl 4-(Oct-1′-ynyl)benzylphosphonate (7). A mixture of 4-(oct-1′-ynyl)benzyl bromide (**6**; 494 mg, 1.77 mmol) and triethyl phosphite (1.5 mL, 8.7 mmol) in a small flask fitted with an open air condenser was heated at reflux (oil bath ca. 160 °C) for 2 h. The mixture was cooled and the excess triethyl phosphite removed in vacuo with warming to 40 °C. The oily residue was transferred to a silica column and eluted with dichloromethane/ethyl acetate mixtures. The solvent was removed from the fraction containing the major product using a rotary evaporator, followed by a vacuum pump. The colorless oil isolated was identified as diethyl 4-(oct-1′-ynyl)benzylphosphonate (**7**; 542 mg, 1.61 mmol, 91%). IR (cyclohexane): ν(C≡C) 2228 w; ν(P=O) 1258 s; δ(P−O−C) 1058 vs; δ(O−C−C) 1031 vs, 964 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.31 (d, J_{HH} = 8 Hz, 2H, H$_3$), 7.18 (dd, J_{HH} = 8 Hz, J_{PH} = 2 Hz, 2H, H$_2$), 3.99 (quartet d, J_{HH} = 7 Hz, J_{PH} = 2 Hz, 4H, H$_8$), 3.09 (d, J_{PH} = 22 Hz, 2H, H$_7$), 2.36 (t, J_{HH} = 7 Hz, 2H, H$_{3'}$), 1.56−1.25 (m, 8H, H$_{4'}$−H$_{7'}$), 1.20 (t, J_{HH} = 7 Hz, 6H, H$_9$), 0.88 (t, J_{HH} = 7 Hz, 3H, H$_{8'}$). ^{13}C NMR (CDCl$_3$): δ 131.5 (d, J_{PC} = 3 Hz, C$_3$), 130.9 (d, J_{PC} = 9 Hz, C$_1$), 129.5 (d, J_{PC} = 6 Hz, C$_2$), 122.6 (d, J_{PC} = 4 Hz, C$_4$), 90.6 (C$_{1'}$), 80.2 (C$_{2'}$), 62.1 (d, J_{PC} = 7 Hz, C$_8$), 33.6 (d, J_{PC} = 137 Hz, C$_7$), 31.3 (C$_{3'}$), 28.6 (C$_{4'}$), 28.5 (C$_{5'}$), 22.5 (C$_{6'}$), 19.3 (C$_{7'}$), 16.3 (d, J_{PC} = 6 Hz, C$_9$), 14.0 (C$_{8'}$). ^{31}P NMR (CDCl$_3$): δ 26.4. MS (EI): 336 ([M]$^+$, 97), 321 ([M − Me]$^+$, 8), 307 ([M − C$_2$H$_5$]$^+$, 36), 293 ([M − C$_3$H$_7$]$^+$, 51), 279 ([M − C$_4$H$_9$]$^+$, 39), 267 ([M − C$_5$H$_9$]$^+$, 46), 199 ([M − P(O)(OEt)$_2$]$^+$, 72), 169 ([M − P(O)(OEt)$_2$ − C$_2$H$_6$]$^+$, 53), 155 ([M − P(O)(OEt)$_2$ − C$_3$H$_8$]$^+$, 72), 141 ([M − P(O)(OEt)$_2$ − C$_4$H$_{10}$]$^+$, 70), 128 ([M − P(O)(OEt)$_2$ − C$_5$H$_{11}$]$^+$, 100), 114 ([M − P(O)(OEt)$_2$ − C$_6$H$_{13}$]$^+$, 75). HR-MS (EI): calcd for C$_{19}$H$_{29}$O$_3$P, 336.1854; found, 336.1843.

Synthesis of 4,4′-(*E*)-Diiodostilbene. A solution of 4,4′-(*E*)-dibromostilbene (306 mg, 0.905 mmol) in THF (150 mL) was cooled to −77 °C, and a solution of *tert*-butyllithium (1.57 M, 2.65 mL, 4.19 mmol) was added. After it was stirred for 10 min, the solution was warmed to 0 °C before it was recooled to −77 °C. A solution of I$_2$ (0.86 g, 3.4 mmol) in THF (30 mL) was added over 3 min, and the reaction mixture was warmed to room temperature and then transferred to a separating funnel. Diethyl ether (100 mL) was added and the organic phase washed with aqueous sodium thiosulfate solution, followed by brine solution, and then dried with magnesium sulfate. Following filtration, the solvent was removed on a rotary evaporator, affording 4,4′-(*E*)-diiodostilbene as a pale yellow solid (354 mg, 0.819 mmol, 91%). The identity of the product was confirmed by comparison of its ^{1}H NMR spectral data with those of a sample prepared by a lower-yielding literature procedure.[54]

Synthesis of 1,2-(*E*)-Bis{4′-(ethynyl)phenyl}ethene (8). A mixture of 4,4′-(*E*)-diiodostilbene (591 mg, 1.37 mmol), (trimethylsilyl)acetylene (1.0 mL, 7.08 mmol), dichlorobis(triphenylphosphine)palladium(II) (30 mg, 0.043 mmol), and copper(I) iodide (10 mg, 0.052 mmol) in triethylamine (60 mL) was stirred at room temperature for 2 h. The precipitate was removed by filtration through a sintered-glass funnel, and the filtrate was taken to dryness in vacuo. The residue was dissolved in methanol (150 mL) and CH$_2$Cl$_2$ (50 mL) and then potassium carbonate (540 mg, 3.91 mmol) was added and the mixture stirred at room temperature for 1.5 h. The filtered solution was taken to dryness on a rotary evaporator (without heating) to yield a pale yellow solid. Further purification on a silica column with dichloromethane/petroleum spirit (1/4) eluant afforded a white solid identified as 1,2-(*E*)-bis{4′-(ethynyl)phenyl}ethene (**8**; 108 mg, 0.47 mmol, 35%). ^{1}H NMR (CDCl$_3$): δ 7.47 (d, J_{HH} = 8 Hz, 4H, H$_2$ or H$_3$), 7.44 (d, J_{HH} = 8 Hz, 4H, H$_2$ or H$_3$), 7.08 (s, 2H, H$_7$), 3.12 (s, 2H, H$_{2'}$). ^{13}C NMR (CDCl$_3$): δ 137.4 (C$_1$), 132.5 (C$_3$), 128.9 (C$_7$), 126.5 (C$_2$), 121.3 (C$_4$), 83.6 (C$_{1'}$), 78.1 (C$_{2'}$). MS (EI): 228 ([M]$^+$, 100), 226 ([M − 2H]$^+$, 50).

Synthesis of 1,2-(*E*)-Bis{4′-(oct-1″-ynyl)phenyl}ethene (9). A mixture of 4,4′-(*E*)-dibromostilbene (780 mg, 2.31 mmol), 1-octyne (1.36 mL, 9.22 mmol), dichlorobis(triphenylphosphine)palladium(II) (97 mg, 0.14 mmol), and copper(I) iodide (29 mg, 0.15 mmol) in triethylamine (80 mL) was heated at 70 °C for 6 h. After the mixture was cooled to room temperature, all volatile materials were removed in vacuo and diethyl ether (ca. 100 mL) was added. The ethereal mixture was transferred to a separating funnel and washed successively with water, ammonium chloride solution, and brine, followed by drying with magnesium sulfate. The filtered solution was taken to dryness on a rotary evaporator to yield a pale yellow solid. Further purification on a silica column with dichloromethane/petroleum spirit (1/9) eluant afforded a white solid identified as 1,2-(*E*)-bis{4′-(oct-1″-ynyl)phenyl}ethene (**9**; 284 mg, 0.72 mmol, 31%). Mp: 135 °C. UV−vis (THF): 316 sh (28.5), 329 sh (42.1), 343 (52.2), 361 (36.1) nm (10^3 L mol^{-1} cm^{-1}). ^{1}H NMR (CDCl$_3$): δ 7.40 (d, J_{HH} = 8 Hz, 4H, H$_2$), 7.35 (d, J_{HH} = 8 Hz, 4H, H$_3$), 7.03 (s, 2H, H$_7$), 2.40 (t, J_{HH} = 7 Hz, 4H, H$_{3'}$), 1.59−1.30 (m, 16H, H$_{4'}$−H$_{7'}$), 0.89 (t, J_{HH} = 7 Hz, 6H, H$_{8'}$). ^{13}C NMR (CDCl$_3$): δ 136.3 (C$_1$), 131.8 (C$_3$), 128.4 (C$_7$), 126.3 (C$_2$), 123.3 (C$_4$), 91.6 (C$_{1'}$), 80.6 (C$_{2'}$), 31.4 (C$_{3'}$), 28.7 (C$_{4'}$), 28.6 (C$_{5'}$), 22.6 (C$_{6'}$), 19.5 (C$_{7'}$), 14.0 (C$_{8'}$). MS (EI): 396 ([M]$^+$, 100). Anal. Calcd for C$_{30}$H$_{36}$ (396.62): C, 90.85; H, 9.15. Found: C, 91.20; H, 8.80.

Synthesis of 1,4-Bis{2′-(*E*)-[4″-(oct-1‴-ynyl)phenyl]ethenyl}benzene (10). Sodium hydride (109 mg, 60% dispersion in oil, 2.73 mmol) was added to a stirred mixture of 4-(oct-1′-ynyl)benzaldehyde (**5**; 573 mg, 2.39 mmol) and 1,4-bis(diethyl methylphosphonate)benzene (360 mg, 1.13 mmol) in dimethoxyethane (30 mL), and the mixture was heated to 60 °C for 1 h. The resulting yellow-orange solution containing a flocculant precipitate was cooled and the volume reduced to 10 mL in vacuo. Methanol (20 mL) was added, and the precipitate was collected using a sintered-glass funnel, washed with methanol, and dried using a water pump. Recrystallization from chloroform/methanol gave 1,4-bis{2′-(*E*)-[4″-(oct-1‴-ynyl)phenyl]ethenyl}benzene (**10**; 118 mg, 0.237 mmol, 21%) as fine pale yellow needles. Mp: 240 °C dec. UV−vis (THF): 257 (12.9), 363 sh (40.2), 377 (47.4), 393 sh (32.6) nm (10^3 L mol^{-1} cm^{-1}). ^{1}H NMR (CDCl$_3$): δ 7.48 (s, 4H, H$_{10}$), 7.42 (d, J_{HH} = 8 Hz, 4H, H$_2$), 7.36 (d, J_{HH} = 8 Hz, 4H, H$_3$), 7.07 (s, 4H, H$_7$ and H$_8$), 2.40 (t, J_{HH} = 7 Hz, 4H, H$_{3'}$), 1.57−1.30 (m, 16H, H$_{4'}$−H$_{7'}$), 0.89 (t, J_{HH} = 6 Hz, 6H, H$_{8'}$). ^{13}C NMR (CDCl$_3$): δ 136.7, 136.4 (C$_1$, C$_9$), 131.9 (C$_3$), 128.6, 128.1 (C$_7$, C$_8$), 126.9, 126.3 (C$_2$, C$_{10}$), 123.2 (C$_4$), 91.6 (C$_{1'}$), 80.6 (C$_{2'}$), 31.4 (C$_{3'}$), 28.8 (C$_{4'}$), 28.6 (C$_{5'}$), 22.6 (C$_{6'}$), 19.6 (C$_{7'}$), 14.1 (C$_{8'}$). MS (EI): 498 ([M]$^+$, 2). Anal. Calcd for C$_{38}$H$_{42}$ (498.75): C, 91.51; H, 8.49. Found: C, 91.72; H, 8.28.

Synthesis of 1,3,5-Tris{2′-(*E*)-[4″-(oct-1‴-ynyl)phenyl]ethenyl}benzene (11). A mixture of 1,3,5-tris(diethyl methylphosphonate)benzene (1.52 g, 2.88 mmol), 4-(oct-1′-ynyl)benzaldehyde (**5**; 1.94 g, 9.05 mmol), and sodium hydride (0.368 g, 60% dispersion in oil, 9.20 mmol) in dimethoxyethane (100 mL) was heated at 65 °C for 2 h. Diethyl ether (500 mL) was added to the cooled solution, followed by extraction with 2 × 100 mL of water and 2 × 100 mL of brine. The organic phase was dried with magnesium sulfate and the filtered solution taken to dryness on a rotary evaporator. The crude product was recrystallized from dichloromethane/methanol, yielding 1.24 g (1.75 mmol, 61%) of 1,3,5-tris{2′-(*E*)-[4″-(oct-1‴-ynyl)phenyl]ethenyl}benzene (**11**) as a flaky white solid. Mp: 118 °C. UV−vis (THF): 274 sh (14.8), 291 sh (28.5), 325 sh (81.6), 335 (92.9), 350 (69.8), 383 sh (3.1) nm (10^3 L mol^{-1} cm^{-1}). ^{1}H NMR (CDCl$_3$): δ 7.48 (s, 3H, H$_2$), 7.44, 7.39 (2 × d, J_{HH} = 8 Hz, 2 × 6H, H$_{10}$ and H$_{11}$), 7.09 (m, 6H, H$_7$ and H$_8$), 2.42 (t, J_{HH} = 7 Hz, 6H, H$_{3'}$), 1.61−1.32 (m, 24H, H$_{4'}$−H$_{7'}$), 0.91 (t, J_{HH} = 7 Hz, 9H, H$_{8'}$). ^{13}C NMR (CDCl$_3$): δ 137.6, 136.2 (C$_1$, C$_9$), 131.8 (C$_{11}$), 128.5, 128.4 (C$_7$, C$_8$), 126.3 (C$_{10}$), 124.0, 123.3 (C$_2$, C$_{12}$), 91.5 (C$_{1'}$), 80.7 (C$_{2'}$), 31.4 (C$_{3'}$), 28.7 (C$_{4'}$), 28.6 (C$_{5'}$), 22.6 (C$_{6'}$), 19.5 (C$_{7'}$), 14.1 (C$_{8'}$). MS (EI): 708 ([M]$^+$, 21), 680 ([M − C$_2$H$_4$]$^+$, 12), 650 ([M − C$_4$H$_{10}$]$^+$, 3), 57 ([C$_4$H$_9$]$^+$, 100). Anal. Calcd for C$_{54}$H$_{60}$ (709.07): C, 91.47; H, 8.53. Found: C, 91.70; H, 8.31.

General Procedure I for the Reaction of M$_2$Ir$_2$(CO)$_{10}$(η^5-C$_5$H$_4$Me)$_2$ (M = Mo (1), W (2)) with Monoynes. The alkyne (in excess) was added to a red-brown solution of M$_2$Ir$_2$(CO)$_{10}$(η^5-C$_5$H$_4$Me)$_2$ (**1**/**2**) in CH$_2$Cl$_2$ (ca. 20 mL) and the resultant mixture heated at reflux until TLC and/or IR indicated the disappearance of **1**/**2**. Over the course of the reaction the color changed from red-brown to green-brown. The

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[54] Sengupta, S.; Bhattacharyya, S.; Sadhukhan, S. K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 275.

reaction mixture was taken to dryness on a rotary evaporator, and the residue was dissolved in a small volume (ca. 3 mL) of CH_2Cl_2 and applied to preparative TLC plates for chromatographic separation of the products.

Reaction of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (1) with Phenylacetylene. Following the general procedure I, phenylacetylene (100 μL, 0.90 mmol) was reacted with **1** (107 mg, 0.106 mmol) in CH_2Cl_2 (20 mL) at reflux for 4 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (1/1) eluant gave one major band ($R_f = 0.61$), the contents of which were extracted with CH_2Cl_2 and recrystallized from CH_2Cl_2/methanol at 3 °C, to afford dark green needle crystals of $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**12**; 52.1 mg, 0.049 mmol, 46%). IR (CH_2Cl_2): ν(CO) 2065 vs, 2037 vs, 2010 m, 1991 m, 1823 s, 1774 s cm^{-1}. UV−vis (THF): 283 sh (20.6), 343 (9.4), 392 (6.1), 431 sh (3.1), 619 (1.9) nm (10^3 L mol^{-1} cm^{-1}). ^{1}H NMR ($CDCl_3$): δ 10.02 (s, 1H, PhCC*H*), 7.25−6.60 (m, 5H, Ph), 4.65−4.33 (m, 8H, C_5H_4Me), 1.99 (s, 6H, C_5H_4*Me*). MS (SI): 1062 ($[M]^+$, 100), 1034 ($[M - CO]^+$, 28), 1006 ($[M - 2CO]^+$, 66), 978 ($[M - 3CO]^+$, 29), 950 ($[M - 4CO]^+$, 48), 922 ($[M - 5CO]^+$, 35), 894 ($[M - 6CO]^+$, 23). Anal. Calcd for $C_{28}H_{22}Ir_2Mo_2O_8$ (1062.76): C, 31.64; H, 2.09. Found: C, 32.01; H, 2.05. The second ($R_f = 0.22$, brown) and third ($R_f = 0.10$, brown) bands appeared to be in trace amounts and were not isolated.

Reaction of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (1) with Diphenylacetylene. Following the general procedure I, diphenylacetylene (59 mg, 0.33 mmol) was reacted with **1** (63.3 mg, 0.0624 mmol) in CH_2Cl_2 (20 mL) at reflux for 20 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (3/2) eluant gave one band ($R_f = 0.67$), the contents of which were crystallized from CH_2Cl_2/methanol at 3 °C to afford dark green crystals of $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**13**; 57.2 mg, 0.0503 mmol, 81%). IR (CH_2Cl_2): ν(CO) 2069 vs, 2043 vs, 2016 m, 1998 m, 1813 s, 1763 m cm^{-1}. UV−vis (THF): 283 sh (22.1), 361 (8.1), 407 (5.4), 450 sh (2.3), 634 (1.7) nm (10^3 L mol^{-1} cm^{-1}). ^{1}H NMR ($CDCl_3$): δ 7.21−7.02 (m, 10H, Ph), 4.57−4.42 (m, 8H, C_5H_4Me), 2.03 (s, 6H, C_5H_4*Me*). MS (SI): 1136 ($[M]^+$, 71), 1108 ($[M - CO]^+$, 37), 1080 ($[M - 2CO]^+$, 39), 1052 ($[M - 3CO]^+$, 84), 1024 ($[M - 4CO]^+$, 71), 996 ($[M - 5CO]^+$, 69), 968 ($[M - 6CO]^+$, 72), 940 ($[M - 7CO]^+$, 73), 912 ($[M - 8CO]^+$, 100). Anal. Calcd for $C_{34}H_{24}Ir_2Mo_2O_8$ (1136.80): C, 35.92; H, 2.13. Found: C, 35.70; H, 2.08.

Reaction of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (1) with 1-Phenyl-1-propyne. Following the general procedure I, 1-phenyl-1-propyne (0.10 mL, 93 mg, 0.70 mmol) was reacted with **1** (120.0 mg, 0.118 mmol) in CH_2Cl_2 (20 mL) at reflux for 5 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (3/2) eluant gave three bands. The contents of the first band ($R_f = 0.82$, red-brown) contained trace amounts of unreacted **1**, as identified by solution IR. The contents of the second and major band ($R_f = 0.53$) were crystallized from CH_2Cl_2/methanol at 3 °C to afford dark green crystals of $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}MeC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**14**; 63.4 mg, 0.0590 mmol, 50%). IR (CH_2Cl_2): ν(CO) 2066 vs, 2039 vs, 2011 m, 1994 m, 1814 s, 1765 m cm^{-1}. UV−vis (THF): 313 sh (9.0), 347 sh (6.5), 405 (6.0), 456 sh (1.5), 633 (1.8) nm (10^3 L mol^{-1} cm^{-1}). ^{1}H NMR ($CDCl_3$): δ 7.22−7.03 (m, 5H, Ph), 4.73−4.37 (m, 8H, C_5H_4Me), 3.02 (s, 3H, PhCC*Me*), 1.99 (s, 6H, C_5H_4*Me*). MS (SI): 1074 ($[M]^+$, 21), 1046 ($[M - CO]^+$, 25), 1018 ($[M - 2CO]^+$, 100), 990 ($[M - 3CO]^+$, 68), 962 ($[M - 4CO]^+$, 66), 934 ($[M - 5CO]^+$, 64), 906 ($[M - 6CO]^+$, 54), 878 ($[M - 7CO]^+$, 52). Anal. Calcd for $C_{29}H_{22}Ir_2Mo_2O_8$ (1074.77): C, 32.41; H, 2.06. Found: C, 32.30; H, 2.10. The third band ($R_f = 0.19$) contained trace amounts of an unidentified orange compound.

Reaction of $W_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (2) with 1-Phenyl-1-propyne. Following the general procedure I, 1-phenyl-1-propyne (0.20 mL, 186 mg, 1.40 mmol) was reacted with **2** (50.3 mg, 0.0431 mmol) at reflux for 4 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (3/2) eluant gave three bands. The first band ($R_f = 0.85$) contained trace amounts of an unidentified yellow compound. The second band ($R_f = 0.59$, red-brown) contained trace amounts of unreacted **2**, as identified by solution IR. The contents of the third and major band ($R_f = 0.29$) were crystallized from CH_2Cl_2/methanol at 3 °C to afford dark green microcrystals of $W_2Ir_2(\mu_4\text{-}\eta^2\text{-}MeC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**15**; 20.6 mg, 0.020 mmol, 79%). IR (CH_2Cl_2): ν(CO) 2058 vs, 2029 vs, 2008 m, 1986 w, 1812 m, 1761 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.22−7.02 (m, 5H, Ph), 4.78−4.60 (m, 8H, C_5H_4Me), 3.26 (s, 3H, PhCC*Me*), 2.09 (s, 6H, C_5H_4*Me*). MS (SI): 1249 ($[M]^+$, 95), 1193 ($[M - 2CO]^+$, 25), 1165 ($[M - 3CO]^+$, 100), 1109 ($[M - 5CO]^+$, 62), 1053 ($[M - 7CO]^+$, 46), 1025 ($[M - 8CO]^+$, 55). Anal. Calcd for $C_{29}H_{22}Ir_2O_8W_2$ (1250.59): C, 27.85; H, 1.77. Found: C, 27.92; H, 1.81.

Reaction of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (1) with 4-(Oct-1′-ynyl)benzaldehyde (5). Following the general procedure I, 4-(oct-1′-ynyl)benzaldehyde (**5**; 104 mg, 0.485 mmol) was reacted with **1** (122 mg, 0.120 mmol) in CH_2Cl_2 (20 mL) at reflux for 20 h. Purification by preparative TLC with CH_2Cl_2 eluant gave two bands. The contents of the first and major band ($R_f = 0.67$) were crystallized from CH_2Cl_2/methanol at 3 °C to afford dark green crystals of $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4CHO\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**16**; 82.4 mg, 0.0703 mmol, 59%). IR (CH_2Cl_2): ν(CO, cluster) 2067 vs, 2040 vs, 2011 m, 1995 m, 1817 s, 1770 m; ν(CO, aldehyde) 1700 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.91 (s, 1H, CHO), 7.69 (d, $J_{HH} = 8$ Hz, 2H, C_6H_4), 7.18 (d, $J_{HH} = 8$ Hz, 2H, C_6H_4), 4.85−4.35 (m, 8H, C_5H_4Me), 2.79 (t, $J_{HH} = 7$ Hz, 2H, C$H_2(CH_2)_4$Me), 1.96 (s, 6H, C_5H_4*Me*), 1.50−1.35 (m, 8H, $CH_2(CH_2)_4$Me), 0.94 (t, $J_{HH} = 6$ Hz, 3H, $(CH_2)_5$*Me*). MS (SI): 1088 ($[M - 3CO]^+$, 41), 1060 ($[M - 4CO]^+$, 97), 1032 ($[M - 5CO]^+$, 83), 1004 ($[M - 6CO]^+$, 79), 976 ($[M - 7CO]^+$, 100), 948 ($[M - 8CO]^+$, 87). Anal. Calcd for $C_{35}H_{32}Ir_2Mo_2O_9$ (1172.91): C, 35.84; H, 2.75. Found: C, 35.88; H, 2.69. The second band ($R_f = 0.25$) contained trace amounts of an unidentified brown solid.

Reaction of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (1) with Diethyl 4-(Oct-1′-ynyl)benzylphosphonate (7). Following the general procedure I, diethyl 4-(oct-1′-ynyl)benzylphosphonate (**7**; 105 mg, 0.312 mmol) was reacted with **1** (110 mg, 0.108 mmol) in CH_2Cl_2 (20 mL) at reflux for 17 h. Purification by preparative TLC with CH_2Cl_2/ethyl acetate (7/3) eluant gave one band ($R_f = 0.58$), the contents of which were crystallized from CH_2Cl_2/ethanol at 3 °C to afford dark green needle crystals of $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4CH_2P(O)(OEt)_2\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**17**; 92.4 mg, 0.0714 mmol, 66%). IR (CH_2Cl_2): ν(CO) 2065 vs, 2038 vs, 2009 m, 1992 m, 1813 s, 1764 m; ν(P=O) 1258 s; δ(P−O−C) 1055 vs; δ(O−C−C) 1029 vs, 967 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.09 (dd, $J_{HH} = 8$ Hz, $J_{PH} = 2$ Hz, 2H, C_6H_4), 6.98 (d, $J_{HH} = 8$ Hz, 2H, C_6H_4), 4.83−4.32 (m, 8H, C_5H_4Me), 4.00 (m, 4H, OCH_2Me), 3.03 (d, $J_{PH} = 22$ Hz, 2H, CH_2P), 2.80 (t, $J_{HH} = 7$ Hz, 2H, C$H_2(CH_2)_4$Me), 1.93 (s, 6H, C_5H_4*Me*), 1.50−1.25 (m, 8H, $CH_2(CH_2)_4$Me), 1.23 (t, $J_{HH} = 7$ Hz, 6H, OCH_2*Me*), 0.93 (t, $J_{HH} = 6$ Hz, 3H, $(CH_2)_5$*Me*). ^{31}P NMR ($CDCl_3$): δ 26.2. MS (SI): 1294 ($[M]^+$, 26), 1266 ($[M - CO]^+$, 13), 1238 ($[M - 2CO]^+$, 35), 1210 ($[M - 3CO]^+$, 38), 1182 ($[M - 4CO]^+$, 100), 1154 ($[M - 5CO]^+$, 61), 1126 ($[M - 6CO]^+$, 45), 1098 ($[M - 7CO]^+$, 55), 1070 ($[M - 8CO]^+$, 45). Anal. Calcd for $C_{39}H_{43}Ir_2Mo_2O_{11}P$ (1295.02): C, 36.17; H, 3.35. Found: C, 35.89; H, 3.33.

Reaction of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_5)_2$ (3) with 1,2-(*E*)-Bis{4′-(ethynyl)phenyl}ethene (8). A mixture of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_5)_2$ (**3**; 84.2 mg, 0.085 mmol) and 1,2-(*E*)-bis{4′-(ethynyl)phenyl}ethene (**8**; 9.0 mg, 0.039 mmol) in CH_2Cl_2 (30 mL) was heated at reflux for 3 h. The green-brown solution was cooled and taken to dryness and the resulting brown residue applied to preparative TLC plates. Elution with ethyl acetate/petroleum spirit (1/1) gave three bands. The contents of the first band ($R_f = 0.93$, red-brown) were identified by solution IR as unreacted $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_5)_2$ (5.2 mg, 5.3 μmol). The second band ($R_f = 0.32$) contained an unidentified green solid (1.7 mg). IR (CH_2Cl_2): ν(CO) 2067 vs, 2041 vs, 2008 m, 1993 w, 1975 m, 1817 s, 1776 m cm^{-1}. The contents of the third and major band ($R_f = 0.16$) had limited solubility and were crystallized from CH_2Cl_2/methanol at 3 °C to afford dark green microcrystals identified as $[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_5)_2]_2\{\mu_8\text{-}\eta^4\text{-}HC_2\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}4\text{-}C_2H\}$ (**18**; 37.1 mg, 0.018 mmol, 46%). IR (CH_2Cl_2): ν(CO) 2067 vs, 2041 vs, 2014 m, 1995 m, 1825 s, 1780 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.17 (s, 2H, C≡C*H*), 7.40 (br d, J_{HH} = 8 Hz, 4H, C_6H_4), 6.90 (br d, J_{HH} = 8 Hz, 4H, C_6H_4), 6.62 (br s, 2H, (*E*)-C*H*=C*H*), 4.84 (s, 20H, C_5H_5). MS (SI): 2088 ($[M]^+$, 32), 2032 ($[M - 2CO]^+$, 41), 2004 ($[M - 3CO]^+$, 50), 1976 ($[M - 4CO]^+$, 42), 1948 ($[M - 5CO]^+$, 52), 1920 ($[M - 6CO]^+$, 42), 1892 ($[M - 7CO]^+$, 45), 1864 ($[M - 8CO]^+$, 49), 1836 ($[M - 9CO]^+$, 48), 1640 ($[M - 16CO]^+$, 100). The low solubility of **18** in common organic solvents rendered purification by recrystallization very difficult—no material sufficiently pure for acceptable microanalysis was obtained.

General Procedure II for the Reaction of $Mo_2Ir_2(CO)_{10}$(η^5-$C_5H_4Me)_2$ (M = Mo (1), W (2)) with Di- and Triynes. The di-/triyne was added to a red-brown solution of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (**1**/**2**) (in excess) in CH_2Cl_2 or THF (ca. 20 mL) and the resultant mixture heated at reflux until TLC and/or IR indicated no further change. Over the course of the reaction the color changed from red-brown to green-brown. The reaction mixture was taken to dryness on a rotary evaporator, and the residue was dissolved in a small volume (ca. 3 mL) of CH_2Cl_2 and applied to preparative TLC plates for chromatographic separation of the products.

Reaction of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (1) with 1,4-Bis(oct-1′-ynyl)benzene. Following the general procedure II, **1** (86.0 mg, 0.085 mmol) was reacted with 1,4-bis(oct-1′-ynyl)benzene (12.0 mg, 0.041 mmol) in THF (15 mL) at reflux for 16 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (7/3) eluant gave four bands. The contents of the first band (R_f = 0.84, red-brown) were identified by solution IR as unreacted **1** (2.3 mg, 2.3 μmol). The second (R_f = 0.73, green) and third (R_f = 0.66, green) bands appeared to be in trace amounts and were not isolated. The contents of the fourth and major band (R_f = 0.48) were crystallized from CH_2Cl_2/methanol at 3 °C to afford a dark green powder identified as $[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2C_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**19**; 51.6 mg, 0.023 mmol, 57%). IR (CH_2Cl_2): ν(CO) 2065 vs, 2039 vs, 2009 m, 1994 m, 1815 s, 1766 m cm^{-1}. UV–vis (THF): 317 sh (20.0), 386 sh (17.9), 409 (18.4), 450 sh (8.3), 633 (3.1) nm (10^3 L mol^{-1} cm^{-1}). ^{1}H NMR ($CDCl_3$): δ 6.91 (s, 4H, C_6H_4), 4.88–4.36 (m, 16H, C_5*H_4*Me), 2.75 (t, J_{HH} = 8 Hz, 4H, C*H_2*$(CH_2)_4$Me), 1.97 (s, 12H, C_5H_4*Me*), 1.50–1.36 (m, 16H, CH_2(C*H_2*$)_4$Me), 0.96 (t, J_{HH} = 6 Hz, 6H, $(CH_2)_5$*Me*). MS (SI): 2210 ($[M]^+$, 72), 2182 ($[M - CO]^+$, 40), 2154 ($[M - 2CO]^+$, 36), 2126 ($[M - 3CO]^+$, 73), 2098 ($[M - 4CO]^+$, 44), 2070 ($[M - 5CO]^+$, 50), 2042 ($[M - 6CO]^+$, 60), 2014 ($[M - 7CO]^+$, 71), 1986 ($[M - 8CO]^+$, 93), 1958 ($[M - 9CO]^+$, 94), 1930 ($[M - 10CO]^+$, 62), 1902 ($[M - 11CO]^+$, 45), 1874 ($[M - 12CO]^+$, 44), 1846 ($[M - 13CO]^+$, 60), 1818 ($[M - 14CO]^+$, 72), 1790 ($[M - 15CO]^+$, 90), 1762 ($[M - 16CO]^+$, 100). Anal. Calcd for $C_{62}H_{58}Ir_4Mo_4O_{16}$ (2211.70): C, 33.67; H, 2.64. Found: C, 33.46; H, 2.65.

Reaction of $W_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (2) with 1,4-Bis(oct-1′-ynyl)benzene. Following the general procedure II, **2** (40.0 mg, 0.034 mmol) was reacted with 1,4-bis(oct-1′-ynyl)benzene (4.5 mg, 0.015 mmol) in CH_2Cl_2 at reflux for 24 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (7/3) eluant gave four bands. The contents of the first band (R_f = 0.89, red-brown) contained trace amounts of unreacted **2**, as identified by solution IR. The contents of the second band (R_f = 0.73) afforded a dark green solid identified as $W_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2C_6H_4\text{-}4\text{-}C{\equiv}C(CH_2)_5Me\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**21**; 5.2 mg, 0.0039 mmol, 11%). IR (CH_2Cl_2): ν(CO) 2058 s, 2031 vs, 2005 sh, 1989 m, 1812 m, 1760 w cm^{-1}. MS (SI): 1349 ($[M - C_5H_4Me]^+$, 48), 1321 ($[M - C_5H_4Me - CO]^+$, 10), 1265 ($[M - C_5H_4Me - 3CO]^+$, 23), 1237 ($[M - C_5H_4Me - 4CO]^+$, 100), 1209 ($[M - C_5H_4Me - 5CO]^+$, 46), 1181 ($[M - C_5H_4Me - 6CO]^+$, 58), 1153 ($[M - C_5H_4Me - 7CO]^+$, 73), 1125 ($[M - C_5H_4Me - 8CO]^+$, 77). Lack of sufficient material precluded microanalysis. The contents of the third band (R_f = 0.54) afforded an unidentified dark brown solid (5.1 mg). IR (CH_2Cl_2): ν(CO) 2054 m, 2040 w, 2029 w, 2006 m, 1991 w, 1967 w, 1942 w, 1922 w, 1917 w, 1889 w, 1869 m cm^{-1}. MS (SI): 1184 (10), 1059 (15), 1037 (43), 992 (36), 957 (50), 910 (21), 876 (17), 861 (26), 832 (76), 804 (100). The contents of the fourth and major band (R_f = 0.44) were crystallized from CH_2Cl_2/methanol at 3 °C to afford a dark green solid identified as $[W_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2C_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**20**) (31.4 mg, 0.0122 mmol, 79%). IR (CH_2Cl_2): ν(CO) 2054 vs, 2029 s, 2009 sh, 1988 m, 1811 m, 1759 m cm^{-1}. ^{1}H NMR: δ 7.67 (d, J_{HH} = 7 Hz, 2H, C_6H_4), 7.51 (d, J_{HH} = 7 Hz, 2H, C_6H_4), 4.94–3.95 (m, 16H, C_5*H_4*Me), 2.90 (br t, 4H, C*H_2*$(CH_2)_4$Me), 2.14 (s, 12H, C_5H_4*Me*), 1.50–1.25 (m, 16H, CH_2(C*H_2*$)_4$Me), 0.90 (t, J_{HH} = 6 Hz, 6H, $(CH_2)_5$*Me*). MS (SI): 2564 ($[M]^+$, 66), 2536 ($[M - CO]^+$, 22), 2480 ($[M - 3CO]^+$, 32), 2424 ($[M - 5CO]^+$, 25), 2396 ($[M - 6CO]^+$, 52), 2368 ($[M - 7CO]^+$, 100), 2340 ($[M - 8CO]^+$, 60), 2312 ($[M - 9CO]^+$, 59), 2256 ($[M - 11CO]^+$, 54). MS (FAB): 2564 ($[M]^+$, 78), 2480 ($[M - 3CO]^+$, 18), 2396 ($[M - 6CO]^+$, 30), 2368 ($[M - 7CO]^+$, 25), 2340 ($[M - 8CO]^+$, 12), 2312 ($[M - 9CO]^+$, 14), 2256 ($[M - 11CO]^+$, 14), 2228 ($[M - 12CO]^+$, 58), 2200 ($[M - 13CO]^+$, 46), 2172 ($[M - 14CO]^+$, 74), 2116 ($[M - 16CO]^+$, 82). Anal. Calcd for $C_{62}H_{58}Ir_4O_{16}W_4$ (2563.33): C, 29.05; H, 2.28. Found: C, 29.08; H, 2.31.

Reaction of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (1) with 1,2-(*E*)-Bis{4′-(oct-1″-ynyl)phenyl}ethene (9). Following the general procedure II, **1** (86.3 mg, 0.085 mmol) was reacted with 1,2-(*E*)-bis{4′-(oct-1″-ynyl)phenyl}ethene (**9**; 13.2 mg, 0.033 mmol) in CH_2Cl_2 (20 mL) at reflux for 20 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (9/1) eluant gave three bands. The contents of the first band (R_f = 0.96, red-brown) were identified by solution IR as unreacted **1** (21.3 mg, 0.021 mmol). The second band (R_f = 0.91, green) appeared to be in a trace amount and was not isolated. The contents of the third and major band (R_f = 0.58) were crystallized from CH_2Cl_2/ethanol at 3 °C to afford dark green platelike crystals identified as $[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**22**; 44.4 mg, 0.019 mmol, 58%). A crystal grown by this method was selected for a single-crystal X-ray structural study. IR (CH_2Cl_2): ν(CO) 2065 vs, 2038 vs, 2010 m, 1993 m, 1814 s, 1765 m cm^{-1}. UV–vis (THF): 317 (32.7), 411 (39.4), 509 sh (3.2), 629 (3.5) nm (10^3 L mol^{-1} cm^{-1}). ^{1}H NMR ($CDCl_3$): δ 7.29 (d, J_{HH} = 8 Hz, 4H, C_6H_4), 7.04 (d, J_{HH} = 8 Hz, 4H, C_6H_4), 6.98 (s, 2H, (*E*)-C*H*=C*H*), 4.86–4.36 (m, 16H, C_5*H_4*Me), 2.83 (t, J_{HH} = 8 Hz, 4H, C*H_2*$(CH_2)_5$Me), 1.95 (s, 12H, C_5H_4*Me*), 1.44–1.35 (m, 16H, CH_2(C*H_2*$)_4$Me), 0.94 (t, J_{HH} = 6 Hz, 6H, $(CH_2)_5$*Me*). MS (SI): 2088 ($[M - 8CO]^+$, 20), 2060 ($[M - 9CO]^+$, 16), 2032 ($[M - 10CO]^+$, 12), 2004 ($[M - 11CO]^+$, 10), 1976 ($[M - 12CO]^+$, 16), 1948 ($[M - 13CO]^+$, 14), 1920 ($[M - 14CO]^+$, 8), 1892 ($[M - 15CO]^+$, 8), 1864 ($[M - 16CO]^+$, 22). Anal. Calcd for $C_{70}H_{64}Ir_4Mo_4O_{16}$ (2313.83): C, 36.34; H, 2.79. Found: C, 36.10; H, 2.73.

Reaction of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (2) with 1,2-(*E*)-Bis{4′-(oct-1″-ynyl)phenyl}ethene (9). Following the general procedure II, **2** (85.5 mg, 0.072 mmol) was reacted with 1,2-(*E*)-bis{4′-(oct-1″-ynyl)phenyl}ethene (**7**; 12.8 mg, 0.033 mmol) in CH_2Cl_2 at reflux for 26 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (9/1) eluant gave three bands. The contents of the first band (R_f = 0.91, red-brown) contained trace amounts of unreacted **2**, as identified by solution IR. The contents of the second band (R_f = 0.59) were crystallized from CH_2Cl_2/MeOH at 3 °C to afford a dark brown crystalline solid identified as $W_3Ir_3(CO)_{12}(\eta^5\text{-}C_5H_4Me)_3$ (6.4 mg, 0.0038 mmol, 6%).[41] IR (CH_2Cl_2): ν(CO) 2056 s, 2037 vs, 1992 vs, 1927 m, 1870 m, 1812 s, 1755 m, 1606 w, 1424 m cm^{-1}. The contents of the third and major band (R_f = 0.36) were crystallized from CH_2Cl_2/methanol at 3 °C to afford a dark green crystalline solid identified as $[W_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**23**; 71.7 mg, 0.027 mmol, 83%). IR (CH_2Cl_2): ν(CO) 2055 vs, 2027 s, 1997 sh, 1982 m, 1809 m, 1758 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.35−7.03 (m, 8H, C_6H_4), 6.99 (s, 2H, (*E*)-C*H*═C*H*), 4.88−4.38 (m, 16H, C_5H_4Me), 3.48 (s, 3H, OMe), 2.96 (br t, J_{HH} = 8 Hz, 4H, C*H*$_2$(CH_2)$_5$Me), 2.10 (s, 12H, C_5H_4*Me*), 1.42−1.20 (m, 16H, CH_2(C*H*$_2$)$_4$Me), 0.94 (t, J_{HH} = 6 Hz, 6H, (CH_2)$_5$*Me*). MS (FAB): 2666 ([M]$^+$, 66), 2582 ([M − 3CO]$^+$, 26), 2498 ([M − 6CO]$^+$, 16), 2470 ([M − 7CO]$^+$, 100), 2442 ([M − 8CO]$^+$, 52), 2414 ([M − 9CO]$^+$, 42), 2386 ([M − 10CO]$^+$, 34), 2358 ([M − 11CO]$^+$, 38), 2330 ([M − 12CO]$^+$, 46), 2302 ([M − 13CO]$^+$, 40). Anal. Calcd for $C_{70}H_{60}Ir_4O_{16}W_4$·MeOH (2661.52 + 32.04): C, 31.66; H, 2.39. Found: C, 31.59; H, 2.27.

Reaction of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (1) with 1,4-Bis{2′-(*E*)-[4″-(oct-1‴-ynyl)phenyl]ethenyl}benzene (10). Following the general procedure II, **1** (83.8 mg, 0.083 mmol) was reacted with 1,4-bis{2′-(*E*)-[4″-(oct-1‴-ynyl)phenyl]ethenyl}benzene (**10**; 17.5 mg, 0.035 mmol) in CH_2Cl_2 at reflux for 18 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (4/1) eluant gave four bands. The contents of the first band (R_f = 0.82, red-brown) were identified by solution IR as unreacted **1** (23.9 mg, 0.024 mmol). The contents of the second and major band (R_f = 0.60) were crystallized from CH_2Cl_2/methanol at 3 °C to afford dark green platelike crystals identified as $[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2\text{-}[4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CH]_2C_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**24**; 52.4 mg, 0.022 mmol, 62%). IR (CH_2Cl_2): ν(CO) 2065 vs, 2038 vs, 2009 m, 1992 m, 1816 s, 1764 m cm^{-1}. UV−vis (THF): 280 sh (33.3), 351 (30.1), 415 (59.7), 506 sh (3.0), 630 (3.0) nm (10^3 L mol^{-1} cm^{-1}). ^{1}H NMR ($CDCl_3$): δ 7.48 (s, 4H, inner C$_6$*H*$_4$), 7.32 (d, J_{HH} = 8 Hz, 4H, outer C_6H_4), 7.09 (d, J_{HH} = 16 Hz, 2H, CH═C*H*C$_6$H$_4$C*H*═CH), 7.04 (d, J_{HH} = 8 Hz, outer C_6H_4), 7.00 (d, J_{HH} = 16 Hz, C*H*═CHC$_6$H$_4$CH═C*H*), 4.87−4.37 (m, 16H, C$_5$*H*$_4$Me), 2.84 (t, J_{HH} = 8 Hz, 4H, C*H*$_2$(CH_2)$_5$Me), 1.97 (s, 12H, C_5H_4*Me*), 1.48−1.35 (m, 16H, CH_2(C*H*$_2$)$_4$Me), 0.92 (t, J_{HH} = 6 Hz, 6H, (CH_2)$_5$*Me*). MS (SI): 2414 ([M]$^+$, 42), 2358 ([M − 2CO]$^+$, 27), 2330 ([M − 3CO]$^+$, 36), 2302 ([M − 4CO]$^+$, 40), 2246 ([M − 6CO]$^+$, 47), 2218 ([M − 7CO]$^+$, 58), 2190 ([M − 8CO]$^+$, 92), 2162 ([M − 9CO]$^+$, 100), 2134 ([M − 10CO]$^+$, 76). Anal. Calcd for $C_{78}H_{70}Ir_4Mo_4O_{16}$ (2416.05): C, 38.78; H, 2.92. Found: C, 38.47; H, 3.15. The third (R_f = 0.41, green) and fourth (R_f = 0.10, green) bands appeared to be in trace amounts and were not isolated.

Reaction of $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (1) with 1,3,5-Tris{2′-(*E*)-[4″-(oct-1‴-ynyl)phenyl]ethenyl}benzene (11). Following the general procedure II, **1** (103.1 mg, 0.102 mmol) was reacted with 1,3,5-tris{2′-(*E*)-[4″-(oct-1‴-ynyl)phenyl]ethenyl}benzene (**11**; 23.0 mg, 0.032 mmol) in CH_2Cl_2 (25 mL) at reflux for 16 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (4/1) eluant gave three bands. The contents of the first band (R_f = 0.94, red-brown) were identified by solution IR as unreacted **1** (34 mg, 0.034 mmol). The second band (R_f = 0.77) contained an unidentified green solid (4.4 mg). IR (CH_2Cl_2): ν(CO) 2066 vs, 2038 vs, 2010 m, 1993 s, 1814 s, 1765 m cm^{-1}. The contents of the third and major band (R_f = 0.55) were crystallized from CH_2Cl_2/ethanol at 3 °C to afford dark green crystals identified as $[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_3\{\mu_{12}\text{-}\eta^6\text{-}1,3,5\text{-}C_6H_3[(E)\text{-}CH{=}CHC_6H_4\text{-}4'\text{-}C_2(CH_2)_5Me]_3\}$ (**25**; 57.8 mg, 16.1 μmol, 50%). A crystal grown by this method was selected for a single-crystal X-ray structural study. IR (CH_2Cl_2): ν(CO) 2065 vs, 2038 vs, 2010 m, 1993 m, 1814 s, 1765 m cm^{-1}. UV−vis (THF): 320 (75.7), 382 (69.9), 480 (13.9), 630 sh (4.4) nm (10^3 L mol^{-1} cm^{-1}). ^{1}H NMR ($CDCl_3$): δ 7.52 (s, 3H, central C$_6$*H*$_3$), 7.34 (d, J_{HH} = 8 Hz, 6H, outer C_6H_4), 7.13 (d, J_{HH} = 15 Hz, 3H, C_6H_3-(*E*)-C*H*═CH), 7.08 (d, J_{HH} = 8 Hz, 6H, outer C$_6$*H*$_4$), 7.07 (d, J_{HH} = 15 Hz, 3H, C_6H_3-(*E*)-CH═C*H*), 4.88−4.39 (m, 24H, C$_5$*H*$_4$Me), 2.86 (br t, J_{HH} = 8 Hz, 6H, C*H*$_2$(CH_2)$_5$Me), 1.98 (s, 18H, C_5H_4*Me*), 1.47−1.35 (m, 24H, CH_2(C*H*$_2$)$_4$Me), 0.95 (t, J_{HH} = 6 Hz, 9H, (CH_2)$_5$*Me*). MS (SI): 3274 ([M − 11CO]$^+$, 36), 3246 ([M − 12CO]$^+$, 43), 3218 ([M − 13CO]$^+$, 55), 3190 ([M − 14CO]$^+$, 42), 3162 ([M − 15CO]$^+$, 40). Anal. Calcd for $C_{114}H_{102}Ir_6Mo_6O_{24}$ (3584.89): C, 38.19; H, 2.87. Found: C, 37.95; H, 3.05.

Reaction of $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4CHO\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (16) with $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4CH_2\text{-}P(O)(OEt)_2\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (17). A solution of $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4CH_2P(O)(OEt)_2\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**17**; 85.6 mg, 66 μmol) in THF (10 mL) was cooled to 0 °C, and sodium methoxide solution (0.35 mL, 88 μmol, 0.25 mol L^{-1} in methanol) was added with stirring. After the mixture was warmed to room temperature, a solution of $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4CHO\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**16**; 75.0 mg, 64 μmol) in THF (5 mL) was added slowly, and this mixture was stirred at room temperature for 16 h, followed by heating to 50 °C for 2 h. The cooled mixture was transferred to a small separating funnel and CH_2Cl_2 (40 mL) added. The organic phase was washed with water (2 × 30 mL) then dried with $MgSO_4$ and filtered and the filtrate taken to dryness on a rotary evaporator. The green-brown residue was dissolved in CH_2Cl_2 (ca. 2 mL) and applied to preparative TLC plates. Elution with CH_2Cl_2 gave four bands. The first (R_f = 0.96, green) band appeared to be in a trace amount and was not isolated. The contents of the second band (R_f = 0.73) were crystallized from CH_2Cl_2/methanol at 3 °C to afford a dark green solid, identified by solution IR and ^{1}H NMR as $[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**22**; 16.8 mg, 7.3 μmol, 11%). The contents of the third band (R_f = 0.68, green) were identified by ^{1}H NMR as unreacted $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4CHO\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**16**; 18.5 mg, 15.8 μmol). The contents of the fourth band (R_f = 0.09, green) were extracted into CH_2Cl_2 and the solvent removed in vacuo to afford an unidentified green solid (1.6 mg). IR (CH_2Cl_2): ν(CO) 2067 vs, 2040 vs, 2010 m, 1996 m, 1817 s, 1770 m cm^{-1}. A large amount of brown material remained on the baseline but could not be extracted with more polar solvents.

Reaction of $W_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (2) with Hexa-1,5-diyne. $W_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (**2**; 22.3 mg, 0.0187 mmol) was added to excess hexa-1,5-diyne (105.0 mg, 1.344 mmol) in CH_2Cl_2 (30 mL), and the mixture was heated at reflux for 5 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (8.5/1.5) as eluent gave one major band. The contents of this band (R_f = 0.43) were crystallized from CH_2Cl_2/methanol at 3 °C to afford a blue powder identified as $W_2Ir_2\{\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2C{\equiv}CH\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**26**; 5.7 mg, 0.0047 mmol, 25%). IR (CH_2Cl_2): ν(CO) 2057 vs, 2026 vs, 2007 sh, 1982 m, 1819 m, 1768 m cm^{-1}. ^{1}H NMR: δ 8.29 (s, 1H, *H*C$_2$(CH_2)$_2$C≡CH), 5.34−4.97 (m, 8H, C$_5$*H*$_4$Me), 2.60 (t, J_{HH} = 8 Hz, 2H, HC$_2$C*H*$_2$CH$_2$C≡CH), 2.23 (s, 1H, HC$_2$(CH_2)$_2$C≡C*H*), 2.14 (s, 6H, C_5H_4*Me*), 2.02 (t, J_{HH} = 8 Hz, 2*H*, HC$_2$CH$_2$C*H*$_2$C≡CH). Lack of sufficient material precluded microanalysis.

Excess $W_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (**2**; 12.2 mg, 0.0091 mmol) was added to **26** (5.7 mg, 0.0047 mmol) in CH_2Cl_2 (4 mL), and the mixture was heated at reflux for 14 h. Purification by preparative TLC with CH_2Cl_2/petroleum spirit (4/1) as eluent gave three bands. The contents of the first band (R_f = 0.90) were identified by solution IR as **2** (9.0 mg, 0.0075 mmol). The contents of the second band (R_f = 0.31) were crystallized from CH_2Cl_2/MeOH at 3 °C to afford a dark brown powder identified as $[W_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}HC_2(CH_2)_2C_2H\}$ (**27**; 7.5 mg, 0.0032 mmol, 61%). IR (CH_2Cl_2): ν(CO) 2036 vs, 1992 sh, 1959 m, 1928 w, 1868 m, 1726 w cm^{-1}. ^{1}H NMR: δ 8.29 (s, 2H, HC$_2$(CH_2)$_2$C$_2$H), 5.98−5.08 (m, 16H, C$_5$*H*$_4$Me), 2.29−2.24 (m, 4H, HC$_2$C$_2$*H*$_4$C$_2$H), 2.18 (s, 12H, C_5H_4*Me*). MS (SI): 2346 ([M]$^+$, 10), 2318 ([M − CO]$^+$, 12), 2290 ([M − 2CO]$^+$, 9), 2262 ([M − 3CO]$^+$, 9), 2234 ([M − 4CO]$^+$, 9), 2206 ([M − 5CO]$^+$, 10), 2178 ([M − 6CO]$^+$, 11), 2150 ([M − 7CO]$^+$, 12), 2122 ([M − 8CO]$^+$, 14), 2094 ([M − 9CO]$^+$, 16), 2066 ([M − 10CO]$^+$, 22), 2038 ([M − 11CO]$^+$, 28), 2010 ([M − 12CO]$^+$, 26), 1982 ([M − 13CO]$^+$, 25), 1954 ([M − 14CO]$^+$, 26). Microanalysis was unable to be undertaken, due to the limited amount of material obtained. The contents of the third band (R_f = 0.21) afforded an unidentified purple compound (2.5 mg). IR (CH_2Cl_2): ν(CO) 2045 s, 2006 sh, 1963 m, 1903 w, 1810 m, 1461 m cm^{-1}.

Table 1. Crystal Data for 15, 22, and 25

	15	**22**	**25**
formula	$C_{29}H_{22}Ir_2O_8W_2$	$C_{70}H_{64}Ir_4Mo_4O_{16}$	$C_{114}H_{102}Ir_6Mo_6O_{24}$
fw	1250.63	2313.91	3585.01
cryst size (mm)	0.32 × 0.05 × 0.02	0.19 × 0.13 × 0.08	0.24 × 0.20 × 0.06
color, habit	dark green, needle	dark green, prism	dark green, plate
cryst syst	monoclinic	triclinic	trigonal
space group	*Pc* (No. 7)	$P\bar{1}$ (No. 2)	$R\bar{3}$ (No. 148)
a (Å)	9.7099(2)	9.6923(2)	26.2521(6)
b (Å)	9.9514(2)	10.4511(2)	
c (Å)	14.8062(3)	18.9394(3)	33.2008(8)
α (deg)		74.615(1)	
β (deg)	105.411(1)	83.982(1)	
γ (deg)		68.9618(9)	
V ($Å^3$)	1379.24(5)	1726.32(6)	19815.6(8)
Z	2	2	6
D_{calcd} (g cm^{-3})	3.01	2.23	1.80
μ (mm^{-1})	18.019	8.464	6.640
θ_{max} (deg)	30.1	30.1	25.0
index ranges	$-13 \le h \le 13$	$-13 \le h \le 13$	$-55 \le h \le 53$
	$0 \le k \le 14$	$-14 \le k \le 14$	$-56 \le k \le 56$
	$-20 \le l \le 20$	$-25 \le l \le 26$	$-21 \le l \le 29$
N_{measd}	37 598	55 415	60 383
N_{unique} (R_{int})	4039 (0.0364)	10103 (0.0805)	7734 (0.0847)
N_{obsd} ($I > n\sigma(I)$)	3900 (2σ)	6243 (2σ)	5181 (3σ)
abs corr	integration	multiscan	multiscan
T_{min}, T_{max}	0.083, 0.60	0.35, 0.51	0.18, 0.67
N_{param} (restraints)	368	418 (12)	415
R ($I > n\sigma(I)$)[a]	0.028 (2σ)	0.038 (2σ)	0.104 (3σ)
R_w ($I > n\sigma(I)$)[b]	0.030 (2σ)[c]	0.041 (2σ)[d]	0.155 (3σ)[c]
GOF	1.15	0.86	3.61
largest diff peak, hole (e $Å^{-3}$)	1.44, −2.38	1.07, −2.06	5.07, −2.78

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [c] $w = [\sigma_c^2(F_o) + 0.00022(F_o^2)]^{-1}$. [d] $w = [\sigma_c^2(F_o) + 0.00040(F_o^2)]^{-1}$.

Electrochemical Studies. The cyclic voltammograms were recorded using a MacLab 400 interface and MacLab potentiostat from ADInstruments. The supporting electrolyte was 0.25 M $(NBu^n_4)PF_6$ in distilled, deoxygenated CH_2Cl_2. Solutions containing on the order of millimolar concentrations of complex were maintained under argon. Measurements were carried out using a platinum-disk working electrode, platinum auxiliary electrode, and a Ag/AgCl reference electrode, using the ferrocene/ferrocenium redox couple as an internal reference (0.56 V). Additional cyclic voltammetry studies on **12**, **14**, **19**, and **22** were carried out under similar conditions, but using decamethylferrocene/decamethylferrocenium as an internal one-electron standard with a Ag-wire pseudo reference. The UV−vis spectroelectrochemical spectra were recorded on a Cary 5E spectrophotometer over the range 4000−45 000 cm^{-1} (2500−222 nm). Solution spectra of the oxidized species at 243 K were obtained by electrogeneration (Thompson 401E potentiostat) at a Pt-gauze working electrode within a cryostatted optically transparent thin-layer electrochemical (OTTLE) cell, path length 0.5 mm, mounted within the spectrophotometer.[55]

X-ray Crystallographic Studies. A single crystal was mounted on the side of a fine glass capillary using epoxy glue (**15**, **22**) or Paratone oil (**25**), and data were collected at 200 K on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The unit cell refinement, data reduction,[56] and absorption correction (**15**;[57] **22**, **25**[58,59]) were implemented from within maXus.[60] The structures were solved by Patterson (**15**, **25**)[61] or direct (**22**)[62] methods and expanded using difference Fourier techniques[63] from within the teXsan software package.[64] Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in idealized positions which were frequently recalculated. The final cycle of least-squares refinement on *F* was based on $N_{observn}$ reflections and N_{param} parameters and converged to *R* and R_w. The absolute configuration for **15** was determined by comparison of the *R* factors for each of the two configurations when refined to convergence. The data collection and structural refinement details are summarized in Table 1, and selected bond lengths and angles for **15** and **22** are given in Tables 2 and 3. Labeled molecular structures are shown in Figures 2−4. The molecule **22** lies on inversion centers and **25** on a 3-fold rotation axis passing through the central ring; symmetry-expanded diagrams are shown (unless stated otherwise). The bond lengths and angles for **25** have not been tabulated because they were deemed unreliable as a result of the poor-quality data collected (the data as presented are from the best of seven individual crystals which were examined; all crystals rapidly degraded, presumably from solvent loss,

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $W_2Ir_2(\mu_4\text{-}\eta^2\text{-}MeC_2Ph)(CO)_8(\eta\text{-}C_5H_4Me)_2$ (15)

Ir1−Ir2	2.7023(4)	Ir2−C4	1.92(1)
Ir1−W1	2.8237(4)	Ir2−C6	2.40(1)
Ir1−W2	2.8021(5)	Ir2−C8	2.38(1)
Ir2−W1	2.7797(5)	W1−C5	2.000(9)
Ir2−W2	2.8109(4)	W1−C6	1.99(1)
Ir1−C27	2.095(8)	W2−C7	2.000(9)
Ir2−C28	2.134(9)	W2−C8	1.98(1)
W1−C27	2.358(9)	C1−O1	1.12(1)
W1−C28	2.332(9)	C2−O2	1.11(1)
W2−C27	2.332(9)	C3−O3	1.12(1)
W2−C28	2.329(9)	C4−O4	1.13(1)
W1−Cp†[a]	1.976	C5−O5	1.16(1)
W2−Cp†	1.988	C6−O6	1.17(1)
Ir1−C1	1.921(9)	C7−O7	1.16(1)
Ir1−C2	1.93(1)	C8−O8	1.17(1)
Ir1−C5	2.37(1)	C26−C27	1.54(1)
Ir1−C7	2.37(1)	C27−C28	1.49(1)
Ir2−C3	1.917(9)	C28−C29	1.50(1)

Ir2−Ir1−W1	60.35(1)	Ir1−C5−O5	123.2(7)
Ir2−Ir1−W2	61.38(1)	Ir1−C7−O7	123.1(7)
W1−Ir1−W2	96.01(1)	Ir1−C1−O1	177.8(9)
Ir1−Ir2−W1	61.99(1)	Ir1−C2−O2	178(1)
Ir1−Ir2−W2	61.06(1)	Ir2−C3−O3	174.0(9)
W1−Ir2−W2	96.81(1)	Ir2−C4−O4	177.0(9)
Ir1−W1−Ir2	57.66(1)	Ir2−C6−O6	122.9(8)
Ir1−W2−Ir2	57.56(1)	Ir2−C8−O8	123.8(7)
Ir1−C27−W1	78.5(3)	W1−C5−O5	156.6(8)
Ir1−C27−W2	78.3(3)	W1−C6−O6	158.9(9)
Ir1−C27−C28	107.4(6)	W2−C7−O7	157.7(8)
Ir2−C28−W1	76.8(3)	W2−C8−O8	156.3(8)
Ir2−C28−W2	78.0(3)	C26−C27−C28	127.8(8)
Ir2−C28−C27	106.0(6)	C27−C28−C29	126.9(8)

[a] Cp† = centroid of η^5-C_5H_4Me ring.

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(63) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 Program System, Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

(64) teXsan: Single-Crystal Structure Analysis Software, Version 1.8; Molecular Structure Corp., The Woodlands, TX 77381, 1997.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Mo_2Ir_2(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (22)

Ir1−Ir2	2.6931(4)	Mo1−C6	1.972(8)
Ir1−Mo1	2.8188(6)	Mo2−C7	1.982(7)
Ir1−Mo2	2.8347(6)	Mo2−C8	1.972(8)
Ir2−Mo1	2.8071(7)	C1−O1	1.120(9)
Ir2−Mo2	2.7940(6)	C2−O2	1.129(8)
Ir1−C27	2.109(6)	C3−O3	1.113(9)
Ir2−C28	2.126(6)	C4−O4	1.112(8)
Mo1−C27	2.348(6)	C5−O5	1.154(9)
Mo1−C28	2.338(6)	C6−O6	1.181(8)
Mo2−C27	2.385(6)	C7−O7	1.178(8)
Mo2−C28	2.360(6)	C8−O8	1.173(9)
Mo1−Cp† [a]	1.993	C27−C28	1.446(9)
Mo2−Cp†	1.993	C28−C29	1.498(7)
Ir1−C1	1.897(8)	C29−C30	1.416(8)
Ir1−C2	1.911(7)	C29−C34	1.392(8)
Ir1−C5	2.386(8)	C30−C31	1.393(8)
Ir1−C7	2.324(7)	C31−C32	1.385(8)
Ir2−C3	1.914(8)	C32−C33	1.387(8)
Ir2−C4	1.929(7)	C32−C35	1.469(8)
Ir2−C6	2.324(7)	C33−C34	1.373(8)
Ir2−C8	2.285(7)	C35−C35*	1.31(1)
Mo1−C5	1.987(7)		

Ir2−Ir1−Mo1	61.18(1)	Ir1−C1−O1	174.9(8)
Ir2−Ir1−Mo2	60.66(1)	Ir1−C2−O2	179.2(8)
Mo1−Ir1−Mo2	96.90(2)	Ir1−C5−O5	124.1(6)
Ir1−Ir2−Mo1	61.62(1)	Ir1−C7−O7	123.6(6)
Ir1−Ir2−Mo2	62.18(1)	Ir2−C3−O3	175.0(7)
Mo1−Ir2−Mo2	98.12(2)	Ir2−C4−O4	176.8(7)
Ir1−Mo1−Ir2	57.20(1)	Ir2−C6−O6	122.6(6)
Ir1−Mo2−Ir2	57.16(1)	Ir2−C8−O8	122.8(6)
Ir1−C27−Mo1	78.3(2)	Mo1−C5−O5	156.2(7)
Ir1−C27−Mo2	77.9(2)	Mo1−C6−O6	156.2(6)
Ir1−C27−C28	107.5(4)	Mo2−C7−O7	154.5(6)
Ir2−C28−Mo1	77.8(2)	Mo2−C8−O8	155.1(6)
Ir2−C28−Mo2	76.9(2)	C27−C28−C29	126.6(6)
Ir2−C28−C27	106.8(4)	C32−C35−C35*	127.5(7)

[a] Cp† = centroid of η^5-C_5H_4Me ring.

during data collection). The hexyl chain of **22** was found to be disordered over two positions, with the two conformations (C21−C25/C21a−C25a) refined with equal occupancies and restraints placed on some of the intrachain distances.

Results

Syntheses of Organic π-Delocalized Frameworks. The π-delocalized bridges chosen to link the group 6−iridium clusters have been built up using two established synthetic methodologies: the cross-coupling of an aryl halide with a terminal alkyne in the presence of palladium(II) and copper(I) iodide catalysts (Sonogashira coupling) has been used for the introduction of the alkyne groups,[65,66] and the Horner−Emmons−Wittig reaction employing a phosphonate ester (RP(O)(OR′)$_2$, R′ = alkyl group) has been used for the generation of (*E*)-alkene groups.[67] The synthetic procedures are summarized in Schemes 1−3. New compounds were characterized by IR and ^{1}H and ^{13}C NMR spectroscopy and EI mass spectrometry.

The palladium-catalyzed coupling of 4-bromobenzaldehyde with 1-octyne afforded 4-(oct-1′-ynyl)benzaldehyde (**5**) (Scheme 1). The mild brominating agent triphenylphosphine dibromide was used to convert 4-(oct-1′-ynyl)benzyl alcohol into the corresponding 4-(oct-1′-ynyl)benzyl bromide (**6**). An Arbuzov reaction was then used to convert the benzyl bromide **6** into diethyl 4-(oct-1′-ynyl)benzylphosphonate (**7**).

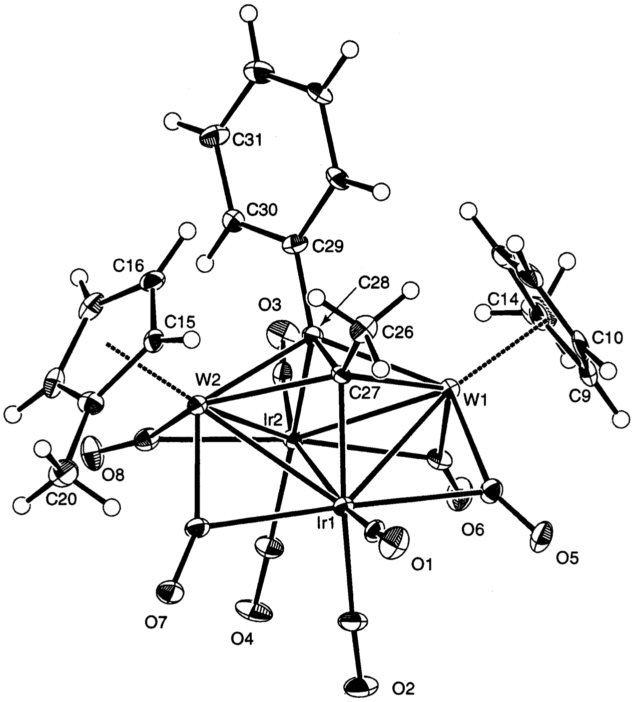

Figure 2. Molecular structure and atomic numbering scheme for **15**. Displacement ellipsoids are shown at the 30% probability level; hydrogens have an arbitrary radius.

1,2-(*E*)-Bis{4′-((trimethylsilyl)ethynyl)phenyl}ethene was synthesized from 4,4′-diiodostilbene and (trimethylsilyl)acetylene, using palladium-catalyzed coupling (Scheme 2). The trimethylsilyl-containing product was not isolated but instead was deprotected in situ with potassium carbonate to afford the diterminal alkyne 1,2-(*E*)-bis{4′-(ethynyl)phenyl}ethene (**8**). The diyne 1,2-(*E*)-bis{4′-(oct-1″-ynyl)phenyl}ethene (**9**) was prepared similarly, utilizing 1-octyne. The longer homologue 1,4-bis{2′-(*E*)-[4″-(oct-1‴-ynyl)phenyl]ethenyl}benzene (**10**) was prepared by a double Horner−Emmons−Wittig coupling of **5** with 1,4-bis(diethyl methylphosphonate)benzene. The branched triyne 1,3,5-tris{2′-(*E*)-[4″-(oct-1‴-ynyl)phenyl]ethenyl}benzene (**11**) was synthesized similarly, using Sonogashira and Horner−Emmons−Wittig protocols (Scheme 3).

Reactions of $M_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (M = Mo, W) with Monoynes. The clusters $M_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4R)_2$ (R = Me, M = Mo (**1**), W (**2**); R = H, M = Mo (**3**)) have been coupled with a range of monoynes. Heating the methylcyclopentadienyl clusters in refluxing dichloromethane with a variety of internal alkynes or phenylacetylene afforded dark green crystals of $M_2Ir_2(\mu_4\text{-}\eta^2\text{-}R^1C_2R^2)(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4Me)_2$ (M = Mo, R^2 = Ph, R^1 = H (**12**), Ph (**13**), Me (**14**); M = W, R^2 = Ph, R^1 = Me (**15**); M = Mo, R^1 = *n*-hexyl, R^2 = C_6H_4-4-CHO (**16**), C_6H_4-4-$CH_2P(O)(OEt)_2$ (**17**)), following chromatographic workup and crystallization, in good to excellent yields (Scheme 4). This group of clusters contains simple monoyne cluster adducts (**12**−**15**), in some cases model compounds for monocluster fragments of the linked clusters described below, as well as

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[65] Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

[66] Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280.

[67] Wadsworth, W. S. J. *Org. React.* **1977**, *25*, 73.

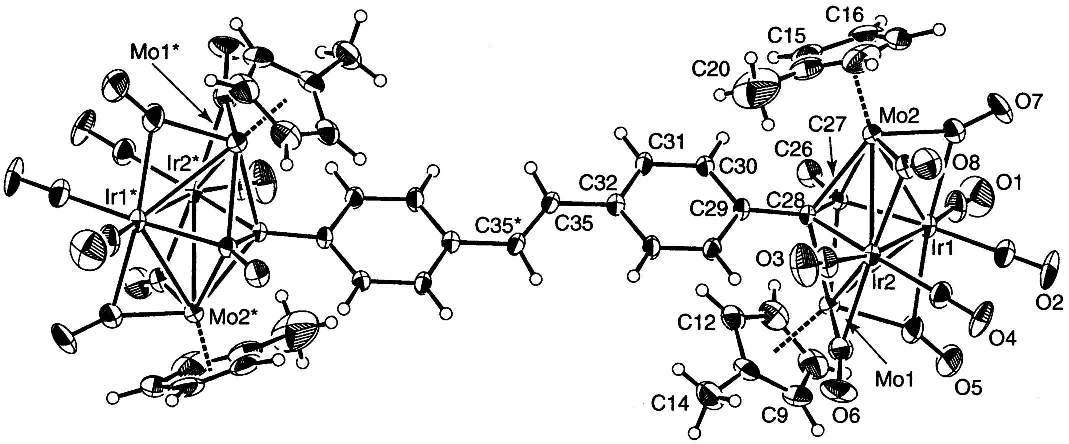


Figure 3. Molecular structure and atomic numbering scheme for **22**. Displacement ellipsoids are shown at the 30% probability level; hydrogens have an arbitrary radius. The hydrogens and C21−C25 of the hexyl chains have been omitted for clarity.

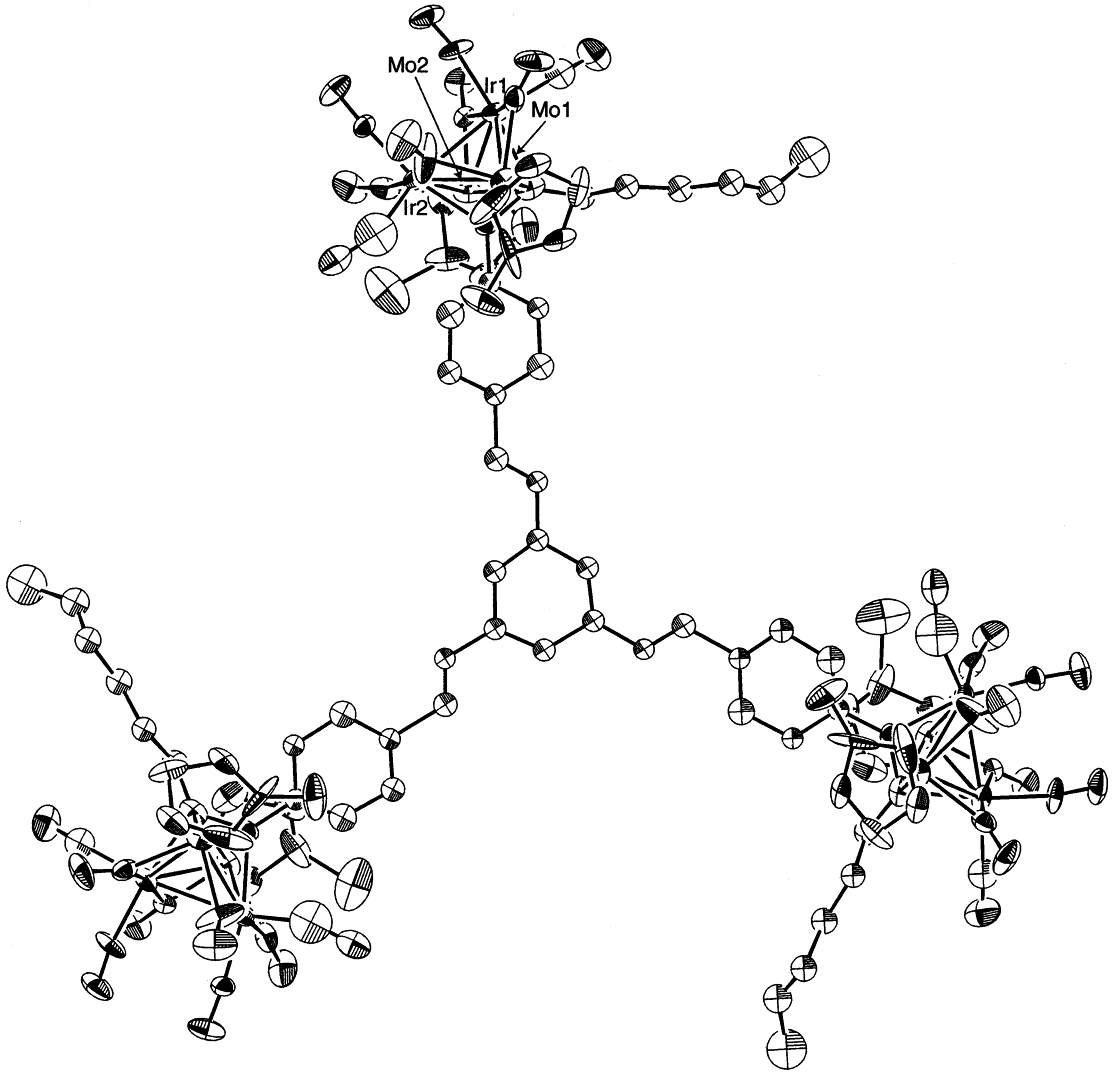
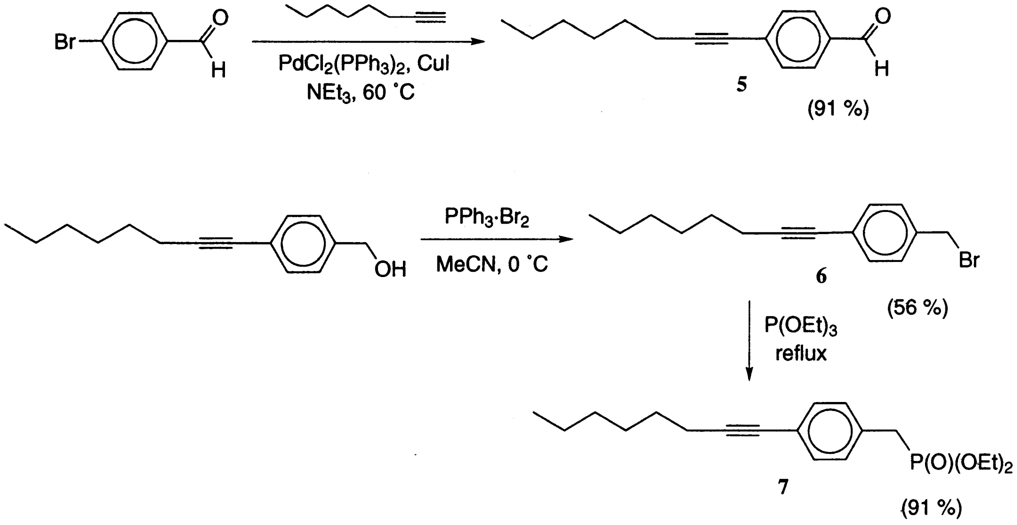


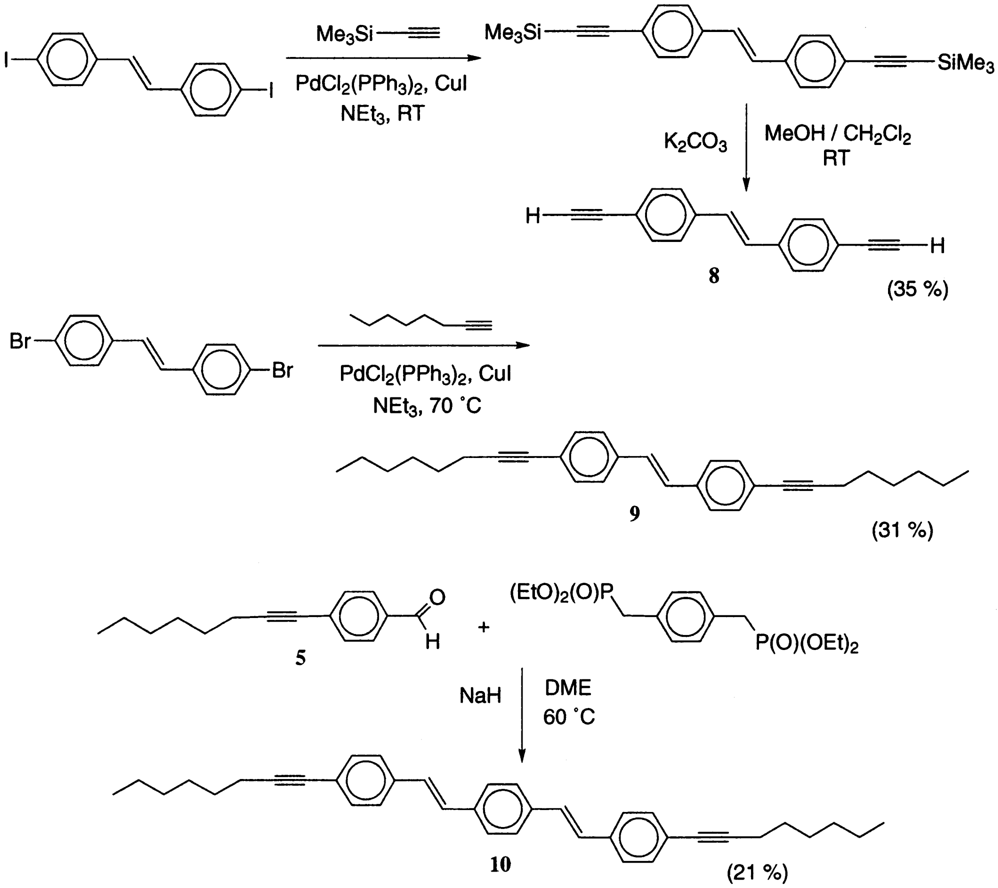
Figure 4. Molecular structure and atomic numbering scheme for **25**. Displacement ellipsoids are shown at the 30% probability level. The hydrogens have been omitted for clarity.

functionalized monoyne cluster adducts (**16**, **17**), for which coupling chemistry at the functionalized alkyne ligand provides one route to linked cluster compounds. The cluster products have been characterized by a combination of IR, ^{1}H NMR, and UV−vis spectroscopy, SI mass spectrometry, and, in the case of **15**, a single-crystal X-ray diffraction study. The solution IR spectra exhibit a distinctive ν(CO) pattern: four bands in the terminal carbonyl region at 2069−1986 cm^{-1} and two in the bridging carbonyl region at 1825−1761 cm^{-1}, accompanied, in the case of **16**, by the ν(CO) band of the aldehyde group at 1700 cm^{-1}. The ^{1}H NMR spectra

Scheme 1



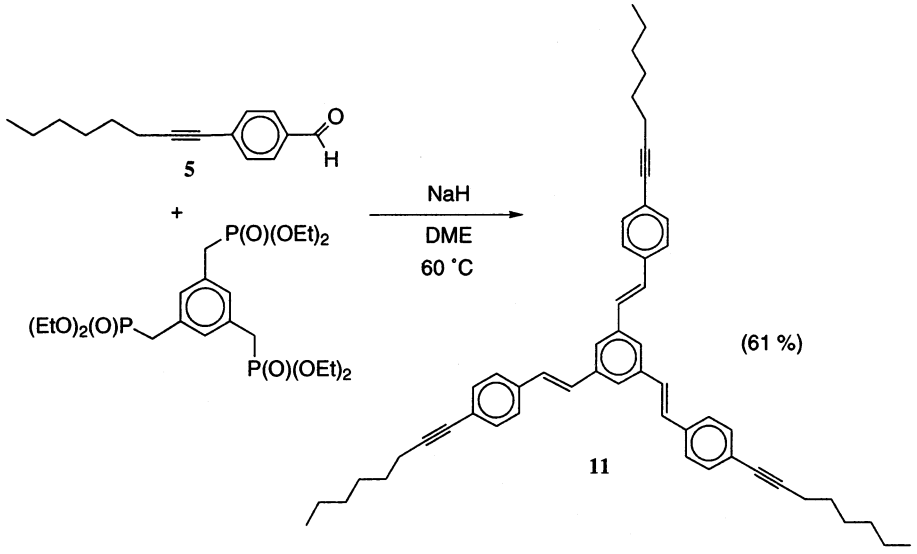
Scheme 2



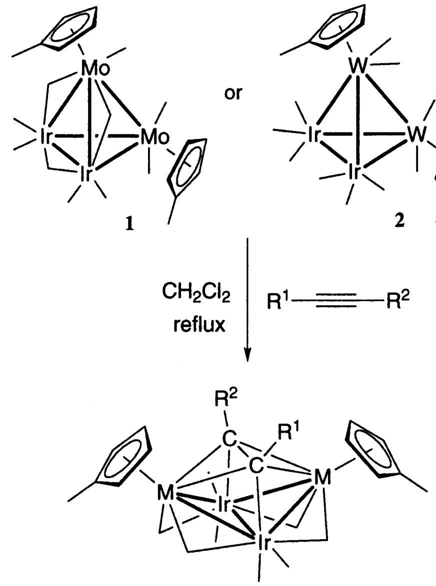
contain resonances arising from the cyclopentadienyl groups and alkyne residue. Multiplets in the region δ 4.85−4.32 and a singlet at ca. δ 2.00 are assigned to the ring and methyl protons of the methylcyclopentadienyl groups, respectively, accompanied by characteristic resonances for the "acetylene" proton of **12** (δ 10.02) and the aldehyde proton of **16** (δ 9.91). The SIMS spectra contain peaks corresponding to the molecular ion and successive loss of carbonyl ligands. The visible electronic spectra for a selection of Mo-containing examples include an absorption maximum in the range 619−634 nm and a maximum/shoulder band over the range 392−446 nm, the former being responsible for the green color of these clusters.

Syntheses of Di- and Tricluster Compounds Linked through π-Delocalized Frameworks. Our initial attempt to prepare a linked-cluster adduct involved reaction of the cyclopentadienyl-ligated cluster $Mo_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_5)_2$ (**3**)[28] with 1,2-(E)-bis{4′-(ethynyl)phenyl}ethene (**8**), which afforded the dicluster product $[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_5)_2]_2\{\mu_8\text{-}\eta^4\text{−}HC_2\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}4\text{-}C_2H\}$ (**18**) (Scheme 5). The solution IR spectrum of **18** exhibits the characteristic four-terminal, two-bridging ν(CO) pattern seen for the monocluster examples

Scheme 3

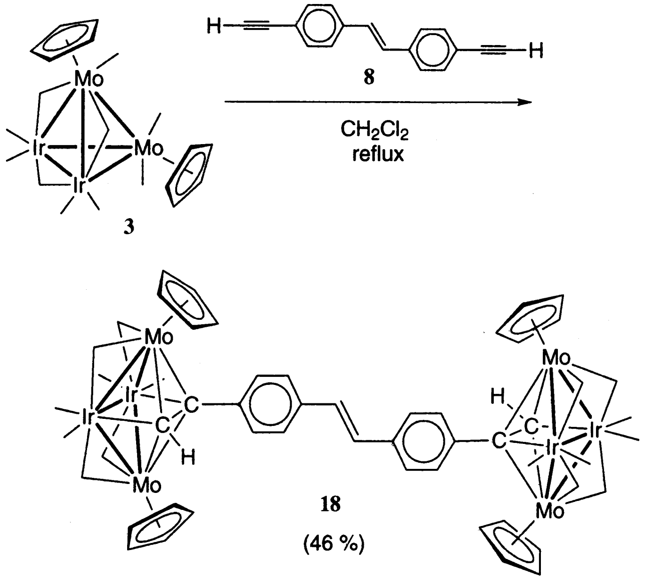


Scheme 4



	M	R^1	R^2	Yield (%)
12	Mo	H	Ph	46
13	Mo	Ph	Ph	81
14	Mo	Me	Ph	50
15	W	Me	Ph	79
16	Mo	*n*-hexyl	C_6H_4-4-CHO	59
17	Mo	*n*-hexyl	C_6H_4-4-$CH_2P(O)(OEt)_2$	66

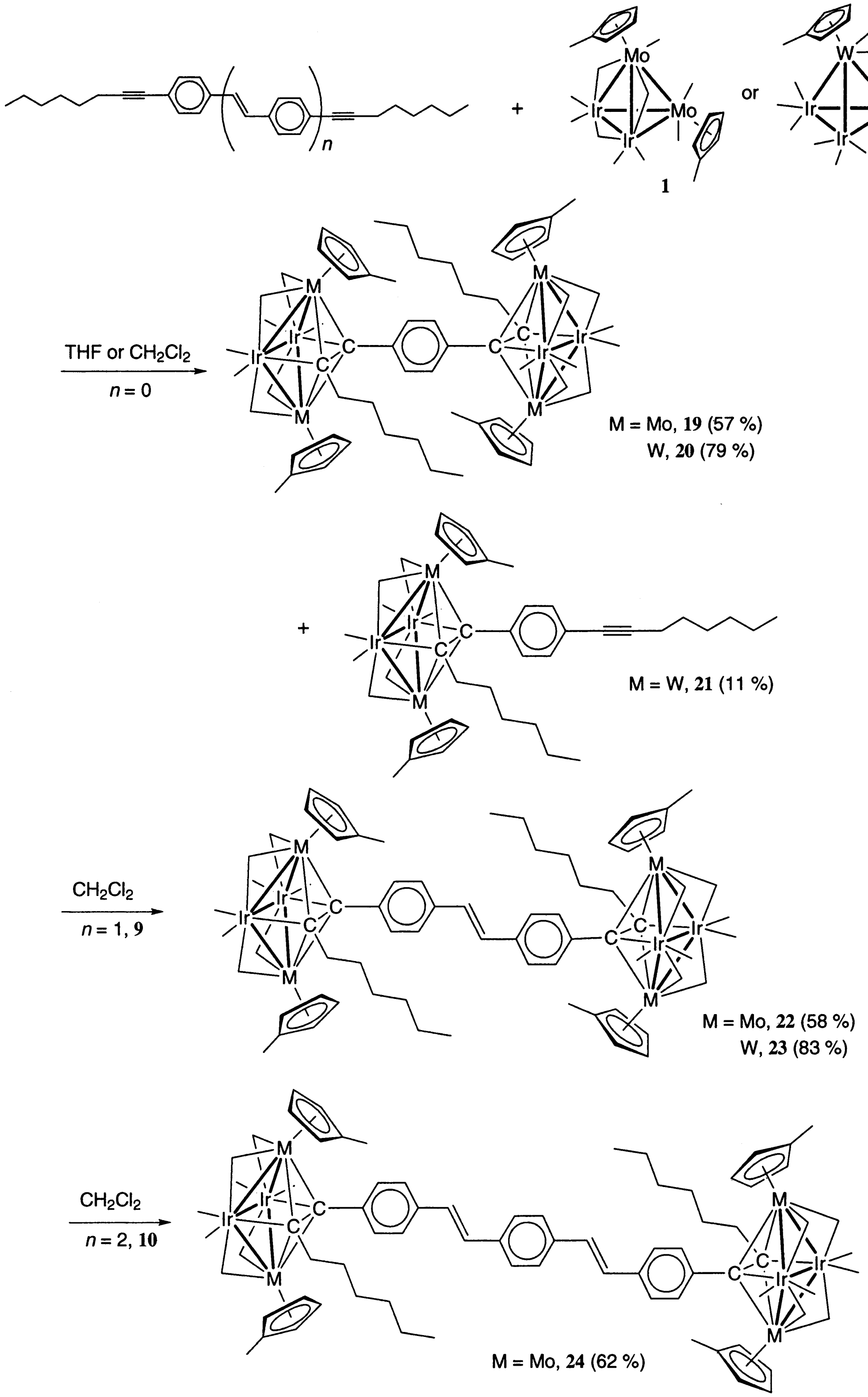
Scheme 5



described above, the "acetylene" protons appear at δ 9.17 in the ^{1}H NMR, and the SIMS spectrum contains peaks corresponding to the molecular ion and successive loss of all carbonyl ligands.

The poor solubility of **18** made purification and characterization difficult, prompting a reconsideration of the linked-cluster design to enhance solubility: the terminal hydrogen of the diyne was (conceptually) replaced with a hexyl group, and the methylcyclopentadienyl-ligated species $M_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ (**1**/**2**) were used as precursor clusters. The reactions of ca. 2.4 equiv of $M_2Ir_2(CO)_{10}(\eta^5\text{-}C_5H_4Me)_2$ with 1,4-bis(oct-1′-ynyl)benzene, 1,2-(*E*)-bis{4′-(oct-1″-ynyl)phenyl}ethene (**9**), and 1,4-bis{2′-(*E*)-[4″-(oct-1‴-ynyl)phenyl]ethenyl}benzene (**10**) in refluxing dichloromethane or THF afforded the linked-cluster adducts $[M_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2\text{-}[4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CH]_nC_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ ($n = 0$, M = Mo (**19**), W (**20**); $n = 1$, M = Mo (**22**), W (**23**); $n = 2$, M = Mo (**24**)) as the major products in good yield (57–83%) (Scheme 6). Unreacted cluster, added in excess to ensure the reactions proceed through to the dicluster product, is recoverable during the TLC purification. A small amount of the monocluster compound $W_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2C_6H_4\text{-}4\text{-}C{\equiv}C(CH_2)_5\text{-}Me\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**21**) was formed from the reaction between **2** and 1,4-bis(oct-1′-ynyl)benzene, possibly a result of the lower reactivity of tungsten–iridium clusters compared with molybdenum–iridium clusters[30] and of the use of a short-chain diyne, for which steric considerations may be important. In a fashion similar to the reactions with diynes, refluxing a dichloromethane solution of **1** with the triyne **11** for 16 h, followed by

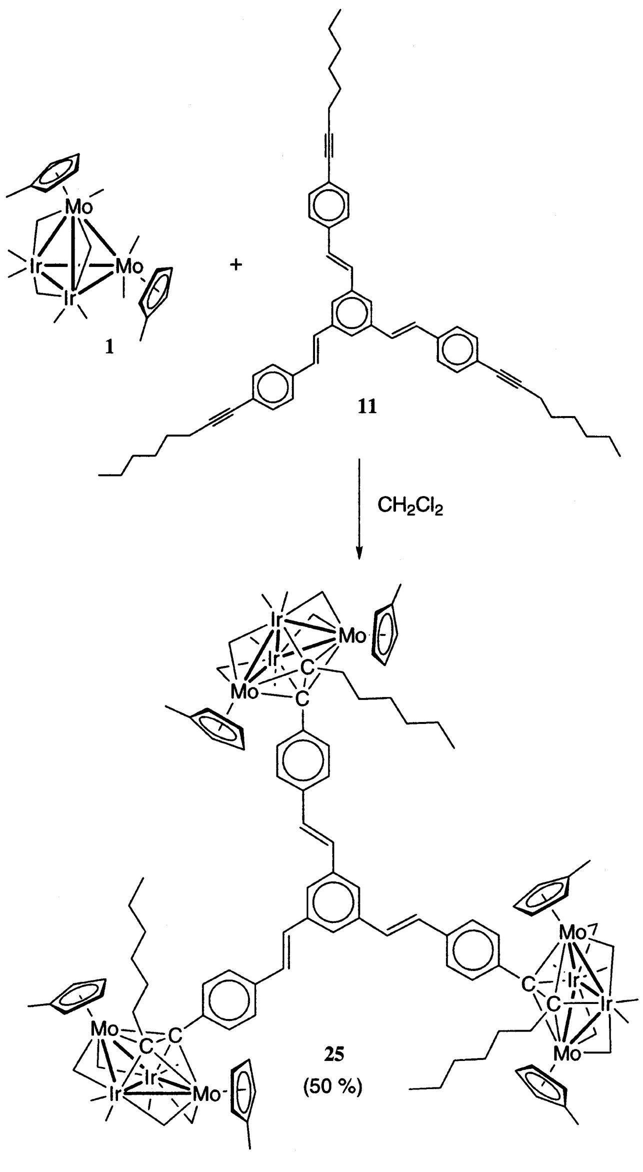
Scheme 6



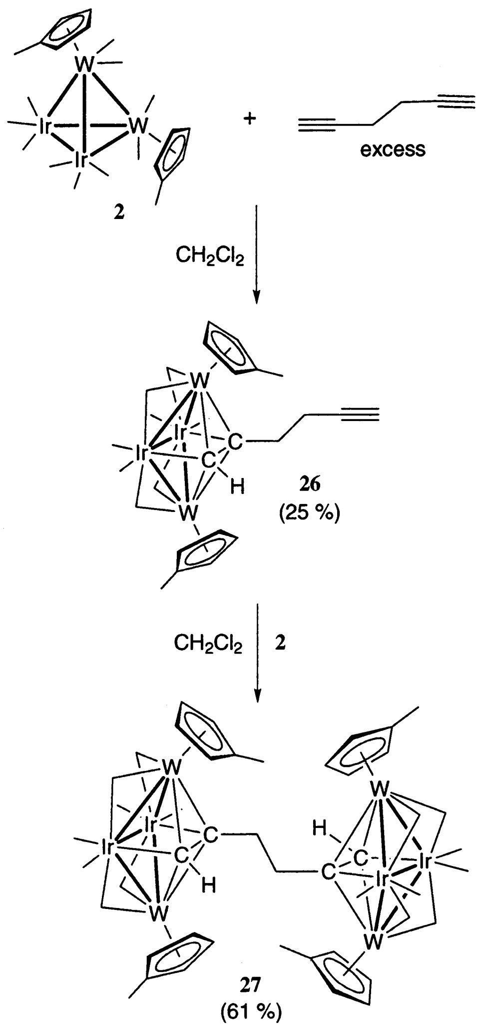
TLC purification and recrystallization, afforded the tricluster adduct $[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_3\{\mu_{12}\text{-}\eta^6\text{-}1,3,5\text{-}C_6H_3[(E)\text{-}CH{=}CHC_6H_4\text{-}4'\text{-}C_2(CH_2)_5Me]_3\}$ (**25**) as the major product in 50% yield (Scheme 7). One example of a dicluster complex linked by a saturated bridge was prepared, using the same methodology but in a stepwise manner (Scheme 8); reaction of **2** with excess 1,5-hexadiyne afforded $W_2Ir_2\{\mu_4\text{-}\eta^2\text{-}HC_2(CH_2)_2C{\equiv}CH\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**26**) in low yield, further addition of **2** to **26** affording $[W_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}HC_2(CH_2)_2C_2H\}$ (**27**) in good yield.

The products have been characterized by IR, ^1H NMR, and UV–vis spectroscopy, SI mass spectrometry, and, in the case of **22** and **25**, single-crystal X-ray diffraction studies. The solution IR spectra exhibit the distinctive $\nu(CO)$ pattern for the $M_2Ir_2C_2$ cluster core. Molecular ion peaks are present in the SIMS spectra of **19**, **20**, **23**, **24**, and **27**; curiously, **21**, **22**, and **25** appear to be

Scheme 7



Scheme 8



more susceptible to fragmentation, the highest peaks in their spectra being assigned to $[M - C_5H_4Me]^+$, $[M - 8CO]^+$, and $[M - 11CO]^+$ fragment ions, respectively.

Coupling of Cluster–Alkyne Complexes To Form a Linked Dicluster Compound. All of the linked-cluster adducts described so far have been synthesized by reaction of the appropriate cluster precursor with a preformed, multifunctional, π-delocalized organic framework. An alternative strategy, mentioned earlier, is to coordinate functionalized monoynes to a cluster core and then to couple two (or more) of these "alkyne-derived building blocks" at the functional group to generate the π-delocalized organic framework with clusters intact. Following this idea, the aldehyde-functionalized cluster $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2C_6H_4\text{-}4\text{-}CHO\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**16**) was added to a solution of the phosphonate anion cluster, the latter formed by addition of sodium methoxide to a THF solution of $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2C_6H_4\text{-}4\text{-}CH_2P(O)(OEt)_2\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**17**) (Scheme 9), to afford the linked cluster $[Mo_2Ir_2(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**22**) in 11% yield. The conditions required to effect Wittig–Horner–Emmons coupling appeared to cause significant decomposition of the cluster unit. The direct coordination of **1** to the diyne 1,2-(*E*)-bis{4′-(oct-1″-ynyl)phenyl}ethene (**9**) (Scheme 6) is therefore the preferred route for the synthesis of **22**, on the basis of reaction yield.

Crystal Structure Studies of 15, 22, and 25. The identities of **15**, **22,** and **25** have been confirmed by single-crystal X-ray diffraction studies. Crystal data are listed in Table 1, and important bond lengths and angles are collected in Tables 2 (**15**) and 3 (**22**) (the structural study of **25** is sufficient only to confirm atom connectivity and spatial disposition of the constituent atoms). ORTEP plots showing the molecular geometries and atomic numbering schemes are shown in Figures 2 (**15**), 3 (**22**), and 4 (**25**). The molecule of **22** lies on an inversion center, and the molecule of **25** lies on a 3-fold rotation axis; in both cases, the symmetry-expanded structure is displayed.

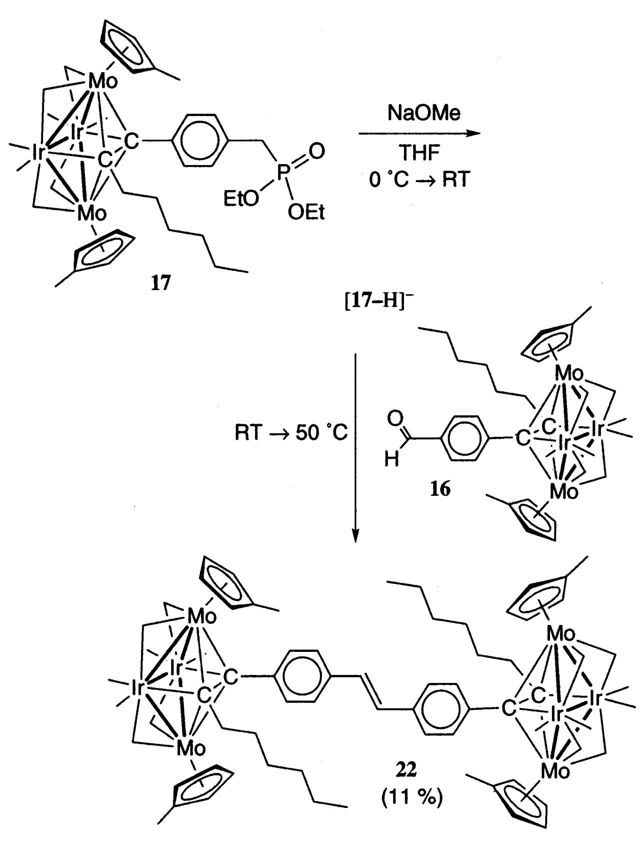
The metal cluster units in **15**, **22**, and **25** possess M_2Ir_2 cores arranged in "butterfly" geometries, with the iridium atoms forming the hinge and the group 6 metal atoms residing at the wing tips. Insertion of the alkynes into the M–M bonds of the tetrahedral precursors results in cluster units with closo-pseudooctahedral cores. Each iridium atom is ligated by two terminal

Table 4. Cyclic Voltammetric Data for Mono-, Di-, and Tricluster Compounds

	oxidn 2		oxidn 1		redn 1		redn 2	
compd	E_p, V	$i_{p,c}/i_{p,a}$	$E_{1/2}$, V [E_p(f) − E_p(r), mV]	$i_{p,c}/i_{p,a}$	E_p, V	$i_{p,a}/i_{p,c}$	E_p, V	$i_{p,a}/i_{p,c}$
Monocluster Compounds								
$Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**12**)	0.96 [100][a]	0.85	0.69 [60]	1	−1.33	irrev		
$Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**13**)	1.18	irrev	0.80 [60]	0.65	−1.22	irrev		
$W_2Ir_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**4**)	0.90	irrev	0.58 [60]	0.75	−1.36	irrev		
$Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}MeC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**14**)	1.19	irrev	0.66 [75]	1	−1.32	irrev		
$W_2Ir_2(\mu_4\text{-}\eta^2\text{-}MeC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**15**)	0.96	irrev	0.45 [74]	1	−1.48	irrev		
Dicluster Compounds								
$[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2C_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**19**)	1.20	irrev	0.70 [65]	1	−1.22	irrev	−1.44	irrev
$[W_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2C_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**20**)	0.94	irrev	0.56 [65]	1	−1.26	irrev	−1.52	irrev
$[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**22**)	1.19	irrev	0.71 [60]	1	−1.23	irrev		
$[W_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**23**)	0.93	irrev	0.54 [60]	1	−1.43	irrev		
$[W_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}HC_2(CH_2)_2C_2H\}$ (**27**)	0.52 [75]	0.50	0.30 [60]	1	−1.32	irrev		
Tricluster Compound								
$[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_3\{\mu_{12}\text{-}\eta^6\text{-}1,3,5\text{-}C_6H_3[(E)\text{-}CH{=}CHC_6H_4\text{-}4'\text{-}C_2(CH_2)_5Me]_3\}$ (**24**)			0.66 [60]	1	−1.35	irrev		

[a] $E_{1/2}$, V [E_p(f) − E_p(r), mV].

Scheme 9



carbonyls, each group 6 metal atom is ligated by a η^5-methylcyclopentadienyl group, and each M−Ir bond is unsymmetrically bridged by a carbonyl ligand (W−C_{av} = 1.993 Å, Ir−C_{av} = 2.380 Å (**15**); Mo−C_{av} = 1.978 Å, Ir−C_{av} = 2.329 Å (**22**)). The metal core bond distances are similar to those of the previously reported analogues $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_5)_2$[28] and $W_2Ir_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4Me)_2$.[53] The alkyne groups coordinate in a μ_4-η^2-fashion, lying parallel to the Ir−Ir bonds; coordination results in significant lengthening of the C≡C bond (ca. 1.20 Å for free alkynes; cf. 1.49(1) Å (**15**), 1.446(9) Å (**22**)). Distances and angles within the alkyne ligands are not unexpected.

Electrochemical Studies. Most of the di- and tricluster compounds prepared in the current study have been examined by cyclic voltammetry; the results of these investigations, together with those of several of the monocluster compounds, are collected in Table 4 (the latter serve as a benchmark for the redox behavior of an isolated, noncommunicating cluster). Tabulated data were obtained at room temperature; selected examples were also examined at reduced temperatures (230−240 K), no significant differences from results at room temperature being observed (specifically, no increase in reversibility of any redox process was seen on lowering the temperature).

Cyclic voltammograms of **4** and **12**−**15** are broadly similar, representative examples (those of **12** and **14**) being shown in Figure 5. The two oxidation waves E/e and F/f are observed (oxidations 1 and 2 in Table 4, respectively). Oxidation process 1 (E/e) decreases in reversibility on alkyne substituent variation as H > Me > Ph. Process 2 (F/f) is quasi-reversible for **12** but irreversible for the other complexes, for which adsorption of an oxidized species onto the electrode surface was sometimes seen, evinced by the irregular appearance of a large symmetrical peak at ca. −0.1 V; no increase in reversibility on increasing scan rate (up to 1600 mV s^{-1}) was detected. Oxidation potentials for the reversible/quasi-reversible process 1 increase as expected for metal variation (W < Mo) and alkyne substituent variation (Me < H < Ph), the latter reflecting the decrease in electron-donating strength of the substituent. Attempts to quantify the electron-transfer stoichiometry for oxidation process 1 in **12** by bulk coulometry and chemical oxidation were inconclusive due to slow chemical decomposition following oxidation. Introduction of equimolar amounts of decamethylferrocene, which is known to exhibit a one-electron-oxidation process, affords oxidation peak heights consistent with oxidation process 1 (E/e) being one-electron in nature.

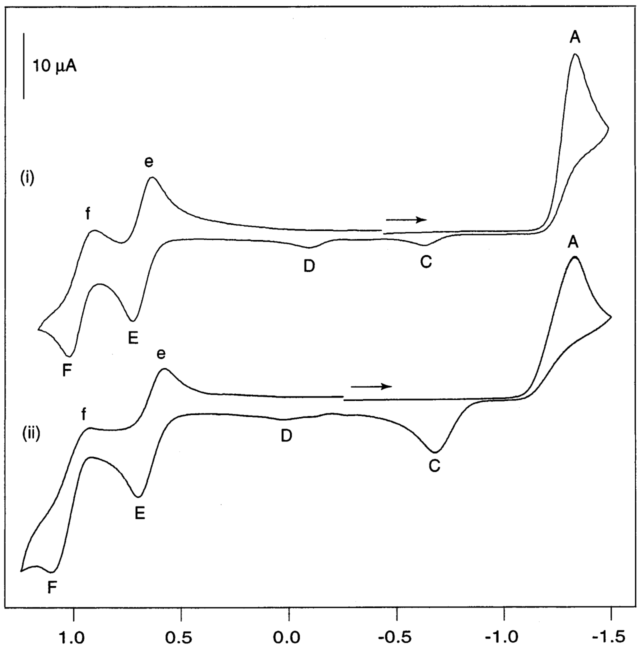


Figure 5. Cyclic voltammograms of (i) ca. 3.7 mM $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**12**) and (ii) ca. 4.9 mM $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}MeC_2Ph)(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ (**14**) in CH_2Cl_2 with 0.25 M $(NBu^n{}_4)PF_6$ as supporting electrolyte (scan rate 200 mV s^{-1}).

A single irreversible reduction process (A) is observed for all five "model" clusters (reduction 1 in Table 4); no increases in reversibility were detected on increasing the scan rate (up to 1600 mV s^{-1}). Oxidation of decomposition species arising from the irreversible reductive process are seen in the return sweep for all compounds (C and D). The size of these two anodic peaks (relative to the sizes of the cathodic peaks) varies with scan rate, suggesting that the species corresponding to these peaks are relatively short-lived.

Cyclic Voltammetry of Di- and Tricluster Compounds. Representative examples of cyclic voltammograms of the dicluster adducts prepared in the current studies (those of **20** and **23**) are shown in Figure 6. Not surprisingly, the linked dicluster compounds **19**, **20**, **22**, and **23** exhibit oxidative behavior similar to that of the monocluster models **14** and **15** (all six have $\mu_4\text{-}\eta^2$-arylalkylalkyne-ligated butterfly cluster cores), particularly with respect to potential and reversibility of the processes. Introduction of equimolar amounts of decamethylferrocene into solutions of **19** and **22** to quantify the oxidation processes affords oxidation peak heights consistent with oxidation process 1 (E/e) being two-electron in nature. The assignment of the *n* values of these reversible oxidation processes is as follows. Decamethylferrocene is a known one-electron-oxidation standard. Monocluster compounds **12** and **14** each have current ratios vs internal equimolar decamethylferrocene which are less than 1 (ca. 0.8−0.86). The significant reduction below 1 is due to the expected significantly larger diffusion coefficient for decamethylferrocene compared to those of these (larger) monocluster molecules. The current ratios for the dicluster molecules are about 1 (ca. 0.94−1.0). An increase in molecular size on proceeding from a monocluster to a linked dicluster molecule will result in a decrease in diffusion coefficient (as above) and a decrease in current ratio for a one-electron process. The current ratio observed for the dicluster molecules is *only* consistent with *n* being greater than 1, and specifically with *n* being 2.

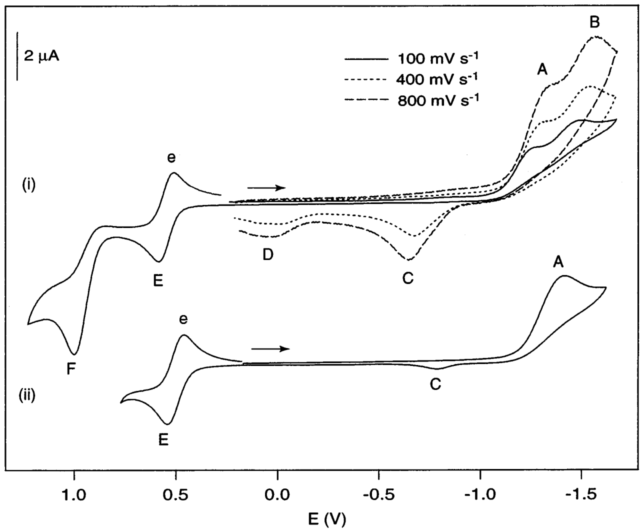


Figure 6. Cyclic voltammograms of (i) ca. 1.1 mM $[W_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2C_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**20**) and (ii) ca. 0.8 mM $[W_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$ (**23**) in CH_2Cl_2 with 0.25 M $(NBu^n{}_4)PF_6$ as supporting electrolyte. The effect of scan rate variation for the reductive processes is shown for **20**.

The presence of two irreversible reduction waves (A and B, corresponding to reductions 1 and 2 in Table 4, respectively) is noted in the cyclic voltammogram of **20** (Figure 6). This behavior is also observed for the other one-ring linked complex **19**. The return waves C and D are associated with A and B; similar to the "model" compounds, these processes vary in size with scan rate (Figure 6). The "extended bridge" examples **22** and **23** do not show a two-step reductive behavior but, rather, a single wave of twice the height. Compound **27**, which has a (saturated) ethylene linkage holding cluster units close together, shows reductive behavior characteristic of the monocluster and extended bridge dicluster compounds (one reduction process only). The branched tricluster adduct **24** shows a single irreversible wave resulting from the simultaneous two-electron reduction of each cluster center, not surprising for cluster units linked by an extended bridge with a nonconjugated 1,3,5-branching unit. The potential of the reduction in **24** is consistent with the bridge being more electron-donating than the shorter stilbenyl linker in **22**.

Spectroelectrochemical Studies. The reversible/partially reversible one-electron oxidation of these clusters has been examined further by UV−vis−near-IR spectroelectrochemistry, representative traces (those of **15** and **20**) being shown in Figure 7. There is no essential difference in electronic spectra on progressive oxidation of the model cluster **15** and the linked dicluster compound **20**. The terminal alkyne adduct **12** was also examined; the spectral progression $\mathbf{12} \rightarrow \mathbf{12}^+$ is similar to those in Figure 7, while the partially reversible second oxidation process affords isosbestic points for the transformation $\mathbf{12}^+ \rightarrow \mathbf{12}^{2+}$, but $\mathbf{12}^{2+}$ cannot be returned to $\mathbf{12}^+$. Given the differing reductive behaviors

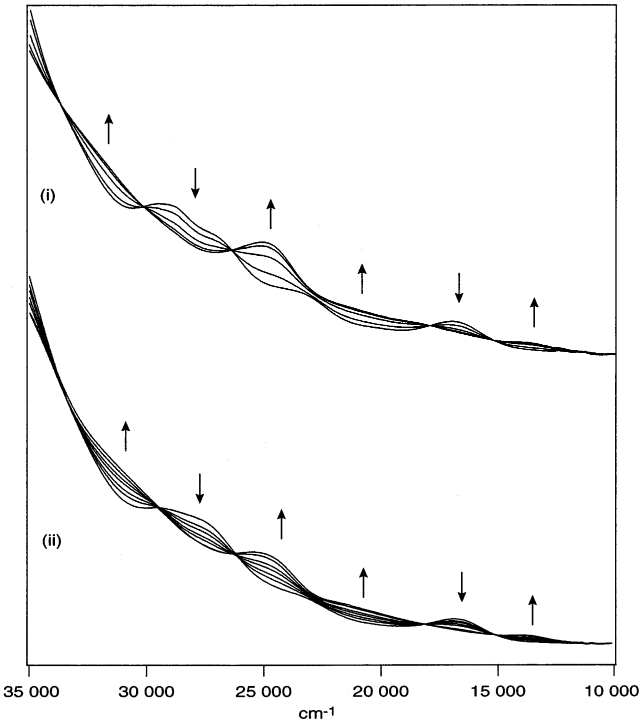


Figure 7. UV−vis−near-IR spectra of (i) $W_2Ir_2(\mu_4-\eta^2-MeC_2Ph)(CO)_8(\eta^5-C_5H_4Me)_2$ (**15**) ($E_{appl} \approx 0.45$ V) and (ii) $[W_2Ir_2(CO)_8(\eta^5-C_5H_4Me)_2]_2\{\mu_8-\eta^4-Me(CH_2)_5C_2C_6H_4-4-C_2(CH_2)_5-Me\}$ (**20**) ($E_{appl} \approx 0.62$ V) in CH_2Cl_2 with 0.25 M $(NBu^n_4)PF_6$ during exhaustive oxidation at 243 K.

of dicluster compounds with a short π-delocalizable bridge (such as **20**) and model clusters such as **15**, particular attention was paid to the possibility of intervalence charge-transfer in **20**, but no low-energy transitions were detected (10 000−4000 cm^{-1}) during exhaustive oxidation of **20** at 0.62 V.

Discussion

The present studies have demonstrated the facile assembly of di- and tricluster compounds in which the cluster modules are at the termini of potentially π-delocalizable bridges and attached via robust $\mu_4-\eta^2$-alkyne−cluster bonding. There are two obvious approaches to compounds of this type: addition of cluster units to a preformed organic di- or triyne and coupling appropriately functionalized cluster−alkyne complexes. The former approach has proven highly successful in the present work, the one example employing the latter approach proceeding in a comparatively lower yield. The low solubility of oligophenylenevinylenes is well-known; this has been circumvented in the present system by appending solubilizing substituents to both the organic di-/triyne (hexyl group) and cluster unit (cyclopentadienyl methyl substituent) to afford compounds with sufficient solubility for subsequent solution studies.

The mono-, di-, and tricluster complexes have accessible oxidation and reduction processes, probed by cyclic voltammetry in the current work. The cyclic voltammograms of these clusters are remarkably similar, the notable difference being an additional reduction process observed for clusters linked by the shortest π-delocalizable bridge. The first oxidation process is reversible/partially reversible across all clusters surveyed, the potential for which varies as expected for systematic structural modifications (metal or alkyne substituent variation) and is consistent with these compositional changes “tuning” cluster electron density.

We have recently reported a detailed study of tetrahedral group 6−iridium clusters, including the precursors for the present work, $M_2Ir_2(CO)_{10}(\eta^5-C_5H_4Me)_2$, by a variety of techniques, including cyclic voltammetry and UV−vis−near-IR spectroelectrochemistry.[42] The precursor clusters have cyclic voltammograms broadly similar to those of the alkyne adducts: namely, an irreversible reduction process associated with two daughter peaks on subsequent reoxidation and a partially reversible oxidation process followed by an irreversible oxidation step. However, the UV−vis−near-IR spectra on oxidation of the precursor clusters differ significantly from those of the cluster−alkyne adducts from the present work, in that a near-IR band at ca. 8000 cm^{-1} appears for the former. Complementary DFT calculations assign this transition as largely σ(M−M) → σ*(M−M) in character. Formation of the alkyne−cluster adducts in the present work proceeds by insertion into the M−M bond, eliminating the possibility of a low-energy σ(M−M) → σ*(M−M) transition.

As noted above, no reports previously have probed linked heterometallic clusters using electrochemical techniques. Several tricobalt clusters linked by naked carbon chains displayed electrochemical responses indicative of interacting redox centers.[7−9] In contrast, triosmium units linked by orthometalated NC_5H_4-4-N=N-4-C_5H_4N and triruthenium units linked by bis(diphenylphosphino)acetylene showed no electrochemically detectable communication.[17,18] The only previous example of electrochemical examination of clusters linked by aryl diynes was of $[Ru_3(\mu-H)(CO)_9]_2(\mu_6-\eta^4-C_2C_6H_4-4-C_2)$ and $[Ru_3(CO)_{10}]_2(\mu_6-\eta^4-HC_2C_6H_4-4-C_2H)$, the authors observing no evidence for communication and concluding that the diyne behaves as an insulator because the chain linearity is perturbed and the alkyne C−C bond order is reduced beyond olefinic character.[19] This explanation required (a) a localized bonding description and (b) consideration of the cluster cores as comprised of metal atoms only. (Note that the triruthenium examples possess distorted-square-pyramidal and distorted-trigonal-bipyramidal core geometries when the alkyne carbons are considered as core atoms, and in both cases these clusters are linked by unsaturated phenylene bridges.) For the group 6−iridium clusters in the present study, the pseudooctahedral core is a geometry for which localized bonding considerations are generally considered inadequate—it is therefore appropriate to consider the current series of compounds as octahedral clusters linked by unsaturated phenylene and phenylenevinylene linkages. A detailed DFT study of clusters from the present system is currently being undertaken in order to rationalize our electrochemical observations.[68]

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[68] Petrie, S.; Stranger, R.; Lucas, N. T.; Humphrey, M. G. Unpublished results.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths and angles, and least-squares planes for **15** and **22**; data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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