

Mixed-Metal Cluster Chemistry. 23. Synthesis and Crystallographic and Electrochemical Studies of Alkyne-Coordinated Group 6–Iridium Clusters Linked by Heterocyclic Groups

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Received April 7, 2003

Reaction between the tetrahedral cluster compound $\text{Mo}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**1**) and 2-iodo-5-(oct-1'-ynyl)thiophene afforded the pseudooctahedral cluster $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-I}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**17**) by formal insertion of the alkyne $\text{C}\equiv\text{C}$ group into the Mo–Mo bond. Similar reactions of **1** or $\text{W}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**2**) with heterocyclic di- or triynes afforded the related mono-, di-, or tricluster compounds $[\text{M}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ [E = S, M = Mo (**20**), W (**21**); E = Se, M = Mo (**30**), W (**31**)], $[\text{M}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-(E)-CH=CH-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ [M = Mo (**22**), W (**24**)], $\text{M}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-(E)-CH=CH-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C}(\text{CH}_2)_5\text{Me}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ [M = Mo (**23**), W (**25**)], $[\text{M}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_3\{\mu_{12}\text{-}\eta^6\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ [M = Mo (**26**), W (**28**)], and $[\text{M}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C}(\text{CH}_2)_5\text{Me}\}$ [M = Mo (**27**), W (**29**)]. Compounds **27** and **29** correspond to the 1,2-dicluster adducts of the linear triyne $\text{Me}(\text{CH}_2)_5\text{C}\equiv\text{C-5-C}_4\text{H}_2\text{S-2-C}\equiv\text{C-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C}(\text{CH}_2)_5\text{Me}$. No 1,3-dicluster isomer was isolated from direct reaction, but the molybdenum-containing 1,3-dicluster isomer was prepared by exploiting organic reaction chemistry on precoordinated functionalized alkyne ligands. Thus, Sonogashira coupling of **17** with trimethylsilylacetylene and subsequent desilylation gave $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-C}\equiv\text{CR}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ [R = SiMe_3 (**18**), H (**19**)]. Sonogashira coupling of **17** and **19** gave the 1,3-isomer $[\text{Mo}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (**32**), as well as the homocoupling product $[\text{Mo}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{CC}\equiv\text{C-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (**33**). The identities of **21**, **29**, and **31** were confirmed by single-crystal X-ray diffraction studies. Cyclic voltammetric scans for these complexes all show a reversible/quasi-reversible oxidation followed by an irreversible oxidation process. Dicluster compounds linked by one heterocycle, and tricluster compounds, show two reduction processes, whereas dicluster compounds with longer bridges reveal only one reduction process.

Introduction

A topic of significant interest in contemporary chemistry is that of linked electroactive modules, where the bridging unit is π -delocalizable and hence potentially conducting.¹ Extensive studies of transition-metal carbonyl clusters have revealed their rich redox behavior; in many cases a range of oxidation states are accessible, the potentials for which are tunable by appropriate ligand modifications.^{2–7} They are therefore attractive termini in such assemblies. Although many examples

of homometallic clusters linked by π -delocalizable bridges are extant,^{8–20} heterometallic clusters have curiously

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been the subject of few reports,^{21–23} despite the possibility of further modification of the cluster electronic environment that heterometal incorporation affords. We recently reported 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–NIR spectroelectrochemistry, the first electrochemical study of linked heterometallic clusters.^{24,25} The bridges were constructed from phenylenevinylene and phenyleneethynylene units. We report herein extension of these studies to embrace heterocyclic bridging units, electrochemical examination of the resultant assemblies, and comparison to our previously reported phenyl-based examples.

Experimental Section

General Conditions. Reactions were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques.²⁶ 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 and triethylamine were 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: CH₂Cl₂ and dimethoxyethane (DME) over CaH₂; THF 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 PF₂₅₄ (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 PF₂₅₄ and visualized under UV light (for colorless compounds).

Starting Materials and Reagents. The reagents 2,5-dibromothiophene, 5-bromo-2-thiophenecarboxaldehyde, 1-octyne, trimethylsilylacetylene, sodium hydride (60% dispersion in oil), *n*-butyllithium solution (Aldrich); copper(I) iodide (Unilab); iodine (M&B); and potassium carbonate (BDH) were purchased commercially and used as received. Literature procedures (or minor variations thereof) were used to synthe-

size dichlorobis(triphenylphosphine)palladium(II),²⁷ diethyl {-(2-bromo-5-thienyl)methyl}phosphonate,²⁸ Mo₂Ir₂(CO)₁₀(η⁵-C₅H₄Me)₂ (**1**),²⁹ and W₂Ir₂(CO)₁₀(η⁵-C₅H₄Me)₂ (**2**).³⁰ 2-Bromo-5-(chloromethyl)thiophene (used in the synthesis of diethyl {(2-bromo-5-thienyl)methyl}phosphonate)²⁸ has previously been prepared by chloromethylation of 2-bromothiophene,³¹ but in the present work was synthesized by reaction of thionyl chloride with 2-bromo-5-(hydroxymethyl)thiophene.³² 2,5-Dibromoselenophene was obtained as the major product from the direct bromination of selenophene with bromine,³³ but it could not be chromatographically separated from the 2,4-dibromoselenophene and 2,3,4,5-tetrabromoselenophene coproducts, so the mixture was used in the preparation of **14**. The *n*-butyllithium (nominally 1.6 M in hexanes) was titrated with diphenylacetic acid in THF prior to use to determine its exact concentration.³⁴ Synthetic and characterization details of 5-bromo-2-iodothiophene (**3**), 2-bromo-5-(trimethylsilylethynyl)thiophene (**4**), 2-bromo-5-ethynylthiophene (**5**), 2-bromo-5-(oct-1'-ynyl)thiophene (**6**), 2-iodo-5-(oct-1'-ynyl)thiophene (**7**), 2,5-di(oct-1'-ynyl)thiophene (**8**), 1,2-(*E*)-bis(5'-bromo-2'-thienyl)ethene (**9**), 1,2-(*E*)-bis(5'-oct-1'-ynyl)-2'-thienyl)ethene (**10**), di(5-bromo-2-thienyl)ethyne (**11**), 2,5-bis(5'-bromo-2'-thienyl)ethynyl)thiophene (**12**), di{5-(oct-1'-ynyl)-2-thienyl}ethyne (**13**), 2,5-di(oct-1'-ynyl)selenophene (**14**), 3,4-dibromo-2,5-di(oct-1'-ynyl)selenophene (**15**), and 3-bromo-5-(oct-1'-ynyl)selenophene (**16**) are available in the Supporting Information.

Instruments. Infrared spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer in a solution cell with CaF₂ windows; spectral frequencies are recorded in cm⁻¹. All analytical spectra were recorded as solutions in either cyclohexane or CH₂Cl₂ (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 and ¹³C NMR spectra were recorded in CDCl₃ (Cambridge Isotope Laboratories) using a Varian Gemini-300 spectrometer (¹H at 300 MHz; ¹³C at 75 MHz, broadband proton decoupled). Spectra are referenced to residual CHCl₃ at 7.24 ppm (¹H) or CDCl₃ at 77.0 ppm (¹³C). 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 CH₂Cl₂) 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, UK, using a VG Autospec mass spectrometer (Ar source with accelerating potential of 6–8 kV, 3-nitrobenzyl alcohol matrix, solutions in CH₂Cl₂). All MS were calculated with the *m/z* based on ³²S, ⁸⁰Se, ⁷⁹Br, ⁹⁶Mo, ¹⁸³W, and ¹⁹²Ir 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.

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Reaction of $\text{Mo}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (1**) with 2-Iodo-5-(oct-1'-ynyl)thiophene (**7**).** 2-Iodo-5-(oct-1'-ynyl)thiophene (**7**) (110 mg, 0.346 mmol) was added to a red-brown solution of $\text{Mo}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**1**) (174 mg, 0.171 mmol) in CH_2Cl_2 (20 mL) and the resultant mixture heated at reflux for 20 h, over which time the color changed from red-brown to green-brown. The reaction mixture was taken to dryness on a rotary evaporator. The residue was dissolved in a small volume (ca. 3 mL) of CH_2Cl_2 and applied to preparative TLC plates. Elution with CH_2Cl_2 /petroleum spirit (1:1) gave five bands. The first ($R_f = 0.77$, orange) and second ($R_f = 0.68$, purple) bands appeared to be in trace amounts and were not isolated. The contents of the third and major band ($R_f = 0.63$) were crystallized from CH_2Cl_2 /methanol at 3 °C to afford dark green needle crystals of $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-I}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**17**) (150 mg, 0.117 mmol, 68%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2066vs, 2039vs, 2011m, 1994m, 1817s, 1770m cm^{-1} . ^1H NMR (CDCl_3): δ 7.03 (d, $J_{\text{HH}} = 4$ Hz, 1H, $\text{C}_4\text{H}_2\text{S}$), 6.46 (d, $J_{\text{HH}} = 4$ Hz, 1H, $\text{C}_4\text{H}_2\text{S}$), 4.76–4.38 (m, 8H, $\text{C}_5\text{H}_4\text{Me}$), 2.69 (t, $J_{\text{HH}} = 8$ Hz, 2H, $\text{CH}_2(\text{CH}_2)_4\text{Me}$), 1.96 (s, 6H, $\text{C}_5\text{H}_4\text{Me}$), 1.50–1.32 (m, 8H, $\text{CH}_2(\text{CH}_2)_4\text{Me}$), 0.94 (t, $J_{\text{HH}} = 6$ Hz, 3H, $(\text{CH}_2)_5\text{Me}$). MS (SI): 1276 ($[\text{M}]^+$, 60), 1248 ($[\text{M} - \text{CO}]^+$, 15), 1220 ($[\text{M} - 2\text{CO}]^+$, 73), 1192 ($[\text{M} - 3\text{CO}]^+$, 28), 1164 ($[\text{M} - 4\text{CO}]^+$, 100), 1136 ($[\text{M} - 5\text{CO}]^+$, 43), 1108 ($[\text{M} - 6\text{CO}]^+$, 25). Anal. Calcd for $\text{C}_{32}\text{H}_{29}\text{Ir}_2\text{Mo}_2\text{O}_8\text{S}$ (1276.83): C, 30.10; H, 2.29. Found: C, 30.21; H, 2.37. The fourth ($R_f = 0.11$, purple) and fifth ($R_f = 0.05$, green) bands appeared to be in trace amounts and were not isolated.

Synthesis of $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-C}\equiv\text{CSiMe}_3\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (18**).** To a solution of $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-I}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**17**) (99.4 mg, 0.0778 mmol) in THF (15 mL) and triethylamine (0.5 mL) were added trimethylsilylacetylene (0.50 mL, 348 mg, 3.5 mmol), dichlorobis(triphenylphosphine)palladium(II) (4 mg, 6 μmol), and copper(I) iodide (5 mg, 26 μmol), and the resultant mixture was stirred at room temperature for 16 h. The volatile materials were removed in vacuo, and the residue was dissolved in a small volume (ca. 3 mL) of CH_2Cl_2 and applied to preparative TLC plates. Elution with CH_2Cl_2 /petroleum spirit (2:5) gave two bands. The contents of the first and major band ($R_f = 0.51$), found to be very soluble in a wide range of organic solvents, were dissolved in DMSO/ CHCl_3 (4:1) and carefully layered with an ethanol/water mixture (7:3). The solvent layers slowly diffused together at 3 °C over 7 days to afford dark green microcrystals of $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-C}\equiv\text{CSiMe}_3\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**18**) (83.5 mg, 0.0670 mmol, 86%). IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2141w; $\nu(\text{CO})$ 2066vs, 2039vs, 2010m, 1993m, 1817s, 1770m cm^{-1} . ^1H NMR (CDCl_3): δ 7.01 (d, $J_{\text{HH}} = 4$ Hz, 1H, $\text{C}_4\text{H}_2\text{S}$), 6.62 (d, $J_{\text{HH}} = 4$ Hz, 1H, $\text{C}_4\text{H}_2\text{S}$), 4.76–4.38 (m, 8H, $\text{C}_5\text{H}_4\text{Me}$), 2.73 (t, $J_{\text{HH}} = 8$ Hz, 2H, $\text{CH}_2(\text{CH}_2)_4\text{Me}$), 1.96 (s, 6H, $\text{C}_5\text{H}_4\text{Me}$), 1.50–1.35 (m, 8H, $\text{CH}_2(\text{CH}_2)_4\text{Me}$), 0.93 (t, $J_{\text{HH}} = 6$ Hz, 3H, $(\text{CH}_2)_5\text{Me}$), 0.23 (s, 9H, SiMe_3). MS (SI): 1246 ($[\text{M}]^+$, 57), 1218 ($[\text{M} - \text{CO}]^+$, 12), 1190 ($[\text{M} - 2\text{CO}]^+$, 42), 1162 ($[\text{M} - 3\text{CO}]^+$, 20), 1134 ($[\text{M} - 4\text{CO}]^+$, 100), 1106 ($[\text{M} - 5\text{CO}]^+$, 38), 1078 ($[\text{M} - 6\text{CO}]^+$, 39), 1050 ($[\text{M} - 7\text{CO}]^+$, 36), 1022 ($[\text{M} - 8\text{CO}]^+$, 69). Anal. Calcd for $\text{C}_{37}\text{H}_{38}\text{Ir}_2\text{Mo}_2\text{O}_8\text{SSi}$ (1247.14): C, 35.63; H, 3.07. Found: C, 35.17; H, 3.02.

Synthesis of $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-C}\equiv\text{CH}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (19**).** A solution of $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-C}\equiv\text{CSiMe}_3\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**18**) (90.0 mg, 0.0722 mmol) in methanol (12 mL, not dried and distilled before use) and CH_2Cl_2 (3 mL) was deoxygenated by bubbling with nitrogen for 2 min, then K_2CO_3 (90 mg, 0.65 mmol) was added. The resultant suspension was stirred (under nitrogen) at room temperature for 30 min. The reaction mixture was transferred to a 250 mL separating funnel, and CH_2Cl_2 (40 mL) was added. After washing with water (2 \times 60 mL), the organic phase was dried with MgSO_4 and filtered, and the filtrate was taken to dryness on a rotary evaporator (without heating) to yield $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-C}\equiv\text{CH}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**19**) (71.4 mg, 0.0608 mmol, 84%). IR ($\text{CH}_2\text{-}$

Cl_2): $\nu(\text{C}\equiv\text{C})$ 2099vw; $\nu(\text{CO})$ 2067vs, 2039vs, 2010w, 1994m, 1818s, 1771m cm^{-1} . ^1H NMR (CDCl_3): δ 7.07 (d, $J_{\text{HH}} = 4$ Hz, 1H, $\text{C}_4\text{H}_2\text{S}$), 6.64 (d, $J_{\text{HH}} = 4$ Hz, 1H, $\text{C}_4\text{H}_2\text{S}$), 4.76–4.38 (m, 8H, $\text{C}_5\text{H}_4\text{Me}$), 3.44 (s, 1H, $\text{C}\equiv\text{CH}$), 2.73 (t, $J_{\text{HH}} = 8$ Hz, 2H, $\text{CH}_2(\text{CH}_2)_4\text{Me}$), 1.96 (s, 6H, $\text{C}_5\text{H}_4\text{Me}$), 1.50–1.35 (m, 8H, $\text{CH}_2(\text{CH}_2)_4\text{Me}$), 0.93 (t, $J_{\text{HH}} = 6$ Hz, 3H, $(\text{CH}_2)_5\text{Me}$). MS (SI): 1174 ($[\text{M}]^+$, 23), 1146 ($[\text{M} - \text{CO}]^+$, 20), 1118 ($[\text{M} - 2\text{CO}]^+$, 45), 1090 ($[\text{M} - 3\text{CO}]^+$, 33), 1062 ($[\text{M} - 4\text{CO}]^+$, 100), 1034 ($[\text{M} - 5\text{CO}]^+$, 51), 1006 ($[\text{M} - 6\text{CO}]^+$, 47), 978 ($[\text{M} - 7\text{CO}]^+$, 49), 949 ($[\text{M} - 8\text{CO} - \text{H}]^+$, 42). The instability of this complex has precluded satisfactory microanalysis.

Similar reactions of **1** and **2** with heterocyclic di- or triynes afforded the related mono-, di-, or tricluster compounds $[\text{M}_2\text{-Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{E-5-C}_2(\text{CH}_2)_5\text{Me}\}$ [E = S, M = Mo (**20**), W (**21**); E = Se, M = Mo (**30**), W (**31**)], $[\text{M}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-(E)-CH=CH-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ [M = Mo (**22**), W (**24**)], $[\text{M}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-(E)-CH=CH-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C}(\text{CH}_2)_5\text{Me}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ [M = Mo (**23**), W (**25**)], $[\text{M}_2\text{-Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_3\{\mu_{12}\text{-}\eta^6\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ [M = Mo (**26**), W (**28**)], and $[\text{M}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C}(\text{CH}_2)_5\text{Me}\}$ [M = Mo (**27**), W (**29**)]; complete synthetic and characterization details are available in the Supporting Information.

Reaction of $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-I}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (17**) and $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-C}\equiv\text{CH}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**19**).** To a solution of $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-I}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**17**) (80.8 mg, 0.063 mmol) and $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-C}\equiv\text{CH}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**19**) (70.0 mg, 0.060 mmol) in THF (10 mL) and triethylamine (0.2 mL) were added dichlorobis(triphenylphosphine)palladium(II) (2.0 mg, 2.9 μmol) and copper(I) iodide (2 mg, 11 μmol), and the resultant mixture was stirred at room temperature for 20 h. The reaction mixture was taken to dryness, and the residue dissolved in a small volume (ca. 3 mL) of CH_2Cl_2 and applied to preparative TLC plates. Multiple developments (5) eluting with CH_2Cl_2 /petroleum spirit (1:1) gave three bands. The contents of the first band ($R_f = 0.92$) were identified by solution IR and ^1H NMR as unreacted $\text{Mo}_2\text{-Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-I}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**17**) (42.2 mg, 0.033 mmol). The contents of the second band ($R_f = 0.67$) were crystallized from CH_2Cl_2 /methanol at 3 °C to afford dark green-brown microcrystals of $[\text{Mo}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (**33**) (37.0 mg, 15.8 μmol , 26%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2066vs, 2039vs, 2011w, 1994m, 1818s, 1770m cm^{-1} . UV–vis (THF): 296sh (30.9), 431 (30.1), 484sh (16.7), 639 (3.0) nm (10^3 L mol $^{-1}$ cm $^{-1}$). ^1H NMR (CDCl_3): δ 7.09 (d, $J_{\text{HH}} = 4$ Hz, 2H, $\text{C}_4\text{H}_2\text{S}$), 6.68 (d, $J_{\text{HH}} = 4$ Hz, 2H, $\text{C}_4\text{H}_2\text{S}$), 4.78–4.39 (m, 16H, $\text{C}_5\text{H}_4\text{Me}$), 2.71 (t, $J_{\text{HH}} = 8$ Hz, 4H, $\text{CH}_2(\text{CH}_2)_4\text{Me}$), 1.96 (s, 12H, $\text{C}_5\text{H}_4\text{Me}$), 1.40–1.32 (m, 16H, $\text{CH}_2(\text{CH}_2)_4\text{Me}$), 0.94 (t, $J_{\text{HH}} = 6$ Hz, 6H, $(\text{CH}_2)_5\text{Me}$). MS (SI): 2346 ($[\text{M}]^+$, 100), 2122 ($[\text{M} - 8\text{CO}]^+$, 36). Anal. Calcd for $\text{C}_{68}\text{H}_{58}\text{Ir}_4\text{Mo}_4\text{O}_{16}\text{S}_2$ (2347.77): C, 34.79; H, 2.49. Found: C, 34.99; H, 2.41. The contents of the third band ($R_f = 0.63$) were crystallized from CH_2Cl_2 /methanol at 3 °C to afford dark green-brown microcrystals of $[\text{Mo}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (**32**) (9.4 mg, 4.0 μmol , 7%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2067vs, 2039vs, 2011w, 1994m, 1819s, 1770m cm^{-1} . UV–vis (THF): 292 (32.3), 341sh (17.3), 427 (30.1), 480sh (17.5), 635 (3.1) nm (10^3 L mol $^{-1}$ cm $^{-1}$). ^1H NMR (CDCl_3): δ 7.14 (d, $J_{\text{HH}} = 4$ Hz, 2H, $\text{C}_4\text{H}_2\text{S}$), 6.66 (d, $J_{\text{HH}} = 4$ Hz, 2H, $\text{C}_4\text{H}_2\text{S}$), 4.78–4.39 (m, 16H, $\text{C}_5\text{H}_4\text{Me}$), 2.73 (t, $J_{\text{HH}} = 8$ Hz, 4H, $\text{CH}_2(\text{CH}_2)_4\text{Me}$), 1.96 (s, 12H, $\text{C}_5\text{H}_4\text{Me}$), 1.42–1.33 (m, 16H, $\text{CH}_2(\text{CH}_2)_4\text{Me}$), 0.94 (t, $J_{\text{HH}} = 6$ Hz, 6H, $(\text{CH}_2)_5\text{Me}$). MS (SI): 2322 ($[\text{M}]^+$, 55), 2098 ($[\text{M} - 8\text{CO}]^+$, 60), 1874 ($[\text{M} - 16\text{CO}]^+$, 100). Anal. Calcd for $\text{C}_{66}\text{H}_{58}\text{Ir}_4\text{Mo}_4\text{O}_{16}\text{S}_2$ (2323.87): C, 34.11; H, 2.52. Found: C, 34.43; H, 2.41.

Electrochemical Studies. The cyclic voltammograms were recorded using a MacLab 400 interface and MacLab poten-

Table 1. Crystal Data for 21, 29, and 31

	21	29	31
formula	C ₆₀ H ₅₆ Ir ₄ O ₁₆ SW ₄	C ₆₆ H ₅₈ Ir ₄ O ₁₆ S ₂ W ₄	C ₆₀ H ₅₆ Ir ₄ O ₁₆ SeW ₄
fw	2569.43	2675.57	2616.25
cryst size (mm)	0.30 × 0.17 × 0.06	0.04 × 0.05 × 0.19	0.30 × 0.11 × 0.06
color, habit	brown, rod	green, needle	dark green, rod
cryst syst	orthorhombic	trigonal	monoclinic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)	<i>R</i> 3 (#148)	<i>P</i> 2 ₁ / <i>c</i> (#14)
<i>a</i> (Å)	10.3508(1)	43.4501(7)	19.9870(2)
<i>b</i> (Å)	19.9540(2)	43.4501(7)	28.9452(3)
<i>c</i> (Å)	29.2639(3)	22.4747(3)	21.2558(2)
α (deg)	90	90	90
β (deg)	90	90	93.8409(5)
γ (deg)	90	120	90
<i>V</i> (Å ³)	6044.16(9)	36745.8(10)	12269.5(2)
<i>Z</i>	4	18	8
<i>D</i> _{calc} (g cm ⁻³)	2.82	2.176	2.83
μ (mm ⁻¹)	16.48	12.23	16.77
θ _{max} (deg)	30.1	27.5	25.0
index ranges	0 ≤ <i>h</i> ≤ 14 -26 ≤ <i>k</i> ≤ 28 -41 ≤ <i>l</i> ≤ 41	-55 ≤ <i>h</i> ≤ 53 -56 ≤ <i>k</i> ≤ 56 -21 ≤ <i>l</i> ≤ 29	-23 ≤ <i>h</i> ≤ 23 -34 ≤ <i>k</i> ≤ 34 -24 ≤ <i>l</i> ≤ 25
<i>N</i> _{measured}	78 908	77 572	149 301
<i>N</i> _{unique} (<i>R</i> _{int})	17 169 (0.0364)	18 658 (0.085)	21 494 (0.048)
<i>N</i> _{obs} [<i>I</i> > 2σ(<i>I</i>)]	13 537	9749 [<i>I</i> > 3σ(<i>I</i>)]	19 627
abs corr	integration	integration	integration
<i>T</i> _{min} , <i>T</i> _{max}	0.053, 0.390	0.227, 0.593	0.078, 0.404
<i>N</i> _{param}	761	492	936
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)] ^a	0.057	0.040 [<i>I</i> > 3σ(<i>I</i>)]	0.045
<i>R</i> _w [<i>I</i> > 2σ(<i>I</i>)] ^b	0.064 ^c	0.057 ^d [<i>I</i> > 3σ(<i>I</i>)]	0.069 ^e
GOF	1.28	1.05	2.38
largest diff peak, hole (e Å ⁻³)	5.73, -5.12	2.90, -2.59	2.28, -1.59

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$. ^c $w = [\sigma_c^2(F_o) + 0.00022(F_o^2)]^{-1}$. ^d $w = [\sigma_c^2(F_o) + 0.0009(F_o^2)]^{-1}$. ^e $w = [\sigma_c^2(F_o) + 0.0004(F_o^2)]^{-1}$.

tiostat from ADInstruments. The supporting electrolyte was 0.25 M (NBu₄)PF₆ in distilled, deoxygenated CH₂Cl₂. Solutions containing ca. 2 × 10⁻³ mol L⁻¹ complex were maintained under argon. Measurements were carried out using a platinum disk working, platinum auxiliary, and Ag/AgCl reference electrodes, using the ferrocene/ferrocenium redox couple as an internal reference (0.56 V).

X-ray Crystallographic Studies. In each case, a single crystal was mounted on the side of a fine glass capillary using oil, and data were collected at 200 K on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Unit cell refinement and data reduction were performed using Denzo/Scalepack,³⁵ and absorption corrections were applied.^{36,37} The structures were solved by Patterson methods^{38a} from within the teXsan software package^{41b} and refined using teXsan (**21**) and Xtal (**31**); see below for procedures applied to **29**. The non-hydrogen atoms in **21** and **31** were refined anisotropically; hydrogen atoms were included in idealized positions, which were frequently recalculated (see variation in procedure for **31** below). The final cycle of least-squares refinement on *F* was based on *N*_{obs}

reflections and *N*_{param} parameters and converged to *R* and *R*_w. The data collection and structural refinement details are summarized in Table 1, and selected bond lengths and angles for **21** and **31** are given in Table 2, with those for **29** being listed in Table 3. Labeled molecular structures are shown in Figures 1 (**21**), 2 (**31**), and 3 (**29**). A comparison of the cluster cores and bridge units for **21** and **31** is shown in Figure 4.

The crystal structure study of **31** revealed two molecules in the asymmetric unit; carbon atoms were refined with isotropic displacement parameters, and least-squares refinement cycles were performed using the block diagonal method. Displacement parameters for some carbon atoms are high, suggesting some disorder; in the case of C122, the atom has been split over two sites, and the relative occupancies have been refined. Alternative sites were not found for C321, so it has been left with unit occupancy. Loose restraints were placed on most C–C bonds in each molecule but not Cn27–Cn28 or Cn30–Cn30. The methyl hydrogen atoms of the η⁵-C₅H₄Me groups were not included.

Two of the four methylcyclopentadienyl ligands in **29** are disordered, and the hexyl groups are partially disordered, but a clear verification of the chemical composition was possible, confirming the essential connectivity of the molecule, and in particular the unsymmetrical coordination of the triyne, coordinating using adjacent alkyne bonds. The metal atoms were readily identified by standard methods, the remaining atoms being identified from electron density difference maps. The location of atoms in the W₂Ir₂(CO)₈(η⁵-C₅H₄Me)₂ fragments was as expected, but constraints and restraints were necessary for their refinement.³⁹ Both the two disordered and the two ordered C₅H₄Me ligands were constrained to be identical, with a refinable planar geometry constrained to maintain local *mm*2 symmetry. Resulting occupancies for the disorder were 0.72(6):0.28 and 0.76(4):0.24. Each C₅H₄Me group had its own *TLX* parametrization⁴⁰ for thermal motion using only a single relocatable libration axis perpendicular to the ring. The minor components at disordered sites were constrained to have the same parametrization as the major components. The Ir, W,

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[\text{W}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2[\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{E-5-C}_2(\text{CH}_2)_5\text{Me}]$ [E = S (21), Se (31)]

bond	31			bond	31		
	21	molecule 1	molecule 2		21	molecule 1	molecule 2
Ir11–Ir12	2.718(1)	2.6894(7)	2.7009(7)	Ir21–Ir22	2.7621(9)	2.7099(6)	2.7077(6)
Ir11–W11	2.813(1)	2.8145(7)	2.8235(7)	Ir21–W21	2.787(1)	2.8108(7)	2.7838(7)
Ir11–W12	2.7886(9)	2.8194(7)	2.8067(7)	Ir21–W22	2.7587(9)	2.7885(7)	2.8011(7)
Ir12–W11	2.7840(9)	2.8126(7)	2.7974(6)	Ir22–W21	2.7758(9)	2.7692(7)	2.8357(7)
Ir12–W12	2.8001(9)	2.8000(7)	2.8179(7)	Ir22–W22	2.7964(9)	2.8126(7)	2.7804(7)
Ir11–C127	2.12(2)	2.120(11)	2.139(11)	Ir21–C227	2.11(2)	2.113(10)	2.134(10)
Ir12–C128	2.11(1)	2.121(10)	2.117(10)	Ir22–C228	2.12(2)	2.127(10)	2.122(10)
W11–C127	2.38(2)	2.367(11)	2.367(11)	W21–C227	2.36(2)	2.354(10)	2.342(10)
W11–C128	2.34(2)	2.329(10)	2.350(10)	W21–C228	2.33(2)	2.320(10)	2.311(11)
W12–C127	2.31(2)	2.321(11)	2.366(11)	W22–C227	2.36(2)	2.341(10)	2.335(11)
W12–C128	2.35(2)	2.290(10)	2.342(10)	W22–C228	2.38(2)	2.341(11)	2.369(10)
C127–C128	1.50(2)	1.507(15)	1.499(15)	C227–C228	1.51(2)	1.483(15)	1.458(15)
C128–C129	1.45(2)	1.504(14)	1.493(14)	C228–C229	1.48(2)	1.491(14)	1.507(15)
C129–E1	1.74(2)	1.877(10)	1.865(10)	C229–E1	1.73(2)	1.906(10)	1.899(10)
C129–C130	1.37(2)	1.400(15)	1.362(14)	C229–C230	1.37(2)	1.364(13)	1.376(14)
C130–C230	1.41(2)	1.386(16)	1.374(15)				
Ir12–Ir11–W11	60.42(2)	61.413(18)	60.797(17)	Ir22–Ir21–W21	60.03(2)	60.178(17)	62.160(18)
Ir12–Ir11–W12	61.12(2)	61.045(18)	61.509(18)	Ir22–Ir21–W22	60.86(2)	61.513(18)	60.597(17)
W11–Ir11–W12	96.52(3)	95.39(2)	96.35(2)	W21–Ir21–W22	97.34(3)	96.34(2)	96.96(2)
Ir11–Ir12–W11	61.49(2)	61.486(18)	61.768(18)	Ir21–Ir22–W21	60.43(2)	61.717(18)	60.237(18)
Ir11–Ir12–W12	60.69(2)	61.770(18)	61.095(18)	Ir21–Ir22–W22	59.51(2)	60.619(18)	61.362(17)
W11–Ir12–W12	96.92(12)	95.87(2)	96.69(2)	W21–Ir22–W22	96.72(3)	96.74(2)	96.24(2)
Ir11–W11–Ir12	58.10(2)	57.101(17)	57.435(17)	Ir21–W21–Ir22	59.54(2)	58.105(17)	57.603(17)
Ir11–W12–Ir12	58.19(2)	57.186(18)	57.396(18)	Ir21–W22–Ir22	59.63(2)	57.869(18)	58.041(17)
C127–C128–C129	124(1)	123.5(9)	123.0(9)	C227–C228–C229	125(2)	127.5(9)	129.2(9)
E1–C129–C130	109(1)	107.2(8)	108.7(8)	E1–C229–C230	109(1)	106.9(7)	107.0(7)
C129–C130–C230	114(2)	117.1(10)	117.4(10)	C229–C230–C130	115(2)	118.6(10)	117.7(9)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[\text{W}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2[\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C}(\text{CH}_2)_5\text{Me}]$ (29)

Ir1–Ir2	2.711(1)	C50–C51	1.461(14)	Ir2–Ir1–W1	60.1(1)	Ir4–Ir3–W3	61.6(1)
Ir1–W1	2.826(1)	C51–C52	1.489(13)	Ir1–Ir2–W1	62.0(1)	Ir3–Ir4–W3	60.3(1)
Ir1–W2	2.817(1)	C52–S1	1.759(10)	Ir1–W1–Ir2	57.9(1)	Ir3–W3–Ir4	58.1(1)
Ir2–W1	2.774(1)	C52–C53	1.504(13)	Ir2–Ir1–W2	60.5(1)	Ir3–Ir4–W4	60.8(1)
Ir2–W2	2.788(1)	C53–C54	1.492(12)	Ir1–Ir2–W2	61.6(1)	Ir3–W4–Ir4	58.2(1)
Ir3–Ir4	2.715(1)	C54–C55	1.480(12)	Ir1–W2–Ir2	57.8(1)	W3–Ir3–W4	96.7(1)
Ir3–W3	2.777(1)	C55–C56	1.364(12)	W1–Ir1–W2	95.7(1)	W3–Ir4–W4	95.8(1)
Ir3–W4	2.791(1)	C55–S2	1.733(9)	W1–Ir2–W2	97.5(1)		
Ir4–W3	2.813(1)	C56–C57	1.391(12)				
Ir4–W4	2.795(1)	C57–C58	1.368(13)				
C47–C48	1.172(17)	C58–S2	1.716(9)				
C48–C49	1.503(16)	C58–C59	1.493(12)				
C49–C50	1.363(15)	C59–C60	1.478(13)				
C49–S1	1.687(12)						

and O atoms were refined as isolated anisotropic atoms, and the C atoms attached to the O atoms were refined as isolated isotropic atoms. C–O distances were restrained to lie between 1.12 and 1.20 Å, conditional restraints applying to make distances outside this range approach the nearest limit of the range. The remaining atoms, i.e., those in the triyne, were refined as isolated atoms while using rigid body thermal parametrizations, breaking the ligand into four fragments. Alkyl C–C distances were restrained to lie between 1.45 and 1.65 Å, conditional restraints applying to make distances outside this range approach the nearest limit of the range. For these distances, restraints to make differences between adjacent bond lengths approach zero were also used. A 1:1 disorder over alternative sites was used for one terminal methyl, viz., C66, and for two adjacent atoms, C44 and C45. The four *TLX* parametrizations centered on C41 (for C41 to C45), on C53 (for C46 to C53 and S1), on C59 (for C54 to C59 and S2), and on C60 (for C60 to C66). The hydrogen atoms were included in sensible geometric positions after each refinement cycle and given the thermal parameters implied by the above models.

Results and Discussion

Syntheses of Heterocyclic Bridges. The heterocyclic bridges chosen to link the group 6–iridium

clusters have been constructed using cross-coupling of a haloheterocycle with a terminal alkyne in the presence of palladium(II) and copper(I) iodide catalysts (Sonogashira coupling) to introduce C≡C groups,^{41,42} and the Horner–Emmons–Wittig reaction employing a phosphonate ester, RP(O)(OEt)₂, to form *E*-alkene groups. The synthetic procedures are summarized in Schemes 1–3. New compounds were characterized by IR and ¹H and ¹³C NMR spectroscopies, EI mass spectrometry, and either satisfactory microanalysis (solids) or high-resolution EI mass spectrometry (liquids).

Functionalization of monothiophene units is summarized in Scheme 1. Commercially available 2,5-dibromothiophene was monotranshalogenated on sequential treatment with 1 equiv of *n*-butyllithium followed by iodine, to afford 2-bromo-5-iodothiophene (**3**). Sonogashira coupling of **3** with trimethylsilylacetylene afforded the protected alkyne 2-bromo-5-(trimethylsilylethynyl)thiophene (**4**), deprotection of which (employing tetra-*n*-butylammonium fluoride) gave the

(42) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280.

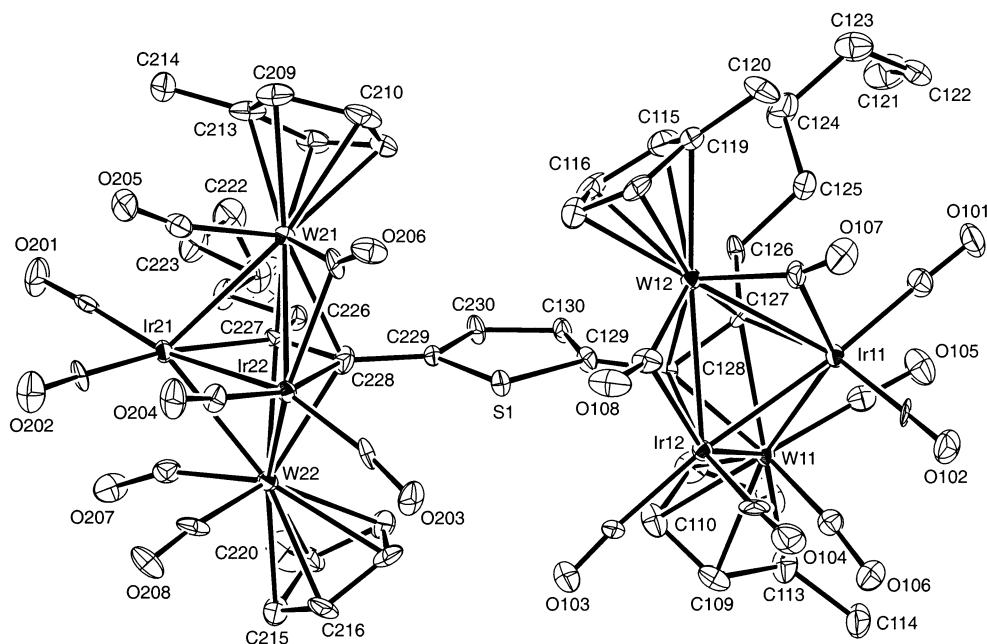


Figure 1. Molecular structure and atomic numbering scheme for **21**. Displacement ellipsoids are shown at the 30% probability level; hydrogen atoms have been omitted for clarity.

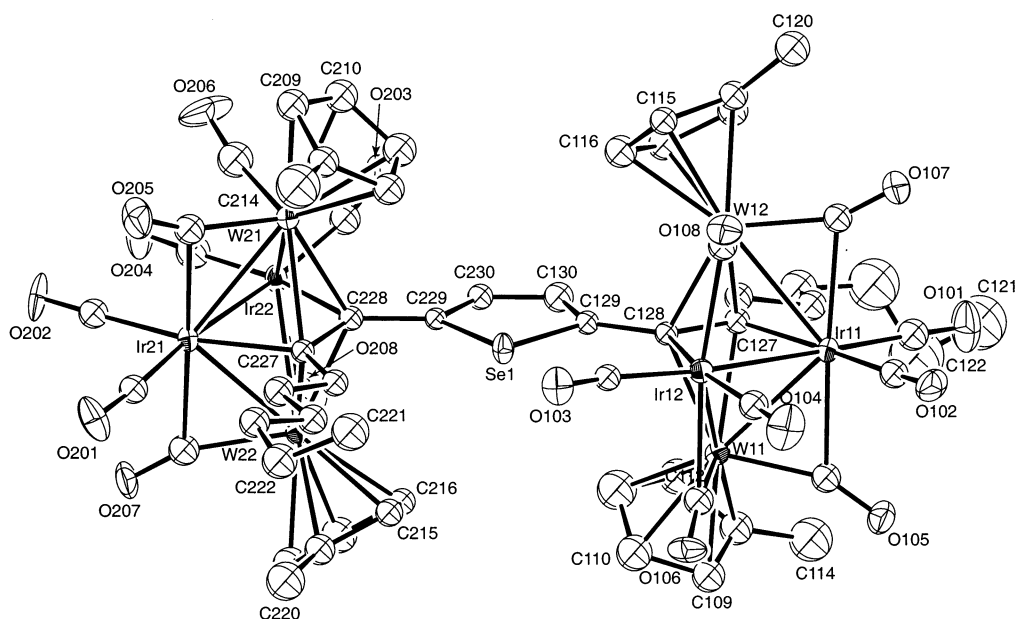


Figure 2. Molecular structure and atomic numbering scheme for **31**. Displacement ellipsoids are shown at the 30% probability level; hydrogen atoms have been omitted for clarity.

terminal alkyne 2-bromo-5-ethynylthiophene (**5**) in almost quantitative yield. A similar coupling of **3** with 1-octyne afforded 2-bromo-5-(oct-1'-ynyl)thiophene (**6**), which was transhalogenated as above to give 2-iodo-5-(oct-1'-ynyl)thiophene (**7**). Bis-coupling of 2,5-dibromothiophene with 1-octyne afforded 2,5-di(oct-1'-ynyl)thiophene (**8**).

Procedures to couple thiophene units to form di- and trithiophene assemblies are summarized in Scheme 2. Emmons–Horner coupling of 5-bromo-2-thiophenecarboxaldehyde with diethyl {(2-bromo-5-thienyl)methyl}phosphonate afforded 1,2-(*E*)-bis(5'-bromo-2'-thienyl)ethene (**9**), subsequent Sonogashira coupling with 2 equiv of 1-octyne giving 1,2-(*E*)-bis{5'-(oct-1'-ynyl)-2'-thienyl}ethene (**10**) in excellent yield. Sonogashira protocols were also used to couple **3** and **5**, affording a

mixture of di(5-bromo-2-thienyl)ethyne (**11**) and 2,5-bis-{(5'-bromo-2'-thienyl)ethynyl}thiophene (**12**); coupling the former with 1-octyne gave di{5-(oct-1'-ynyl)-2-thienyl}ethyne (**13**).

Syntheses of ethynylselenophenes are summarized in Scheme 3. Bromination of selenophene afforded a mixture of di- and tetrabromo derivatives which could not be separated chromatographically. This mixture was treated with 1-octyne in the presence of Pd(II) and Cu(I) salts to afford the expected products 2,5-di(oct-1'-ynyl)selenophene (**14**), 3,4-dibromo-2,5-di(oct-1'-ynyl)selenophene (**15**), and 3-bromo-5-(oct-1'-ynyl)selenophene (**16**), for which chromatographic separation could be effected.

Syntheses of Functionalized Cluster–Alkyne Complexes. The dicluster compounds of interest in the

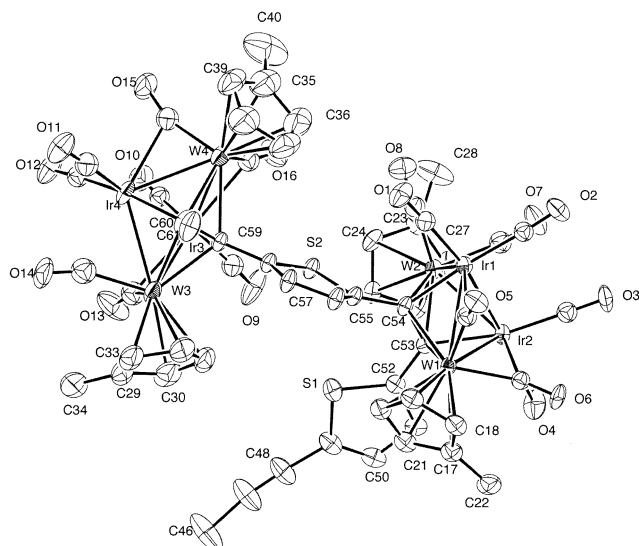


Figure 3. Molecular structure and atomic numbering scheme for **29**. Displacement ellipsoids are shown at the 30% probability level; hydrogen atoms and the disordered hexyl groups have been omitted for clarity.

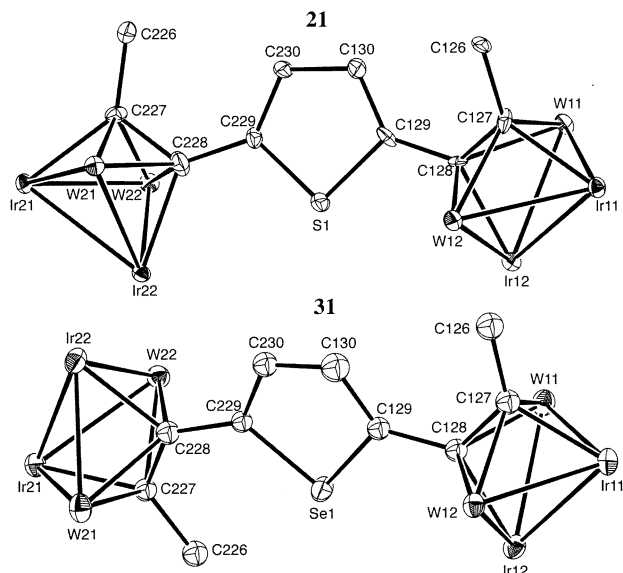


Figure 4. Comparison of the cluster cores and bridge units for **21** and **31**; the carbonyl groups, methylcyclopentadienyl groups, hexyl chain carbons C_{n21} – C_{n25} , and hydrogen atoms have been omitted for clarity. Displacement ellipsoids are shown at the 30% probability level.

existing studies can conceptually be prepared by two general routes: adding cluster units to preformed organic di- or triynes or coupling appropriately functionalized cluster–alkyne complexes. In the present studies, the former approach has been pursued with both $\text{Mo}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**1**) and $\text{W}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**2**), while the latter has been investigated for the molybdenum-containing cluster only. Scheme 4 summarizes procedures to prepare the functionalized cluster–alkyne complexes required to pursue the second option. Heating **1** in refluxing dichloromethane with 2-iodo-5-(oct-1'-ynyl)thiophene (**7**) afforded $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-I}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**17**), for which organic chemistry at the iodo substituent is possible without cluster disruption: Sonogashira coupling of **17** with trimethylsilylacetylene gave

$\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-C}\equiv\text{CSiMe}_3\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**18**), subsequent deprotection affording $\text{Mo}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-5-C}_4\text{H}_2\text{S-2-C}\equiv\text{CH}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**19**). Clusters **17**–**19** have been characterized by a combination of IR and ^1H NMR spectroscopies and SI mass spectrometry. The solution IR spectra exhibit the distinctive $\nu(\text{CO})$ pattern identified with related cluster–alkyne adducts:^{24,25,43,44} four bands in the terminal carbonyl region and two in the bridging carbonyl region, accompanied, in the case of **18** and **19**, by weak $\nu(\text{C}\equiv\text{C})$ bands at 2141 and 2099 cm^{-1} , respectively. The ^1H NMR spectra contain resonances arising from the methylcyclopentadienyl and thienyl groups in the appropriate ratios accompanied by resonances corresponding to SiMe_3 (**18**: δ 0.23) and $\equiv\text{CH}$ (**19**: δ 3.44). The SIMS spectra contain peaks corresponding to the molecular ion and successive loss of carbonyl ligands.

Syntheses of Di- and Tricluster Compounds Linked through π -Delocalized Frameworks.

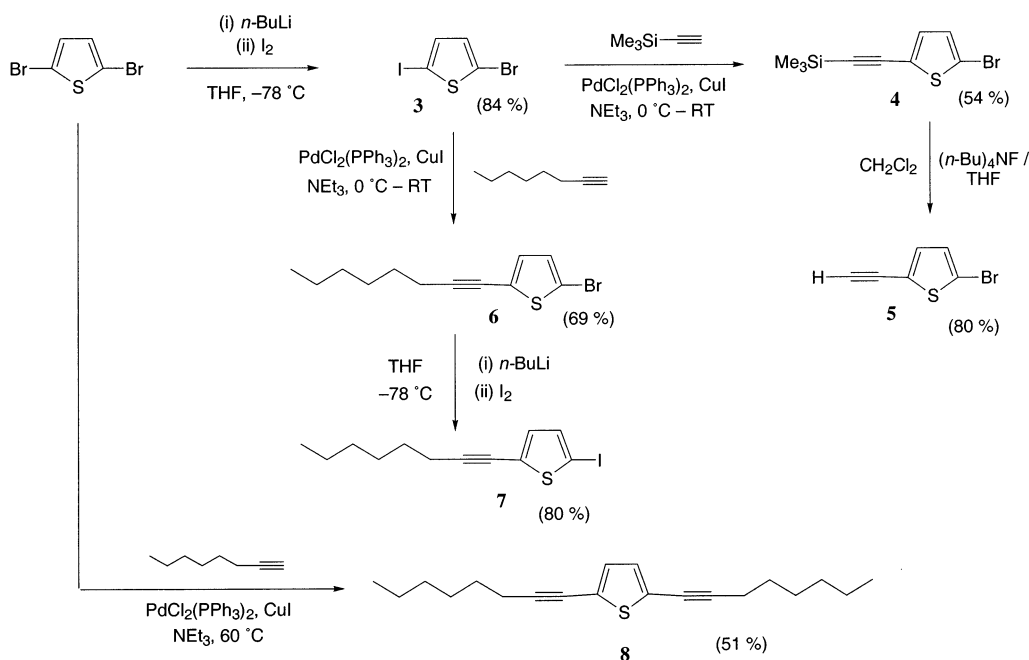
The reactions of excess $\text{Mo}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**1**) or $\text{W}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**2**) with 2,5-di(oct-1'-ynyl)thiophene (**8**) in refluxing dichloromethane afforded the dicluster products $[\text{M}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ [$\text{M} = \text{Mo}$ (**20**), W (**21**)]. Similar reactions with 1,2-(*E*)-bis{5'-(oct-1'-ynyl)-2'-thienyl}ethene (**10**) gave the expected dicluster products $[\text{M}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-(E)-CH=CH-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ [$\text{M} = \text{Mo}$ (**22**), W (**24**)], together with small amounts of the reaction intermediate monocluster products $\text{M}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-(E)-CH=CH-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C}(\text{CH}_2)_5\text{Me}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ [$\text{M} = \text{Mo}$ (**23**), W (**25**)] (Scheme 5). In a similar fashion, the reaction of 2–2.5 equiv of **1** or **2** with the linear triyne di{5-(oct-1'-ynyl)-2-thienyl}ethyne (**13**) in dichloromethane at reflux for 24 h afforded the tricluster adducts $[\text{M}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_3\{\mu_{12}\text{-}\eta^6\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ [$\text{M} = \text{Mo}$ (**26**), W (**28**)] as the major products in fair yield, accompanied by minor products identified as the dicluster adducts $[\text{Mo}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8\text{-}\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C}(\text{CH}_2)_5\text{Me}\}$ [$\text{M} = \text{Mo}$ (**27**), W (**29**)] (Scheme 6). The products have been characterized by a combination of IR, ^1H NMR, and (for the molybdenum-containing examples) UV–vis spectroscopies and SI mass spectrometry. The solution IR spectra exhibit the distinctive $\nu(\text{CO})$ pattern for the $\text{M}_2\text{Ir}_2\text{C}_2$ cluster core. The SIMS spectra of **20**–**22**, **24**, **26**, **28**, and **29** contain molecular ion peaks; the highest m/z peaks in the spectra of **23**, **25**, and **27** have been assigned to $[\text{M} - 4\text{CO}]^+$, $[\text{M} - \text{C}_2\text{H}_5]^+$, and $[\text{M} - \text{C}\equiv\text{C}(\text{CH}_2)_5\text{Me}]^+$ fragment ions, respectively. The ^1H NMR spectra feature methylcyclopentadienyl and thienyl resonances in the appropriate ratios for mono-, di-, and tricluster adducts; the aromatic regions of **27** and **29** display four doublets consistent with coordination of the clusters to adjacent $\text{C}\equiv\text{C}$ sites, rather than the symmetrical product that would be expected on steric grounds.

Refluxing dichloromethane solutions containing 2–2.5 equiv of $\text{M}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (**1/2**) with 2,5-di(oct-1'-ynyl)selenophene **14**, followed by TLC purification

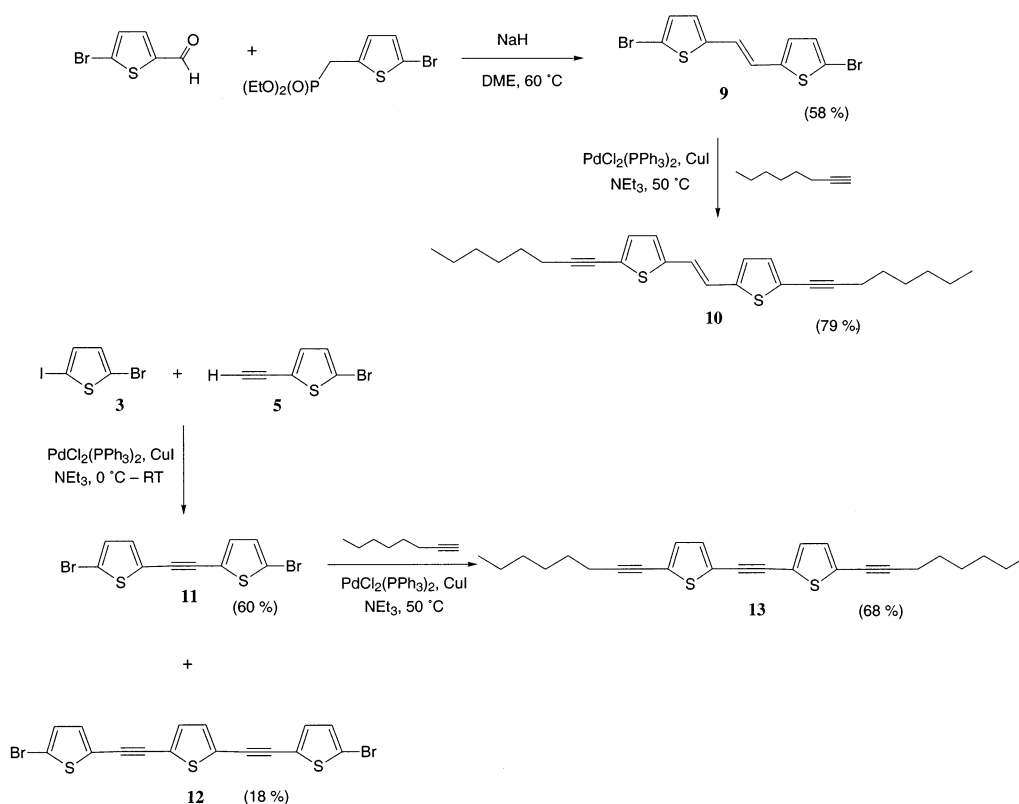
(43) Lucas, N. T.; Humphrey, M. G.; Healy, P. C.; Williams, M. L. *J. Organomet. Chem.* **1997**, 545–546, 519.

(44) Waterman, S. M.; Humphrey, M. G.; Tolhurst, V.-A.; Bruce, M. I.; Low, P. J.; Hockless, D. C. R. *Organometallics* **1998**, 17, 5789.

Scheme 1



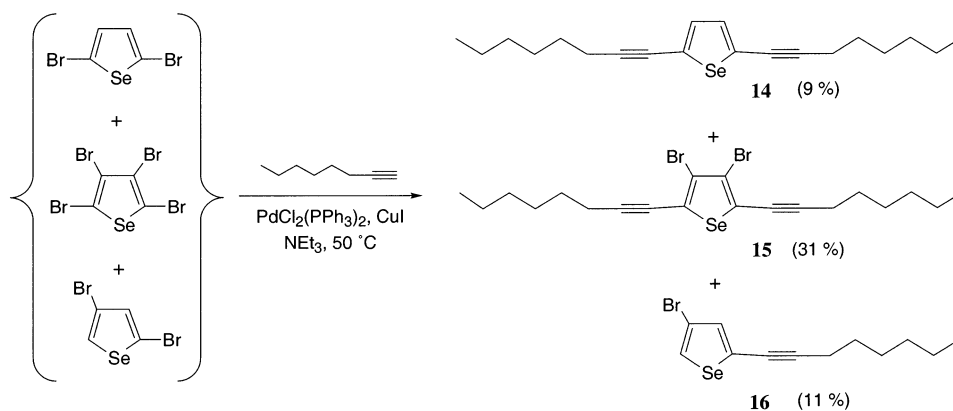
Scheme 2



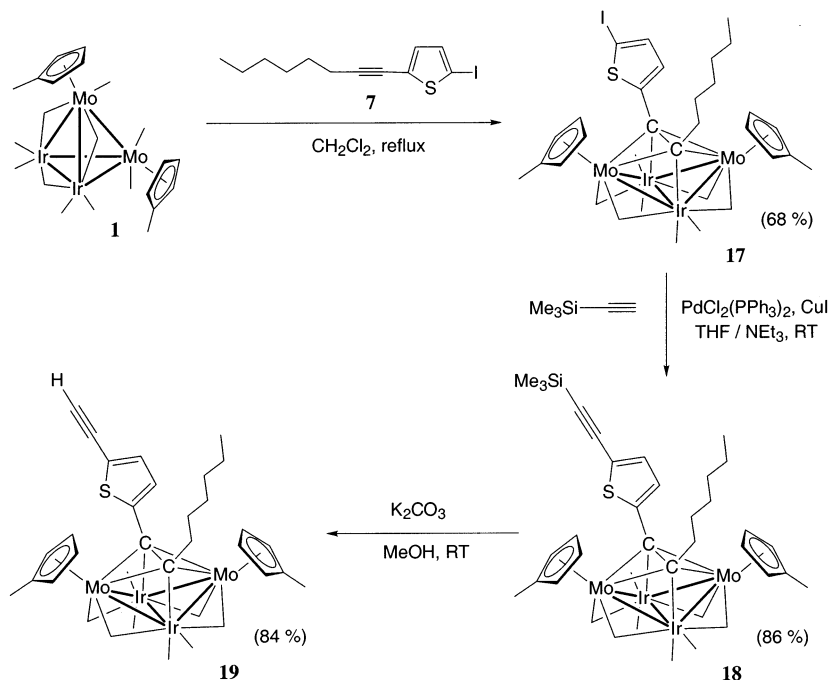
and recrystallization, afforded the dicluster adducts $[M_2Ir_2(CO)_8(\eta^5-C_5H_4Me)_2]_2\{\mu_8-\eta^4-Me(CH_2)_5C_2-2-C_4H_2Se-5-C_2(CH_2)_5Me\}$ [$M = Mo$ (**30**), W (**31**)] (Scheme 7), which as above were characterized by IR, 1H NMR, and UV-vis spectroscopies and SI mass spectrometry. The solution IR are consistent with the expected core geometry, and the 1H NMR spectra contain signals assigned to the selenienyl ring and methylcyclopentadienyl and hexyl groups in the appropriate ratios. The SIMS spectra contain molecular ions and fragment ions corresponding to stepwise loss of carbonyls.

All of the linked cluster adducts described so far have been synthesized by reaction of the appropriate cluster precursor with a preformed di- or triyne π -delocalized organic framework. An alternate strategy, mentioned earlier, is to coordinate functionalized monoynes to a cluster core, then 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 procedure, $Mo_2Ir_2\{\mu_4-\eta^2-Me(CH_2)_5C_2-5-C_4H_2S-2-I\}(CO)_8(\eta^5-C_5H_4Me)_2$ (**17**) and $Mo_2Ir_2\{\mu_4-\eta^2-Me(CH_2)_5C_2-5-C_4H_2S-2-C\equiv CH\}(CO)_8(\eta^5-C_5H_4-$

Scheme 3



Scheme 4



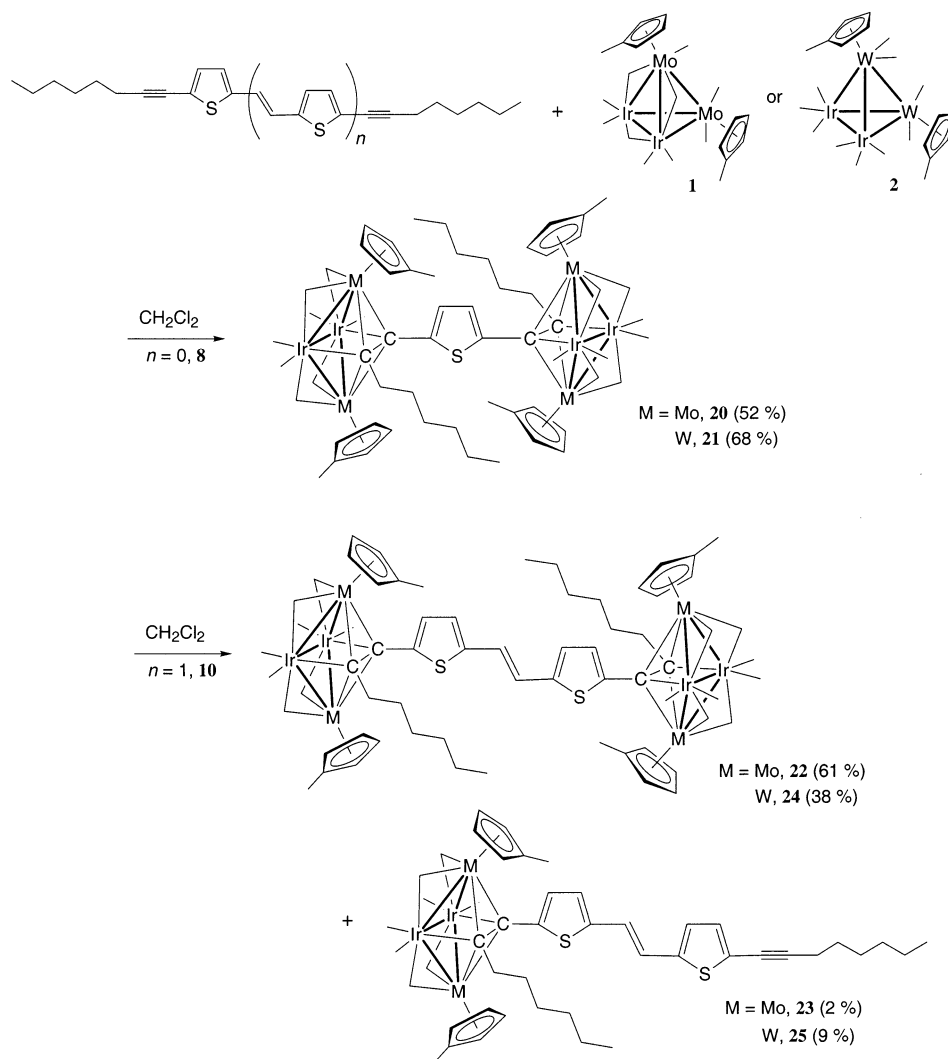
Me)₂ (**19**) were reacted to afford two products, which were separable by TLC (Scheme 8) and identified as the desired product [Mo₂Ir₂(CO)₈(η-C₅H₄Me)₂]₂{μ₈-η⁴-Me(CH₂)₅C₂-4-C₄H₂SC≡CC₄H₂S-4-C₂(CH₂)₅Me} (**32**) and the homocoupled product [Mo₂Ir₂(CO)₈(η-C₅H₄Me)₂]₂{μ₈-η⁴-Me(CH₂)₅C₂-2-C₄H₂S-5-C≡CC≡C-5-C₄H₂S-2-C₂(CH₂)₅Me} (**33**) (Scheme 8). The products have been characterized by IR, ¹H NMR, and UV-vis spectroscopies and SI mass spectrometry. The solution IR spectra exhibit the expected ν(CO) pattern for the Mo₂-Ir₂C₂ cluster, and the SIMS spectra contain molecular ions. There are many similarities in the ¹H NMR spectra of the products, the most significant differences being in the thiophene ring resonances (doublets at δ 7.14, 6.66 (**32**), cf. δ 7.09, 6.68 (**33**)).

Crystal Structure Studies. The identities of **21**, **29**, and **31** have been confirmed by single-crystal X-ray diffraction studies. ORTEP plots showing the molecular geometries and atomic numbering schemes are shown in Figures 1 (**21**), 2 (**31**), and 3 (**29**), and crystal data, selected bond lengths and angles for **21** and **31**, and selected bond lengths and angles for **29** are collected in Tables 1, 2, and 3, respectively.

The structures consist of W₂Ir₂C₂ cluster moieties linked by 2,5-thienyl (**21**, **29**) or 2,5-selenienyl (**31**) bridges. In each cluster unit, the iridium atoms form the hinge and η⁵-methylcyclopentadienyl-ligated tungsten atoms occupy the wing-tip positions of metal cores adopting butterfly geometries. The metal-metal bond lengths in **21**, **29**, and **31** are in agreement with previously reported single cluster examples.^{25,44,45} Two terminal carbonyl groups ligate each iridium, while the four remaining carbonyl ligands unsymmetrically bridge the W-Ir bonds [Ir-C 2.25(2)-2.84(2), W-C 1.93(2)-2.02(2) Å]. The C27-C28 bond lengths [1.50(2)/1.51(2) (**21**); 1.51(2), 1.50(2)/1.48(2), 1.46(2) (**31**) Å] are, as expected, between those corresponding to formal single and double bond orders. Interestingly, the core C-C vectors adopt a *syn* disposition relative to the thiophene ring in **21**, in contrast to the selenophene analogue **31**, in which the two C-C moieties lie on opposite sides of the central ring (Figure 4). All C-C bond lengths within the thiophene, selenophene, and hexyl chains in **21** and

(45) Lucas, N. T.; Notaras, E. G. A.; Humphrey, M. G. *Acta Crystallogr.* **2001**, *E57*, m143.

Scheme 5



31 are in agreement with typical interatomic distances.⁴⁶

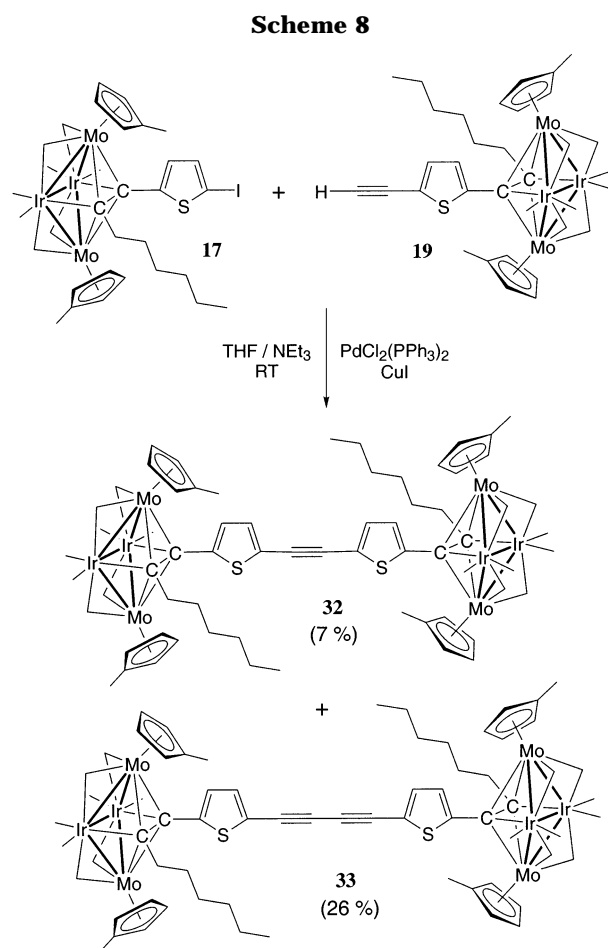
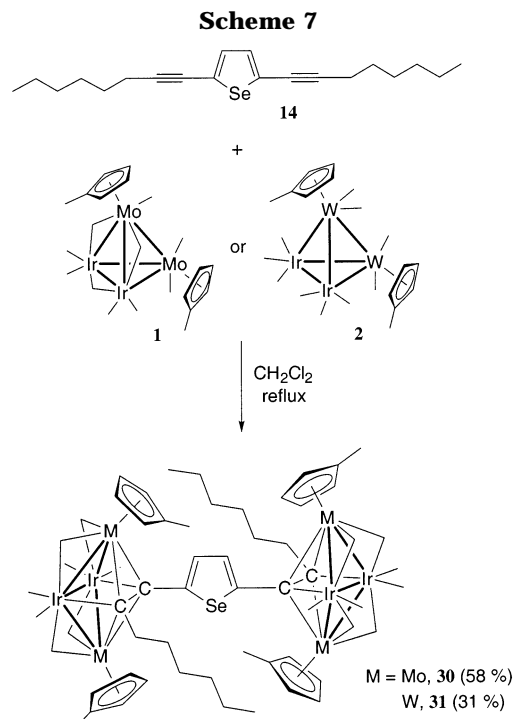
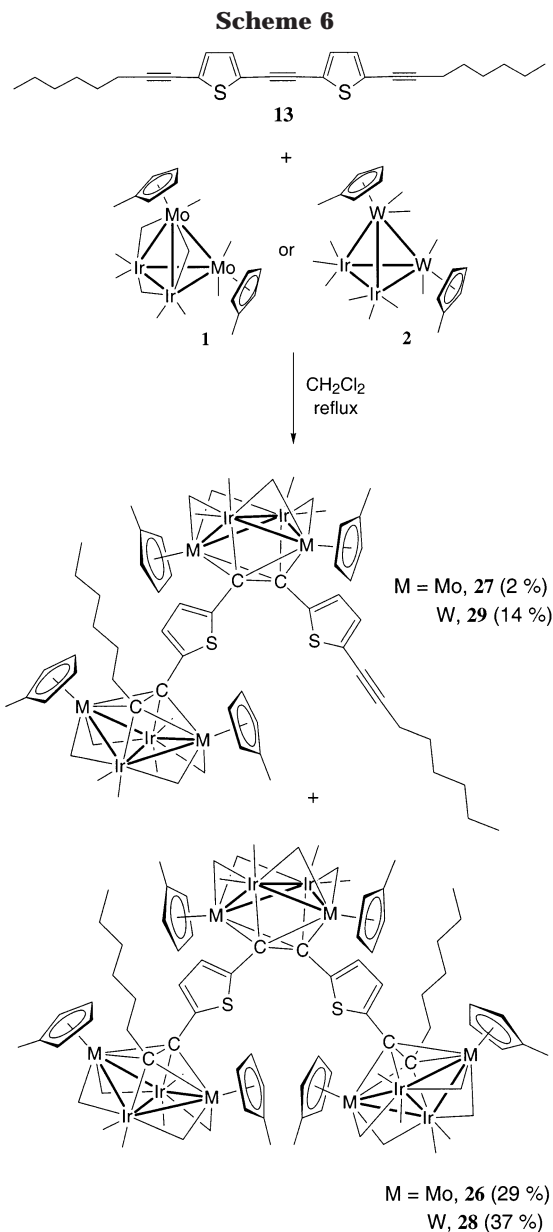
Electrochemical Studies. We have previously reported cyclic voltammetric studies of the monocluster compounds $\text{M}_2\text{Ir}_2\{\mu_4\text{-}\eta^2\text{-RC}_2\text{Ph}\}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ [R = Ph, M = Mo (**34**), W (**35**); R = Me, M = Mo (**36**), W (**37**)] (which serve as benchmarks for the redox behavior of isolated, noncommunicating, clusters) and a range of di- and tricluster compounds with linking phenylenevinylene²⁵ and phenyleneethynylene²⁴ bridging units. We have now extended this study to embrace some of the di- and tricluster compounds prepared in the current work, the results of these investigations being listed in Table 4. Note: no significant variation to tabulated data was observed upon decreasing temperature (to 230 K) or increasing scan rate (to 1600 mV s^{-1}); the listed data were obtained at room temperature (293 K) with a scan rate of 200 mV s^{-1} .

Cyclic voltammograms of **20**, **21**, and **29–31**, in which the cluster units are linked by one heterocycle, are similar to those of dicluster compounds with one linking phenyl group;²⁵ they possess a reversible oxidation

process at less positive potentials, an irreversible oxidation process at more positive potentials, and two irreversible reduction processes. Cyclic voltammograms of **22**, **24**, **32**, and **33**, in which the cluster units are linked by two heterocycles in the bridging unit, are similar to those of dicluster compounds with $\text{C}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4$ or $\text{C}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4$ bridges,^{24,25} containing one reversible and one irreversible oxidation process, together with one irreversible reduction process. The tricluster compounds **26** and **28** similarly show oxidative and reductive behavior analogous to that shown by their phenyleneethynylene-linked tricluster analogues,²⁴ with one reversible and one irreversible oxidation process and two irreversible reduction processes. Potentials for the reversible oxidation processes increase on replacement of tungsten by molybdenum and phenylene by thienyl and selenienyl bridging units.

Discussion. In previous reports we have summarized the facile construction of di- and tricluster compounds in which the cluster modules are linked by phenylenevinylene²⁵ or phenyleneethynylene²⁴ bridges. The present study extends this work to related examples linked by heterocycle-containing bridging groups. Two approaches to construct dicluster compounds were employed in our earlier reports, viz., adding cluster units to preformed organic diynes, and coupling ap-

(46) Allen, F. H.; Kennard, O.; Watson, D. G.; Brummer, L.; Orpen, A. G.; Taylor, R. In *International Tables for Crystallography, Volume C*; Wilson, A. J. C., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; p 685.



appropriately functionalized cluster-alkyne complexes. The present study confirms that both routes can be utilized to form dicluster compounds linked by heterocycle-containing bridges and that the two synthetic approaches complement each other: whereas reaction of $M_2Ir_2(CO)_{10}(\eta^5-C_5H_4Me)_2$ (**1/2**) with di{5-(oct-1'-ynyl)-2-thienyl}ethyne **13** afforded the "1,2-isomers" $[M_2Ir_2(CO)_8(\eta^5-C_5H_4Me)_2]_2\{\mu_8-\eta^4-Me(CH_2)_5C_2-2-C_4H_2S-5-C_2-2-C_4H_2S-5-C\equiv C(CH_2)_5Me\}$ [M = Mo (**27**), W (**29**)] together with the tricluster adducts $[M_2Ir_2(CO)_8(\eta^5-C_5H_4Me)_2]_3\{\mu_{12}-\eta^6-Me(CH_2)_5C_2-2-C_4H_2S-5-C_2-2-C_4H_2S-5-C_2(CH_2)_5Me\}$ [M = Mo (**26**), W (**28**)], combining $Mo_2Ir_2\{\mu_4-\eta^2-Me(CH_2)_5C_2-5-C_4H_2S-2-I\}(CO)_8(\eta^5-C_5H_4Me)_2$ (**17**) with $Mo_2Ir_2\{\mu_4-\eta^2-Me(CH_2)_5C_2-5-C_4H_2S-2-C\equiv CH\}(CO)_8(\eta^5-C_5H_4Me)_2$ (**19**) gave the "1,3-isomer" $[Mo_2Ir_2(CO)_8(\eta^5-C_5H_4Me)_2]_2\{\mu_8-\eta^4-Me(CH_2)_5C_2-2-C_4H_2S-5-C\equiv C-2-C_4H_2S-5-C_2(CH_2)_5Me\}$ (**32**). The latter reaction necessitated a functional group organic reaction (Sonogashira coupling) on the cluster-alkyne adducts and also afforded a butadiyne-linked dicluster compound by homocoupling of the terminal alkyne-functionalized cluster complex **19**. All of this chemistry is analogous

to that reported by us previously in the phenylenevinylene²⁵ and phenyleneethynylene systems,²⁴ and, taken together, the earlier and current reports provide access to a unique series of mixed-metal di- and tricluster compounds in which the cluster modules are linked by a variety of unsaturated bridging units. The present

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

compound	oxidation 2		oxidation 1		reduction 1		reduction 2	
	E_p	i_{pc}/i_{pa}	$E_{1/2}$ [$E_p^f - E_p^r$ mV]	i_{pc}/i_{pa}	E_p	i_{pa}/i_{pc}	E_p	i_{pa}/i_{pc}
Monocluster compounds								
$\text{Mo}_2\text{Ir}_2(\mu_4-\eta^2\text{-PhC}_2\text{Ph})(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (34) ^a	1.18	irrev	0.80 [60]	0.65	-1.22	irrev		
$\text{W}_2\text{Ir}_2(\mu_4-\eta^2\text{-PhC}_2\text{Ph})(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (35) ^a	0.90	irrev	0.58 [60]	0.75	-1.36	irrev		
$\text{Mo}_2\text{Ir}_2(\mu_4-\eta^2\text{-MeC}_2\text{Ph})(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (36) ^a	1.19	irrev	0.66 [75]	1	-1.32	irrev		
$\text{W}_2\text{Ir}_2(\mu_4-\eta^2\text{-MeC}_2\text{Ph})(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ (37) ^a	0.96	irrev	0.45 [74]	1	-1.48	irrev		
Dicluster compounds								
$[\text{Mo}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8-\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (20)	1.15	irrev	0.76 [70]	1	-1.14	irrev	-1.37	irrev
$[\text{W}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8-\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (21)	1.93	irrev	0.59 [65]	1	-1.19	irrev	-1.51	irrev
$[\text{W}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8-\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C}(\text{CH}_2)_5\text{Me}\}$ (29)	0.95	irrev	0.63 [65]	1	-1.15	irrev	-1.57	irrev
$[\text{Mo}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8-\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{Se-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (30)	1.20	irrev	0.77 [60]	1	-1.11	irrev	-1.36	irrev
$[\text{W}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8-\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{Se-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (31)	0.97	irrev	0.60 [65]	1	-1.19	irrev	-1.51	irrev
$[\text{Mo}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8-\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-(E)-CH=CH-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (22)	1.15	irrev	0.74 [60]	1	-1.21	irrev		
$[\text{W}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8-\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-(E)-CH=CH-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (24)	1.15	irrev	0.59 [60]	1	-1.34	irrev		
$[\text{Mo}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8-\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (32)	1.19	irrev	0.77 [65]	1	-1.29	irrev		
$[\text{Mo}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2\{\mu_8-\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}\equiv\text{C}\equiv\text{C-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (33)	1.20	irrev	0.76 [60]	1	-1.20	irrev		
Tricluster compounds								
$[\text{Mo}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_3\{\mu_{12}-\eta^6\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (26)	1.20	irrev	0.77 [65]	1	-1.24	irrev	-1.49	irrev
$[\text{W}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_3\{\mu_{12}-\eta^6\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$ (28)	0.93	irrev	0.57 [75]	1	-1.07	irrev	-1.55	irrev

^a Ref 25.

study also provides the first X-ray structural confirmation of the identity of a "1,2-isomer" across the three series of compounds (**29**).

The electrochemical behavior of the compounds reported herein is similarly analogous to the related compounds in our earlier reports. Quantification with an internal decamethylferrocene standard suggested that the reversible oxidation process in compounds of this type is one-electron in nature (although this is still uncertain, given the (expected) significantly different diffusion coefficients of decamethylferrocene and these clusters), and peak height comparison suggested that the irreversible reduction process is two-electron in nature;²⁵ local density approximation calculations suggested that the former occurs with retention of the pseudooctahedral core geometry of the resting state whereas the latter possibly proceeds with loss of carbonyl.²⁴ In all compounds incorporating two clusters linked by one phenyl-, thienyl-, or selenienyl-containing bridge, the number of reduction processes observed increases, but the irreversible nature of these processes

renders speculation regarding intercluster electronic communication unwarranted. The difference in potential between these reduction processes increases on replacing phenyl with selenienyl/thienyl, but, once again, their irreversible nature precludes further comment.

Acknowledgment. We thank the Australian Research Council (ARC) for financial support and Johnson-Matthey Technology Centre for the generous loan of iridium salts (M.G.H.). M.G.H. holds an ARC Australian Senior Research Fellowship, and N.T.L. was an Australian Postgraduate Awardee.

Supporting Information Available: Synthetic and characterization details for **3-16** and **20-31** and tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths and angles, and least-squares plane for **21**, **29**, and **31**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM030253B