Synthesis, Structure, and Electrochemistry of $[(\eta^5\text{-}C_5H_5)_2Mo_2WFe_2(O)_2(S)_2(CO)_9(CCPh)_2]$

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Summary: Thermolysis of a toluene solution containing $[Fe_2W(CO)_{10}(\mu_3\text{-}S)_2]$ *(**1**) and* $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CCPh)]$ *(**2**) in the presence of air at 70 °C yields the mixed-metal cluster* $[(\eta^5\text{-}C_5H_5)_2Mo_2WFe_2(O)_2(S)_2(CO)_9(CCPh)_2]$ *(**3**). The structure of **3** has been established crystallographically. It consists of a triangular* Fe_2W *unit, each face of which is capped by a sulfido ligand. Each Fe atom bears three carbonyl groups, while the W atom is attached to two different Mo-containing moieties. It is π-bonded to the C≡C bond of a* $(\eta^5\text{-}C_5H_5)Mo(CO)_3(C{\equiv}CPh)$ *unit, and it is also bonded to a second Mo atom, and this bond is bridged by an oxo group and a* μ_2,η^2*-CCPh group. Also attached to this Mo atom is a terminal oxo group. Compound **3** has been investigated electrochemically.*

Introduction

The versatility of mononuclear acetylides as basic building blocks in cluster growth reactions to prepare mixed-metal clusters of high nuclearity containing multisite cluster bound polycarbon ligands has been exploited extensively.[1−5] Previously, we have reported on the reactions of some mononuclear acetylide complexes with the chalcogen-bridged iron carbonyl clusters $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$, where E = S, Se, Te. Motivation for this study was to explore the stabilizing role of the chalcogen ligands in the formation of new acetylide-bridged mixed-metal clusters and to investigate unusual acetylide coupling reactions on these clusters. Our investigations revealed that indeed new types of acetylide- and chalcogen-bridged mixed-metal clusters could be obtained by this method, and moreover, a variety of unusual acetylide bonding and coupling could be observed on the new chalcogen-bridged complexes. For example, the reaction between $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$, where E = S, Se, Te, and $[(\eta^5\text{-}C_5Me_5)W(CO)_3(C{\equiv}CPh)]$ resulted in the isolation of the new clusters $[W_2Fe_3(\eta^5\text{-}C_5Me_5)_2(CO)_6(\mu_3\text{-}E)_2\{\mu_4\text{-}CC(Ph)C(Ph)C\}]$, which shows novel tail-to-tail coupling of the acetylide fragments in this cluster environment.[6] The reaction of $[Fe_3(CO)_9(\mu_3\text{-}Se)_2]$ and $[(\eta^5\text{-}C_5Me_5)W(CO)_3(C{\equiv}CPh)]$ in the presence of air yields the unusual diselenaoxoacetylide compound $[(\eta^5\text{-}C_5Me_5)W(O)(Se_2)(CCPh)]$. When the same reaction was carried out under a nitrogen atmosphere, the pentaselenaacetylide compound $[(\eta^5\text{-}C_5Me_5)W(Se_2)(Se_3\text{-}CCPh)]$ was isolated.[7] In this paper, we report on the reaction of the square-pyramidal metal cluster $[Fe_2W(CO)_{10}(\mu_3\text{-}S)_2]$ with $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CCPh)]$, the structure of the unusual cluster formed which has both oxo and acetylide groups, and its electrochemical behavior.

Results and Discussion

When a toluene solution of $[Fe_2W(CO)_{10}(\mu_3\text{-}S)_2]$ (**1**) and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CCPh)]$ (**2**) was heated at 70 °C in the presence of air, an immediate color change was observed. Chromatographic workup yielded a brown compound in pure form, which was characterized as $[(\eta^5\text{-}C_5H_5)_2Mo_2WFe_2(O)_2(S)_2(CO)_9(CCPh)_2]$ (**3**) (Scheme 1). No new products were observed when the reaction was carried out under anaerobic conditions; after reflux in toluene for 3 h, the only observable products in the reaction mixture were trace amounts of the known dimers $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}1,2\text{-}PhC{\equiv}CC{\equiv}CPh)]$ and $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}1,2\text{-}PhC{\equiv}C(CO)C{\equiv}CPh)]$.[8] The structural features of **3** were identified on the basis of IR and ^1H NMR spectroscopy. The IR spectrum of **3** shows bands due to terminally bonded carbonyl groups and a peak at 900 cm $^{-1}$ attributable to the Mo(=O) unit.[9−12] The ^1H NMR spectrum confirms the presence of two types of $\eta^5\text{-}C_5H_5$ groups, as well as a multiplet for the phenyl group protons. For an unambiguous determination of the structure of **3**, single crystals were grown and X-ray structure analysis carried out. Dark brown crystals of **3** were grown from hexane/dichloromethane solvent mixtures at 0 °C. Its molecular structure (Figure 1) can be described as consisting of an Fe_2S_2W trigonal-bipyramidal unit in which the S atoms occupy the apical positions.[13−16] Each Fe atom

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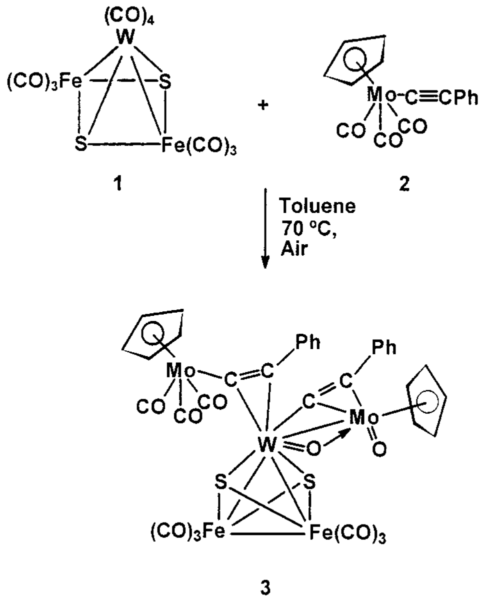
Scheme 1



bears three carbonyl groups, while the W atom is attached to two different Mo-containing moieties. It is π-bonded to the C≡C bond of a $(\eta^5\text{-}C_5H_5)Mo(CO)_3(C{\equiv}CPh)$ unit, and as a result the acetylenic bond is reduced to an olefinic bond (C(41)−C(42), 1.298(4) Å). The W atom is also bound to a second Mo atom via a metal−metal bond, and this bond is bridged by an oxo group and a μ_2,η^2-CCPh group (C(51)−C(52), 1.286(4) Å). Also attached to this Mo atom is a terminal oxo group (Mo(2)−O(16), 1.687(2) Å), comparable in length with the Mo(=O) bonds reported earlier: 1.697(6) and 1.713(7) Å in $[(\eta^5\text{-}C_5H_5)_2Mo_2({=}O)(\mu\text{-}Te)(\mu\text{-}NC_6H_5)]$,[17] 1.700(2) Å in *trans*-$[(\eta^5\text{-}C_5H_5)_2Mo({=}O)_2(\mu\text{-}S)_2]$,[18] 1.705(4) Å in *trans*-$[(\eta^5\text{-}C_5H_5)_2Mo_2({=}O)_2(\mu\text{-}Se)_2]$,[9] and 1.691(5) Å in *cis*-$[(\eta^5\text{-}C_5H_5)_2Mo_2({=}O)_2(\mu\text{-}Se)_2]$.[9,11]

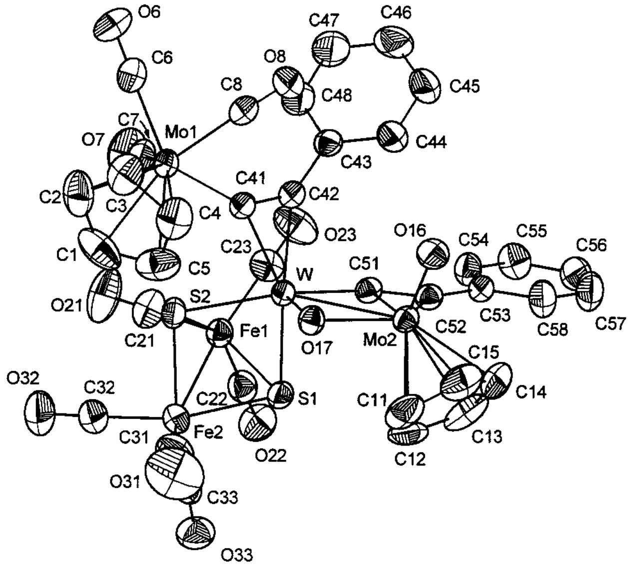


Figure 1. Molecular structure of **3** with 30% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): Fe(1)−Fe(2) = 2.5303(7), Fe(1)−W = 3.0677(9), W−Mo(2) = 2.9038(7), C(41)−C(42) = 1.298(4), C(51)−C(52) = 1.286(4), W−C(51) = 2.002(3), Mo(2)−C(51) = 2.169(3), Mo(1)−C(41) = 2.185(3), W−S(1) = 2.4774(10), W−S(2) = 2.4428(9), Fe(1)−S(1) = 2.2860(10), Fe(1)−S(2) = 2.2847(11), Fe(2)−S(1) = 2.2712(10), Fe(2)−S(2) = 2.2650(11); Mo(1)−C(41)−C(42) = 146.3(2), C(41)−C(42)−C(43) = 142.2(3), W−O(17)−Mo(2) = 96.34(9), W−C(51)−Mo(2) = 88.14(11), Mo(2)−C(51)−C(52) = 71.24(18), Mo(2)−C(52)−C(53) = 143.5(2), Fe(2)−Fe(1)−W = 80.48(2), C(51)−C(52)−C(53) = 142.4(3).

Although the exact mechanism of formation of **3** cannot be established at present, there are some structural features of **3** which deserve mention. There is a formal conversion of the Fe_2WS_2 square-pyramidal core of **1** into a trigonal-pyramidal geometry of this unit in which the three metal atoms occupy the equatorial positions. A satisfactory electron count around the metal atoms in **3** can be made on the assumption that each S atom contributes one electron to each of the Fe atoms and two electrons to the W atom and that the linkage between the W atom and the oxo-bearing Mo atom is a double bond. Alternatively, if one considers that the unit $\{(\eta^5\text{-}C_5H_5)Mo(CO)_3(C{\equiv}CPh)\}$ (ligand 1) contributes two electrons and that the $Fe_2(CO)_6S_2$ unit (ligand 2) contributes six electrons to the W atom, then the W−Mo unit in **3**, written as $[(\text{ligand 1})(\text{ligand 2})W(\mu\text{-}O)(\mu\text{-}C{=}CPh)Mo(\eta\text{-}C_5H_5)]$, can be regarded as having 32 cluster valence electrons and hence is electronically unsaturated. However, the W−Mo(2) separation of 2.9038(7) Å is appreciably longer than those found in other electronically unsaturated dimetal complexes with 32 cluster valence electrons: $[MoW(\mu\text{-}C_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$, 2.657(2) Å;[19] $[MoW\{\mu\text{-}\sigma\text{-}\eta\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2\}(CO)_3(\eta\text{-}EtC_2Et)(\eta^5\text{-}C_9H_7)]$, 2.604(1) Å;[20] $[MoW(\mu\text{-}PPh_2)\{\mu\text{-}C(OH)C(C_6H_4Me\text{-}4)(CO)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{11})]$, 2.713(1) Å; $[MoW(\mu\text{-}PPh_2)(CO)_3(\eta^5\text{-}C_9H_7)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$, 2.708(1) Å.[21] In fact, the W−Mo(2) separation in **3** is more comparable to those found in the electronically saturated trimetal 48-electron cluster $[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (2.881(3) and 2.867(3) Å)[22] and the dimetal 34-electron cluster $[MoW\{(\mu\text{-}C(C_6H_4\text{-}OMe\text{-}2)C(Me)O\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (2.935(1) Å).[23]

Interestingly though, the cluster $[MoW(\mu\text{-}C_4Me_4)\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2\}(\eta\text{-}C_7H_7)]$, which is electronically unsaturated with 30 cluster valence electrons, has a Mo−W separation of 2.922(1) Å.[24] Thus, we see examples of electronically unsaturated complexes with 30 cluster valence electrons having a large Mo−W separation (~2.9 Å) and others with 32 cluster valence electrons having a shorter W−Mo separation (~2.6−

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2.7 Å). It would therefore appear, as has been suggested by Stone et al. earlier,[24] that the metal−metal distances are strongly influenced by the steric and bonding requirements of the bridging ligands. A second description of the structure, which gives a 34-electron count to the W−Mo portion of **3**, assumes that the bridging oxo ligand is a net 4-electron donor, of the type W═O→Mo. Assignment of a double bond between W and O atoms is supported by the short W−O(17) distance, 1.822(2) Å, which is similar to the W═O bond distances observed in the fragments W═O→M (M = Ru, Os) in several $WOs_3(\mu\text{-}O)$, $WRu_4(\mu\text{-}O)$, and $WRu_5(\mu\text{-}O)$ clusters reported previously.[25] The Mo(2)−O(17) distance of 2.068(2) Å is considerably longer and is consistent with a single bond. The W−Mo portion of **3** is therefore saturated, according to this description, and the W−Mo(2) bond can be regarded as a single bond. Another feature of some significance in **3** is the attachment of the W atom, which is completely stripped of its carbonyl groups, to two different molybdenum−acetylide units. While one of the molybdenum−acetylide units remains almost unchanged and is attached to the W atom by means of a π-bond between the acetylide group and the tungsten atom, the second molybdenum acetylide moiety undergoes oxidation, resulting in complete removal of the carbonyl groups and incorporation of two oxo groups. Its attachment to the W atom by means of a direct metal−metal bond which contains a bridging oxo group can be compared with the oxo-bridged compounds $[(\eta^5\text{-}C_5H_5)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}Te)]$ and $[(\eta^5\text{-}C_5H_5)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)]$, which were obtained from the thermolysis of $[(\eta^5\text{-}C_5H_5)_2Mo_2Fe_2(CO)_7(\mu_3\text{-}S)(\mu_3\text{-}Te)]$ in the presence of air.[11]

Redox Properties of Complex 3. The redox properties of complex **3** have been studied by cyclic voltammetric and differential pulse voltammetric techniques in dichloromethane solution using a platinum working electrode. It exhibits one irreversible oxidation process, $E_{p,a}$, at 1.56 V and one quasi-reversible reduction process, $E°_{298}$, at −1.62 V ($\Delta E_p = 130$ mV) versus SCE (Figure 2) (under identical experimental conditions the ferrocene/ferrocenium couple appears at 0.58 V versus SCE[26]). The peak potential ($E_{p,a}$) of the oxidation process varies depending on the scan rate; a shift of 100 mV has been observed on changing the scan rate from 50 to 500 mV s^{-1} (Figure 2, inset). The peak current of the oxidation wave varies linearly with the square root of the scan rate. The increase in current height of the small reduction wave $E_{p,c}$ at 0.7 V with that of the oxidation wave $E_{p,a}$ at 1.56 V at higher scan rates implies that the $E_{p,c}$ value at 0.7 V is essentially the counterpart of the oxidation wave, $E_{p,a}$, at 1.56 V. This also indicates that the degree of reversibility of the process increases to a certain extent at higher scan rates. However, the general irreversible nature of the oxidation process remains unchanged even at a higher scan rate (1 V s^{-1}). The one-electron nature of the quasi-reversible reduction process is established from the current height consideration.[27] Although the anodic current height ($i_{p,a}$) of the irreversible oxidation process is ~1.5 times that of the quasi-reversible reduction process, the differential pulse voltammograms show the oxidation wave to have the same height as that of the reduction process, implying a one-electron process (Figure 2). The observed electron-transfer processes may be assigned to be the one-electron irreversible oxidation and quasi-reversible reduction of the oxomolybdenum center of **3**. The assignment of the observed oxidation and reduction processes specifically at the Mo center is made on the basis of the consideration that the oxomolybdenum center is known to be a facile electron-transfer center.[28]

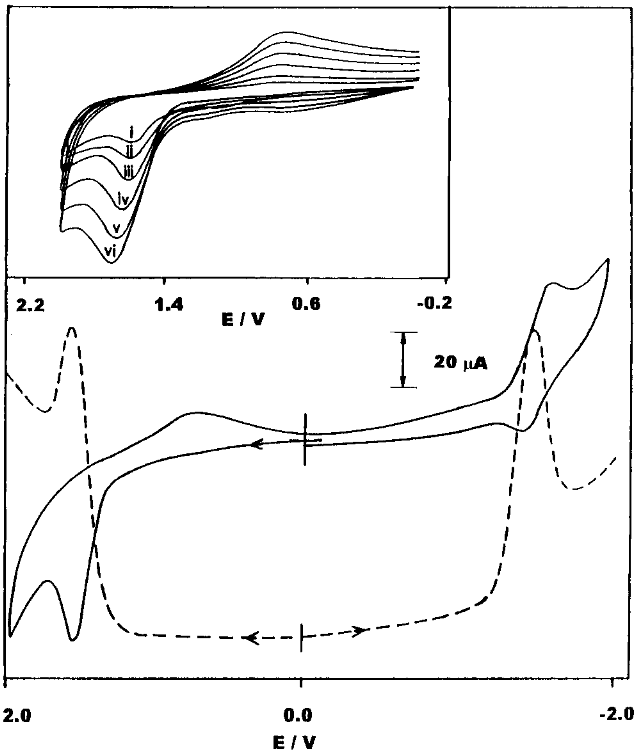

Figure 2. Cyclic voltammogram (−) and differential pulse voltammogram (- - -) of **3** in dichloromethane solvent (scan rate 50 mV s^{-1}). The inset shows the cyclic voltammograms at different scan rates (mV s^{-1}): (i) 50; (ii) 100; (iii) 200; (iv) 300; (v) 400; (vi) 500 (positive side only).

The electronic spectrum of this complex has been recorded in dichloromethane solvent in the range of 700−190 nm. The complex exhibits multiple transitions in the UV−visible region (Experimental Section). On the basis of their high intensities, the bands are assigned to be charge transfer in nature.

Conclusion

On use of aerobic conditions, an unusual reaction of $[CpMo(CO)_3C{\equiv}CPh]$ with $[Fe_2WS_2(CO)_{10}]$ is observed. In the formation of cluster **3** we see two different metal−acetylide units incorporated within the cluster framework. Although designation of formal oxidation states to metal centers is frequently unclear in cluster complexes, in **3** we can assign formal oxidation states of 0

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and +5 to the two Mo centers. Such a contrast in the oxidation states of two metal atoms in the same cluster molecule is unusual. Further work is in progress to investigate the role of the chalcogen and the reactivity of such clusters which contain both the oxo and acetylide moieties.

Experimental Section

Reactions and manipulations were carried out using standard Schlenk line techniques under an atmosphere of prepurified nitrogen, unless otherwise stated. Solvents were purified, dried, and distilled under an argon or nitrogen atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FTIR spectrophotometer, as hexane solutions in 0.1 mm path length cells; ^{1}H NMR spectra were recorded on a Varian VXR-300S spectrometer in $CDCl_3$. Elemental analyses were performed using a Carlo-Erba automatic analyzer. Electrochemical measurements were carried out using a PAR Model 273 A potentiostat/galvanostat. A platinum-wire working electrode (length 0.3 cm and diameter 0.5 mm), a platinum-wire auxiliary electrode, and a saturated calomel electrode (SCE) were used in a three-electrode configuration. Tetraethylammonium perchlorate (TEAP) was the supporting electrolyte, and the solute concentration was $\sim 10^{-3}$ M. The half-wave potential $E°_{298}$ was set equal to 0.5 ($E_{p,a} + E_{p,c}$), where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic cyclic voltammetric peak potentials, respectively. For irreversible processes $E_{p,a}$ and $E_{p,c}$ are considered. Electronic spectra were recorded using a Shimadzu UV-2100 spectrophotometer. The compound [CpMo(CO)$_3$C≡CPh] (**2**) was prepared by an established procedure.[29] The new compound [$Fe_2W(CO)_{10}(\mu_3\text{-}S)_2$] was prepared by the method used previously for obtaining the related compounds [$Fe_2W(CO)_{10}(\mu_3\text{-}Se)_2$] and [$Fe_2W(CO)_{10}(\mu_3\text{-}Te)_2$].[30]

Preparation of [$Fe_2W(CO)_{10}(\mu_3\text{-}S)_2$]. A THF solution (120 mL) of [$W(CO)_6$] (256 mg, 0.73 mmol) was irradiated with 366 nm UV light in an immersion type photolysis instrument for 15 min under a constant argon purge. The lemon yellow solution of [$W(CO)_5(THF)$] was added to a hexane solution (50 mL) containing [$Fe_2(CO)_6(\mu\text{-}S)_2$] (25 mg, 0.73 mmol), and the reaction mixture was stirred at room temperature for 3 h. The solvent was removed in vacuo, and the residue was subjected to chromatographic workup on a silica gel column, 30 cm in length and 2 cm in diameter. Elution with hexane yielded trace amounts of [$W(CO)_6$] and [$Fe_2(CO)_6(\mu\text{-}S)_2$] followed by a major maroon band of compound **1** (125 mg, 45%).

Data for **1** are as follows. IR (hexane; cm^{-1}): ν(CO), 2093 (w), 2055 (vs), 2048 (vs), 2012 (s, br), 1972 (w). Mp: 130 °C dec. Anal. Calcd (found) for $C_{10}Fe_2O_{10}S_2W$: C, 18.8 (18.8).

Reaction of [$Fe_2WS_2(CO)_{10}$] with [CpMo(CO)$_3$C≡CPh]. A toluene solution (30 mL) of [$Fe_2WS_2(CO)_{10}$] (10 mg, 0.0156 mmol) and [CpMo(CO)$_3$C≡CPh] (30 mg, 0.0864 mmol) was heated at 70 °C for 15 min with constant stirring. The solvent was removed in vacuo, and the residue was subjected to chromatographic workup using silica gel TLC plates (20 × 20 cm, 0.20 mm thickness). On elution with a hexane−dichloromethane mixture (60:40, v/v), compound **3** was separated (4 mg, 23%) together with unreacted [CpMo(CO)$_3$C≡CPh]. Several other compounds could be seen on the TLC plate but could not be isolated due to decomposition. Attempts to isolate these compounds by column chromatography were also unsuccessful.

Data for **3** are as follows. IR (hexane; cm^{-1}): ν(CO), 2062 (vs), 2036 (s), 2023 (vs), 1997 (s), 1978 (m), 1965 (s); ν(Mo=O), 900. UV (dichloromethane; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 478 (6617), 330 sh (29 278), 284 (42 059), 232 (69 706). ^{1}H NMR (δ, ppm): δ 5.96 (s, C_5H_5), 6.24 (s, C_5H_5), 7.48−7.61 (m, C_6H_5). Mp: 192 °C dec. Anal. Calcd (found) for $C_{35}Fe_2H_{20}Mo_2O_{11}S_2W$: C, 35.89 (35.6); H, 1.72 (1.90).

Crystal Structure Determination. A single crystal of complex **3** was grown from dichloromethane−hexane solvent mixtures at 0 °C. Data were collected on a Nonius MACH3 four-circle diffractometer (graphite-monochromatized Mo Kα radiation) for the cell determination and intensity data collection. The unit cell parameters were derived and refined by using randomly selected reflections in the θ range ∼22−28°. The structure was solved by direct methods using the SHELXS93 program and refined by using SHELXL97 software.[31] The non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms were geometrically fixed and refined using a riding model. Absorption correction was employed using ψ scans[32] ($T_{max} = 1.000$, $T_{min} = 0.719$). The size of the crystal was 0.5 × 0.2 × 0.1 mm.

Crystal data for $C_{35}Fe_2H_{20}Mo_2O_{11}S_2W$ (**3**): $M_r = 1168.06$, triclinic, $P\bar{1}$, $a = 9.650(18)$ Å, $b = 13.058(2)$ Å, $c = 16.367(5)$ Å, $\alpha = 88.127(18)°$, $\beta = 88.312(2)°$, $\gamma = 68.876(14)°$, $Z = 2$, $V = 1923.6(8)$ Å^3, $T = 293(2)$ K, $\mu = 4.514$ mm^{-1}, 7261 [6770] collected reflections, R1 = 0.0719, wR2 = 0.0420 [for $I > 2\sigma(I)$], R1 = 0.0231, wR2 = 0.0433 (for all data).

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Supporting Information Available: Details of the structure determination for **3**, including tables listing atomic coordinates, thermal parameters, and bond distances and angles and figures showing structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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