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Synthesis, Structure, and Electrochemistry of Acetylide and Oxo Incorporated Mixed Fe/Mo and Fe/W Chalcogen-Bridged Clusters

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Thermolysis of a benzene solution containing $[Fe_2Mo(CO)_{10}(\mu_3\text{-}Se)_2]$ (**1**) and $[(\eta^5\text{-}C_5Me_5)W(CO)_3C{\equiv}CPh]$ (**2**) under an optimum concentration of oxygen in the reaction medium yields the cluster $[(\eta^5\text{-}C_5Me_5)MoWFe_2(O)(\mu_3\text{-}Se)(\mu_4\text{-}Se)(CO)_8(CCPh)]$ (**3**), containing a monooxygenated metal center. Under an argon atmosphere, thermolysis of $[Fe_2Mo(CO)_{10}(\mu_3\text{-}S)_2]$ (**4**) with $[(\eta^5\text{-}C_5Me_5)W(CO)_3C{\equiv}CPh]$ (**2**) in benzene leads to an oxygen-free mixed metal cluster $[(\eta^5\text{-}C_5Me_5)MoWFe_4(\mu_3\text{-}S)_3(\mu_4\text{-}S)(CO)_{14}(CCPh)]$ (**9**). Interestingly, on reacting a benzene solution of **4** with **2** and $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3C{\equiv}CPh]$ (**5**) under an increased concentration of oxygen in the reaction medium gave way to clusters $[(\eta^5\text{-}C_5Me_5)WMo_2(\mu\text{-}O)_2(\mu\text{-}S)(\mu_3\text{-}CCPh)\{Fe_2(CO)_6(\mu_3\text{-}S)_2\}_2]$ (**6**), $[(\eta^5\text{-}C_5Me_5)WMo(O)_2(\mu\text{-}O)(\mu\text{-}CCPh)\{Fe_2(CO)_6(\mu_3\text{-}S)_2\}]$ (**7**), and $[(\eta^5\text{-}C_5Me_5)Mo_3(\mu\text{-}O)_2(\mu\text{-}S)(\mu_3\text{-}CCPh)\{Fe_2(CO)_6(\mu_3\text{-}S)_2\}_2]$ (**8**) with higher oxygen content. The structures of the newly formed clusters **3**, **6**, **7**, **8**, and **9** were established crystallographically and the oxo-containing Mo and W clusters investigated electrochemically.

Introduction

Organometallic oxo complexes serve as realistic models for metal-mediated oxidation and other homogeneous and heterogeneous reactions with high-valent metal species as catalysts.[1,2] As a result, a large number of oxo complexes have been synthesized and their reactivities with organic substrates have been studied. To probe the oxo ligand in promoting various transformations on metal complexes, considerable interest exists in the synthesis of complexes containing both oxo and hydrocarbyl ligands.

The conventional method of preparing organometallic oxo complexes from carbonyl complexes involves a thermally or photochemically induced reaction in the presence of air or oxygen.[3,4] However, several other methods have been reported for obtaining a diverse array of organometallic complexes bearing oxo ligands. For instance, the use of trimethylamine-*N*-oxide was found to be essential in the air oxidation of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ ($R = R' = CO_2Me$ or Ph; $R = H$, $R' = Ph$; or $R = H$, $R' = CO_2Me$) to form $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}RCCR')]$.[5] Treatment of a THF solution of $[(\eta^5\text{-}C_5H_5)W(NO)(o\text{-}tolyl)_2]$ with water affords its structural isomer $[(\eta^5\text{-}C_5H_5)W(O)(N\text{-}o\text{-}tolyl)(o\text{-}tolyl)]$.[6] The oxo-bridged mixed metal complex $[(\eta^5\text{-}C_5Me_5)Ti(\mu_3\text{-}O)_3Rh(COD)_3]$ has been obtained from the reaction of $[(\eta^5\text{-}C_5Me_5)TiMe_3]$ with $[Rh(\mu_2\text{-}OH)(COD)]_2$.[7] Oxidation of $[(\eta^5\text{-}C_5Me_5)MCl_4]$ ($M = Mo$ or W) with hydrogen peroxide provides a high yield synthesis of the oxo-peroxo complexes $[(\eta^5\text{-}C_5Me_5)M(O)(O_2)Cl]$.[8] Several oxo-containing cluster complexes have also been reported.[9−11] At least in some cases, the formation and type of metal-oxo complex have been found to be highly sensitive to the reaction conditions used. For instance, $[(\eta^5\text{-}C_5Me_5)_2V]$ reacts with different concentrations of oxygen to form three types of complexes: 1:2 molar excess of oxygen gives $[(\mu\text{-}\eta^3\text{-}C_5Me_5O_3)V(O)]_2$; in the presence of trace amounts of oxygen, $[(\eta^5\text{-}C_5Me_5)V]_4(\mu\text{-}O)_6$ is formed; and when a large excess of oxygen is used, $[(\eta^5\text{-}C_5Me_5)_6V_8(O)_{17}]$ is obtained.[12]

We became interested in oxo-containing complexes after a serendipitous discovery of the complex $[(\eta^5\text{-}C_5H_5)_2Mo_2WFe_2(O)_2(S)_2(CO)_9(CCPh)_2]$[13] during our work

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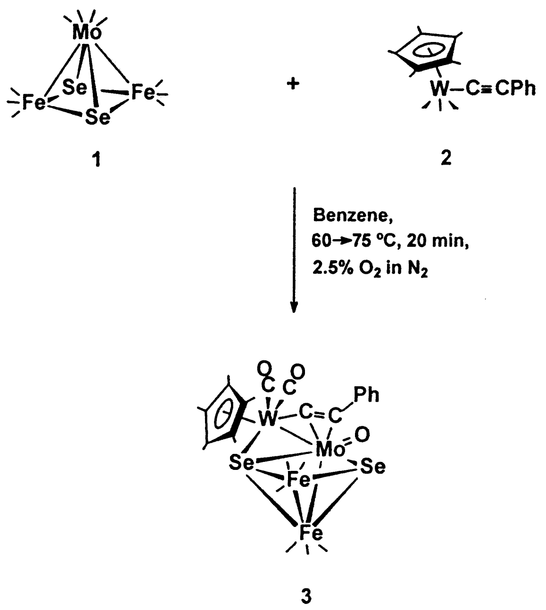
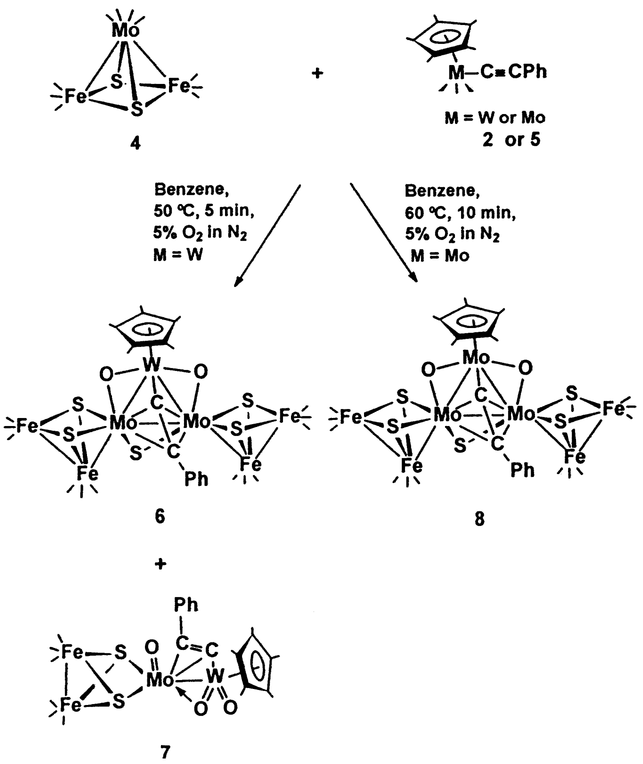
Scheme 1



Scheme 2



on acetylide-bridged cluster complexes.[14−18] In our efforts to systematize the synthesis of other chalcogen-stabilized mixed metal clusters containing both the acetylide and the oxo groups, we have isolated a number of such species, formation of which takes place only under limited concentration of oxygen in the reaction medium. We hereby report on the reactions of [$Fe_2Mo(CO)_{10}(\mu_3\text{-}Se)_2$] and [$Fe_2Mo(CO)_{10}(\mu_3\text{-}S)_2$] with [$LM(CO)_3C{\equiv}CPh$] [where L = ($\eta^5$-$C_5Me_5$), ($\eta^5$-$C_5H_5$) and M = Mo or W], the structures of the new clusters obtained, and their electrochemical behavior.

Results and Discussion

Reaction of [$Fe_2Mo(CO)_{10}(\mu_3\text{-}E)_2$] (E = S, Se) with [($\eta^5$-$C_5Me_5$)$M(CO)_3$-$C{\equiv}CPh$] (M = Mo, W) under Aerobic Conditions. When a benzene solution of [$Fe_2Mo(CO)_{10}(\mu_3\text{-}E)_2$] (E = S, Se) and [($\eta^5$-$C_5Me_5$)$M(CO)_3C{\equiv}CPh$] (M = Mo, W) was exposed to air, rapid decomposition of both starting materials was observed without observation of formation of any new products. At lower concentrations of oxygen, 2.5−5% O_2 in N_2, [$Fe_2Mo(CO)_{10}(\mu_3\text{-}Se)_2$] (**1**) reacts with [($\eta^5$-$C_5Me_5$)$W(CO)_3C{\equiv}CPh$] (**2**) to form the oxo- and acetylide-bridged cluster [(η^5-C_5Me_5)$MoWFe_2(O)(\mu_3\text{-}Se)(\mu_4\text{-}Se)(CO)_8(CCPh)$] (**3**) (Scheme 1) and [$Fe_2Mo(CO)_{10}(\mu_3\text{-}S)_2$] (**4**) reacts with [($\eta^5$-$C_5Me_5$)$W(CO)_3C{\equiv}CPh$] (**2**) to form the clusters [(η^5-C_5Me_5)$WMo_2(\mu\text{-}O)_2(\mu\text{-}S)(\mu_3\text{-}CCPh)\{Fe_2(CO)_6(\mu_3\text{-}S)_2\}_2$] (**6**) and [($\eta^5$-$C_5Me_5$)$WMo(O)_2(\mu\text{-}O)(\mu\text{-}CCPh)\{Fe_2(CO)_6(\mu_3\text{-}S)_2\}$] (**7**) (Scheme 2). Compound **4** also reacts with the molybdenum acetylide complex [(η^5-C_5Me_5)$Mo(CO)_3C{\equiv}CPh$] (**5**) under similar conditions to form [(η^5-C_5Me_5)$Mo_3(\mu\text{-}O)_2(\mu\text{-}S)(\mu_3\text{-}CCPh)\{Fe_2(CO)_6(\mu_3\text{-}S)_2\}_2$] (**8**). In this reaction we did not observe any formation of [(η^5-C_5Me_5)$Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}CCPh)\{Fe_2(CO)_6(\mu_3\text{-}S)_2\}$], the S-analogue of **7**.

Structural features of **3**, **6**, **7**, and **8** were identified on the basis of IR and ^{1}HNMR spectroscopy. The IR spectrum of **3** shows bands due to terminally bonded carbonyl groups and a band at 943 cm^{-1} attributable to Mo(=O) group.[19−22] Its NMR spectrum confirms the presence of only one type of (η^5-C_5Me_5) group. For an unambiguous determination of the structure of **3**, its single crystals were grown from hexane/dichloromethane solvent mixtures at 0 °C, and X-ray structure analysis was carried out. Its molecular structure (Figure 1) can be described as consisting of a distorted square pyramidal Fe_2MoSe_2 core in which the apical site is occupied by one of the iron atoms. Both iron atoms bear three carbonyls, the molybdenum has one terminal oxo group, and one of the Mo−Se edges is bridged by a (η^5-C_5Me_5)$W(CO)_2$ group. The W−Mo bond is bridged by a η^1,η^2-CCPh group. The Mo−O(7) bond distance, 1.685(3) Å, is comparable in length with the Mo(=O), 1.687(2) Å, reported earlier for [(η^5-C_5H_5)$_2MoWFe_2(O)_2(S)_2(CO)_9(CCPh)_2$].[13] The Fe−Mo bond distance, 2.9488(8) Å, is longer than the Fe−Mo distances of 2.823(4) and 2.794(4) Å reported for the square pyramidal cluster [$Fe_2Mo(CO)_{10}(\mu_3\text{-}Se)_2$][23] and only slightly shorter than the somewhat long Mo−Fe bond distance of 3.083(5) Å reported for the hourglass cluster [$Fe_4Mo(CO)_{14}(\mu_3\text{-}Se)_2$-

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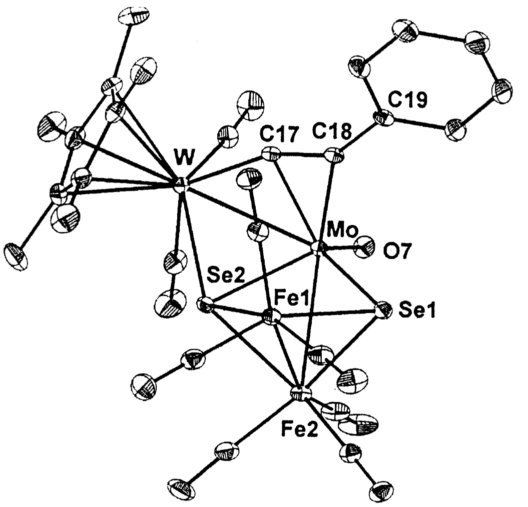

Figure 1. ORTEP diagram of [(η^5-C_5Me_5)MoWFe$_2$(O)(μ_3-Se)(μ_4-Se)(CO)$_8$(CCPh)] (**3**) with 50% probability ellipsoids. Selected bond distances (Å) and bond angles (deg): Fe(1)−Fe(2) = 2.5511(10), Fe(2)−Mo = 2.9488(8), Se(1)−Mo = 2.4528(6), Se(2)−Mo = 2.5641(6), Se(2)−W = 2.7057(5), Mo−O(7) = 1.685(3), Mo−W = 2.9244(6), C(17)−C(18) = 1.303(6), W−C(17)−C(18) = 160.7(3), C(17)−C(18)−C(19) = 144.5(4).

(μ_3-Te)$_2$], which contains a 10-coordinate Mo atom.[24] The acetylide carbon atoms form a shorter bond, C(17)−C(18) 1.303(6) Å, than in the similarly bonded acetylide group (1.34(2) Å) in the other known example of a mixed metal complex containing both an oxo and an acetylide moiety, [Cp*Re(O)(μ-C_2Ph)W(CO)$_2$Cp].[25] All other bond metricals appear unexceptional.

The IR spectra of **6**, **7**, and **8** indicate the presence of only terminally bonded carbonyls, and the stretching patterns for compounds **6** and **8** are similar. Additionally, the spectra for **6** and **8** show a band at 826 and 845 cm^{-1}, respectively, consistent with the presence of bridging oxo groups, while the spectrum of **7** shows bands at 958 and 818 cm^{-1} for terminally bonded and bridging oxo groups, respectively. The presence of a (η^5-C_5Me_5) group in each compound is confirmed by the presence of a single band in the ^{1}H NMR spectra.

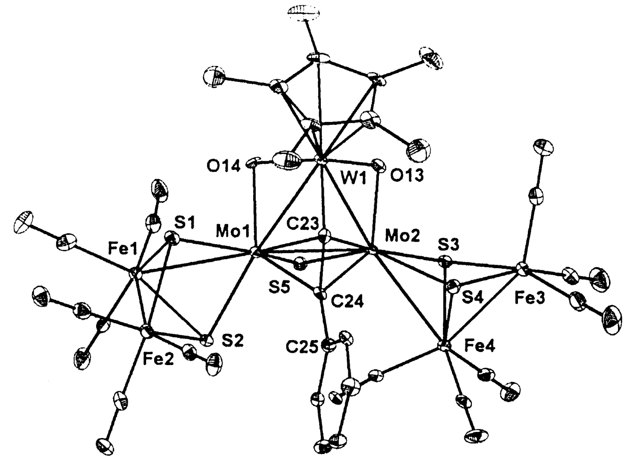

Figure 2. ORTEP diagram of [(η^5-C_5Me_5)WMo$_2$(μ-O)$_2$(μ-S)(μ_3-CCPh){Fe$_2$(CO)$_6$(μ_3-S)$_2$}$_2$] (**6**) with 50% probability ellipsoids. Selected bond distances (Å) and bond angles (deg): Fe(1)−Fe(2) = 2.5502(17), Fe(3)−Fe(4) = 2.5498(17), Fe(1)−Mo(1) = 2.8208(15), Fe(4)−Mo(2) = 2.8561(13), Mo(1)−Mo(2) = 2.6914(11), Mo(1)−W(1) = 2.7768(8), Mo(2)−W(1) = 2.7320(8), Mo(1)−O(14) = 2.096(5), W(1)−O(14) = 1.834(6), Mo(2)−O(13) = 1.962(5), W(1)−O(13) = 1.898(5), Mo(1)−S(5) = 2.295(2), Mo(2)−S(5) = 2.317(2), C(23)−C(24) = 1.372(10), C(23)−C(24)−C(25) = 134.2(7), W(1)−C(23)−Mo(1) = 84.3(3), W(1)−C(23)−Mo(2) = 81.4(3), W(1)−O(13)−Mo(2) = 90.1(2), W(1)−O(14)−Mo(1) = 89.6(2), Mo(1)−S(5)−Mo(2) = 71.40(7).

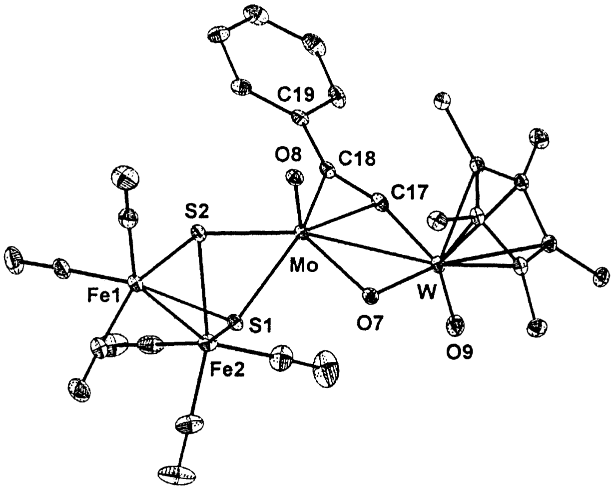

Figure 3. ORTEP diagram of [(η^5-C_5Me_5)WMo(O)$_2$(μ-O)(μ-CCPh){Fe$_2$(CO)$_6$(μ_3-S)$_2$}] (**7**) with 50% probability ellipsoids. Selected bond distances (Å) and bond angles (deg): Fe(1)−Fe(2) = 2.5219(8), Mo−S(1) = 2.4302(9), Mo−S(2) = 2.4375(10), Mo−O(8) = 1.673(3), Mo−W = 2.8571(4), Mo−O(7) = 2.017(3), W−O(7) = 1.873(3), W−O(9) = 1.711(3), C(17)−C(18) = 1.276(6), W−C(17)−C(18) = 157.6(3), C(17)−C(18)−C(19) = 144.7(4), O(7)−W−O(9) = 105.88(14), O(8)−Mo−O(7) = 104.85(13).

Crystals of **6**−**8** were grown from hexane/dicloromethane solvent mixtures at 0 °C, and single-crystal X-ray analyses were undertaken. The molecular structures of **6** and **8** (Figures 2 and 4, respectively) show an identical cluster core geometry consisting of two distorted square pyramid MoFe$_2$S$_2$ units joined via a Mo−Mo bond which is bridged by a (η^5-C_5Me_5)W group in **6** and by a (η^5-C_5Me_5)Mo group in **8**. The edges of the Mo$_2$W triangle of **6** and the Mo$_3$ triangle of **8** are bridged by a sulfido and two oxo groups, and the face is capped by a phenylacetylide moiety. Each iron atom bears three terminal carbonyls. The sulfido-bridged Mo−Mo bond in **6** (2.6914(11) Å) is slightly shorter than the two types of Mo−Mo bonds in **8**: the sulfido-bridged one, Mo(1)−Mo(2) (2.7397(3) Å), and the oxo-bridged, Mo(1)−Mo(3) (2.7217(3) Å) and Mo(2)−Mo(3) (2.7221(3) Å). The oxo bridges are symmetrical with the Mo−O distances of 2.096(5) and 1.962(5) Å in **6** and 1.8972(14)−1.9467(14) Å in **8** being slightly shorter than the Mo to bridging oxo distances in [Cp$_2$Mo$_2$(O)$_2$(μ-O)(μ-Te)] and [Cp$_2$Mo$_2$(O)$_2$(μ-O)(μ-S)] (2.202(3)−2.236(3) Å).[21] All other bonding parameters are unexceptional.

The molecular structure of **7** (Figure 3) can be described as consisting of an open Fe$_2$S$_2$ butterfly unit in which sulfur atoms are attached to the molybdenum atom of a Mo(=O)W(=O)(η^5-C_5Me_5)(μ-O)(μ-CCPh) unit. The two terminal oxo groups in **7** prefer to adopt the somewhat rare trans geometry, similar to the terminal oxo groups in the Te-bridged [Cp$_2$Mo$_2$(O)$_2$(μ-O)(μ-Te)].[21]

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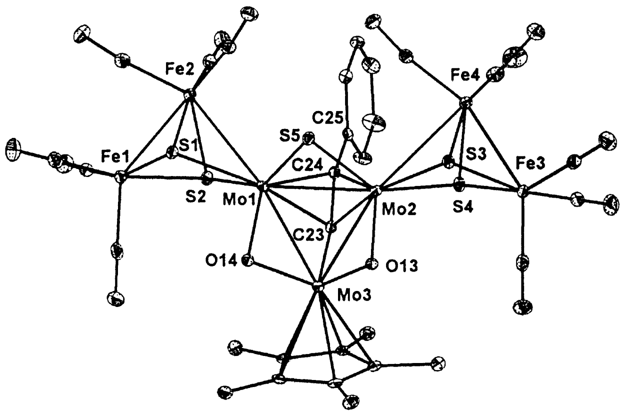
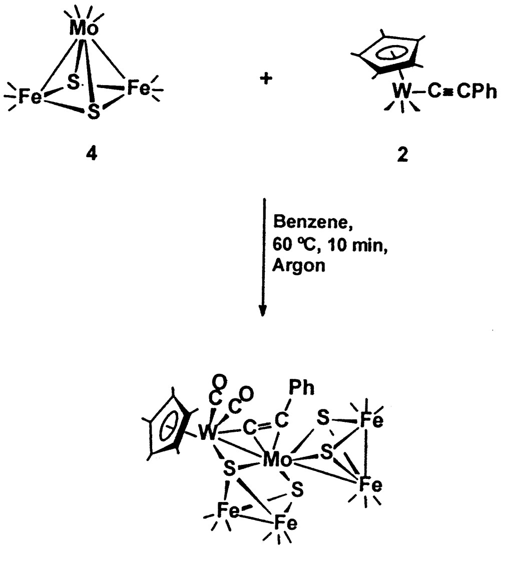


Figure 4. ORTEP diagram of [(η^5-C_5Me_5)Mo_3(μ-O)$_2$(μ-S)(μ_3-CCPh){$Fe_2(CO)_6$(μ_3-S)$_2$}$_2$] (**8**) with 50% probability ellipsoids. Selected bond distances (Å) and bond angles (deg): Fe(1)−Fe(2) = 2.5487(5), Fe(3)−Fe(4) = 2.5472(4), Fe(2)−Mo(1) = 2.9188(4), Fe(4)−Mo(2) = 2.9695(4), Mo(1)−Mo(3) = 2.7217(3), Mo(1)−Mo(2) = 2.7397(3), Mo(2)−Mo(3) = 2.7221(3), Mo(1)−O(14) = 1.9467(14), Mo(3)−O(14) = 1.8972(14), Mo(2)−O(13) = 1.9251(14), Mo(3)−O(13) = 1.9110(14), Mo(1)−S(5) = 2.3153(6), Mo(2)−S(5) = 2.3178(6), C(23)−C(24) = 1.327(3), C(23)−C(24)−C(25) = 138.8(2), Mo(3)−C(23)−Mo(2) = 80.92(7), Mo(3)−C(23)−Mo(1) = 81.17(7), Mo(1)−O(14)−Mo(3) = 90.14(6), Mo(2)−O(13)−Mo(3) = 90.40(6), Mo(1)−S(5)−Mo(2) = 72.504(17).

Each iron atom has three terminal carbonyls. The Mo−W bond is bridged unsymmetrically by a four-electron oxo group: Mo−O(7) = 2.017(3) Å, W−O(7) = 1.873(3) Å are comparable to the Mo−O and W−O distances of 2.068(2) and 1.822(2) Å, respectively, in [(η^5-C_5H_5)$_2$MoWFe$_2$(O)$_2$(S)$_2$(CO)$_9$(CCPh)$_2$], which also features an unsymmetrical bridging of a Mo−W bond by an oxo group.[13] The W−O distance of 1.793(5) Å in [(C_5Me_5)W(O)$_2$Ru$_4$(CO)$_{10}$(μ_4-PPh)(CCPh)],[10] in which a W−Ru bond is unsymmetrically bridged by an oxo group, is, however, shorter than the distance in our compound **7**. The terminal Mo═O(8) bond distance of 1.673(3) Å in **7** is similar to that in **3** as well as in [Cp_2Mo_2(O)$_2$(μ-O)(μ-Te)] (1.693(4) Å) and [Cp_2Mo_2(O)$_2$(μ-O)(μ-S)] (1.694(8) Å),[21] and the W−O(9) distance of 1.711(3) Å is close to that of a double bond between tungsten and an oxo group (1.711(6) Å) observed in [(η^5-C_5Me_5)W(O)$_2$(CCPh)Ru$_6$(μ_6-C)(CO)$_{14}$].[26]

Reaction of [$Fe_2Mo(CO)_{10}$(μ_3-E)$_2$] (E = S, Se) with [(η^5-C_5Me_5)M(CO)$_3$C≡CPh] (M = Mo, W) under Anaerobic Conditions. At room temperature, no observable reaction was observed between compound **1** and the molybdenum or the tungsten acetylide compounds **2** and **5**, respectively. On mild thermolysis, cluster **1** gradually decomposes after a period of 1 h, and **2** and **5** are recovered intact from the reaction medium without observation of any new product. A similar observation was made when **4** was made to interact with **5**. There is, however, a sole new product isolable from the reaction of **4** with the tungsten acetylide compound **2** under the conditions shown in Scheme 3. The new compound has been characterized as [(η^5-C_5Me_5)MoWFe$_4$(μ_3-S)$_3$(μ_4-S)(CO)$_{14}$(CCPh)] (**9**). Its IR spectrum shows a complex six-band terminal carbonyl stretching pattern, and the ^{1}H NMR spectrum shows a single peak for the (η^5-C_5Me_5) group. Dark green crystals of **9** were grown from hexane/dichloromethane solvent mixtures at 0 °C, and a single-crystal X-ray analysis was undertaken. The molecular structure of **9**, shown in Figure 5, consists of an Fe_2MoS_2 distorted square pyramid unit in which the basal Mo atom is bonded to the two sulfur atoms of an open Fe_2S_2 butterfly unit. The Mo atom also bonds to a (η^5-C_5Me_5)W(CO)$_2$ group. A phenylacetylide group bridges the Mo−W bond, and there are three carbonyls on each iron atom. The W atom also bonds to one of the sulfurs of the $Fe_2S_2(CO)_6$ unit.

Scheme 3



9

The Mo−W bond distance [2.9512(4) Å] is comparable to the Mo−W bond distances in other related clusters: 2.922(1) Å in [MoW(μ-C_4Me_4){σ,η^5-CH(C_6H_4Me-4)$C_2B_9H_8$-

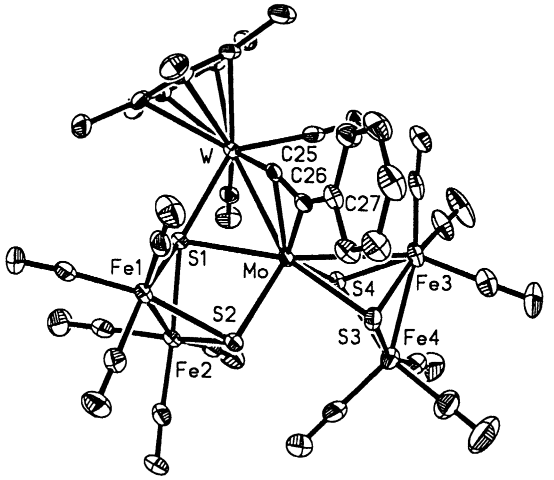


Figure 5. ORTEP diagram of [(η^5-C_5Me_5)MoWFe$_4$(μ_3-S)$_3$(μ_4-S)(CO)$_{14}$(CCPh)] (**9**) with 50% probability ellipsoids. Selected bond distances (Å) and bond angles (deg): Fe(1)−Fe(2) = 2.5545(7), Fe(3)−Fe(4) = 2.5422(8), Mo−S(1) = 2.4359(9), Mo−S(2) = 2.3917(9), Mo−S(3) = 2.4300(9), Mo−S(4) = 2.4025(9), W−S(1) = 2.4856(9), Mo−W = 2.9512(4), Mo−Fe(3) = 3.0263(6), C(25)−C(26) = 1.296(5), W−C(25)−C(26) = 162.8(3), C(25)−C(26)−C(27) = 142.4(3), W−C(25)−Mo = 91.26(13), Mo−C(25)−C(26) = 71.6(2), Mo−C(26)−C(27) = 145.7(3).

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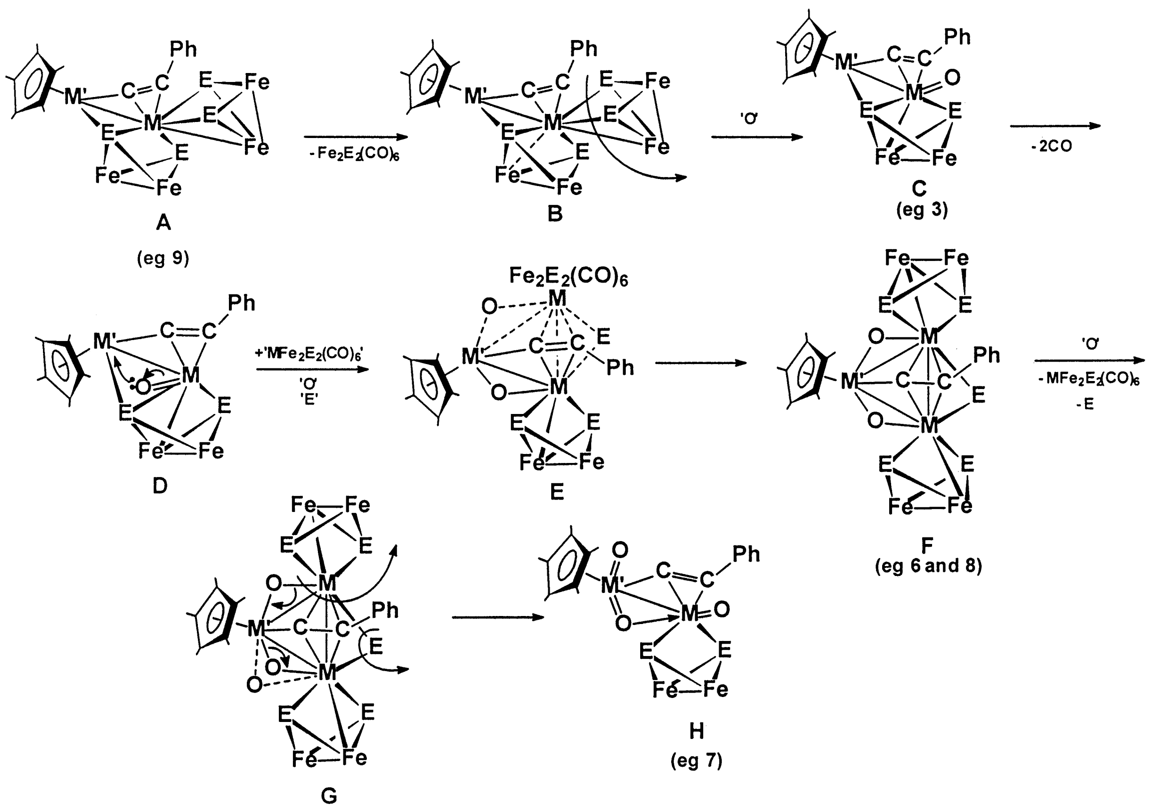
Scheme 4



$Me_2\}(\eta\text{-}C_7H_7)]$[27] and 2.935(1) Å in $[MoW(\mu\text{-}C(C_6H_4\text{-}OMe\text{-}2)C(Me)O\}(CO)_4(\eta\text{-}C_5H_5)_2]$.[28] The Mo–Fe(3) bond distance of 3.0263(6) Å is long and comparable to the other long Fe–Mo bond length (3.052(2) Å) in the hourglass cluster $[Fe_4Mo(CO)_{14}(\mu_3\text{-}S)_2(\mu_3\text{-}Te)_2]$.[29] The acetylide carbon atoms have a bond length of 1.296(5) Å, which is similar to the olefinic C–C bond, 1.298(4) Å, in the related oxo- and acetylide-bridged cluster $[(\eta^5\text{-}C_5H_5)_2MoWFe_2(O)_2(S)_2(CO)_9(CCPh)_2]$.[13]

Geometry around the quadruply bridging Se atom in **3** suggests that it acts as a four-electron donor, and on the basis of the 18-electron rule, the electron count for the two Fe atoms and the W atom are satisfied, while the high-valent Mo atom falls short by four electrons. In the two isostructural clusters **6** and **8**, the Fe atoms satisfy the electron count requirements, whereas the oxo-bonded Mo and W atoms fall short by two electrons each. An electron count of 16 each can be assigned to the Mo and W atoms in **7** if it is assumed that a W to Mo donor–acceptor bond exists; the two Fe atoms are electron precise. In contrast to cluster **3**, the quadruply bridging S atom in **9** has tetrahedral coordination and acts as a six-electron donor, thus satisfying the electron count for the four Fe atoms and the W atom; the Mo atom falls short of the 18-electron count by two.

Formation of each of the clusters reported here is highly sensitive to the reaction conditions used, in particular to the concentration of oxygen present in the reaction medium. The type of bridging chalcogen in the starting cluster and the metal acetylide complex used also determines the general stability of these compounds and their isolability. Our attempts to experimentally demonstrate any interconversion among the four structure types depicted by **3** and **6**–**9** proved unsuccessful. Scheme 4 represents the formal relationship that can be envisioned to exist between these structure types and the possible mechanism by which, starting from a non-oxo cluster (**9**), stepwise oxidations can lead to the formation of the other three types of clusters, containing one (**3**), two (**6** and **8**), and three (**7**) oxo groups. Thus, a formal replacement of an $Fe_2E_2(CO)_6$ unit of A (e.g., **9**) by an oxo group and formation of a new bond between an Fe atom and the Mo atom as in B would yield C (e.g., **3**). Transformation of structure C to that represented by the clusters **6** and **8** through D and E is more complicated and involves formal additions of an $Fe_2ME_2(CO)_6$ unit, an oxo, and an E group and a change in the terminal oxo of C into a bridging ligand. Loss of two carbonyls would yield intermediate D, and new metal–metal bond formations in E would complete the transformation to F (e.g., **6** and **8**). Addition of a third oxo group and formal loss of the doubly bridging E and an $Fe_2ME_2(CO)_6$ unit in G would give rise to structure H (e.g., **7**). Although we understand the speculative nature of the transformations depicted in this scheme, we feel it necessary and important to point out the relationship between the structure types of which clusters **3** and **6**–**9** are representatives.

Redox Properties. The redox properties of Mo– and W–oxo complexes (**3**, **6**, **7**, and **8**) have been studied by cyclic voltammetric technique in dichloromethane solution using a platinum wire working electrode in the potential range ± 2.0 V versus SCE. In all cases, the

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E_{pa} and E_{pc} are measured versus SCE (under identical experimental conditions the ferrocene/ferrocenium couple appears at 0.58 V versus SCE[30]).

Complex **3** exhibits one irreversible oxidation wave at 1.48 V corresponding to the oxidation of its $Mo^{IV}=$oxo center to the $Mo^{V}=O$ state. The two molybdenum centers [Mo(2) and Mo(3)] in the trimolybdenum complex **8** are in a chemically equivalent environment, whereas the chemical environment around the Mo(1) center is different with respect to Mo(2) and Mo(3). The formal oxidation states of Mo(1) and Mo(2)/Mo(3) can be considered as +IV and +V, respectively. Complex **8** exhibits two irreversible oxidative responses [$E_{pa1} = 0.57$ V and $E_{pa2} = 1.27$ V] and one reductive response at $E_{pc} = -1.68$ V. Similarly, complex **6**, comprising two equivalent Mo(V) centers and one W(IV) center, displays two irreversible oxidation processes at $E_{pa1} = 0.59$ V and $E_{pa2} = 1.23$ V and one irreversible reduction at $E_{pc} = -1.34$ V. Complex **7** exhibits two irreversible oxidative responses at $E_{pa1} = 0.75$ V and $E_{pa2} = 1.44$ V and two reductive responses at $E_{pc1} = -1.18$ V and $E_{pc2} = -1.75$ V, which are considered to be associated with the oxo–Mo and –W centers.[13,31] The irreversible nature of the observed voltammograms and the involved inherent electron delocalization problem in the cluster system precluded the assignment of the responses corresponding to the specific metal centers.

Experimental Section

Reactions and manipulations for the preparation of **1**, **2**, and **5** were carried out using standard Schlenk line techniques under an atmosphere of prepurified nitrogen, unless otherwise stated. The reaction leading to the formation of **3** was carried out under an atmosphere of 2.5% of O_2 in N_2, and those for obtaining **6**–**8** were performed in the presence of 5% oxygen in a nitrogen gas atmosphere. The gas mixtures were supplied by Indian Oxygen Ltd., and the compositions were confirmed by GC analysis using a MS 5A, 10 m × 1/8 in. column in a GC Prototype (Mak Analytica) instrument. 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; ^1H 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 scan rate used was 50 mV s^{-1}. The compounds $[Fe_2Mo(CO)_{10}(\mu_3\text{-}Se)_2]$ (**1**), $[Cp^*W(CO)_3(C\equiv CPh)]$ (**2**), $[Fe_2Mo(CO)_{10}(\mu_3\text{-}S)_2]$ (**4**), and $[Cp^*Mo(CO)_3(C\equiv CPh)]$ (**5**) were prepared by established procedures.[32,33]

Tungsten hexacarbonyl, molybdenum hexacarbonyl, and pentamethyl cyclopentadiene were purchased from Strem Chemical Co., phenyl acetylene was purchased from Aldrich Chemical Co., and these were used without further purification.

Synthesis of $[(\eta^5\text{-}C_5Me_5)MoWFe_2(O)(\mu_3\text{-}Se)(\mu_4\text{-}Se)(CO)_8(CCPh)]$ (3). A benzene solution (40 mL) of $[Fe_2MoSe_2(CO)_{10}]$ (**1**) (0.015 g, 0.023 mmol) and $[(\eta^5\text{-}C_5Me_5)W(CO)_3C\equiv CPh]$ (**2**) (0.012 g, 0.023 mmol) was heated from 60 to 75 °C for 20 min under constant purge of a mixture of gas (2.5% O_2 in N_2) 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), some unreacted $[Fe_2MoSe_2(CO)_{10}]$ and $[(C_5Me_5)W(CO)_3C\equiv CPh]$ eluted first, followed by a major purple-colored band, **3** (9 mg, 42%).

3. IR [hexane; cm^{-1}]: ν (CO), 2062 (s), 2031 (vs), 1999 (vs), 1988 (m), 1940(w); ν (Mo=O), 943. ^1H NMR (δ, ppm): δ 2.32 (s, 15H, C_5Me_5), 7.38–7.51 (m, 5H, C_6H_5). Mp: 155 °C dec. Anal. Calc (found) for $C_{18}Fe_2H_{15}MoO_9Se_2W$: C, 23.26 (23.0); H, 1.63 (1.80).

Synthesis of $[(\eta^5\text{-}C_5Me_5)Mo_2WFe_4(\mu_3\text{-}S)_4(\mu_2\text{-}S)(O)_2(CO)_{12}(CCPh)]$ (6) and $[(\eta^5\text{-}C_5Me_5)MoWFe_2(O)_3(\mu_3\text{-}S)_2(CO)_6(CCPh)]$ (7). A benzene solution (40 mL) of $[Fe_2MoS_2(CO)_{10}]$ (**4**) (0.015 g, 0.027 mmol) and $[(C_5Me_5)W(CO)_3C\equiv CPh]$ (**2**) (0.007 g, 0.013 mmol) was heated at 60 °C for 10 min under constant purge of a mixture of gas (5% O_2 in N_2) with stirring. After removal of the solvent in vacuo, the residue was subjected to chromatographic workup on silica gel TLC plates (20 × 20 cm, 0.20 mm thickness) by using a 60:40 v/v hexane/dichloromethane mixture as eluant. Some $[Fe_2(\mu_2\text{-}S)_2(CO)_6]$ was formed due to the decomposition of $[Fe_2Mo(\mu_3\text{-}S)_2(CO)_{10}]$, which eluted first, followed by unreacted $[(\eta^5\text{-}C_5Me_5)W(CO)_3C\equiv CPh]$ and a major maroon-colored band of compound **6** (0.010 g, 26.9%). Last, the brown-colored compound **7** (0.006 g, 24.35%) was extracted.

6. IR [hexane; cm^{-1}]: ν (CO), 2063 (vs), 2034 (s), 2009 (s), 1989 (w); ν (μ_2-O), 826. ^1H NMR (δ, ppm): δ 2.26 (s, 15H, C_5Me_5), 7.34–7.56 (m, 5H, C_6H_5). Mp: 185 °C dec. Anal. Calc (found) for $C_{30}H_{20}Fe_4Mo_2WO_{14}S_5$: C, 26.42 (26.22); H, 1.48 (1.50).

7. IR [hexane; cm^{-1}]: ν (CO), 2064 (s), 2026 (vs), 1995 (s), 1985 (m); ν (Mo=O), 958; (μ_2-O), 818. ^1H NMR (δ, ppm): δ 2.25 (s, 15H, C_5Me_5), 7.61–8.12 (m, 5H, C_6H_5). Mp: 180 °C dec. Anal. Calc (found) for $C_{24}H_{20}Fe_2MoWO_9S_2$: C, 31.75 (31.56); H, 2.22 (2.28).

Synthesis of $[(\eta^5\text{-}C_5Me_5)Mo_3Fe_4(\mu_3\text{-}S)_4(\mu_2\text{-}S)(O)_2(CO)_{12}(CCPh)]$ (8). Under a constant purge of a mixture of gas (5% O_2 in N_2) with constant stirring, a benzene solution (40 mL) of $[Fe_2MoS_2(CO)_{10}]$ (**4**) (0.015 g, 0.027 mmol) and $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3C\equiv CPh]$ (**5**) (0.006 g, 0.013 mmol) was heated at 50 °C for 5 min. After removal of the solvent in vacuo, 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), maroon-colored compound **8** was separated (0.014 g, 40%) from some unreacted $[(C_5Me_5)Mo(CO)_3C\equiv CPh]$.

8. IR [hexane; cm^{-1}]: ν (CO), 2063 (vs), 2034 (s), 2009 (s), 1990 (w); ν(μ_2-O), 845. ^1H NMR (δ, ppm): δ 2.27 (s, 15H, C_5Me_5), 7.34–7.56 (m, 5H, C_6H_5). Mp: 178 °C dec. Anal. Calc (found) for $C_{30}H_{20}Fe_4Mo_3O_{14}S_5$: C, 28.24 (28.04); H, 1.58 (1.60).

Synthesis of $[(\eta^5\text{-}C_5Me_5)MoWFe_4(\mu_3\text{-}S)_3(\mu_4\text{-}S)(CO)_{14}(CCPh)]$ (9). To a solution of $[Fe_2MoS_2(CO)_{10}]$ (**4**) (0.015 g, 0.027 mmol) in dry benzene (40 mL) was added $[(\eta^5\text{-}C_5Me_5)W(CO)_3C\equiv CPh]$ (**2**) (0.007 g, 0.013 mmol), and the mixture was heated at 60 °C for 10 min under constant purge of argon with 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). Use of a 70:30 v/v hexane/dichloromethane mixture as eluant initially gave the same orange-colored band of $[Fe_2(\mu_2\text{-}S)_2(CO)_6]$ from the decomposition of $[Fe_2Mo(\mu_3\text{-}S)_2(CO)_{10}]$. Further elution gave some

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Table 1. Crystal Data and Structure Refinement Parameters for 3, 6, 7, 8, and 9

	3	6	7	8	9
formula	$C_{26}H_{20}Fe_2MoO_9Se_2W$	$C_{30}H_{20}Fe_4Mo_2O_{14}S_5W$	$C_{24}H_{20}Fe_2MoO_9S_2W$	$C_{30}H_{20}Fe_4Mo_3O_{14}S_5$	$C_{32.5}H_{21}ClFe_4MoO_{14}S_4W$
fw	1025.83	1363.89	908.01	1275.98	1302.37
cryst syst	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	8.6531(12)	14.237(2)	8.5175(8)	11.3592(6)	11.3384(8)
b, Å	10.8941(16)	17.006(3)	15.7030(16)	13.5829(8)	22.3526(16)
c, Å	15.745(2)	17.856(3)	21.868(2)	13.7884(8)	17.0944(12)
α, deg	88.618(6)	83.606(6)	90	76.262(3)	90
β, deg	89.522(6)	79.022(6)	91.307(3)	72.911(3)	92.737(3)
γ, deg	86.134(6)	74.427(6)	90	76.793(3)	90
V, Å^3	1480.4(4)	4079.9(12)	2924.1(5)	1946.26(19)	4327.5(5)
Z	2	4	4	2	4
D(calc), Mg/m^3	2.301	2.220	2.063	2.177	1.999
$2\theta_{max}$, deg	50	50	50	50	50
F(000)	968	2616	1744	1244	2516
abs coeff, mm^{-1}	7.755	5.101	5.503	2.716	4.548
goodness-of-fit on F^2	1.074	0.909	1.106	0.946	0.954
final R indices [$I > 2\sigma(I)$]	R1=0.0317, wR2=0.0783	R1=0.0435, wR2=0.0828	R1=0.0343, wR2=0.0868	R1=0.0235, wR2=0.0458	R1=0.0306, wR2=0.0604
R indices (all data)	R1=0.0365, wR2=0.0798	R1=0.0954, wR2=0.0966	R1=0.0454, wR2=0.0976	R1=0.0368, wR2=0.0482	R1=0.0574, wR2=0.0664

unreacted [(η^5-C_5Me_5)W$(CO)_3$C≡CPh] followed by the blackish green colored compound **9** (0.012 g, 35%).

9. IR [hexane; cm^{-1}]: ν (CO), 2072 (w), 2056 (vs), 2036 (s), 2028 (vs), 2009 (w), 1994 (w). ^{1}H NMR (δ, ppm): δ 2.41 (s, 15H, C_5Me_5), 7.29−7.36 (m, 5H, C_6H_5). Mp: 145 °C dec. Anal. Calc (found) for $C_{32}H_{20}Fe_4MoO_{14}S_4W$: C, 30.51 (30.33); H, 1.60 (1.64).

Crystal Structure Determination of 3, 6, 7, 8, and 9. Purple-colored crystals of **3**, maroon-colored crystals of **6** and **8**, brown-colored crystals of **7,** and blackish green crystals of **9** suitable for crystal structure determination were grown from a hexane/dichloromethane solution at 0 °C. The crystals were mounted on glass fibers and transferred to the cold gas stream (−140 °C) of a Bruker SMART 1000CCD area detector equipped with an LT-2 low-temperature attachment. Monochromated Mo Kα radiation (λ = 0.71073 Å) was used for the measurements. Appropriate empirical absorption corrections using the program SADABS were applied. The crystal structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares methods based upon F^2 (SHELXL-93).[34] Hydrogens were included using a riding model or as rigid methyls. Compound **9** contains severely disordered CH_2Cl_2 molecules in which the carbon atoms could not be located. Pertinent crystallographic data for **3**, **6**, **7**, **8**, and **9** are summarized in Table 1.

Conclusion

By careful control of the oxygen concentration used, a series of non-oxo- and oxo-containing, acetylide-bridged mixed metal clusters have been prepared. The new clusters **3** and **6**−**9** represent four different structure types. Variation in reaction conditions used in each reaction is slight, but the differences are necessary for isolation of each product. While changes in time or temperature affect the yields of products, concentration of oxygen used is critical for isolation of each of the oxo-containing clusters. Although we were unsuccessful in demonstrating the interconversion among these four structures, we believe that the structures do have a formal relationship and it is the instability of certain structures for particular metal and chalcogen compositions in the cluster core that prevents their isolation. The oxo Mo and W centers of the respective clusters are found to be redox active, exhibiting successive irreversible oxidative and reductive responses.

Acknowledgment. P.M. and S.M. are grateful to the Council of Scientific and Industrial Research, Government of India, for a research grant and a research fellowship, respectively.

Supporting Information Available: Details of the structure determination for **3**, **6**, **7**, **8**, and **9**, including tables listing full bond lengths, bond angles, and torsion angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020420S

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