3694 *Organometallics* **2004,** *23,* 3694−3700

Photochemical Reactions of $Fe(CO)_5$ with Monometal Alkynyls and Free Alkynes: Synthesis and Characterization of $[(\eta^5\text{-}C_5Me_5)Fe_2Mo(CO)_7\{\mu_3\text{-}\eta^1{:}\eta^4{:}\eta^2\text{-}C(H)C(Ph)C(Ph)C\}]$ and Diferrocenylquinones

Pradeep Mathur,[*,†,‡] Anjan K. Bhunia,[†] Shaikh M. Mobin,[‡] Vinay K. Singh,[†] and Chimalakonda Srinivasu[†]

Chemistry Department, Indian Institute of Technology, Powai, Bombay 400 076, India, and National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology, Powai, Bombay 400 076, India

Received April 10, 2004

Photolysis of a benzene solution containing $Fe(CO)_5$ and $[(\eta^5\text{-}C_5R_5)Mo(CO)_3(C{\equiv}CPh)]$ yielded mixed-metal clusters $[(\eta^5\text{-}C_5R_5)Fe_2Mo(CO)_8(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}CCPh)]$ (R = H, **1**; Me, **2**) and $[(\eta^5\text{-}C_5H_5)Fe_3Mo(CO)_{11}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^1\text{-}CCPh)]$ (**3**). When a mixture of $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(C{\equiv}CPh)]$, $Fe(CO)_5$, and phenylacetylene was photolyzed, coupling of the acetylide and acetylene was observed and the mixed-metal cluster $[(\eta^5\text{-}C_5Me_5)Fe_2Mo(CO)_7(\mu_3\text{-}\eta^1{:}\eta^4{:}\eta^2\text{-}C(H)C(Ph)C(Ph)C)]$ (**4**) was obtained. Interestingly, use of a bulky substituent on the free acetylene in the reaction mixture did not produce analogues of **4**. Reaction of $Fe(CO)_5$ with ferrocenylacetylene produced three different compounds, tetracarbonyl(2-ferrocenylmaleoyl)iron (**5**), 2,5-diferrocenylquinone (**6**), and 2,6-diferrocenylquinone (**7**). All new compounds were characterized by IR and ^1H and ^{13}C NMR spectroscopy. Structures of **2**−**7** were established crystallographically.

Introduction

Interest in the organometallic chemistry of alkynes has continued since Reppe discovered the cyclomerization of acetylene to cyclooctatetraene.[1−4] Since that initial discovery, work on reactivity of metal-acetylenic systems has been extended to use of alkynes as bridging ligands in cluster formation, metal acetylides, and acetylide coupling on cluster frameworks.[5−8] We and others have shown that the nature of coupling of acetylides, when it does occur, is strongly influenced by the nature of the metal core in the clusters.[9−15] In our earlier work on the use of chalcogen-bridged metal carbonyl clusters for formation of new acetylide-incorporated mixed-metal clusters, the nature of the chalcogen used, the metal atom present, and the reaction conditions determined the type of acetylide coupling observed. For instance, under anaerobic conditions, we have observed mixed-metal clusters $[Fe_3M_2(\eta^5\text{-}C_5R_5)_2(CO)_6(\mu_3\text{-}E)_2\{\mu_4\text{-}CC(Ph)C(Ph)C\}]$ and $[Fe_2M_2(\eta^5\text{-}C_5R_5)_2(CO)_4(\mu_3\text{-}E)_2\{\mu_4\text{-}CC(Ph)(CO)C(Ph)C\}]$ (M = Mo, W; R = H, Me; E = S, Se, Te), which feature tail-to-tail coupling of acetylide ligands with and without CO.[16] In contrast, under aerobic conditions, we have isolated complexes containing both oxo and acetylide ligands in the same molecule, as in $[W(\eta^5\text{-}C_5Me_5)(O)(Se_2)(CCPh)]$ and $[Fe_2MoW(\eta^5\text{-}C_5Me_5)_2(O)(\mu_3\text{-}Se)(\mu_4\text{-}Se)(CO)_8(CCPh)]$.[17,18] When monometal acetylides, $[(\eta^5\text{-}C_5Me_5)M(CO)_3(C{\equiv}CPh)]$ (M = Mo, W), were treated with $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ in the presence of different acetylenes $HC{\equiv}CR$ (R = Ph, $\{(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)Fe\}$, here after denoted as Fc), we isolated mixed-metal clusters $[Fe_3M(\eta^5\text{-}C_5Me_5)(CO)_6(\mu_3\text{-}S)\{\mu_3\text{-}CCPh\}\{\mu_3\text{-}C(H){=}C(R)S\}]$ (M = Mo, W; R = Ph, n-Bu) and $[Fe_3M(\eta^5\text{-}C_5Me_5)(CO)_7(\mu_3\text{-}S)\{\mu_3\text{-}CCPh\}\{\mu_3\text{-}C(Fc){=}C(H)S\}]$ (M = Mo, W), which feature head-to-tail flip of the coordinated acetylide group or new carbon-chalcogen formation depending upon the nature of the free acetylene used.[19] In this paper, we report the contrast in the reactions of $PhC{\equiv}CH$ and ferrocenyl-

---

[*] Corresponding author. E-mail: mathur@iitb.ac.in.

[†] Chemistry Department.

[‡] National Single Crystal X-ray Diffraction Facility.

(1) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *561*, 1.

(2) Cooke, J.; Takats, J. *J. Am. Chem. Soc.* **1997**, *119*, 11088.

(3) Young, F. R., III; O'Brien, D. H.; Pettersen, R. C.; Levenson, R. A.; Minden, D. L. V. *J. Organomet. Chem.* **1976**, *114*, 157.

(4) Efraty, A.; Bystrek, R.; Geaman, J. A.; Huang, M. H. A.; Herber, R. H. *Synthesis* **1971**, *6*, 305.

(5) Shiu, C.-W.; Chi, Y.; Chung, C.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1998**, *17*, 2970.

(6) Akita, M.; Terada, M.; Moro-oka, Y. *Chem. Commun.* **1997**, 265.

(7) Sappa E. *J. Cluster Sci.* **1994**, *5*, 211 and 535.

(8) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

(9) Carty, A. J.; Enright, G. D.; Hogarth, G. *Chem. Commun.* **1997**, 1883.

(10) Blenkiron, P.; Enright, G. D.; Carty, A. J. *Chem. Commun.* **1997**, 483.

(11) Chi, Y.; Carty, A. J.; Blenkiron, P.; Delgado, E.; Enright, G. D.; Wang, W.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1996**, *15*, 5269.

(12) Akita, M.; Sugimoto, S.; Terada, M.; Moro-oka, Y. *J. Organomet. Chem.* **1993**, *447*, 103.

(13) Delgado, E.; Chi, Y.; Wang, W.; Hogarth, G.; Low, P. J.; Enright, G. D.; Peng, S.-M.; Lee, G.-H.; Carty, A. J. *Organometallics* **1998**, *17*, 2936.

(14) Wu, C.-H.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1990**, 3025.

(15) Mathur, P.; Ahmed, M. O.; Kaldis, J. H.; McGlinchey, M. J. *J. Chem. Soc., Dalton Trans.* **2002**, 619.

(16) Mathur, P.; Ahmed, M. O.; Dash, A. K.; Walawalkar, M. G.; Puranik, V. G. *J. Chem. Soc., Dalton Trans.* **2000**, 2916.

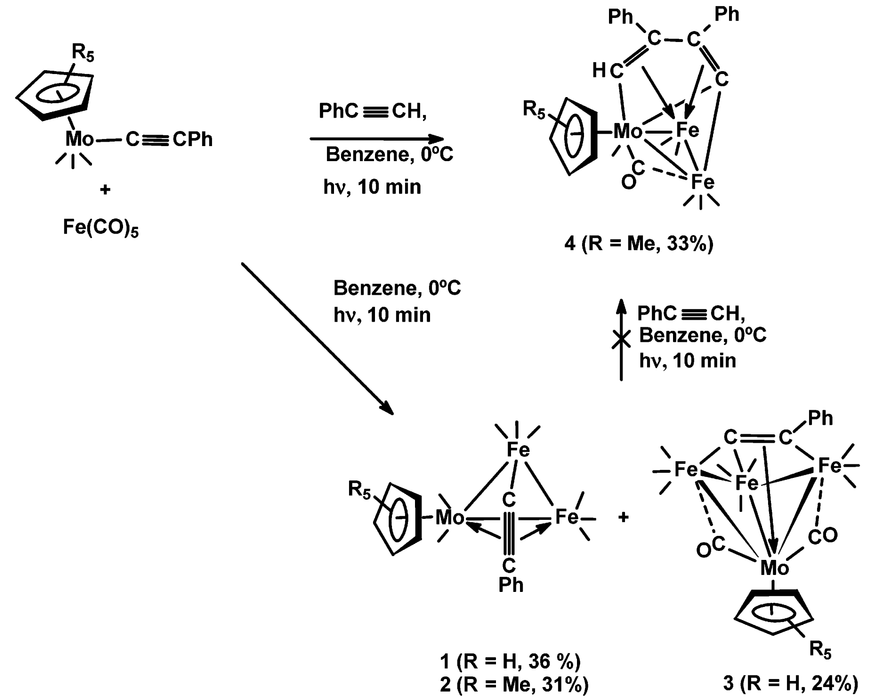
(17) Mathur, P.; Mukhopadhyay, S.; Lahiri, G. K.; Chakraborty, S.; Thöne, C. *Organometallics* **2002**, *21*, 5209.

(18) Mathur, P.; Ahmed, M. O.; Dash, A. K.; Kaldis, J. H. *Organometallics* **2000**, *19*, 941.

(19) Mathur, P.; Bhunia, A. K.; Srinivasu, Ch.; Mobin, S. M. *J. Organomet. Chem.* **2003**, *670*, 144.

10.1021/om049739y CCC: $27.50
Publication on Web 06/19/2004

Scheme 1



acetylene with metal acetylide complexes [(η^5-C$_5$R$_5$)Mo(CO)$_3$(C≡CPh)] (R = H, Me) and Fe(CO)$_5$.

Results and Discussion

Photolysis of Solutions Containing Fe(CO)$_5$, [(η^5-C$_5$R$_5$)Mo(CO)$_3$(C≡CPh)] (R = H, Me), and Phenylacetylene. When a benzene solution containing Fe(CO)$_5$ and [(η^5-C$_5$R$_5$)Mo(CO)$_3$(C≡CPh)] (R = H, Me) was photolyzed under continuous bubbling of argon for 10 min, formation of new mixed-metal clusters [(η^5-C$_5$R$_5$)Fe$_2$Mo(CO)$_8$(μ_3-η^1:η^2:η^2-CCPh)] (R = H, **1**; Me, **2**) and [(η^5-C$_5$H$_5$)Fe$_3$Mo(CO)$_{11}$(μ_4-η^1:η^1:η^2:η^1-CCPh)] (**3**) were observed (Scheme 1).

Compounds **1**−**3** were characterized by IR and ^{1}H and ^{13}C NMR spectroscopy. All three compounds are stable in the solid state and decompose in solution over a period of days. The IR spectra of compounds **1** and **2** show the presence of terminal carbonyls, whereas compound **3** shows the presence of terminal and semibridging carbonyl groups. ^{1}H and ^{13}C NMR spectra of compounds **1**−**3** confirm the presence of (η^5-C$_5$R$_5$) and (CCPh) units in addition to carbonyl groups. Crystals of **2** and **3** were grown from hexane/dichloromethane solvent mixtures at −5 °C, and single-crystal X-ray analyses were undertaken. ORTEP diagrams of **2** and **3** are shown in Figures 1 and 2, respectively.

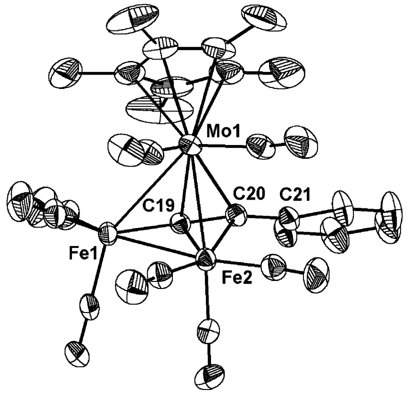


Figure 1. ORTEP diagram of [(η^5-C$_5$Me$_5$)Fe$_2$Mo(CO)$_8$(μ_3-η^1:η^2:η^2:η^2-CCPh)] (**2**) with 30% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): Mo(1)−Fe(1) = 2.8968(7), Fe(1)−Fe(2) = 2.6332(8), Mo(1)−Fe(2) = 2.7254(7), Fe(1)−C(19) = 1.797(4), Mo(1)−C(19) = 2.230(4), Mo(1)−C(20) = 2.285(4), C(19)−C(20) = 1.318(5), C(20)−C(21) = 1.462(6); Fe(2)−Mo(1)−Fe(1) = 55.755(19), Fe(2)−Fe(1)−Mo(1) = 58.824(19), Fe(1)−Fe(2)−Mo(1) = 65.42(2), Fe(1)−C(19)−Fe(2) = 86.37(16), Fe(1)−C(19)−Mo(1) = 91.36(16), Fe(2)−C(19)−Mo(1) = 79.15(13).

The molecular structure of **2** consists of a triangular Fe$_2$Mo core, in which a (η^5-C$_5$Me$_5$) group and two carbonyl groups are bonded to the molybdenum atom. The triply bridging acetylide group of **2** adopts a η^1:η^2:η^2-bonding mode such that it is formally σ-bonded to one of the Fe atoms and forms a transverse bridge over an Fe−Mo bond. Each iron atom has three terminally bonded carbonyl groups. The bridged Fe−Mo bond (Fe(2)−Mo(1), 2.7254(7) Å) is shorter than the unbridged Fe−Mo bond (Fe(1)−Mo(1), 2.8968(7) Å). A similar difference between the bridged (2.830(2) Å) and unbridged (2.916(2) Å) Os−W bond lengths is seen in the related structure [(η^5-C$_5$H$_5$)Os$_2$W(CO)$_8$(CCPh)].[20] The unbridged Fe−Mo bond distance in **2** is somewhat longer than the unbridged Fe−Mo bond distances in other clusters that feature a Mo$_2$Fe core structure: 2.625(1) Å in [Fe$_2$Mo(CO)$_5$(η^5-C$_5$H$_5$){μ_3-η^2-HCCPh}(μ-CO)(μ-PPh$_2$)] and 2.714(2) Å in [Fe$_2$Mo(CO)$_6$(η^5-C$_5$H$_5$){μ_3-η^2-HCCPh}(μ-CO)(μ-PPh$_2$)].[21] The Fe−Fe bond distance of 2.6332(8) Å in **2** is marginally longer than the Fe−Fe bond distance of 2.503(3) Å in [Fe$_2$W(CO)$_8$(η^5-C$_5$H$_5$) (μ-C$_2$C$_6$H$_4$Me-4)][22] and 2.568(1) Å in [Fe$_2$Mo(CO)$_5$(η^5-C$_5$H$_5$){μ_3-η^2-HCCPh}(μ-CO)(μ-PPh$_2$)], but similar to

---

[20] Hwang, D.-K.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1990**, *9*, 2709.

[21] Mays, M. J.; Raithby, P. R.; Sarveswaran, K.; Solan, G. A. *J. Chem. Soc., Dalton Trans.* **2002**, 1671, and references therein.

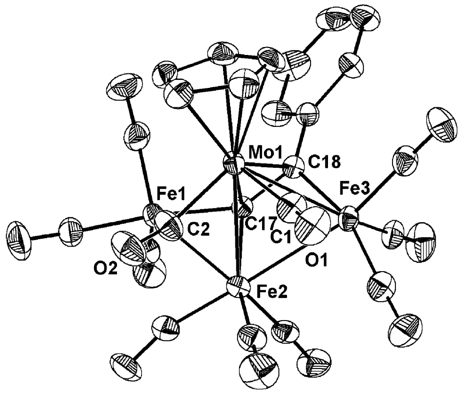


Figure 2. ORTEP diagram of $[(\eta^5\text{-}C_5H_5)Fe_3Mo(CO)_{11}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^1\text{-}CCPh)]$ (**3**) with 30% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): Mo(1)−Fe(2) = 2.7401(8), Mo(1)−Fe(3) = 2.7879(8), Mo(1)−Fe(1) = 2.9044(8), Fe(1)−Fe(2) = 2.5886(10), Fe(2)−Fe(3) = 2.7041(10), Mo(1)−C(17) = 2.201(4), Mo(1)−C(18) = 2.371(4), Fe(1)−C(17) = 1.858(4), Fe(2)−C(17) = 1.969(4), Fe(3)−C(18) = 1.970(4), C(17)−C(18) = 1.353(6); Fe(2)−Mo(1)−Fe(3) = 58.56(2), Fe(2)−Mo(1)−Fe(1) = 54.50(2), Fe(1)−Fe(2)−Mo(1) = 65.99(2), Fe(3)−Fe(2)−Mo(1) = 61.60(2), Fe(1)−Fe(2)−Fe(3) = 107.26(3), Fe(3)−Mo(1)−Fe(1) = 96.94(2), Fe(2)−Fe(1)−Mo(1) = 59.51(2), Fe(2)−Fe(3)−Mo(1) = 59.83(2), Mo(1)−C(1)−O(1) = 160.6(5), Mo(1)−C(2)−O(2) = 162.1(6).

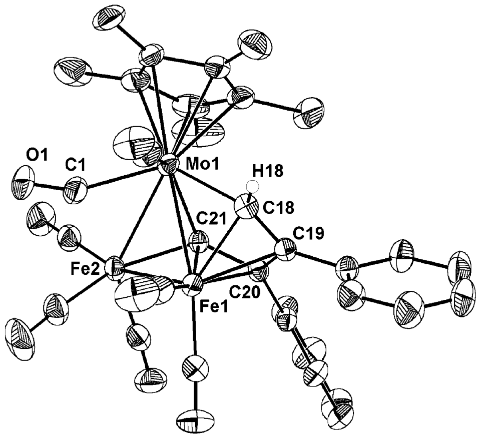


Figure 3. ORTEP diagram of $[(\eta^5\text{-}C_5Me_5)Fe_2Mo(CO)_7(\mu_3\text{-}\eta^2{:}\eta^4{:}\eta^1\text{-}C(H)C(Ph)C(Ph)C)]$ (**4**) with 30% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): Mo(1)−Fe(1) = 2.6972(10), Mo(1)−Fe(2) = 2.7713(11), Fe(1)−Fe(2) = 2.5824(13), Mo(1)−C(18) = 2.168(7), Mo(1)−C(21) = 2.059(6), Fe(1)−C(18) = 2.046(7), Fe(1)−C(19) = 2.140(6), Fe(1)−C(20) = 2.132(6), Fe(2)−C(21) = 1.885(6), C(18)−C(19) = 1.407(9), C(19)−C(20) = 1.454(8), C(20)−C(21) = 1.425(8); Mo(1)−C(18)−C(19) = 118.9(4), Mo(1)−C(1)−O(1) = 152.9(7), Mo(1)−Fe(2)−Fe(1) = 60.38(3), Mo(1)−C(21)−Fe(1) = 83.0(2), Mo(1)−C(21)−C(20) = 123.1(4), C(18)−C(19)−C(20) = 112.3(5), C(19)−C(20)−C(21) = 110.3(5), C(20)−C(21)−Mo(1) = 118.9(4).

the Fe−Fe bond distance of 2.680(3) Å in $[Fe_2Mo(CO)_6(\eta^5\text{-}C_5H_5)\{\mu_3\text{-}\eta^2\text{-}HCCPh\}(\mu\text{-}CO)(\mu\text{-}PPh_2)]$.[21] On formation of **2**, there is a lengthening of bond distance between the two acetylide carbons (1.318(5) Å), similar to the C−C lengthening in clusters $[Fe_2W(CO)_8(\eta^5\text{-}C_5H_5)(\mu\text{-}C_2C_6H_4Me\text{-}4)]$ (1.30(2) Å) and $[(\eta^5\text{-}C_5Me_4Et)_2Fe_4(CO)_9(\mu_4\text{-}\eta^2\text{-}C_2)]$ (1.292(9) Å).[23]

The molecular structure of **3** comprises an open Fe_3Mo butterfly arrangement, with atoms Mo(1) and Fe(2) in the hinge positions. A $(\eta^5\text{-}C_5H_5)$ group is bonded to the molybdenum atom. Each iron atom associates with three carbonyls, whereas the molybdenum atom bears two carbonyls, which are bent toward the wing-tip Fe atoms, forming semibridges (Mo(1)−C(2)−O(2) = 162.1(6)° and Mo(1)−C(1)−O(1) = 160.6(5)°). The $\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^1$-bonding mode of the acetylide group in the Fe_3Mo cluster framework of **3** is similar to that seen in the related cluster $[Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)(CCPh)]$.[24] The acetylide C−C bond distance of 1.353(6) Å in **3** is shorter than the C−C bond distance of 1.38(2) Å in $[Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)(CCPh)]$ and 1.45(3) Å in $[Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)(CCCH_2OMe)]$.[25] The average Fe−Mo bond distance of 2.811 Å in **3** is similar to the average Fe−Mo bond distances of 2.7949 Å in $[Fe_3Mo(CO)_6(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}S)(\mu_3\text{-}C(H){=}C(Ph)S)(\mu_3\text{-}CCPh)]$,[19] 2.8164 Å observed in $[Fe_3Mo_2(CO)_8(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}S)_2\{\mu_5\text{-}CC(Ph)CC(Ph)\}]$, and 2.8001 Å in $[Fe_4Mo_2(CO)_9(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}S)_2\{\mu_4\text{-}CC(Ph)_2]$.[15] The average Fe−Fe bond distance of 2.6463 Å observed in **3** is longer than the average Fe−Fe bond distance of 2.5347 Å in $[Fe_3Mo(CO)_6(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}S)(\mu_3\text{-}C(H){=}C(Ph)S)(\mu_3\text{-}CCPh)]$ but comparable with an average Fe−Fe bond distance of 2.6644 Å in $[Fe_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C{=}CHCH_3)]$.[26]

In continuation of our interest in acetylide coupling reactions, we have investigated the possibility of acetylide-alkyne coupling. Under photolytic and thermal conditions, we did not observe any new cluster formation in the reaction of **1**−**3** with phenylacetylene. This contrasts with the reactivity of $[Os_2W(CO)_8(\eta^5\text{-}C_5H_5)(CCR)]$ (R = Ph, Bu^t), which reacts with alkyne to form clusters $[Os_2W(CO)_7(\eta^5\text{-}C_5H_5)\{C(R^I)C(R^I)CCR\}]$ (R^I = Tol, CO_2Et), bearing an acetylide-alkyne coupled unit.[27] However, when a benzene solution containing a mixture of $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(C{\equiv}CPh)]$, $Fe(CO)_5$, and $PhC{\equiv}CH$ was photolyzed, the formation of an alkyne-acetylide coupled mixed-metal cluster $[(\eta^5\text{-}C_5Me_5)Fe_2Mo(CO)_7(\mu_3\text{-}\eta^2{:}\eta^4{:}\eta^1\text{-}C(H)C(Ph)C(Ph)C)]$ (**4**) was observed in moderate yield. The new cluster is stable in the solid state and decomposes in solution over a period of 2−3 days. Compound **4** was identified on the basis of IR and ^1H and ^{13}C NMR spectroscopy. The infrared spectrum of **4** shows peaks in the carbonyl stretching region due to terminal carbonyl groups and additional bands at 1896 and 1844 cm^{-1}, suggesting the presence of semibridging carbonyls. ^1H and ^{13}C NMR spectra of **4** show the presence of $(\eta^5\text{-}C_5Me_5)$, (CCPh), and (HCCPh) groups, in addition to the carbonyls. Crystals of **4** were grown from hexane/ dichloromethane solvent mixtures at −5 °C, and a single-crystal X-ray analysis was undertaken. The molecular structure of **4** (Figure 3) consists of an Fe_2Mo triangle with two terminal carbonyls on one Fe atom and three on the other.

The molybdenum atom bears a $(\eta^5\text{-}C_5Me_5)$ ligand and two carbonyls, one of which is terminal and the other

---

(22) Green, M.; Marsden, K.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *Chem. Commun.* **1983**, 446.

(23) Akita, M.; Chung, M.-C.; Terada, M.; Miyauti, M.; Tanaka, M.; Moro-oka, Y. *J. Organomet. Chem.* **1998**, *565*, 49.

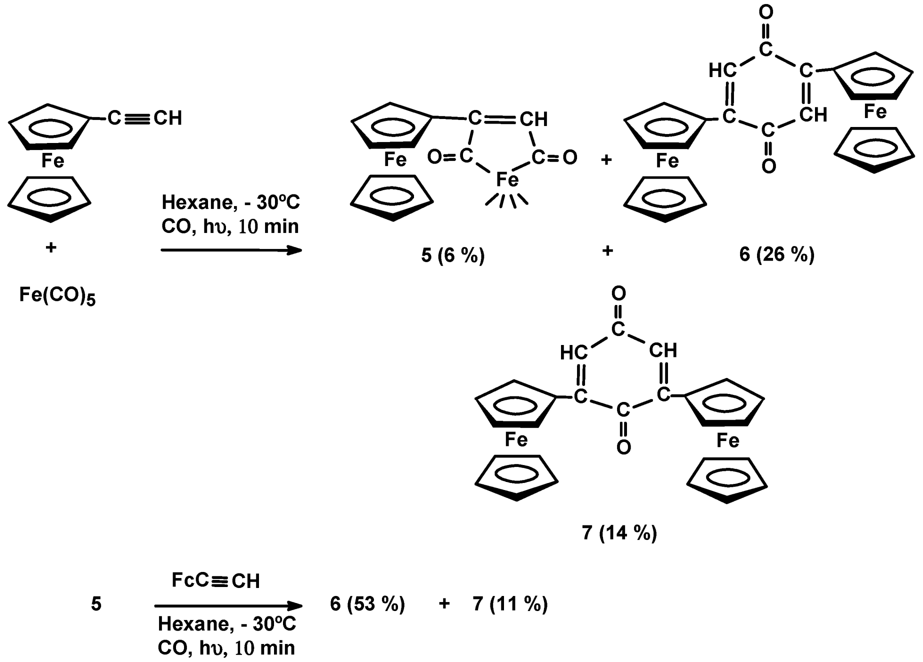
(24) Chi, Y.; Wu, C.-H. *Organometallics* **1990**, *9*, 2305.

(25) Su, P.-C.; Chiang, S.-J.; Chang, L.-L.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 4844.

(26) Bradley, J. S.; Harris, S.; Hill, E. W. *J. Chem. Soc., Dalton Trans.* **1997**, 3139.

(27) Chi, Y.; Huttner, G.; Imhof, W. *J. Organomet. Chem.* **1990**, *384*, 93.

Scheme 2



bent toward one of the Fe atoms, forming a semibridge (Mo(1)−C(1)−O(1) = 152.9(7)°). The average Mo−Fe bond distance of 2.734 Å observed in **4** is similar to the Fe−Mo bond distance of 2.701 Å (av) observed in the related acetylide-bridged Fe$_2$Mo trinuclear cluster [Fe$_2$Mo(CO)$_5$(η^5-C$_5$H$_5$){μ_3-η^2-HCCPh}(μ-CO)(μ-PPh$_2$)],[21] but shorter than the average Mo−Fe bond distance of 2.8035 Å in sulfido-bridged [Cp$_2$Mo$_2$Fe$_2$(μ_3-S)$_2$(CO)$_6$(μ-CO)$_2$].[28] The Fe−Fe bond distance of 2.5824(13) Å in **4** is comparable with the Fe−Fe bond distance of 2.5931(8) Å in [(η^5-C$_5$Me$_5$)Fe$_2$Mo(CO)$_6$(μ_3-S)(μ-SCCH$_2$Ph)] and 2.6332(8) Å in **2**. A {C(H)═C(Ph)C(Ph)═C} ligand triply bridges the Fe$_2$Mo face in the manner shown in Scheme 1, with the internal C−C bond (1.454(8) Å) being slightly longer than the two terminal C−C bonds (1.407(9) and 1.425(8) Å). The alkyne-acetylide coupling seen in **4** may be compared with the tail-to-tail acetylide coupling in [Fe$_3$W$_2$(η^5-C$_5$Me$_5$)$_2$(CO)$_6$(μ_3-S)$_2${μ_4-CC(Ph)C(Ph)C}], where also the middle C−C bond (1.439(5) Å) is longer than the terminal C−C bonds (1.428(5) and 1.421(6) Å).[29]

Photolysis of Fe(CO)$_5$ with Ferrocenylacetylene. When we carried out the photolysis of a benzene solution containing [(η^5-C$_5$Me$_5$)Mo(CO)$_3$(C≡CR)] (R = H, Me), Fe(CO)$_5$, and ferrocenylacetylene, we obtained tetracarbonyl(2-ferrocenylmaleoyl)iron (**5**), 2,5-diferrocenylquinone (**6**), and 2,6-diferrocenylquinone (**7**) in low yields. We did not observe any ferrocenyl analogue of compound **4**. After complete characterization of **5**−**7**, we optimized their yields by carrying out the photolysis of a hexane solution containing Fe(CO)$_5$ and ferrocenylacetylene under CO atmosphere. Further, we observed that, on photolysis, the Fe(CO)$_4$ group of the ferrole **5** could be substituted by a second molecule of ferrocenylacetylene to give the quinones **6** as the major product and **7** in minor yield (Scheme 2).

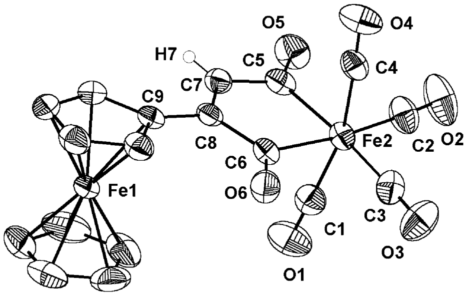


Figure 4. ORTEP diagram of tetracarbonyl(2-ferrocenylmaleoyl)iron (**5**) with 30% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): Fe(2)−C(5) = 2.018(3), Fe(2)−C(6) = 2.033(3), Fe(2)−C(1) = 1.812(3), Fe(2)−C(2) = 1.844(4), Fe(2)−C(3) = 1.842(4), Fe(2)−C(4) = 1.820(3), C(5)−O(5) = 1.209(4), C(6)−O(6) = 1.203(3), C(8)−C(9) = 1.460(3), C(7)−C(8) = 1.336(4), C(6)−C(8) = 1.507(4), C(5)−C(7) = 1.470(4); C(7)−C(8)−C(6) = 114.3(3), C(8)−C(7)−C(5) = 118.4(3), Fe(2)−C(6)−C(8) = 112.8(2), C(7)−C(5)−Fe(2) = 112.6(2), C(6)−Fe(2)−C(5) = 81.93(13), C(7)−C(5)−O(1) = 122.5(3).

Compounds **5**−**7** are stable in solid and solution state over a period of days. The infrared spectrum of **5** contains a ν(C═O) band at 1682 cm^{-1} in addition to terminal ν(C═O) vibrations due to the Fe(CO)$_4$ unit. Compounds **6** and **7** show the presence of carbonyl groups in the ketonic region at 1638 and 1619 cm^{-1}, respectively. ^{1}H and ^{13}C NMR spectra of compounds **5**−**7** confirm the presence of (CCH), ferrocenyl, ketonic carbonyl groups, and terminal carbonyl groups. Suitable crystals of **5**−**7** were grown from hexane/dichloromethane mixtures at −5 °C, and their structures were established crystallographically.

The molecular structure of **5** (Figure 4) consists of a ferracyclopentendione ring containing a ferrocenyl substituent, and four carbonyls are bonded to the iron atom. The Fe(2)−C bond distances present in the ferracyclopentendione ring (Fe(2)−C(5) = 2.018(3) Å and Fe(2)−C(6) = 2.003(3) Å) are longer than the other four Fe(2)−C bond distances (Fe(2)−C(1) = 1.812(3) Å, Fe-

---

(28) Braunstein, P.; Tiripicchio, A.; Camellini, M. T.; Sappa, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 307.

(29) Mathur, P.; Ahmed, M. O.; Dash, A. K.; Walawalkar, M. G. *J. Chem. Soc., Dalton Trans.* **1999**, 1795.

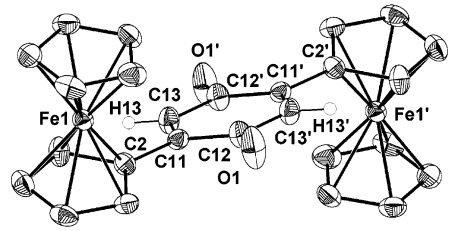


Figure 5. ORTEP diagram of 2,5-diferrocenylquinone (**6**) with 30% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): C(2)−C(11) = 1.486(7), C(11)−C(13) = 1.356(6), C(11)−C(12) = 1.423(7), C(12)−O(1) = 1.317(6), Fe(1)−C(2) = 2.043(5); C(2)−C(11)−C(13) = 120.6(4), C(11)−C(13)−C(12) = 123.1(5), C(13)−C(12)−O(1) = 118.3(5), Fe(1)−C(2)−C(11) = 126.6(3).

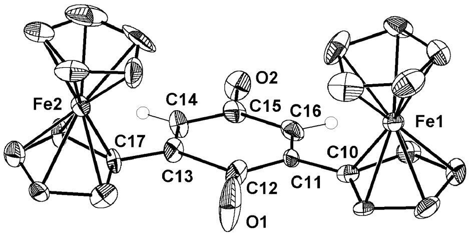


Figure 6. ORTEP diagram of 2,6-diferrocenylquinone (**7**) with 30% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): C(11)−C(12) = 1.39(2), C(12)−C(13) = 1.61(2), C(13)−C(14) = 1.32(2), C(14)−C(15) = 1.42(2), C(13)−C(17) = 1.51(2), C(15)−C(16) = 1.49(2), C(11)−C(16) = 1.37(2), O(1)−C(12) = 1.205(11), O(2)−C(15) = 1.252(8), C(10)−C(11) = 1.41(2); C(11)−C(12)−C(13) = 119.1(7), O(1)−C(12)−C(13) = 114(2), C(16)−C(11)−C(12) = 121.0(13), C(14)−C(13)−C(12) = 115.2(15).

(2)−C(2) = 1.844(4) Å, Fe(2)−C(3) = 1.842(4) Å, Fe(2)−C(4) = 1.820(3) Å). The C(5)−O(5) bond distance of 1.209(4) Å in **5** is almost the same as the other (C(6)−O(6) = 1.203(3) Å). The C(7)−C(8) bond length of 1.336(4) Å in **5** shows double-bond character and is comparable with a C−C bond length of 1.314(3) Å observed in the related compound tetracarbonyl(2-methyl-3-prop-1-ynylmaleoyl)iron.[30]

The molecular structures of **6** and **7** are shown in Figures 5 and 6, respectively.

The skeleton in each is a quinone core. Compound **6** has an inversion center and contains two ferrocenyl groups at the 2,5-positions, whereas compound **7** has a plane of symmetry and holds two ferrocenyl groups at the 2,6-positions.

The C−C bond lengths of the quinone unit in **6** (C(11)−C(12) = 1.423(7) Å, C(11)−C(13) = 1.356(6) Å) are shorter than the C−C bond lengths of the quinone unit in the related structure [{(η^5-C_5Me_4Et)Fe$(CO)_2$}$_2$-$C_6H_2O_2$],[23] but comparable with compound **7** (C(14)−C(15) = 1.42(2) Å, C(13)−C(14) = 1.32(2) Å). The C−O bond length of 1.317(6) Å in **6** is longer than the C−O bond length of 1.24(1) Å observed in [{(η^5-C_5Me_4Et)Fe$(CO)_2$}$_2C_6H_2O_2$]. In compound **7**, the two C−O bond lengths are unequal (C(12)−O(1) = 1.205(11) Å, C(15)−O(2) = 1.252(8) Å) and shorter than in **6**.

Several earlier examples of cyclodimerization of acetylenes with or without CO have been reported.[31] A few [Fe$(CO)_4$(RC≡CR)] complexes have been prepared by low-temperature photolysis of Fe$(CO)_5$ and RC≡CR (R = CF_3, H, Me),[32] but their structural characterization remains unreported. They are reported to react further at low temperature with RC≡CR to form *p*-quinone derivatives, [{η^2:η^2-$R_4C_4(CO)_2$}Fe$(CO)_3$]. Curiously, the well-known acetylene complex of osmium, [Os$(CO)_4$(η^2-C_2H_2)], does not react with acetylenes, while [Os$(CO)_4$(η^2-C_2Me_2)] reacts with but-2-yne to give the cyclopentadienone species [Os$(CO)_3$\{η^4-$C_4Me_4C(O)$\}] instead of the *p*-quinone or the osmacyclopentendione[33] osmium analogue of compound **5** obtained by us. Although in our hands even spectroscopic observation of [Fe$(CO)_4$(FcC≡CH)] proved unsuccessful, formation of **5** in our photolytic reactions of ferrocenylacetylene and Fe$(CO)_5$ probably occurs via an initial coordination of a “Fe$(CO)_4$” unit to the acetylenic group of ferrocenylacetylene, followed by CO insertion to form a ferracyclopentendione ring (Scheme 3). Displacement of the “Fe$(CO)_4$” group by a second ferrocenylacetylene molecule then gives rise to the quinone isomers **6** and **7**. There are reports of reactions of iron carbonyls with acetylenes to give various ferroles in low yields by reacting acetylenes and iron carbonyls in water[34] or in alkaline solutions[35] and by refluxing a mixture of $Fe_3(CO)_{12}$ and alkynes in hydrocarbon solvents.[36] Cyclobutendiones $C_2R_2(CO)_2$ have been obtained from the decomplexation reactions of the nickel maleoyl complex [Ni(bpy)C_2R_2-$(CO)_2$][37] and some acyloxyferrole complexes.[38] However, our reaction leading to formation of **5** and demonstration of it as an intermediate in the formation of quinones is unprecedented. Efforts are in progress toward examining the generality of replacing the Fe$(CO)_4$ unit of **5** by organic molecules other than acetylenes and thus providing a possible method for obtaining compounds related to the quinones.

Experimental Section

General Procedure. Reactions and manipulations were performed using standard Schlenk techniques under an atmosphere of prepurified argon. Solvents were purified, dried, and distilled under an argon atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as dichloromethane solutions in a 0.1 mm path length NaCl cell and NMR spectra on a Varian VXRO-300S spectrometer in $CDCl_3$. Elemental analyses were performed on a Carlo-Erba automatic analyzer. The compounds [(η^5-C_5R_5)Mo$(CO)_3$(C≡CPh)] (R = H, Me)[39] and ferrocenylacetylene[40] were prepared by established procedures. Iron pentacarbonyl and phenylacetylene were purchased from Fluka and Merck, respectively, and were used without further purification. Photochemical

---

(30) Pettersen, R. C.; Cihonski, J. L.; Young, F. R., III; Levenson, R. A. *Chem. Commun.* **1975**, 370.

(31) Fehlhammer, W. R.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.;Pergamon Press: Oxford, 1983; Vol. 4, p 545.

(32) Cooke, J.; Takats, J. *J. Am. Chem. Soc.* **1997**, *119*, 11088.

(33) Washington, J.; McDonald, R.; Takats, J.; Menashe, N.; Reshef, D.; Shvo, Y. *Organometallics* **1995**, *14*, 3996.

(34) Hock, A. A.; Mills, O. S. *Acta Crystallogr.* **1961**, *14*, 139.

(35) Sternberg, H. W.; Friedel. R. A.; Markby, R.; Wender, I. *J. Am. Chem. Soc.*, **1956**, *78*, 3621.

(36) Aime, S.; Milone, L.; Sappa, E.; Tiripicchio, A.; Lanfredi, A. M. M. *J. Chem. Soc., Dalton Trans.* **1979**, 1664.

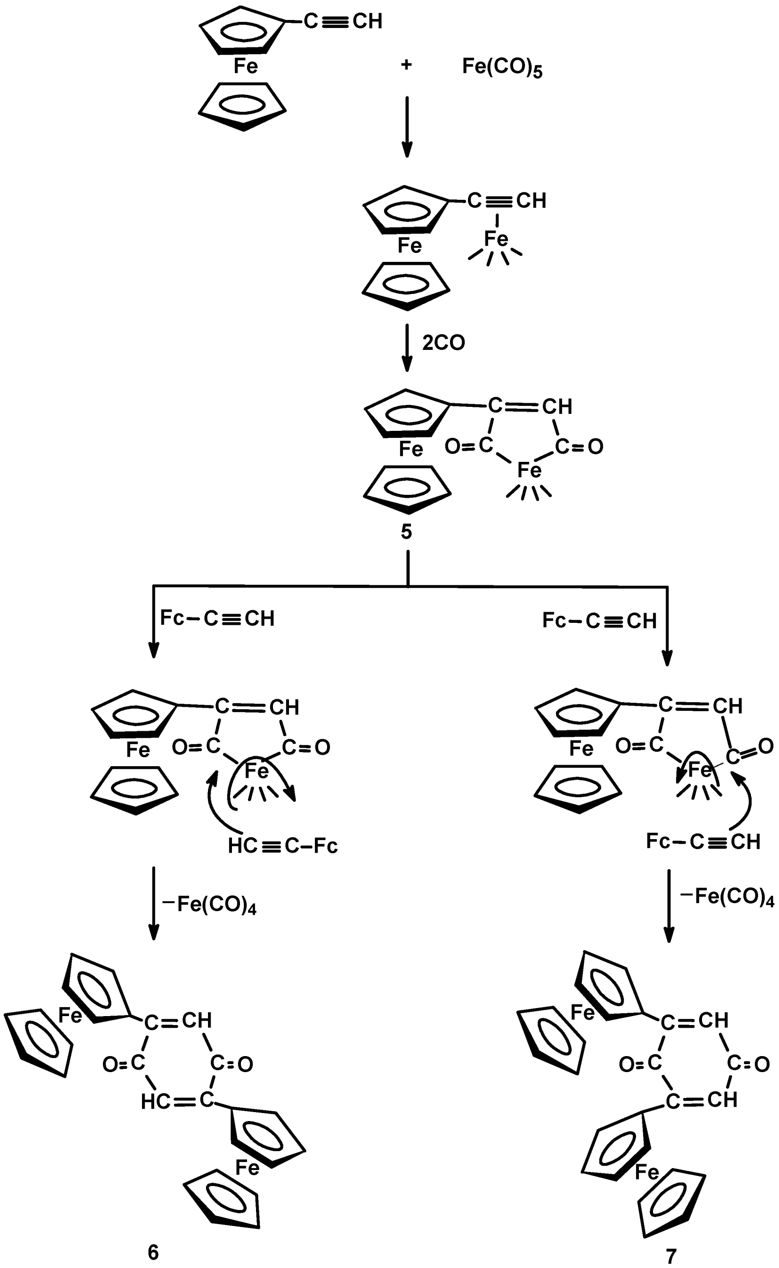
(37) Hoberg. H.; Herrera, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *29*, 927.

(38) Periasamy, M.; Mukkanti, A.; Raj, D. S. *Organometallics* **2004**, *23*, 619.

(39) Bruce, M. I.; Humphrey, M. G.; Matisons, J. G.; Roy, S. K.; Swincer, A. G. *Aust. J. Chem.* **1984**, *37*, 1955.

(40) Doisneau, G.; Balavonie, G.; Khan, T. F. *J. Organomet. Chem.* **1992**, *425*, 113.

Scheme 3



reactions were carried out in a water-cooled double-walled quartz vessel having a 125 W immersion type mercury lamp manufactured by Applied Photophysics Ltd.

Preparation of $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}_2\text{Mo(CO)}_8(\mu_3\text{-CCPh})]$ (R = H, 1; Me, 2) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}_3\text{Mo(CO)}_{11}(\mu_4\text{-CCPh})]$ (3). A benzene solution containing Fe(CO)$_5$ (30 mg, 0.15 mmol) and $[(\eta^5\text{-C}_5\text{R}_5)\text{Mo(CO)}_3(\text{C}{\equiv}\text{CPh})]$ [R = H (53 mg, 0.15 mmol) or Me (64 mg, 0.15 mmol)] was subjected to photolysis for 10 min at 0 °C in a photochemical reaction vessel under a continuous argon flow. After removal of the volatiles, the residue was extracted with dichloromethane and passed through a Celite pad to remove insoluble material. The filtrate was concentrated and subjected to chromatographic workup on silica gel TLC plates. Elution with a dichloromethane/hexane (10:90 v/v) mixture yielded a major red band of $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}_2\text{Mo(CO)}_8(\mu_3\text{-CCPh})]$ (R = H, **1**; Me, **2**) and a minor green band of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}_3\text{Mo(CO)}_{11}(\mu_4\text{-CCPh})]$ (**3**).

1: Yield: 33 mg (36%). IR (ν(CO), cm^{-1}, *n*-hexane): 2066 (s), 2024 (s), 2005 (vs), 1991 (w), 1964 (s). ^{1}H NMR (δ, CDCl$_3$): 5.28 (s, 5H, C$_5$H$_5$), 7.26−7.35 (m, 5H, C$_6$H$_5$). ^{13}C NMR (δ, CDCl$_3$): 91.5 (C$_5$H$_5$), 124.6 (CCPh), 128.4−130.8 (C$_6$H$_5$), 188.2 (CCPh), 211, 213 (CO). Mp (°C): 163−166 (dec). Anal. Calcd for C$_{21}$H$_{10}$Fe$_2$MoO$_8$: C, 42.18; H, 1.69. Found: C, 42.33; H, 1.76.

2: Yield: 31 mg (31%). IR (ν(CO), cm^{-1}, *n*-hexane): 2059 (s), 2016 (s), 1999 (vs), 1984 (w), 1955 (s). ^{1}H NMR (δ, CDCl$_3$): 2.08 (s, 15H, C$_5$ Me$_5$), 7.30−7.37 (m, 5H, C$_6$H$_5$). ^{13}C NMR (δ, CDCl$_3$): 11.1 (CH$_3$), 104.6 (C$_5$Me$_5$), 125.0 (CCPh), 126.4−135.4 (C$_6$H$_5$), 191.4 (CCPh), 213.3, 224.2 (CO). Mp (°C): 157−159 (dec). Anal. Calcd for C$_{26}$H$_{10}$Fe$_2$MoO$_8$: C, 46.74; H, 3.02. Found: C, 46.79; H, 3.11.

3: Yield: 27 mg (24%). IR (ν(CO), cm^{-1}, *n*-hexane): 2073 (s), 2043 (vs), 2021 (s), 2005 (m), 1973 (m), 1931 (w), 1877(m), 1856(w). ^{1}H NMR (δ, CDCl$_3$): 5.24 (s, 5H, C$_5$H$_5$), 7.37−7.40 (m, 5H, C$_6$H$_5$). ^{13}C NMR (δ, CDCl$_3$): 92.3 (C$_5$H$_5$), 132.6−135.2 (C$_6$H$_5$), 163.7, 182.4 (CCPh), 213, 218 (CO). Mp (°C): 127−131 (dec). Anal. Calcd for C$_{24}$H$_{10}$Fe$_3$MoO$_{11}$: C, 39.07; H, 1.37. Found: C, 38.92; H, 1.32.

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}_2\text{Mo(CO)}_7\{\mu_3\text{-C(H)C(Ph)C(Ph)C}\}]$ (4). A benzene solution containing $[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo(CO)}_3(\text{C}{\equiv}\text{CPh})]$ (50 mg, 0.12 mmol), Fe(CO)$_5$ (23 mg, 0.12 mmol), and PhC≡CH (73 mg, 0.6 mmol) was subjected to

Table 1. Crystal Data and Structure Refinement Parameters for 2−7

	2	**3**	**4**	**5**	**6**	**7**
empirical formula	$C_{26}H_{20}Fe_2MoO_8$	$C_{24}H_{10}Fe_3MoO_{11}$	$C_{33}H_{26}Fe_2MoO_7$	$C_{18}H_{10}Fe_2O_6$	$C_{26}H_{20}Fe_2O_2$	$C_{26}H_{20}Fe_2O_2$
fw	668.06	737.81	742.18	433.96	476.12	476.12
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/a$	*Pbca*	$P2_12_12_1$
a, Å	10.8610(7)	14.1570(11)	9.0530(12)	13.6460(9)	9.5430(15)	8.5770(7)
b, Å	14.9630(9)	9.4960(6)	10.6620(11)	6.0060(7)	11.7330(16)	9.9040(10)
c, Å	17.0970(11)	19.2440(14)	18.504(3)	20.4780(14)	17.563(3)	23.3060(11)
α, deg			87.076(10)		90.000	90.000
β, deg	105.105(5)	90.984(6)	79.318(12)	96.767(6)	90.000	90.000
γ, deg			83.152(10)		90.000	90.000
V, $Å^3$	2682.5(3)	2586.7(3)	1741.8(4)	1.666.6(3)	1966.5(5)	1979.8(3)
Z	4	4	2	4	2	4
D_{calcd}, Mg m^{-3}	1.654	1.895	1.415	1.729	1.608	1.597
abs coeff, mm^{-1}	1.573	2.182	1.217	1.773	1.496	1.486
F(000)	1336	1448	748	872	976	976
cryst size, mm	0.3 × 0.2 × 0.15	0.3 × 0.25 × 0.15	0.275 × 0.215 × 0.215	0.3 × 0.175 × 0.125	0.3 × 0.25 × 0.25	0.25 × 0.215 × 0.10
θ range, deg	1.83 to 24.93	1.44 to 24.92	1.12 to 24.93	2.00 to 24.94	2.31 to 24.92	1.74 to 24.91
index ranges	$0 \le h \le 12$, $0 \le k \le 17$, $-20 \le l \le 19$	$0 \le h \le 16$, $0 \le k \le 11$, $-22 \le l \le 22$	$0 \le h \le 10$, $-12 \le k \le 12$, $-21 \le l \le 21$	$0 \le h \le 16$, $0 \le k \le 7$, $-24 \le l \le 24$	$0 \le h \le 11$, $0 \le k \le 13$, $0 \le l \le 20$	$0 \le h \le 10$, $0 \le k \le 11$, $-27 \le l \le 27$
no. of reflns	4073/4073	3985/3985	5485/5485	2656/2656	1425/1425	1632/1632
no. of collected/ unique reflns	[*R*(int) = 0.0000]	[*R*(int) = 0.0000]	[*R*(int) = 0.0000]	[*R*(int) = 0.0000]	[*R*(int) = 0.0000]	[*R*(int) = 0.0000]
no. of data/restraints/ params	4073/0/354	3985/0/389	5485/0/412	2656/0/275	5485/0/412	1632/0/295
goodness-of-fit on F^2	1.078	1.110	1.190	1.072	1.103	1.079
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0364, wR2 = 0.0874	R1 = 0.0477, wR2 = 0.1146	R1 = 0.0517, wR2 = 0.1674	R1 = 0.0332, wR2 = 0.0758	R1 = 0.0486, wR2 = 0.1221	R1 = 0.0457, wR2 = 0.1065
R indices (all data)	R1 = 0.0467, wR2 = 0.0957	R1 = 0.0557, wR2 = 0.1228	R1 = 0.0635, wR2 = 0.1795	R1 = 0.0429, wR2 = 0.0827	R1 = 0.0648, wR2 = 0.1353	R1 = 0.0648, wR2 = 0.1218
largest diff peak and hole, e $Å^{-3}$	0.369 and −0.773	1.200 and −1.430	1.796 and −0.875	0.409 and −0.473	0.854 and −0.478	0.582 and −0.680

photolysis for 10 min at 0 °C in a photochemical reaction vessel under a continuous argon flow. The solvent was removed in vacuo, and the residue was dissolved in a minimum amount of dichloromethane. This solution was filtered through Celite to remove insoluble material and then subjected to chromatographic workup on silica gel TLC plates. Elution with a dichloromethane/hexane (10:90 v/v) mixture yielded a green band, $[(\eta^5\text{-}C_5Me_5)Fe_2Mo(CO)_7\{\mu_3\text{-}C(H)C(Ph)C(Ph)C\}]$ (**4**). Yield: 29 mg (33%). IR (ν(CO), cm^{-1}, *n*-hexane): 2049 (s), 2027 (w), 2008 (vs), 1973 (s), 1896 (s), 1844 (w). ^1H NMR (δ, $CDCl_3$): 2.10 (s, 15H, C_5Me_5), 7.30−7.10 (m, 10H, C_6H_5), 8.58 (s, 1H, CH). ^{13}C NMR (δ, $CDCl_3$): 13.1 (CH_3), 109.6 ($C_5(CH_3)_5$), 128.6−131.2 (C_6H_5), 138.6, 143.8 (C_4Ph), 208.6, 214.2 (CO). Mp (°C): 131−133 (dec). Anal. Calcd for $C_{33}H_{26}Fe_2MoO_7$: C, 53.40; H, 3.53. Found: C, 53.94; H, 3.64.

Preparation of Tetracarbonyl(2-ferrocenylmaleoyl)-iron (5), 2,5-Diferrocenylquinone (6), and 2,6-Diferrocenylquinone (7). A hexane solution of FcC≡CH (153 mg, 0.73 mmol) and $Fe(CO)_5$ (72 mg, 0.36 mmol) was subjected to photolysis for 10 min at −30 °C under a continuous bubbling of carbon monoxide. After removal of the solvent in vacuo, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a dichloromethane/hexane mixture (40:60 v/v) gave three major bands, namely, tetracarbonyl-(2-ferrocenylmaleoyl)iron (blue) (**5**), 2,5-diferrocenylquinone (green) (**6**), and 2,6-diferrocenylquinone (green) (**7**). After workup, 59 mg (38%) of FcC≡CH was recovered.

5: Yield: 13 mg (6%). IR (ν(CO), cm^{-1}, *n*-hexane): 2112 (s), 2053 (s), 2027 (s), 1716 (s), 1682 (w). ^1H NMR (δ, $CDCl_3$): 4.15 (s, 5H, Fc-unsub), 4.57 (s, 2H, Fc-sub), 5.29 (s, 2H, Fc-sub), 7.38 (s, 1H, CH). ^{13}C NMR (δ, $CDCl_3$): 69.5−73.1 (4H, Fc-sub), 70.2 (5H, Fc-unsub), 151.5 (C═CH), 176.1 (C═CH), 199.3, 199.6 (═CO), 202.8 (Fe−CO). Mp (°C): 93−95 (dec). Anal. Calcd for $C_{18}H_{10}Fe_2O_6$: C, 49.82; H, 2.32. Found: C, 50.08; H, 2.49.

6: Yield: 29 mg (26%). IR (ν(CO), cm^{-1}, *n*-hexane): 2084 (s), 2058 (s), 2044 (w), 2008 (s), 1780 (w), 1670 (w), 1638 (s). ^1H NMR (δ, $CDCl_3$): 4.16 (s, 10H, Fc-unsub), 4.61 (s, 4H, Fc-sub), 4.99 (s, 4H, Fc-sub), 6.83 (s, 2H, CH). ^{13}C NMR (δ, $CDCl_3$): 69.8−72.2 (8H, Fc-sub), 70.5 (10H, Fc-unsub), 127.6 (C═CH), 147.8 (FcC═CH), 185.9 (CO). Mp (°C): 131−133 (dec). Anal. Calcd for $C_{26}H_{20}Fe_2O_2$: C, 65.59; H, 4.23. Found: C, 65.93; H, 4.42.

7: Yield: 16 mg (14%). IR (ν(CO), cm^{-1}, *n*-hexane): 2063 (w), 2027 (s), 2044 (w), 1964 (w), 1896 (s), 1778 (s), 1737 (w), 1619 (w). ^1H NMR (δ, $CDCl_3$): 4.18 (s, 10H, Fc-unsub), 4.61 (s, 4H, Fc-sub), 4.97 (s, 4H, Fc-sub, 6.83 (s, 2H, CH). ^{13}C NMR (δ, $CDCl_3$): 69.8−72.0 (8H, Fc-sub), 70.4 (10H, Fc-unsub), 127.2 (C═CH), 148.8 (FcC═CH), 186.5 (CO). Mp (°C): 139−141 (dec). Anal. Calcd for $C_{26}H_{20}Fe_2O_2$: C, 65.59; H, 4.23. Found: C, 65.82; H, 4.36.

Crystal Structure Determination of 2−7. Suitable X-ray quality crystals of **2**−**7** were grown by slow evaporation of a dichloromethane/*n*-hexane solvent mixture at −5 °C, and an X-ray crystallographic data were collected from single-crystal samples of **2** (0.3 × 0.2 × 0.15), **3** (0.3 × 0.25 × 0.15), **4** (0.275 × 0.215 × 0.215), **5** (0.3 × 0.175 × 0.125), **6** (0.3 × 0.25 × 0.25), and **7** (0.25 × 0.215 × 0.1), mounted on glass fibers. Relevant crystallographic data and structure refinement details are listed in Table 1. A Nonius MACH3 diffractometer (graphite monochromatized Mo Kα radiation) was used for the cell determination and intensity data collection. The structure was solved by direct methods (SHELXS) and refined by full-matrix least squares against F^2 using SHELXL-97 software.[41] Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

Acknowledgment. One of us (P.M.) is grateful to the Department of Science and Technology, Government of India, for research funding. V.K.S. is grateful to the CSIR for a fellowship.

Supporting Information Available: Details of the structure determination for **2**−**7**, including tables listing full bond length, bond angles, and torsion angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049739Y

---

[41] Sheldrick, G. M. *SHELXL 97*, Program for crystal structure solution and refinement; University of Göttingen, 1997.