Thermal and Photochemical Formation of Dinuclear Molybdenadithiolene Complexes in One-Pot Reactions among $[(Cp)_2Mo_2(CO)_6]$, Elemental Sulfur and Dimethyl Acetylenedicarboxylate

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One-pot reaction among $[(Cp)_2Mo_2(CO)_6]$, elemental sulfur, and dimethyl acetylenedicarboxylate (DMAD) affords several types of dinuclear molybdenadithiolene complexes. The thermal reaction gives $[(Cp)(CO)_2Mo\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Mo(Cp)]$(**2**), while the photoreaction gives mainly isomeric $[(Cp)Mo(CO)\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Mo(CO)(Cp)]$(**3**). The former dicarbonylmolybdenum complex easily undergoes decarbonylation, while the latter is thermally stable.

A metalladithiolene ring is a very unique metal chelate ring which exhibits aromaticity and unsaturation.[1] In addition to the extensive studies on the mononuclear metalladithiolene complexes, interest is now directed to polynuclear metalladithiolene complexes for which new physical and chemical properties and thus novel functionalities are expected.

With respect to the polynuclear molybdenadithiolene complexes having CpMo unit, a few studies have been done. King first prepared dinuclear molybdenadithiolene complexes in the reaction between $[(Cp)_2Mo_2(CO)_6]$ and $S_2C_2(CF_3)_2$.[2] The group of DuBois reported the same type of molybdenadithiolenes with 1,2-benzenedithiolato ligand.[3] Rosselet *et al.* have determined the X-ray structures of two molybdenadithiolene complexes which have been synthesized by King.[4]

We have developed the construction of the metalladithiolene rings: the first method is the one-pot reaction among alkyne, mononucluear metal carbonyls and elemental sulfur[5] and the second one is the incorporation of a part of sulfur containing ring compounds into metal complexes as a ligand in the thermal or photochemical reactions.[6]

The thermal or photochemical one-pot reaction of $[(Cp)_2Mo_2(CO)_6]$, elemental sulfur, and dimethyl acetylenedicarboxylate (DMAD) gives several types of dinuclear molybdenadithiolene complexes. Interestingly thermal and photochemical reactions give different types of molybdenadithiolenes.

The reflux of a benzene solution of $[(Cp)_2Mo_2(CO)_6]$ (**1**) (0.10 mmol), S_8 (0.11mmol), and DMAD (4.0 mmol) for 1 h affords $[(Cp)(CO)_2Mo\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Mo(Cp)]$ (**2**), and $[(Cp)Mo\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Mo(Cp)\{S_2C_2(CO_2Me)_2\}]$(**5**).

The irradiation of a benzene solution of the same mixture with a medium pressure mercury lamp gives **2**, $[(Cp)Mo(CO)\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Mo(CO)(Cp)]$ (**3**), in which each metal atom is bonded to one CO, **5** and a small amount of $[(Cp)Mo\{\mu\text{-}S_2C_2(CO_2Me)_2\}Mo(Cp)\{\mu\text{-}S_2C_2(CO_2Me)_2\}]$(**4**). The complexes, **2**, **4**, and **5** are analogs of molybdenadithiolene complexes reported by King in the reaction between $[(Cp)_2Mo_2\text{-}(CO)_6]$ and $S_2C_2(CF_3)_2$.[2]

The most remarkable difference between thermal and photochemical reactions is that the thermal reaction affords dicarbonyl complex **2**, while photo-reaction yields mainly isomeric dicarbonyl complex **3**. The yields of products in thermal and photochemical reactions are summarized in Table 1.[7]

The structures of molybdenadithiolene complexes have been determined by X-ray crystal analysis. The ORTEP drawings of **2** and **3** are shown below.

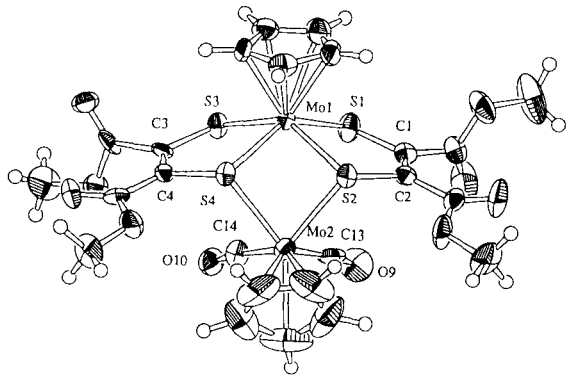


Figure 1. ORTEP drawing of $[(Cp)(CO)_2Mo\{\mu\text{-}S_2C_2\text{-}(CO_2Me)_2\}_2Mo(Cp)]$(**2**). Selected bond lengths (Å) and angles (°), Mo(1)-Mo(2), 3.262(2), Mo(1)-S(1), 2.4323(4); Mo(1)-S(2), 2.379(3); S(1)-C(1), 1.73(1); S(2)-C(2), 1.78(1); C(1)-C(2), 1.34(2); Mo(2)-C(13), 1.99(2); S(1)-Mo(1)-S(2), 82.8(1), Mo(1)-S(1)-C(1), 104.8(5), Mo(1)-S(2)-C(2), 106.2(4), Mo(1)-S(2)-Mo(2), 83.9(1).

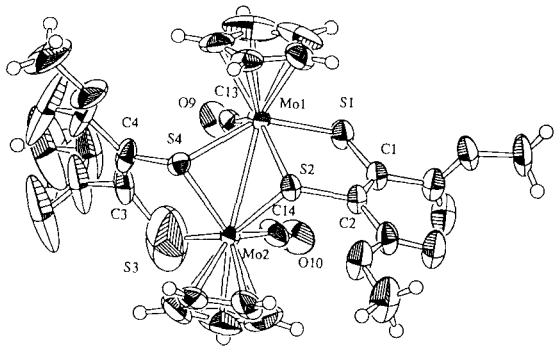


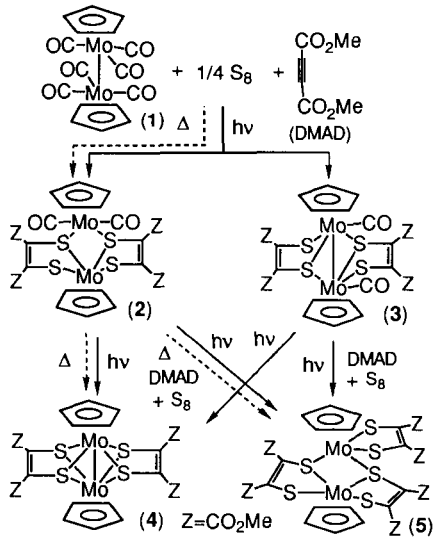
Figure 2. ORTEP drawing of $[(Cp)Mo(CO)\{\mu\text{-}S_2C_2\text{-}(CO_2Me)_2\}_2Mo(CO)(Cp)]$ (**3**). Selected bond lengths (Å) and angles (°), Mo(1)-Mo(2), 3.040(2), Mo(1)-S(1), 2.449(2), Mo(1)-S(2), 2.394(3), S(1)-C(1), 1.7929(7), S(2)-C(2), 1.769(6), C(1)-C(2), 1.340(9); Mo(1)-C(13), 2.008(8); S(1)-Mo(1)-S(2), 82.91(6), Mo(1)-S(1)-C(1), 104.3(2), Mo(1)-S(2)-C(2), 106.8(2), Mo(1)-Mo(2)-S(2), 50.10(5), Mo(2)-Mo(1)-S(2), 52.91(6), Mo(1)-S(2)-Mo(2), 76.99(6).

Table 1. Thermal and photochemical formation of molybdenadithiolene complexes in one-pot reactions from $[(Cp)_2Mo_2(CO)_6]$, S_8, and DMAD in benzene solutions

Condition	Time	Yield of product /%			
	h	2	3	4	5
Δ[a]	20	30	0	0	41
hν[b]	1	10	50	1	15

[a]reflux under an Ar atmosphere. [b]Irradiation was carried out with a medium pressure Hg lamp through a pyrex cooling jacket under an Ar atmosphere at room temperature.

The molybdenadithiolene complexes **4** and **5** having no coordinated carbonyl are considered to be secondary products from carbonyl-containing complexes. The thermolysis and photolysis of **2** give **4**. The thermal and photochemical reactions of **2** with DMAD and S_8 afford **5**. The complex **3** is resistant to heating but it gives **4** in photolysis and **5** in the irradiation with S_8 and DMAD.



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7 *Identification of metalladithiolene complexes*

$[(Cp)(CO)_2Mo\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Mo(Cp)]$(**2**), mp, 255 °C; ^{1}H NMR($CDCl_3$), δ=3.86(6H, s, $CO_2C\underline{H}_3$), 3.90(6H, s, $CO_2C\underline{H}_3$), 4.75(5H, s, H of Cp ring), and 5.70 (5H, s, H of Cp ring); ^{13}C NMR($CDCl_3$), δ=52.8, 53.2, 93.7, 95.1, 129.5, 163.6, 169.3, and 171.4; IR(KBr), 1930 and 1979 cm^{-1} (νC≡O); MS (EI 70eV, rel intensity)) *m/z*, 734(M^+, 68), 450(86), and 449(100);Calcd for $C_{24}H_{22}O_{10}S_4Mo_2$: C, 36.46; H, 2.80%; Found: C, 36.85; H, 3.03%.; Crystal data F.W., 790.55; Space goup $C2_1/a$ with cell dimensions a = 11.560(3)Å, b = 16.644(2)Å, c = 15.337(2)Å; β = 100.24(1)°; V = 2904.0(8)Å^3, Z = 4, ρ_{calcd} = 1.808 g/cm^3; R = 0.051, Rw = 0.038.

$[(Cp)Mo(CO)\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Mo(CO)(Cp)]$ (**3**), mp, 196-198 °C; ^{1}H NMR($CDCl_3$), δ=3.80(6H, s, $C\underline{H}_3$), 3.82 (3H, s, $C\underline{H}_3$), 3.85(3H, s, $C\underline{H}_3$), 5.32(5H, s, H of Cp ring), and 5.44(5H, s, H of Cp ring); ^{13}C NMR($CDCl_3$), δ=52.5, 52.7, 53.1, 53.5, 92.2, 95.2, 163.0, 164.5, 165.0, 168.0, 228.2 and 232.0; IR(KBr), 1971 cm^{-1} (νC≡O); MS(EI 70eV, rel intensity) *m/z*, 734,(M^+, 21), 702(79), 450(40), and 418(100); Crystal data F.W., 790.55; Space goup $C2/c$ with cell dimensions a = 13.05(1)Å, b = 16.30(4)Å, c = 27.53(3)Å; β = 98.29(8)°; V = 5796(10)Å^3, Z = 8, ρ_{calcd} = 1.81g/cm^3; R = 0.052, Rw = 0.044.

$[(Cp)Mo\{\mu\text{-}S_2C_2(CO_2Me)_2\}Mo(Cp)\{\mu\text{-}S_2C_2(CO_2Me)_2\}]$ (**4**), mp, >300 °C; ^{1}H NMR ($CDCl_3$), δ=3.61(12H,s, $CO_2C\underline{H}_3$), 6.24(10H, s , H of Cp ring); ^{13}C NMR($CDCl_3$), δ=52.7, 97.8, 159.9, and 165.6; MS(EI-70eV, rel intensity) *m/z*, 734(M^+, 47), 450(89), 448(100), and 386(24); Calcd for $C_{22}H_{22}O_8S_4Mo_2$: C, 35.97; H, 3.02%; Found: C, 35.85; H, 3.03%.

$[(Cp)Mo\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Mo(Cp)\{S_2C_2(CO_2Me)_2\}]$ (**5**), mp, >300 °C; ^{1}H NMR($CDCl_3$), δ=3.81(6H, s, $CO_2C\underline{H}_3$), 3.89(6H,s, $CO_2C\underline{H}_3$), 4.00(3H,s , $CO_2C\underline{H}_3$), 4.97(5H, s, H of Cp ring), and 5.20 (5H, s, H of Cp ring); ^{13}C NMR($CDCl_3$), δ=52.8, 53.0, 53.1, 95.6, 95.9, 136.2, 161.1, 162.8, 165.2, 168.8, and 173.7; MS(FAB) *m/z* 940(M^+); (EI 70eV, rel intensity), 702(50), 418(100), and 386(28); $C_{28}H_{28}O_{12}S_6Mo_2$: C, 35.75; H, 3.00%; Found: C, 35.75; H, 2.95%.