

Insertion of CS₂ into a metal acetylide bond and conversion of the bonding mode of S₂CC≡CPh from η² to η³

Pradeep Mathur^{a,b,*}, Abhijit K. Ghosh^a, Sarbani Mukhopadhyay^a,
Chimalakonda Srinivasu^a, Shaikh M. Mobin^b

^a Chemistry Department, Indian Institute of Technology, Powai, Bombay 400076, India

^b National Single Crystal X-Ray Diffraction Facility, Indian Institute of Technology, Powai, Bombay 400076, India

Received 10 December 2002; received in revised form 7 May 2003; accepted 16 May 2003

Abstract

Photolysis of a benzene solution containing [(L)Mo(CO)₃(C≡CPh)] (L = η⁵-C₅H₅ **1**; η⁵-C₅Me₅ **2**) and CS₂ leads to the formation of dithiopropiolato containing complexes, [(L)Mo(CO)₂(η²-S₂CC≡CPh)] (L = η⁵-C₅H₅ **4**; L = η⁵-C₅Me₅ **5**). In presence of air, [(η⁵-C₅H₅)Mo(CO)₃(C≡CPh)] reacts with CS₂ to give **4** as the major and [(η⁵-C₅H₅)Mo(O)(η³-S₂CC≡CPh)] (**6**) as minor products. Similarly, [(η⁵-C₅Me₅)Mo(CO)₃(C≡CPh)] reacts with CS₂ under aerobic conditions to give compound **5** along with [(η⁵-C₅Me₅)Mo(O)(η³-S₂CC≡CPh)] (**7**) as minor product. When solutions of **4** or **5** are photolysed under a constant purge of air, **4** gives **6**, and **5** gives **7** in high yields. Room temperature stirring of **5** with [W(CO)₅(THF)] forms [η⁵-C₅Me₅)Mo(CO)₂CS₂{W(CO)₅}C≡CPh] (**9**). All new compounds have been characterised by IR and ¹H-NMR spectroscopy and the structures of **4**, **6**, **7** and **9** have been established crystallographically.

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Keywords: Acetylides; Mixed-metal; Chalcogen; Crystal structure

1. Introduction

As an unsaturated electrophile and a potential source of C₁ chemistry carbon disulfide has attracted a plethora of research activity, in particular on its reactivity towards transition metal complexes [1]. A diverse array of compounds are known where CS₂ bonds in η¹-end on, η²-side on and bridging co-ordination modes [2–10]. It readily inserts into metal alkyl and metal hydride bonds at room temperature or under mild thermolytic conditions to form dithiocarboxylate or dithioformate complexes where the S₂C motif is bound to the metal in either η² or η³ fashion [11–13]. Although insertion of CS₂ into a M–C (sp³) bond is the most common, there exist some examples of CS₂ additions yielding η³-S₂CR ligand systems [13–22]. In our previous studies we have examined acetylide coupling reactions on chalcogen-bridged mixed metal carbonyl clusters. Various modes

of coupling reactions were observed and these were found to be dependent on the nature of chalcogen bridges as well as the reaction conditions used [23–27]. Under oxidising conditions we were able to isolate some novel oxo-containing mixed-metal clusters with chalcogen and acetylide bridges [28,29]. Here we report another facet to the reactions of metal acetylide complexes, namely the photolytic reaction of molybdenum acetylide complexes with CS₂ under aerobic and anaerobic reaction conditions. Two types of CS₂ insertion into Mo–acetylide bonds are observed with conversion of one type into the other.

2. Results and discussion

On photolysis of a benzene solution of [(L)Mo(CO)₃(C≡CPh)] (L = η⁵-C₅H₅ **1**; η⁵-C₅Me₅ **2**) and CS₂, formation of [(L)Mo(CO)₂(η²-S₂CC≡CPh)] (L = η⁵-C₅H₅ **4**; L = η⁵-C₅Me₅ **5**) was observed (Eq. 1). Compounds **4** and **5** were characterised by IR and ¹H-NMR spectroscopy and their compositions were

* Corresponding author. Tel./fax: +91-22-572-4089.

E-mail address: mathur@chem.iitb.ac.in (P. Mathur).

confirmed by elemental analysis. Both compounds display an identical carbonyl stretching pattern in their IR spectra, and $^1\text{H-NMR}$ show singlets to confirm the presence of $(\eta^5\text{-C}_5\text{H}_5)$ and $(\eta^5\text{-C}_5\text{Me}_5)$ groups for **4** and **5**, respectively, and a multiplet for a phenyl group in each of these compounds. For an unambiguous structure elucidation, crystals of **4** were grown from dichloromethane–hexane solvent mixture at 4°C , and a single crystal X-ray diffraction study was undertaken. Molecular structure of **4** (Fig. 1) shows a $\{(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\}$ unit and a $(\text{S}_2\text{CC}\equiv\text{CPh})$ ligand bonded to the molybdenum atom in η^2 -bonding mode. The two Mo–S bond lengths in **4**, 2.4639(11) and 2.4610(12) Å are almost equal and marginally longer than the Mo–S bond distance range of 2.414–2.455 Å observed in other thio acid complexes [30–36]. A separation of 2.995 Å between molybdenum atom and the α -carbon of the acetylide group is much longer than the Mo–C(acetylide) bond length of 1.196(9) Å in **1** indicating absence of a formal bond between Mo atom and the acetylide group. Delocalisation of π -electron cloud over the S_2C moiety in **4** is indicated by shortening of C(6)–C(7) single bond to 1.415(6) Å and lengthening of C(7)–C(8) to 1.206(6) Å from the normal values associated with C–C single and C $\equiv$ C triple bonds, respectively as in $[\text{Ru}_3(\mu_3\text{-}\eta^2\text{-PhC}_2\text{C}\equiv\text{CBu}^t)(\mu\text{-PPh}_2)_2(\text{CO})_6]$; C–C, 1.439(5) Å, C $\equiv$ C, 1.188(5) Å [37]. The small bond angle of S(2)–Mo–S(1), $68.34(4)^\circ$ is comparable to the S–Mo–S bond angle of $72.4(1)^\circ$ of the $\eta^2\text{-CS}_2$ bonded moiety of $[\text{MoO}(\text{S}_2\text{CNPr}_2)_2]$ [30], and is consistent with the ring constraints imparted by the bidentate S_2C ligand in forming a four-membered ring.

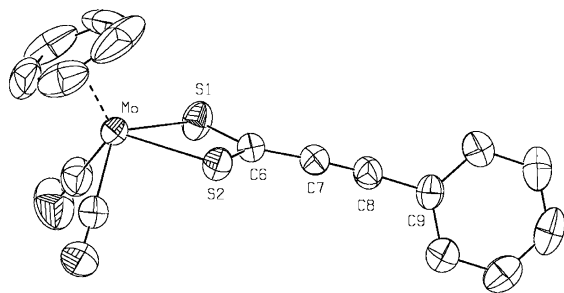
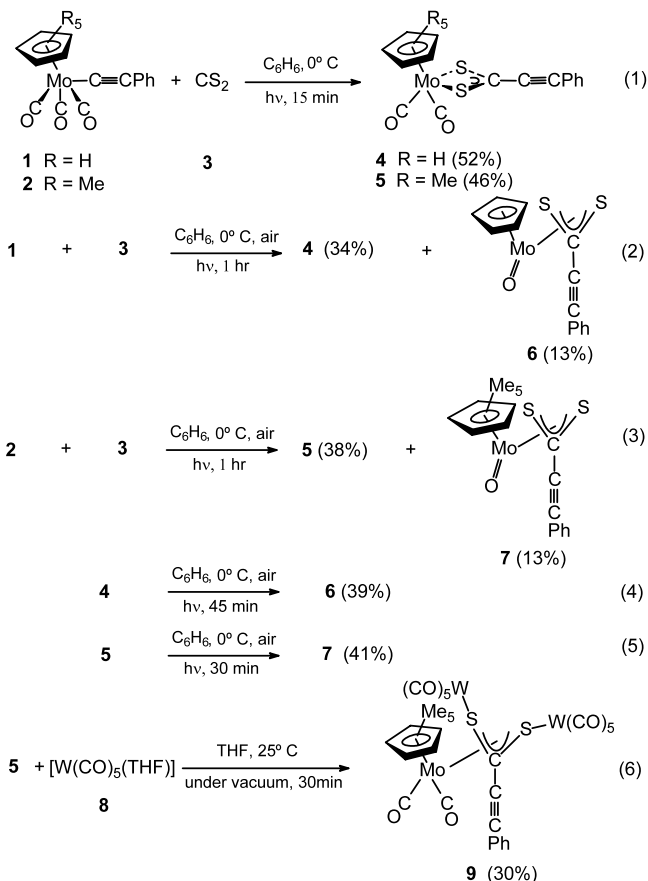


Fig. 1. ORTEP diagram of **4** with 30% probability ellipsoids. Selected bond distance (Å) and bond angles ($^\circ$): Mo–S(1) = 2.4610(12), Mo–S(2) = 2.4639(11), S(1)–C(6) = 1.6770(4), S(2)–C(6) = 1.688(4), C(6)–C(7) = 1.415(6), C(7)–C(8) = 1.206(6), C(8)–C(9) = 1.435(6), S(2)–C(6)–S(1) = $110.6(2)$, S(1)–C(6)–C(7) = $125.2(3)$, S(2)–C(6)–C(7) = $124.0(3)$, C(6)–C(7)–C(8) = $176.8(4)$, C(7)–C(8)–C(9) = $176.5(4)$, S(2)–Mo–S(1) = $68.34(4)$.



From the photolytic reaction between **1** and CS_2 , in presence of air, **4** and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ (**6**) were obtained in yields of 34 and 13%, respectively (Eq. 2). Under similar conditions, reaction between **2** and CS_2 led to the formation of **5** (38%) and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ (**7**) (13%) (Eq. 3). Compound **6** and the analogous $[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ (**7**) were obtained in reasonable yields when a benzene solution of **4** or **5** was photolysed in presence of air (Eq. 4 and Eq. 5). Absence of bands in the carbonyl region, and a band at 975 cm^{-1} (**6**) or 973 cm^{-1} (**7**) assignable to a Mo=O group are the notable features in their IR spectra [28,29]. Presence of $(\eta^5\text{-C}_5\text{H}_5)$, $(\eta^5\text{-C}_5\text{Me}_5)$ and phenyl groups were confirmed by $^1\text{H-NMR}$ spectra. Single crystals of **6** and **7** were grown from dichloromethane–hexane mixture solvent at 0°C and single crystal X-ray diffraction analyses were carried out. Molecular structures of **6** (Fig. 2) and **7** (Fig. 3) are similar and consists of a $\{(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(=\text{O})\}$ or $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(=\text{O})\}$ moiety, respectively and a $(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})$ ligand attached to the Mo atom. The unusual η^3 -bonding mode of this ligand is confirmed on the basis of the following observations: the Mo–C(6) separations of 2.228(4) Å in **6** and 2.216(5) Å in **7** are much shorter than the usual ≈ 3.0 Å separation observed for the more common $\eta^2\text{-S}_2\text{C-R}$ bonded systems [38]; additionally the planarity of the S1–S2–

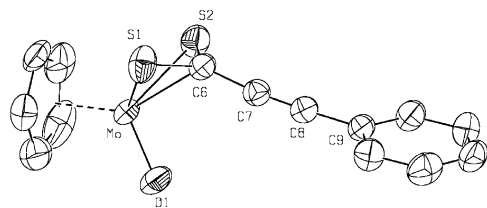


Fig. 2. ORTEP diagram of **6** with 30% probability ellipsoids. Selected bond distances (Å) and bond angles (°): Mo–S(2) = 2.3399(12), Mo–S(1) = 2.3366(10), Mo–C(6) = 2.228(4), Mo–O(1) = 1.689(3), C(6)–S(2) = 1.744(4), C(6)–S(1) = 1.732(3), C(6)–C(7) = 1.428(5), C(7)–C(8) = 1.204(5), C(8)–C(9) = 1.432(5), S(2)–C(6)–S(1) = 120.0(2), S(2)–C(6)–Mo = 70.99(14), S(1)–C(6)–Mo = 71.06(13), Mo–C(6)–C(7) = 127(3), C(6)–C(7)–C(8) = 174.3(4), C(7)–C(8)–C(9) = 177.6(4), S(1)–Mo–S(2) = 80.17(4).

C6–C7 (C_2S_2) found in **4**, is lost in **6** and **7**. The S–Mo–S bond angles, $80.17(4)^\circ$ in **6** and $79.44(7)^\circ$ in **7** are significantly larger than that observed in **4** and is indicative of release of some strain on conversion of the four membered MoS_2C ring in **4** to an open, allyl-type bonding between the Mo atom and the S_2C unit. This is also reflected in the S–C–S angle of $110.6(2)^\circ$ in **4** opening to $120(2)^\circ$ in **6** and $119.6(3)^\circ$ in **7**. The ($C\equiv CPh$) substituent and the oxo on the molybdenum atom are mutually endo in both **6** and **7**; without observation of any exo-isomer in our reaction mixtures.

We observed that $\eta^2-\eta^3$ conversion of the $S_2C-C\equiv CPh$ ligand can also be brought about by the addition of ‘ $W(CO)_5$ ’ groups to the S atoms of **5**. Thus, when a THF solution of **5** was treated with $[W(CO)_5(THF)]$ and the solution stirred at room temperature in vacuum, the adduct, $[\eta^5-C_5Me_5]Mo(CO)_2CS_2\{W(CO)_5\}_2C\equiv CPh$ (**9**) was isolated in 30% yield (Eq. 6). IR spectrum of **9** shows bands due to terminal carbonyls as well as bands

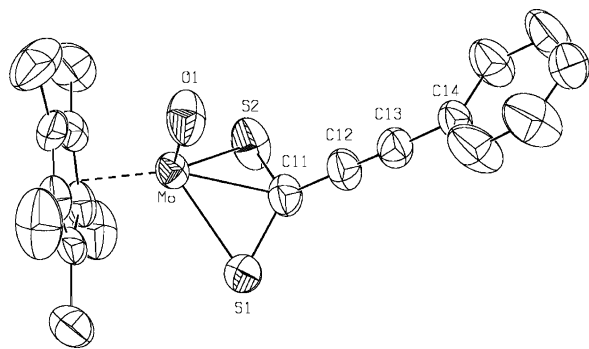


Fig. 3. ORTEP diagram of **7** with 30% probability ellipsoids. Selected bond distances (Å) and bond angles (°): Mo–S(1) = 2.3431(17), Mo–S(2) = 2.3404(16), Mo–C(11) = 2.216(5), Mo–O(1) = 1.689(4), C(11)–C(12) = 1.429(7), C(12)–C(13) = 1.189(7), C(13)–C(14) = 1.451(8), S(1)–C(11) = 1.730(6), S(2)–C(11) = 1.733(5), S(1)–Mo–S(2) = $79.44(7)^\circ$, S(2)–C(11)–S(1) = $119.6(3)^\circ$, Mo–S(1)–C(11) = $63.85(18)^\circ$, Mo–S(2)–C(11) = $63.89(18)^\circ$, S(1)–C(11)–C(12) = $120.5(4)^\circ$, S(2)–C(11)–C(12) = $124.3(8)^\circ$, Mo–C(11)–S(1) = $71.66(19)^\circ$, Mo–C(11)–S(2) = $71.52(19)^\circ$, C(11)–C(12)–C(13) = $177.7(6)^\circ$, C(12)–C(13)–C(14) = $177.9(6)^\circ$.

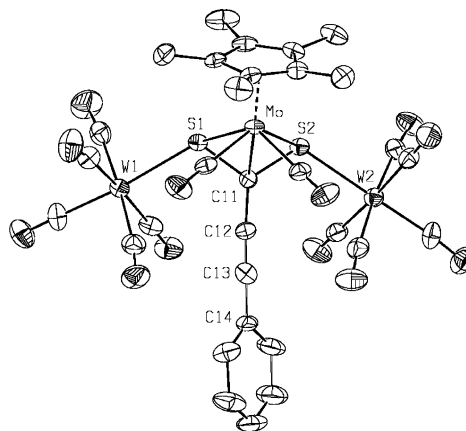


Fig. 4. ORTEP diagram of **9** with 30% probability ellipsoids. Selected bond distances (Å) and bond angles (°): Mo–S(1) = 2.525(3), Mo–S(2) = 2.513(3), Mo–C(11) = 2.220(11), C(11)–C(12) = 1.447(16), C(12)–C(13) = 1.197(18), W(2)–S(2) = 2.536(3), W(1)–S(1) = 2.549(3), C(13)–C(14) = 1.394(18), S(2)–C(11) = 1.755(11), S(1)–C(11) = 1.763(11), Mo–S(1)–C(11) = $59.2(4)^\circ$, Mo–S(2)–C(11) = $59.6(4)^\circ$, S(1)–C(11)–C(12) = $123.1(8)^\circ$, S(2)–C(11)–C(12) = $124.3(8)^\circ$, Mo–C(11)–S(1) = $77.7(4)^\circ$, Mo–C(11)–S(2) = $77.5(4)^\circ$, C(12)–C(13)–C(14) = $177.8(15)^\circ$, Mo–S(2)–W(2) = $128.94(12)^\circ$, Mo–S(1)–W(1) = $132.5(11)^\circ$, C(11)–C(12)–C(13) = $176.4(13)^\circ$, S(1)–C(11)–S(2) = $108.6(6)^\circ$.

due to the C–S and $C\equiv C$ groups. Presence of both ($\eta^5-C_5Me_5$) and phenyl groups were confirmed by 1H -NMR spectra. Crystallographic analysis of **9** was undertaken after obtaining its crystals from dichloromethane–hexane solvent mixtures at $-4^\circ C$. Its molecular structure (Fig. 4), shows an endo- $[\eta^5-C_5Me_5]Mo(CO)_2(\eta^3-S_2CC\equiv CPh)$ unit with a ‘ $W(CO)_5$ ’ group attached to each S atom. The reduced π electron delocalization over the S_2C moiety is reflected in C(11)–C(12) bond length, $1.447(16)$ Å which is comparable to a C–C single bond, $1.443(5)$ Å in $[Ru_3\{\mu_3-Me_3SiCC(C\equiv CSiMe_3)CC=CPh_2\}(\mu-OH)(CO)_9]$ [39]. The C(12)–C(13) bond distance, $1.197(18)$ Å in **9** is similar to the acetylide triple bond distance, $1.196(9)$ Å in $[(\eta^5-C_5H_5)Mo(CO)_3(C\equiv CPh)]$ and $1.197(5)$ Å in $[\{\eta^5-C_5H_5\}Mo(CO)_2]_2\{\mu-1, 2-PhC-C(CO)C\equiv CPh\}]$ [24,40].

3. Conclusion

In this paper we have reported the photolytic insertion of CS_2 into Mo–acetylide bond to give two types of co-ordinated $S_2C-C\equiv CPh$ ligands; one is the η^2 -bonding mode and the second, the rather rare η^3 -bonding mode [13–22]. We observe that the ($\eta^2-S_2C-C\equiv CPh$) can be transformed to ($\eta^3-S_2C-C\equiv CPh$) ligand by two different pathways: by oxidation at the metal atom or by addition of electron-withdrawing metal carbonyl groups to the S atoms of the ($\eta^2-S_2C-C\equiv CPh$) group. Thus, under aerobic photolytic conditions $[(L)Mo(CO)_2(\eta^2-$

$\text{S}_2\text{C}-\text{C}\equiv\text{CPh}]$ (**4** and **5**) convert to $[(\text{L})\text{Mo}(\text{O})(\eta^3-\text{S}_2\text{C}-\text{C}\equiv\text{CPh})]$ (**6** and **7**). Room temperature reaction of $[(\eta^5-\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_2(\eta^2-\text{S}_2\text{C}-\text{C}\equiv\text{CPh})]$ (**5**) with $[\text{W}(\text{CO})_5(\text{THF})]$ forms the adduct $[(\eta^5-\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_2\{\text{SW}(\text{CO})_5\}_2\text{C}-\text{C}\equiv\text{CPh}]$ (**9**) in which the S_2C unit is η^3 bonded to the Mo atom.

4. Experimental

4.1. General procedures

Reactions and manipulations for the preparation of **4–7** and **9** were carried out using standard Schlenk line techniques under an atmosphere of argon 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 FT IR spectrophotometer, as hexane solutions in 0.1 mm path length cells and NMR spectra were recorded on a Varian VXR—300S spectrometer in CDCl_3 . Elemental analyses were performed using a Carlo–Erba automatic analyser. The compounds $[(\text{L})\text{Mo}(\text{CO})_3-\text{C}\equiv\text{CPh}]$ ($\text{L} = \eta^5-\text{C}_5\text{H}_5$, $\eta^5-\text{C}_5\text{Me}_5$) [41] and $[\text{W}(\text{CO})_5(\text{THF})]$ [42] were prepared by established procedures. Photochemical 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.

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.

4.2. Synthesis of $[(\eta^5-\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta^2-\text{S}_2\text{CC}\equiv\text{CPh})]$ (**4**) and $[(\eta^5-\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_2(\eta^2-\text{S}_2\text{CC}\equiv\text{CPh})]$ (**5**)

A benzene solution (50 ml) containing $[(\eta^5-\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\text{C}\equiv\text{CPh})]$ (100 mg, 0.29 mmol) and carbon disulfide (0.02 ml, 0.3 mmol) was photolysed for 15 min at 0°C under continuous bubbling of argon. The solvent was removed in vacuo and the residue was dissolved in minimum amount of dichloromethane. The dichloromethane solution was filtered through Celite to remove insoluble material and the solution was subjected to chromatographic work-up on a silica gel column. Elution with hexane–dichloromethane mixture (60:40, v/v) yielded a violet coloured compound **4**. Yield: 58 mg (52%). M.p. $155\text{--}157^\circ\text{C}$. Anal. Found: C, 48.09; H, 2.60. $\text{C}_{16}\text{H}_{10}\text{MoO}_2\text{S}_2$ Calc.: C, 48.49; H, 2.55%. IR (cm^{-1}): 1980 (s), 1922 (vs) $\nu(\text{CO})$; 2187 (w) $\nu(\text{CC})$; 1066 (m), 891 (s), 764 (sh), 729 (vs) $\nu(\text{CS})$. $^1\text{H-NMR}$ (δ , ppm): δ 5.53 (s, 5H, C_5H_5), 7.31–7.56 (m, 5H, C_6H_5).

Compound **5** was prepared similarly using $[(\eta^5-\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3(\text{C}\equiv\text{CPh})]$ (100 mg, 0.24 mmol) and carbon disulfide (0.02 ml, 0.3 mmol). Yield: 49 mg (46%). M.p. $170\text{--}171^\circ\text{C}$. Anal. Found: C, 54.0; H, 4.53. $\text{C}_{21}\text{H}_{20}\text{MoO}_2\text{S}_2$ Calc.: C, 54.08; H, 4.33%. IR (cm^{-1}): 1979 (s), 1922 (vs) $\nu(\text{CO})$; 2183 (w) $\nu(\text{CC})$; 1064 (m), 887 (s), 760 (sh), 722 (vs) $\nu(\text{CS})$. $^1\text{H-NMR}$ (δ 1.88 (s, 15H, C_5Me_5), 7.32–7.56 (m, 5H, C_6H_5).

4.3. Synthesis of $[(\eta^5-\text{C}_5\text{H}_5)\text{Mo}(\text{O})(\eta^3-\text{S}_2\text{CC}\equiv\text{CPh})]$ (**6**) and $[(\eta^5-\text{C}_5\text{Me}_5)\text{Mo}(\text{O})(\eta^3-\text{S}_2\text{CC}\equiv\text{CPh})]$ (**7**)

A benzene solution (50 ml) of $[(\eta^5-\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\text{C}\equiv\text{CPh})]$ (80 mg, 0.232 mmol) and CS_2 (0.02 ml, 0.3 mmol) was subjected to photolysis for 1 h at 0°C in a photochemical reaction vessel under a continuous flow of air. After removal of the solvent in vacuum, the residue was subjected to chromatographic work up on silica gel column by using hexane–dichloromethane mixture (60:40 v/v) as an eluant. A major band of a violet compound **4** (31 mg, 34%) eluted first followed by an orange band of compound **6** (11 mg, 13%). Compound **6** was obtained in better yield by carrying out photolysis of a benzene solution (50 ml) of $[(\eta^5-\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta^2-\text{S}_2\text{CC}\equiv\text{CPh})]$ (**4**) (34 mg, 0.87 mmol) at 0°C under a constant purge of air for 45 min. Using hexane–dichloromethane mixture (60:40 v/v) as an eluant, trace amounts of **4** were obtained, followed by the major orange band of compound **6** (12 mg, 39%). M.p. $160\text{--}161^\circ\text{C}$. IR (cm^{-1}): 1060 (sh), 745 (vs) $\nu(\text{CS})$; 2187 (w) $\nu(\text{CC})$; 975 (w) $\nu(\text{Mo}=\text{O})$. $^1\text{H-NMR}$ (δ , ppm): δ 6.28 (s, 5H, C_5H_5), 7.26–7.40 (m, 5H, C_6H_5). Anal. Found: C, 47.07; H, 2.95. $\text{C}_{14}\text{H}_{10}\text{MoO}_2\text{S}_2$ Calc. C, 47.20; H, 2.83%.

Compound **7** was similarly obtained by photolysing a benzene solution (50 ml) of $[(\eta^5-\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3(\text{C}\equiv\text{CPh})]$ (80 mg, 0.19 mmol) and CS_2 (0.02 ml, 0.3 mmol) at 0°C in air for 1 h. Chromatographic work up on a silica gel column using hexane–dichloromethane mixture (60:40 v/v) as an eluant afforded compound **5** (34 mg, 38%) followed by **7** (10 mg, 13%). Alternatively, it was obtained in higher yield from direct photolysis of a benzene solution (50 ml) of $[(\eta^5-\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_2(\eta^2-\text{S}_2\text{CC}\equiv\text{CPh})]$ (**5**) (50 mg, 0.11 mmol) at 0°C for 30 min under constant purge of air. Yield: 19 mg (41%). M.p. $175\text{--}177^\circ\text{C}$. Anal. Found: C, 53.21; H, 4.85. $\text{C}_{19}\text{H}_{20}\text{MoOS}_2$. Calc. C, 53.52; H, 4.73%. IR (cm^{-1}): 1060 (sh), 745 (vs) $\nu(\text{CS})$; 2187 (w) $\nu(\text{CC})$; 973 (w) $\nu(\text{Mo}=\text{O})$. $^1\text{H-NMR}$ (δ , PPM): δ 2.12 (s, 15H, C_5Me_5), 7.20–7.50 (m, 5H, C_6H_5).

4.4. Synthesis of $[(\eta^5-\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_2\text{CS}_2\{\text{W}(\text{CO})_5\}_2\text{C}\equiv\text{CPh}]$ (**9**)

To a solution of $[(\eta^5-\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3(\text{C}\equiv\text{CPh})]$ (25 mg, 0.054 mmol) in dry THF (70 ml) was added

[W(CO)₅(THF)]. The reaction mixture was stirred under vacuum for 30 min, during which, the colour of the solution changed from green to brown. The solvent was removed in vacuo. The residue was dissolved in a minimum amount CH₂Cl₂ and was chromatographed using silica gel coated TLC plates. Use of hexane–dichloromethane mixture (60:40 v/v) as an eluant afforded a violet band **9**. Yield: 18 mg (30%). M.p. 240–241 °C (decomposition). Anal. Found: C, 33.11; H, 1.97. C₃₁H₂₀MoW₂O₁₂S₂ Calc. C, 33.40; H, 1.81%. IR (cm⁻¹): 1942 (vs), 1895 (s) ν (CO); 2187 (w) ν (CC); 1060 (sh), 899 (m), 745 (vs) ν (CS). ¹H-NMR (δ , ppm): δ 2.04 (s, 15H, C₅Me₅), 7.39–7.60 (m, 5H, C₆H₅).

4.5. Crystal structure determination of **4**, **6**, **7** and **9**

Suitable X-ray quality crystals of **4**, **6**, **7** and **9** were grown by slow evaporation of CH₂Cl₂-*n*-hexane solvent

mixtures and X-ray diffraction studies were undertaken. Relevant crystallographic data and details of measurements are given in Table 1. Data were collected from single crystals of **4** (0.3 × 0.15 × 0.15 mm³), **6** (0.4 × 0.25 × 0.15 mm³), **7** (0.25 × 0.125 × 0.1 mm³) and **9** (0.35 × 0.10 × 0.15 mm³). Unit cell dimensions were obtained using 25 centered reflections in θ range 5.6900–12.6800 mounted on a Nonius MACH 3 diffractometer equipped with graphite monochromated Mo–K α radiation (0.7093 Å). Intensity data were collected by ω –2 θ scan mode, and corrected by Lorentz polarization and absorption effects using Psi-Scan (ψ -scan). Three standard reflections monitored after every 200 reflections and 3 Intensity controlled reflections monitored every hour showed no significant changes (<3%). The structure was solved by direct methods (SHELXS 97) and refined by full-matrix least squares against F^2 using SHELXL-97 software [43]. Non-hydro-

Table 1
Crystal data and structure refinement details for **4**, **6**, **7** and **9**

	4	6	7	9
Empirical formula	C ₁₆ H ₁₀ MoO ₂ S ₂	C ₁₄ H ₁₀ MoOS ₂	C ₁₉ H ₂₀ MoOS ₂	C ₃₁ H ₂₀ MoO ₁₂ S ₂ W ₂
Formula weight	394.30	354.28	424.41	1112.23
Temperature (K)	293(2)	293(2)	293(2)	221(2)
Wavelength	0.70930	0.70930	0.70930	0.70930
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions				
<i>a</i> (Å)	13.2560(10)	10.469(2)	21.6530(12)	12.7070(10)
<i>b</i> (Å)	9.7660(12)	11.6280(13)	11.2990(11)	19.1550(14)
<i>c</i> (Å)	13.3740(12)	11.544(2)	16.5520(15)	14.7290(13)
α (°)	90.000(8)	90.000(12)	90.000(9)	90.000(6)
β (°)	115.003(6)	102.635(16)	109.305(6)	100.929(7)
γ (°)	90.000(8)	90.000(13)	90.000(6)	90.000(6)
<i>V</i> (Å ³)	1569.1(3)	1371.3(4)	3821.9(6)	3520.1(5)
<i>Z</i> , calculated density (Mg m ⁻³)	4, 1.669	4, 1.716	8, 1.475	4, 2.099
Adsorption coefficient (mm ⁻¹)	1.101	1.244	0.906	7.048
<i>F</i> (0 0 0)	784	704	1728	2096
Crystal size (mm)	0.3 × 0.15 × 0.15	0.4 × 0.25 × 0.15	0.25 × 0.125 × 0.1	0.35 × 0.10 × 0.15
θ range of data collection	1.68–24.91	1.80–24.93	1.99–24.92	1.63–24.92
Index ranges	0 ≤ <i>h</i> ≤ 15, 0 ≤ <i>k</i> ≤ 11, –15 ≤ <i>l</i> ≤ 14	0 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 13, –13 ≤ <i>l</i> ≤ 13	0 ≤ <i>h</i> ≤ 25, 0 ≤ <i>k</i> ≤ 13, –19 ≤ <i>l</i> ≤ 18	0 ≤ <i>h</i> ≤ 15, 0 ≤ <i>k</i> ≤ 22, –17 ≤ <i>l</i> ≤ 17
Reflections collected/unique [<i>R</i> (int) = 0.0000]	2487/2487	2368/2368	2604/2604	5509/5509
Completeness to 2 θ	2 θ = 24.91, 85.0%	2 θ = 27.93, 92.6%	2 θ = 24.92, 36.7%	2 θ = 24.92, 86.2%
Absorption correction	ψ -scan	ψ -scan	ψ -scan	ψ -scan
Max. and min. transmission	1.000 and 0.957	1.000 and 0.871	1.000 and 0.990	1.000 and 0.911
Refinement methods	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2487/0/230	2368/0/196	2604/0/288	5509/0/433
Goodness-of-fit on F^2	1.110	1.125	1.050	1.094
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.321, <i>wR</i> ₂ = 0.0777	<i>R</i> ₁ = 0.0452, <i>wR</i> ₂ = 0.1101	<i>R</i> ₁ = 0.0380, <i>wR</i> ₂ = 0.0675	<i>R</i> ₁ = 0.0754, <i>wR</i> ₂ = 0.1845
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0403, <i>wR</i> ₂ = 0.0872	<i>R</i> ₁ = 0.0473, <i>wR</i> ₂ = 0.1124	<i>R</i> ₁ = 0.0650, <i>wR</i> ₂ = 0.0783	<i>R</i> ₁ = 0.0820, <i>wR</i> ₂ = 0.1954
Largest diff. peak and hole (e Å ⁻³)	0.531 and –0.587	0.855 and –0.874	0.335 and –0.290	3.099 and –6.995

gen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 199392, 199391, 199390 and 199389 for compounds **4**, **6**, **7** and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgements

P.M. is grateful to the Department of Science and Technology, Government of India, for a research grant. A.K.G. and S.M. gratefully acknowledges University Grants Commission and Council of Scientific and Industrial Research, Government of India, respectively for research fellowships.

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