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The cleavage reaction of the Mo–Mo triple bond. The crystal structures of molybdenum complexes $[\text{CpMo}(\text{CO})_2(\text{C}_5\text{H}_4\text{NS})]$, $[\text{CpMo}(\text{CO})_2(\text{C}_9\text{H}_6\text{NS})] \cdot \text{O}=\text{PPh}_3$ and $[\text{CpMo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)]$

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Abstract

The reactions of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ (**1**) with 2,2'-dipyridyl disulphide ($\text{C}_5\text{H}_4\text{NS-})_2$, 8,8'-diquinoyl disulphide ($\text{C}_9\text{H}_6\text{NS-})_2$ and tetramethyl thiuram disulphide ($\text{Me}_2\text{NC}(\text{S})\text{S-})_2$ in toluene solution resulted in the cleavage of the Mo–Mo triple bond to yield molybdenum complexes $[\text{CpMo}(\text{CO})_2(\text{C}_5\text{H}_4\text{NS})]$ (**2**), $[\text{CpMo}(\text{CO})_2(\text{C}_9\text{H}_6\text{NS})]$ (**3**) and $[\text{CpMo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)]$ (**4**), respectively. The molecular structures of **2**, **3** · O=PPh₃ and **4** were determined by X-ray diffraction studies. Crystals of **2** are monoclinic, space group $P2_1/n$, with $Z = 4$, in a unit cell of dimensions $a = 6.448(1)$, $b = 12.616(2)$, $c = 14.772(2)$ Å, $\beta = 92.85(1)^\circ$. The structure was refined to $R = 0.028$ and $R_w = 0.039$ for 1357 observed reflections. Crystals of **3** · O=PPh₃ are triclinic, space group $P\bar{1}$, with $Z = 2$, in a unit cell of dimensions $a = 11.351(3)$, $b = 13.409(3)$, $c = 9.895(2)$ Å, $\alpha = 94.59(2)$, $\beta = 90.35(2)$, $\gamma = 78.07(2)^\circ$. The structure was refined to $R = 0.033$ and $R_w = 0.037$ for 3260 observed reflections. Crystals of **4** are monoclinic, space group $P2_1/a$ and $Z = 4$ with $a = 12.468(5)$, $b = 7.637(2)$, $c = 13.135(4)$ Å, $\beta = 96.62(3)^\circ$. The structure was refined to $R = 0.032$ and $R_w = 0.042$ for 1698 observed reflections. Each of complexes **2–4** contains a cyclopentadienyl ligand, a *cis* pair of carbonyls and a chelate ligand (S,N donor or S,S donor). All the compounds have distorted square-pyramid structures.

1. Introduction

The chemistry of the metal–metal triple bond in $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ (**1**) has been the subject of numerous investigations [1,2]. Its reactions with dialkyl or diphenyl disulphides RSSR led to the formation of binuclear thiolate-bridged complexes of general formula $[\text{Cp}_2\text{Mo}_2(\mu\text{-SR})_2(\text{CO})_4]$ ($\text{R} = \text{Me}$ [3], ^tBu [4], Ph [5] and *p*-MeC₆H₄ [4]) or $[\text{Cp}_2\text{Mo}_2(\mu\text{-SMe})_2(\text{CO})_2]$ [6] containing a Mo–Mo double bond. However, there is no report on its reaction with heterocyclic disulphide. Recently, we examined the reactions of **1** with some heterocyclic disulphides and found that mononuclear

compounds were formed. Here, we report on the synthesis of $[\text{CpMo}(\text{CO})_2(\text{C}_5\text{H}_4\text{NS})]$ (**2**), $[\text{CpMo}(\text{CO})_2(\text{C}_9\text{H}_6\text{NS})]$ (**3**) and the molecular structures of **2** and **3** · O=PPh₃. For comparison, the crystal structure of the closely related complex $[\text{CpMo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)]$ (**4**) [7] is also presented. Part of the work has appeared as a communication [8].

2. Results and discussion

The treatment of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ with $(\text{C}_5\text{H}_4\text{NS-})_2$ and $(\text{Me}_2\text{NC}(\text{S})\text{S-})_2$ in refluxing toluene gave thermally stable complexes $[\text{CpMo}(\text{CO})_2(\text{C}_5\text{H}_4\text{NS})]$ (**2**) and $[\text{CpMo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)]$ (**4**), respectively, while the similar complex $[\text{CpMo}(\text{CO})_2(\text{C}_9\text{H}_6\text{NS})]$ (**3**) with the chelate quinoline-8-thiolate ligand was obtained by the

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TABLE 1. IR and ^1H NMR data for complexes 2–4

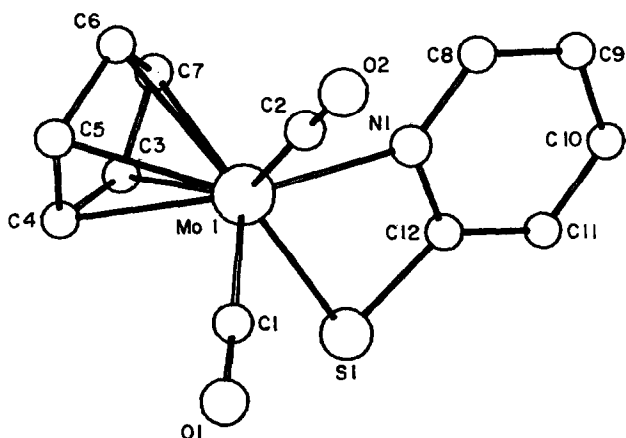
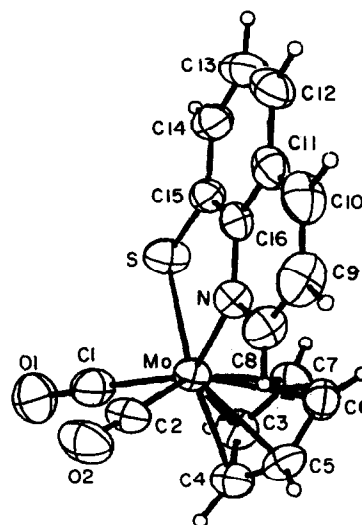
Complex	$\nu(\text{CO})(\text{cm}^{-1})$ ^a	δ (^1H NMR) ^b
$\text{CpMo}(\text{CO})_2(\text{C}_5\text{H}_4\text{NS})$ (2)	1958s, 1840s	7.94 (d, 1H); 7.29 (m, 1H); 6.67 (m, 1H); 6.61 (d, 1H); 5.55 (s, 5H)
$\text{CpMo}(\text{CO})_2(\text{C}_9\text{H}_6\text{NS})$ (3)	1940s, 1845s	9.26 (d, 1H); 8.20 (m, 1H); 7.77 (m, 1H); 7.42–7.06 (m, 3H); 5.48 (s, 5H)
$\text{CpMo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)$ (4)	1945s, 1850s	3.18 (s, 6H); 5.48 (s, 5H)

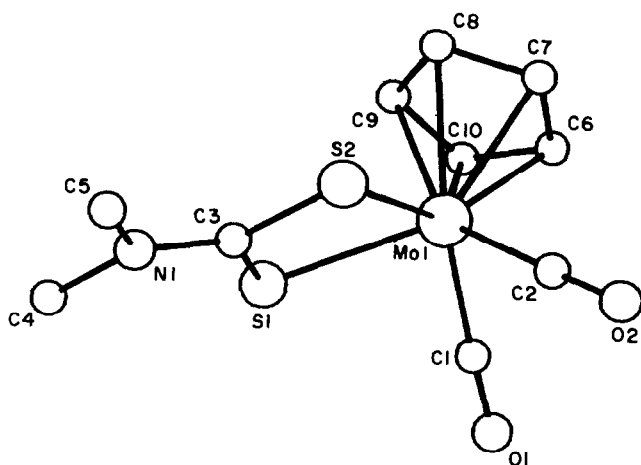
^a Recorded by KBr pellet. ^b Recorded in CDCl_3 .

reaction with $(\text{C}_9\text{H}_6\text{NS}^-)_2$ in toluene at room temperature. Compounds 2, 3 and 4 were characterized by IR and ^1H NMR (Table 1). When compound 3 was mixed with an equal amount of PPh_3 in THF, a crystalline product of similar colour was formed. The elemental analysis of the purified crystals gave a formula corresponding to an adduct, $[\text{CpMo}(\text{CO})_2(\text{C}_9\text{H}_6\text{NS})] \cdot \text{O}=\text{PPh}_3$ ($3 \cdot \text{O}=\text{PPh}_3$). The formation of the co-crystallized molecule $\text{O}=\text{PPh}_3$ was due to oxidation of PPh_3 by molecular oxygen which may be introduced to the reaction system by using untreated solvent THF. The crystals of $3 \cdot \text{O}=\text{PPh}_3$ show no spectroscopic indication of coordination of the $\text{O}=\text{PPh}_3$ molecule. The carbonyl stretching frequencies (1840 and 1945 cm^{-1}) of $3 \cdot \text{O}=\text{PPh}_3$ are identical to those of 3, indicating that, as revealed by the present X-ray analysis, the triphenylphosphine oxide in $3 \cdot \text{O}=\text{PPh}_3$ has no bonding interaction with the Mo moiety but merely acts as a crystalline molecule in the unit cell (*vide infra*). Compound 4 has been reported previously, but the structure has not yet been determined [7]. The structure of 4 described here is consistent with that proposed based on the IR spectrum [7]. The results of X-ray diffraction studies reveal that 2 and 3 have monomeric structures, rather than thiolate-bridged dimers which are always formed when 1 reacts with dialkyl or diphenyl disulphides. The formation of the mononuclear compounds 2 and 3 may be accounted for by a sequence of reactions initially in-

volving oxidative addition of the heterocyclic disulphides, such as dialkyl or diphenyl disulphides, to the Mo–Mo triple bond to form binuclear thiolate-bridged intermediates $[\text{Cp}_2\text{Mo}_2(\mu\text{-SR})_2(\text{CO})_4]$ ($\text{R} = \text{C}_5\text{H}_4\text{N}$ or $\text{C}_9\text{H}_6\text{N}$) which are unstable due to the presence of the other coordinating nitrogen atom in the bidentate ligand and SR group, and then followed by an intramolecular rearrangement of the latter to give 2 and 3.

The molecular structures of 2, 3 and 4 are shown in Figs. 1–3, and selected bond lengths and angles for each compound are listed in Tables 2–4, respectively. The molecular structure of the $\text{O}=\text{PPh}_3$ in the crystals of $3 \cdot \text{O}=\text{PPh}_3$ is shown in Fig. 4. The crystals of $3 \cdot \text{O}=\text{PPh}_3$ are built up from discrete molecules of the complex 3 and triphenylphosphine oxide; the shortest intermolecular contact between complexes with $\text{O}=\text{PPh}_3$ is 3.311 \AA between O(1) and C(26) at $(x, 1 + y, z)$. The coordination environments of the molybdenum atoms in the complexes are very similar. On the assumption that the Cp ligand is counted as a single binding point, the geometry of each compound can be described as an approximate square-pyramidal with Cp–Mo defining the axial position and the C(1)C(2)SN or C(1)C(2)S(1)S(2) atoms defining the basal plane. In complexes 2, 3 and 4, the tetragons C(1)C(2)NS or

Fig. 1. Molecular structure of $[\text{CpMo}(\text{C}_5\text{H}_4\text{NS})]$ (2).Fig. 2. Molecular structure of $[\text{CpMo}(\text{Co})_2(\text{C}_9\text{H}_6\text{NS})]$ (3).

Fig. 3. Molecular structure of $[\text{CpMo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)]$ (**4**).TABLE 4. Selected bond lengths (Å) and angles (°) for $\text{CpMo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)$ (**4**)

Mo–S(1)	2.500(1)	C(1)–Mo–C(2)	76.5(2)
Mo–S(2)	2.506(2)	S(1)–Mo–S(2)	68.7(5)
Mo–C(1)	1.961(5)	Mo–S(1)–C(3)	89.7(2)
Mo–C(2)	1.954(6)	Mo–S(2)–C(3)	89.7(2)
Mo–C(6)	2.272(5)	Mo–C(1)–O(2)	177.4(4)
Mo–C(7)	2.308(6)	Mo–C(2)–O(2)	178.3(5)
Mo–C(8)	2.381(6)	S(1)–C(3)–S(2)	111.8(3)
Mo–C(9)	2.366(6)	C(1)–Mo–S(1)	80.8(1)
Mo–C(10)	2.300(6)	C(1)–Mo–S(2)	121.8(2)
S(1)–C(3)	1.709(5)	C(2)–Mo–S(1)	124.1(2)
S(2)–C(3)	1.702(5)	C(2)–Mo–S(2)	81.5(2)
C(1)–O(1)	1.143(6)		
C(2)–O(2)	1.151(6)		
C(3)–N	1.334(6)		
C(4)–N	1.454(7)		
C(5)–N	1.456(7)		

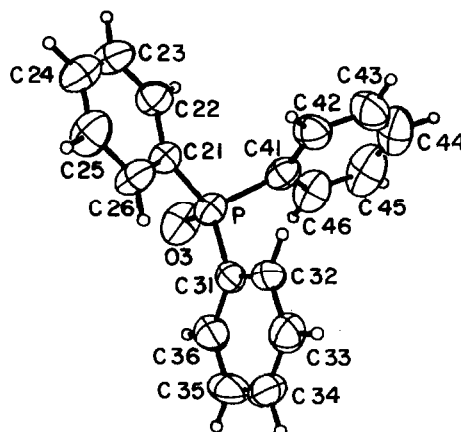
TABLE 2. Selected bond lengths (Å) and angles (°) for $\text{CpMo}(\text{CO})_2(\text{C}_5\text{H}_4\text{NS})$ (**2**)

Mo–C(1)	1.961(6)	C(1)–Mo–C(2)	74.9(2)
Mo–C(2)	1.967(6)	N–Mo–S	64.3(1)
Mo–N	2.178(4)	C(1)–Mo–S	82.6(2)
Mo–S	2.520(2)	C(2)–Mo–N	82.4(2)
Mo–C(3)	2.374(5)	O(1)–C(1)–Mo	178.1(6)
Mo–C(4)	2.295(6)	O(2)–C(2)–Mo	178.6(5)
Mo–C(5)	2.263(6)	N–Mo–C(1)	118.3(2)
Mo–C(6)	2.313(6)	S–Mo–C(2)	123.7(2)
Mo–C(7)	2.394(6)	Mo–N–C(12)	104.5(3)
S–C(12)	1.720(6)	Mo–N–C(8)	135.4(3)
N–C(8)	1.352(6)	Mo–S–C(12)	81.6(2)
N–C(12)	1.350(6)	N–C(12)–S	109.5(4)
C(1)–O(1)	1.145(7)	S–C(12)–C(11)	129.1(5)
C(2)–O(2)	1.145(6)		

TABLE 3. Selected bond lengths (Å) and angles (°) for $[\text{CpMo}(\text{CO})_2(\text{C}_9\text{H}_6\text{NS})] \cdot \text{O}=\text{PPh}_3$ (**3** · $\text{O}=\text{PPh}_3$)

Mo–S	2.475(1)	C(1)–Mo–C(2)	73.0(2)
Mo–N	2.226(3)	C(1)–Mo–S	78.6(1)
Mo–C(1)	1.944(4)	C(2)–Mo–N	81.3(1)
Mo–C(2)	1.955(4)	N–Mo–S	77.4(1)
Mo–C(3)	2.313(4)	O(1)–C(1)–Mo	177.3(4)
Mo–C(4)	2.281(4)	O(2)–C(2)–Mo	178.3(4)
Mo–C(5)	2.312(4)	Mo–S–C(15)	101.7(1)
Mo–C(6)	2.406(4)	Mo–N–C(16)	122.2(2)
Mo–C(7)	2.403(4)	S–C(15)–C(16)	119.9(3)
S–C(15)	1.736(4)	S–C(15)–C(14)	122.1(3)
N–C(8)	1.335(5)	N–C(16)–C(15)	117.9(3)
N–C(16)	1.386(5)	Mo–N–C(8)	119.8(2)
C(14)–C(15)	1.382(5)		
C(15)–C(16)	1.418(6)		

C(1)C(2)S(1)S(2) are not regular. For example, non-bonding distances of $\text{S} \cdots \text{N}$, $\text{C}(1) \cdots \text{C}(2)$, $\text{S} \cdots \text{C}(1)$ and $\text{N} \cdots \text{C}(2)$ are 2.95, 2.32, 2.83 and 2.73 Å in **3**, respectively. The deviation from an idealized square-pyramid geometry around the Mo atom in the complexes is due to the differences in bond lengths between Mo–S, Mo–N or Mo–S, and two Mo–C(0) bonds (these distances are 2.520(2), 2.178(4), 1.961(6) and 1.967(6) Å in **2**; 2.457(2), 2.226(3), 1.944(4) and 1.955(4) Å in **3** and 2.506(1), 2.500(2), 1.961(5), and 1.954(6) Å in **4**, respectively) and in ligand angles of S–Mo–N or S(1)–Mo–S(2), C(1)–Mo–C(2), S–Mo–C(1) and N–Mo–C(2). For example, the angles are 77.4, 73.0, 78.6 and 81.3° in compound **3**, respectively.

Fig. 4. Molecular structure of the co-crystallized molecule $\text{O}=\text{PPh}_3$ in **3** · $\text{O}=\text{PPh}_3$.

The structural differences between **2**, **3** and **4** are that a five-membered chelate ring is defined by a quinoline-8-thiolate ligand and Mo atom in **3** and that a four-membered chelate ring is formed by a pyridine-2-thiolate (S,N donor) ligand in **2** and by a dithiocarbamate (S,S donor) ligand in **4**, respectively, which lead to the largest ligand angle 77.4° for **3** among the complexes. This value of the S–Mo–N ligand angle in **3** is close to those of 76.9° and 74.0° for the corresponding S–Mo–N and N–Mo–N angles in compounds [CpMo(CO)₂(C₅H₄N)C(S)NCH(CH₃)(C₆H₅)] [9] and [CpMo(CO)₂(C₅H₄N)CHNCH(CH₃)(C₆H₅)] [PF₆] [10] in which five-membered chelate rings are present. The values of the ligand angles of the chelate ligands in **2** and **4** (64.3° and 68.7°) are comparable with that (63.8°) of the N–Mo–S angle in a four-membered chelate ring compound [CpMo(CO)₂{SC(CH₃)NCH(CH₃)(C₆H₅)}] [11].

Bernal *et al.* [11], in comparing the molecular parameters of various molybdenum compounds containing sulphur, nitrogen, carbonyl and Cp ligands, observed that when the ligand angle S–Mo–N or S–Mo–S opens up and the S–C(ligand) bond length is long,

there is a short Mo–S distance. A similar pattern is found for compounds **2**, **3** and **4**. Going from **2**, **4** to **3**, an opening up of the ligand angle from $64.3(1)$, $68.7(5)$ to $77.4(1)^\circ$ and changing of the S–C(ligand) bond distance from $1.720(6)$, $1.706(5)$ (averaged) to $1.736(4)$ Å lead to significantly shorter Mo–S distances (from $2.520(2)$, $2.503(2)$ (averaged) to $2.475(1)$ Å). It seems that such a shortening of the Mo–S bond length reflects the better ability of the sulphur and molybdenum electrons to interact in a five-membered chelate ring than in four-membered systems. For similar four-membered chelate systems, a shorter Mo–S distance in **4** than in **2** suggests that the Mo–S electronic interaction in the S,S donor chelate ligand is better than that in the S,N donor chelate ligand.

The bond lengths and angles in the dithiocarbamate ligand in **4** are in agreement with values found in other dithiocarbamate structures [12]. Delocalized π -bonding in the S(1)S(2)C(3)N portion of the ligand is indicated by the C(3)–N ($1.334(6)$ Å) and C(3)–S (averaged $1.706(5)$ Å) distances, which are intermediate between single bond and double bond lengths (C–N, 1.47 ; C=N, 1.27 ; C–S, 1.81 ; C=S, 1.61 Å) [13].

TABLE 5. Summary of crystal data and intensity data

Compound	2	3 · O=PPh ₃	4
Formula	C ₁₂ H ₉ MoNO ₂ S	C ₁₆ H ₁₁ MoNO ₂ S · O=PPh ₃	C ₁₀ H ₁₁ MoNO ₂ S ₂
<i>M</i> (g mol ⁻¹)	328.22	655.56	337.26
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> (Å)	6.448(1)	11.351(3)	12.468(5)
<i>b</i> (Å)	12.616(2)	13.409(3)	7.637(2)
<i>c</i> (Å)	14.772(2)	9.895(2)	13.135(4)
α (°)		94.59(2)	
β (°)	92.85(1)	90.35(2)	96.62(3)
γ (°)		78.07(2)	
<i>U</i> (Å ³)	1200.2(4)	1468.7(6)	1242.5(7)
<i>Z</i>	4	2	4
<i>F</i> (000)	652	668	672
<i>D</i> _c (g cm ⁻³)	1.82	1.48	1.80
Crystal size (mm ³)	0.35 × 0.20 × 0.10	0.52 × 0.32 × 0.08	0.50 × 0.20 × 0.20
μ (Mo K α) (cm ⁻¹)	12.21	5.91	13.38
Radiation		Graphite-monochromated Mo K α	
Scan speed (°/min)	16	4.88	16
Diffractometer	Rigaku AFC5R	Nicolet R3m/E	Rigaku AFC5R
Scan mode	ω -2 θ	ω	ω -2 θ
2 θ range (°)	3–50.0	3–48.0	3–50.0
Temperature (°C)	23	25	23
No. data with $I > 3\sigma(I_0)$	1357	3260	1698
No. parameters refined	154	370	145
<i>R</i>	0.028	0.033	0.032
<i>R</i> _w	0.039	0.037	0.042
Goodness of fit	1.04	0.0996	1.10
(Δ/σ)max	0.09	0.14	0.14
($\Delta\rho$)max (e Å ⁻³)	0.29	0.31	0.55

3. Experimental details

All reactions were carried out under a nitrogen atmosphere using Schlenk techniques unless indicated otherwise. Solvents were dried by standard methods and distilled under nitrogen prior to use. The compound $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ was prepared according to the reported method [14]. $(\text{C}_5\text{H}_4\text{NS}^-)_2$, $(\text{C}_9\text{H}_6\text{NS}^-)_2$ and $(\text{Me}_2\text{NC}(\text{S})\text{S}^-)_2$ were used as received.

IR spectra were recorded on a Perkin-Elmer 683 infrared spectrometer. ^1H NMR spectra were recorded on a Hitachi-60 or a Varian XL-400 spectrometer. Elemental analysis was carried out with a Carlo Erba elemental analyser MOD 1106.

3.1. Reaction of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ with 2,2'-dipyridyl disulphide

A mixture of **1** (0.490 g, 1 mmol), $(\text{C}_5\text{H}_4\text{NS}^-)_2$ (0.220 g, 1 mmol) and toluene (30 ml) was refluxed under nitrogen for 2 h. The resulting brown solution was concentrated under vacuum to ca. 6 ml and then transferred onto a column of alumina. With toluene as eluent, a small amount of compound $[\text{Cp}_2\text{Mo}_2(\text{CO})_6]$ was first eluted. On evaporation to dryness, the second band gave $[\text{CpMo}(\text{CO})_2(\text{C}_5\text{H}_4\text{NS})]$ (**2**) (0.505 g, yield 77%) as red-brown crystals from a dichloromethane/hexane mixture. Anal. Found: C, 44.09; H, 3.24; N, 4.88. $\text{C}_{12}\text{H}_9\text{MoNO}_2\text{S}$ calc.: C, 44.04; H, 2.80; N, 4.30%.

3.2. Reaction of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ with 8,8'-diquinolyl disulphide

A mixture of **1** (0.200 g, 0.46 mmol), $(\text{C}_9\text{H}_6\text{NS}^-)_2$ (0.163 g, 0.51 mmol) and toluene (30 ml) was stirred at

TABLE 6. Fractional atomic coordinates ($\times 10^4$) for $\text{CpMo}(\text{CO})_2(\text{C}_5\text{H}_4\text{NS})$ (**2**)

Atom	x	y	z
Mo	3734.2(6)	34.7(3)	2026.8(3)
S	1018(2)	-25(1)	3194(1)
O(1)	142(8)	1002(4)	816(3)
O(2)	5479(7)	2130(3)	1255(3)
N	4586(6)	785(3)	3320(3)
C(1)	1450(1)	652(4)	1276(4)
C(2)	4860(1)	1357(4)	1544(4)
C(3)	4140(1)	-1817(4)	2263(5)
C(4)	3300(1)	-1614(5)	1388(6)
C(5)	4820(2)	-1072(6)	942(4)
C(6)	6540(1)	-921(5)	1547(6)
C(7)	6070(1)	-1403(5)	2360(4)
C(8)	6270(8)	1306(4)	3673(4)
C(9)	6330(1)	1670(4)	4551(5)
C(10)	4620(1)	1515(5)	5058(4)
C(11)	2900(1)	999(4)	4718(4)
C(12)	2928(8)	630(4)	3827(4)

room temperature for 6 h to yield a purple-red solution. Chromatographic separation as above gave $[\text{CpMo}(\text{CO})_2(\text{C}_9\text{H}_6\text{NS})]$ (**3**) (0.113 g, yield 32%) as blue-purple crystals from a dichloromethane/hexane mixture. Anal. Found: C, 50.99; H, 2.98; N, 3.73. $\text{C}_{16}\text{H}_{11}\text{MoNO}_2\text{S}$ calc.: C, 50.90; H, 2.92; N, 3.71%.

3.3. Reaction of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ with tetramethyl thiuram disulphide

The same manipulation as in the synthesis of **2**, except with $(\text{C}_5\text{H}_4\text{NS}^-)_2$ replaced by $(\text{Me}_2\text{NC}(\text{S})\text{S}^-)_2$, gave $[\text{CpMo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)]$ (**4**) as red-brown crystals (yield 67%). Anal. Found: C, 35.40; H, 3.30; N, 4.22. $\text{C}_{10}\text{H}_{11}\text{MoNO}_2\text{S}$ calc.: C, 35.58; H, 3.26; N, 4.15%.

TABLE 7. Fractional atomic coordinates ($\times 10^4$) for $[\text{CpMo}(\text{CO})_2(\text{C}_9\text{H}_6\text{NS})] \cdot \text{O}=\text{PPh}_3$ ($3 \cdot \text{O}=\text{PPh}_3$)

Atom	x	y	z
Mo	1680(1)	1095(1)	2566(1)
C(1)	1855(4)	-39(3)	1179(5)
O(1)	1947(4)	-692(3)	306(3)
C(2)	2906(4)	1272(3)	1293(4)
O(2)	3637(3)	1358(3)	518(3)
C(3)	-388(3)	1372(3)	2338(4)
C(4)	60(3)	2040(3)	1558(4)
C(5)	543(3)	2728(3)	2447(4)
C(6)	342(4)	2500(3)	3787(4)
C(7)	-224(3)	1669(3)	3722(4)
S	2050(1)	-388(1)	3962(1)
N	3028(3)	1487(2)	4050(3)
C(8)	3420(4)	2355(3)	3985(4)
C(9)	4198(4)	2690(3)	4936(4)
C(10)	4585(4)	2125(3)	5984(4)
C(11)	4190(3)	1209(3)	6129(4)
C(12)	4529(4)	594(4)	7215(4)
C(13)	4075(4)	-252(4)	7308(4)
C(14)	3296(4)	-558(3)	6333(4)
C(15)	2953(3)	4(3)	5233(4)
C(16)	3397(3)	910(3)	5135(4)
P	2107(1)	5609(1)	2281(1)
O(3)	2058(3)	4567(2)	1709(4)
C(21)	3311(3)	6102(3)	1572(4)
C(22)	4501(4)	5644(3)	1807(4)
C(23)	5435(4)	5926(4)	1170(5)
C(24)	5208(4)	6672(3)	297(5)
C(25)	4061(4)	7148(4)	62(5)
C(26)	3090(4)	6869(3)	694(4)
C(31)	728(3)	6529(3)	2070(4)
C(32)	541(4)	7525(3)	2648(4)
C(33)	-544(4)	8190(4)	2526(4)
C(34)	-1645(4)	7875(4)	1827(4)
C(35)	-1300(4)	6896(4)	1239(5)
C(36)	-207(4)	6210(4)	1358(4)
C(41)	2314(4)	5669(3)	4100(4)
C(42)	2874(4)	6360(4)	4824(4)
C(43)	2915(5)	6395(4)	6217(5)
C(44)	2392(5)	5772(4)	6910(5)
C(45)	1838(5)	5087(4)	6222(5)
C(46)	1799(4)	5033(3)	4825(5)

TABLE 8. Fractional atomic coordinates ($\times 10^4$) for $\text{CpMo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)$ (**4**)

Atom	x	y	z
Mo	8516.4(3)	1975.3(5)	7015(3)
S(1)	8052(1)	2275(2)	8808(1)
S(2)	10181(1)	2111(2)	8278(1)
O(1)	6858(3)	-1059(6)	6984(3)
O(2)	9725(3)	-1194(6)	6203(4)
N	9761(3)	2514(6)	10237(3)
C(1)	7474(4)	54(7)	7021(4)
C(2)	9285(4)	-25(7)	6519(4)
C(3)	9396(4)	2339(6)	9247(4)
C(4)	9032(5)	2720(1)	11017(4)
C(5)	10913(4)	2533(9)	10584(4)
C(6)	7846(6)	3021(8)	5451(4)
C(7)	8907(6)	3634(9)	5636(5)
C(8)	8950(6)	4822(8)	6446(6)
C(9)	7935(7)	4907(9)	6751(5)
C(10)	7256(5)	3800(1)	6151(5)

3.4. Preparation of $3 \cdot \text{O}=\text{PPh}_3$

A mixture of PPh_3 (0.069 g, 0.26 mmol) and **3** (0.100 g, 0.26 mmol) was heated in refluxing THF (used as received) (20 ml) for 5 h. The solvent was removed under reduced pressure and the residue was extracted with hexane. The solution was then concentrated *in vacuo*. After the solution had stood for several days, the concentrate gave blue-purple crystals (0.035 g, yield 20%). Anal. Found: C, 61.85; H, 4.20; N, 2.29. $\text{C}_{16}\text{H}_{11}\text{MoNO}_2\text{S} \cdot \text{C}_{18}\text{H}_{15}\text{OP}$ calc.: C, 62.23; H, 3.97; N, 2.13%.

3.5. Crystal structure determinations

Crystals of **2** and **4** suitable for X-ray diffraction studies were grown from a mixture of dichloromethane/hexane. Crystals of $3 \cdot \text{O}=\text{PPh}_3$ were obtained from hexane.

The crystal data and experimental conditions are summarized in Table 5. The structures of **2** and **4** were solved by the direct method, while the structure of $3 \cdot \text{O}=\text{PPh}_3$ was solved by the heavy-atom method. The structure for each compound was refined by the block-diagonal least-squares method. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined with isotropic thermal parameters. The posi-

tional parameters for compounds **2**, $3 \cdot \text{O}=\text{PPh}_3$ and **4** are given in Tables 6, 7 and 8, respectively. Natural atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-Ray Crystallography* [15]. All calculations were performed using the TEXSAN v2.1 program package [16] for **2** and **4**, and the SHELXTL program system [17] for $3 \cdot \text{O}=\text{PPh}_3$.

Additional material available from the authors comprises thermal parameters and remaining bond lengths and angles.

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