

η^3 -Allyl molybdenum dithiophosphate and dithiophosphinate complexes with uni- and bidentate nitrogen donor ligands. X-ray structure of $[\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_2(\text{CO})_4\{\text{S}_2\text{P}(\text{OEt})_2\}_2(\mu\text{-NH}_2\text{NH}_2)]$

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Received 16 June 1994

Abstract

The bis(nitrile) complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCMe})_2\text{Br}]$ (**1**) reacts with ammonium diethyldithiophosphate or sodium diphenyldithiophosphinate to afford $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{PX}_2)(\text{NCMe})]$ (**2**, X = OEt or Ph). The labile nitrile ligand in these complexes can be replaced by unidentate N-donors, L, affording mononuclear $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{PX}_2)(\text{L})]$ (**3**, L = 4-NH₂C₆H₄Me or py). Reactions of **2** with 0.5 equiv. of bidentate donors such as hydrazine or pyrazine produces binuclear complexes $[\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_2(\text{CO})_4(\text{S}_2\text{PX}_2)_2(\mu\text{-N-N})]$ (**4**, N-N = N₂H₄ or pyrazine). An X-ray structure determination carried out on $[\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_2(\text{CO})_4\{\text{S}_2\text{P}(\text{OEt})_2\}_2(\mu\text{-NH}_2\text{NH}_2)]$ (**4a**), showed the hydrazine bridge holding together two pseudo-octahedral 'Mo($\eta^3\text{-C}_3\text{H}_5$)(CO)₂(S₂P(OEt)₂)₂' fragments.

Keywords: Molybdenum; Hydrazine; X-ray structure; Dinuclear; Dithiophosphate; Dithiophosphinate

1. Introduction

Molybdenum and sulfur are involved in several catalytic processes of great practical importance, such as hydrodesulfurization [1], coal liquefaction [2] and nitrogen fixation [3]. This has stimulated the preparation of many molybdenum complexes in the hope that they could be suitable models for the study of the more complex heterogeneous or biological processes. A second avenue of research relies in the potential use of the controlled decomposition of molecular complexes to prepare supported catalysts. In the context of our studies on transition metal complexes containing bidentate sulfur ligands [4], we have recently described several families of molybdenum–tin complexes containing phosphoniodithiocarboxylate and phosphorodithioate [5]. Here we wish to report the preparation of the compounds $[\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\text{S-S}(\text{NCMe}))]$ (S-S = dithiophosphate or dithiophosphinate) which can be used as convenient starting materials for the prepara-

tion of a variety of mono- and bi-nuclear complexes with N-donors. Some of the complexes described here, together with those of the Mo–Sn series mentioned above, perform well as precursors to supported catalysts for coal liquefaction and hydroxyprolysis [6]. Additionally, we include here the X-ray determination of a derivative which contains a hydrazine ligand acting as a single bridge between two molybdenum atoms. Despite possible relevance to nitrogen fixation, the structural reports of species with coordinated hydrazine are scarce and there are only a few cases containing $\mu_2\text{-N}_2\text{H}_4$ [7–12].

2. Results and discussion

The reaction of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCMe})_2\text{Br}]$ (**1**) [13] with ammonium diethyldithiophosphate or with sodium diphenyldithiophosphinate in CH₂Cl₂ leads to the formation of yellow–orange solutions from which crystalline complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{PX}_2)(\text{NCMe})]$ (**2a,b** in Scheme 1) are isolated in good yield after appropriate work-up. The structures proposed for

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Table 1
Selected IR and $^{31}\text{P}\{^1\text{H}\}$ NMR data for the new complexes

Compound	IR (THF) ν (CO) (cm^{-1})	$^{31}\text{P}\{^1\text{H}\}$ NMR ^a (S_2P)
2a [$\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{P}(\text{OEt})_2)(\text{NCMe})$] ^b	1949(s), 1857(s)	100.99
2b [$\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{PPh}_2)(\text{NCMe})$] ^b	1948(s), 1856(s)	83.83
3a [$\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{P}(\text{OEt})_2)(4\text{-NH}_2\text{C}_6\text{H}_4\text{Me})$]	1946(s), 1856(s)	101.47 (br)
3b [$\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{PPh}_2)(4\text{-NH}_2\text{C}_6\text{H}_4\text{Me})$]	1946(s), 1854(s)	82.44 (br)
3c [$\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{P}(\text{OEt})_2)(\text{py})$]	1944(s), 1850(s)	101.35 (br)
3d [$\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{PPh}_2)(\text{py})$]	1943(s), 1847(s)	84.43 (br)
4a [$\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_2(\text{CO})_4(\text{S}_2\text{P}(\text{OEt})_2)_2(\mu\text{-NH}_2\text{NH}_2)$]	1945(s), 1852(s)	100.38 (br)
4b [$\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_2(\text{CO})_4(\text{S}_2\text{P}(\text{OEt})_2)_2(\mu\text{-N}_2\text{C}_4\text{H}_4)$]	1948(s), 1860(s)	103.82 (br)

^a In CDCl_3 solutions, δ (ppm) from internal 85% H_3PO_4 .

^b $\nu(\text{CN})$ at 2285 cm^{-1} .

complexes **2a,b** in Scheme 1 are fully consistent with their analytical (see Experimental details) and spectroscopic data (Tables 1 and 2).

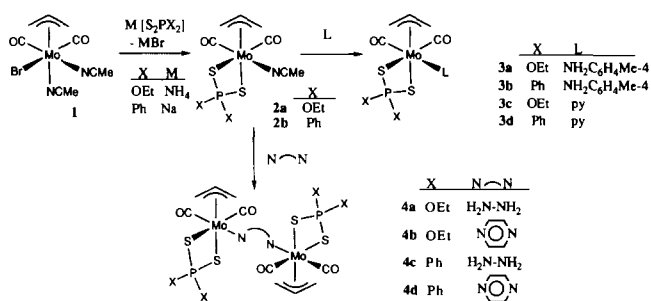
The chemistry of related η^3 -allyl molybdenum compounds with anionic sulfur ligands such as dithiocarbamate and xantate has been explored by Perpiñán and Santos [14], and more recently by Shiu et al. [15]. Despite the formal analogy between phosphorodithioate, dithiocarbamate and xantate, these ligands exhibit a different chemistry with the $\text{Mo}(\eta^3$ -

allyl)(CO)₂ fragment. Thus, it has been reported that, irrespective of the molar ratio used, compound **1** incorporates two xanthate or dithiocarbamate ligands to give anionic [$\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\eta^2\text{-S}_2\text{CX})(\eta^1\text{-S}_2\text{CX})^-$] when the reaction is carried out in acetone [14]. In the case of dialkyldithiocarbamates, the reaction appears to be solvent-dependent, since it has been recently reported that treatment of the starting bis(acetonitrile) complex **1** with dithiocarbamate in acetonitrile solution leads to the precipitation of solids

Table 2
 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for the new complexes ^a

Compound	^1H NMR δ (ppm)	$^{13}\text{C}\{^1\text{H}\}$ NMR δ (ppm)
2a	4.23 [m, 1H, CH of allyl]; 4.07 [m, 4H, CH ₂ of Et]; 3.29 [d(6), 2H, H syn of allyl]; 2.18 [s, 3H, NCCCH ₃]; 1.33 [m, 8H, CH ₃ of Et and H anti of allyl]	225.1 [s, 2 MoCO]; 119.6 [s, NCCCH ₃]; 71.7 [s, C ² of allyl]; 63.1 [d(6), CH ₂ of Et]; 55.9 [s, C ¹ and C ³ of allyl]; 16.0 [d(8), CH ₃ of Et]; 3.2 [s, NCCCH ₃]
2b	8.01–7.40 [m, 10H, CH of Ph]; 4.04 [m, 1H, CH of allyl]; 3.32 [d(7), 2H, H syn of allyl]; 1.61 [s, 3H, NCCCH ₃]; 1.35 [d(10), 2H, H anti of allyl]	225.3 [s, 2 MoCO]; 139.4–128.3 [m, C ₆ H ₅]; 119.1 [s, NCCCH ₃]; 73.9 [s, C ² of allyl]; 56.4 [s, C ¹ and C ³ of allyl]; 2.1 [s, NCCCH ₃]
3a	7.15 [m, 4H, C ₆ H ₄ CH ₃]; 4.09 [m, 4H, CH ₂ of Et]; 3.91 [m, 1H CH of allyl]; 3.21 [d(6), 2H, H syn of allyl]; 2.34 [s, 3H, C ₆ H ₄ CH ₃]; 1.35 [t(7), 6H, CH ₃ of Et]; 1.21 [d(10), 2H, H anti of allyl]	226.2 [s, 2 MoCO]; 140.9, 135.0, 130.6, 120.3 [s, C ₆ H ₄ CH ₃ -4]; 71.7 [s, C ² of allyl]; 64.2 [d(7), CH ₂ of Et]; 56.9 [s, C ¹ and C ³ of allyl]; 21.5 [s, C ₆ H ₄ CH ₃ -4]; 16.6 [s, CH ₃ of Et]
3b	7.89–7.45 [m, 10H, CH of Ph]; 7.15 [m, 4H, C ₆ H ₄ CH ₃]; 3.86 [m, 1H, CH of allyl]; 3.09 [d(7), 2H, H syn of allyl]; 2.32 [s, 3H, C ₆ H ₄ CH ₃]; 1.34 [d(10), 2H, H anti of allyl]	225.5 [s, 2 MoCO]; 141.1–119.2 [m, C ₆ H ₅ and C ₆ H ₄ CH ₃ -4]; 71.4 [s, C ² of allyl]; 56.6 [s, C ¹ and C ³ of allyl]; 20.7 [s, C ₆ H ₄ CH ₃ -4],
3c	7.89–7.45 [m, 5H, CH of py]; 4.11 [m, 4H, CH ₂ of Et]; 3.91 [m, 1H, CH of allyl]; 3.23 [d(6), 2H, H syn of allyl]; 1.39 [t(7), 6H, CH ₃ of Et]; 0.81 [d(10), 2H, H anti of allyl]	226.2 [s, 2 MoCO]; 153.4, 137.8, 124.6 [s, CH of py]; 73.2 [s, C ² of allyl]; 63.8, 62.7 [2 × s, CH ₂ of Et]; 57.6 [s, C ¹ and C ³ of allyl]; 16.4, 16.2 [2 × s, CH ₃ of Et]
3d	8.81–6.97 [m, 15H, CH of Ph and py]; 3.92 [m, 1H, CH of allyl]; 3.23 [d(7), 2H, H syn of allyl]; 1.37 [d(9), 2H, H anti of allyl]	226.1 [s, 2 MoCO]; 152.9, 136.7, 123.6 [s, CH of py]; 131.1–128.9 [m, C ₆ H ₅]; 71.4 [s, C ² of allyl]; 57.8 [s, C ¹ and C ³ of allyl]
4a	4.63 [m, 2H, CH ₂ of allyl]; 4.12 [m, 8H, CH ₂ of Et]; 3.86 [m, 2H, CH of allyl]; 3.25 [t(3), 4H, H syn of allyl]; 1.38 [m, 12H, CH ₃ of Et and H anti of allyl]	224.5 [s, 2 MoCO]; 224.4 [s, 2 MoCO]; 71.4 [s, C ² of allyl]; 64.1 [s, CH ₂ of Et]; 55.7 [s, C ¹ and C ³ of allyl]; 15.8 [d(8), CH ₃ of Et]
4b	8.85 [s, 4H, C ₄ H ₄ N ₂]; 4.05 [m, 1H, CH of allyl]; 3.82 [m, 8H, CH ₂ of Et]; 3.31 [s, 4H, H syn of allyl]; 1.49–1.21 [m, 16H, CH ₃ of Et and H anti of allyl]	224.9 [s, 4 MoCO]; 147.6 [s, CH of C ₄ H ₄ N ₂]; 74.4 [s, C ² of allyl]; 63.8 [d(6), CH ₂ of Et]; 58.4 [s, C ¹ and C ³ of allyl]; 16.5 [d(17), CH ₃ of Et]

^a From CD_2Cl_2 solutions. Coupling constants, in Hz, in parentheses.



which have been formulated as neutral, 16-electron complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\eta^2\text{-S}_2\text{CNR}_2)]$ [15]. In our case, the use of acetonitrile as solvent does not modify the outcome of the reaction, which yields acetonitrile complexes **2a,b**. In fact, complex **2a** can be prepared in a very convenient one-pot synthesis by heating an equimolar mixture of $[\text{Mo}(\text{CO})_6]$, allyl bromide and ammonium diethyldithiophosphate in acetonitrile for 3 h at reflux temperature (see Experimental details). Although this one-pot procedure does produce the dithiophosphinate complex **2b**, better yields are obtained by a two-step method, using isolated **1** in CH_2Cl_2 solution.

The presence of labile NCMe in complexes **2a,b** suggested that they could be used as starting materials to prepare derivatives by acetonitrile replacement reactions. IR monitoring indicates that NCMe is readily displaced from **2a,b** by unidentate N-donor ligands (L), such as pyridine and *p*-toluidine in dichloromethane solution to afford, after work-up, crystalline solids of formula $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{PX}_2)(\text{L})]$ (**3a,d** in Scheme 1). The analytical and spectroscopic data available (see Tables 1 and 2) fully support the structures depicted for these compounds in Scheme 1. IR monitoring shows that compounds **2a,b** react with 1 mol. equiv. of other unidentate donors such as PET_3 , $\text{P}(\text{OMe})_3$, tetramethylthiourea and ${}^t\text{BuNC}$ at room temperature. However, repeated attempts at crystallization produced oily materials which could not be properly characterized.

Reaction of **2a,b** with 0.5 mol. equiv. of bidentate N-donors (N–N) such as hydrazine or pyrazine, leads to the binuclear complexes $[\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_2(\text{CO})_4(\text{S}_2\text{PX}_2)_2(\mu\text{-N-N})]$ (**4a–d** in Scheme 1). In this case, only the derivatives containing dithiophosphate have been crystallized and fully characterized. In contrast, the derivatives with dithiophosphinate were obtained as very insoluble precipitates, which could not be recrystallized for further characterization. Binuclear compounds **4a–d** appear to be produced ultimately even when an excess of the N–N is employed in the reaction. This may be due to solubility factors, which would favour the less-soluble dinuclear complexes over

the mononuclear ones containing unidentate hydrazine or pyrazine. That is, however, difficult to prove, since the most representative spectroscopic signals of all derivatives either mononuclear (**2** and **3**) or binuclear (**4**) are broad and in a very narrow range.

A single crystal of the derivative **4a**, containing dithiophosphate and hydrazine, was subjected to an X-ray analysis to confirm the structure of complexes **4**. Relevant crystallographic details are listed in Table 3 and the results are shown in Fig. 1 and in Tables 4 (atomic parameters) and 5 (bond lengths and angles).

As can be seen in Fig. 1, the molecule of **4a** consists of two $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{P}(\text{OEt})_2)]$ fragments held together by a hydrazine which acts as the only bridge between the two molybdenum atoms. A crystallographically imposed symmetry centre, lying at the midpoint of the N–N bond, relates the atoms of both halves of the molecule which have, therefore, the same geometrical parameters. The coordination around molybdenum can be described as pseudo-octahedral, with the allyl and two carbonyls in one triangular face, and the two sulfur and one nitrogen in the opposite face. As has been usually found in other structures of

Table 3
Crystallographic data for $[\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_2(\text{CO})_4(\text{S}_2\text{P}(\text{OEt})_2)_2(\mu\text{-NH}_2\text{NH}_2)]$ (**4a**)

Formula	$\text{C}_{18}\text{H}_{34}\text{Mo}_2\text{N}_2\text{O}_8\text{P}_2\text{S}_4$
Molecular weight	785.52
Crystal system, space group	triclinic, $P\bar{1}$
<i>a</i> , Å	10.380(2)
<i>b</i> , Å	7.597(2)
<i>c</i> , Å	10.852(2)
α , deg	93.04(3)
β , deg	114.80(2)
γ , deg	91.35(2)
<i>V</i> , Å ³	774.7(3)
<i>Z</i>	1
<i>T</i> , K	200
ρ_{calc} g cm ⁻³	1.68
<i>F</i> (000)	395
$\lambda(\text{Mo K}\alpha)$, Å	0.71073
μ , cm ⁻¹	11.91
Crystal size, mm; colour	0.20 × 0.16 × 0.13; red
Method of collection	$\omega/2\theta$ scan
Scan range, deg	$2 \leq \theta \leq 25$,
Collection limits	$-12 \leq h \leq 11, -9 \leq k \leq 9, 0 \leq l \leq 12$
No. of reflections collected	2878
No. of reflections observed	2521 [$I \geq 3\sigma(I)$]
Absorption correction	DIFABS
Factors: max, min	1.185, 0.794
No. of parameters	181
Data to parameter ratio	13.93
Weighting scheme	$w = [\sigma^2(F) + gF^2]^{-1}$
<i>g</i>	0.0003
Residuals ^a <i>R</i> , <i>R</i> _w	0.028, 0.030

^a $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $R_w = \{\Sigma(w(|F_o| - |F_c|)^2) / \Sigma w|F_o|^2\}^{1/2}$.

(η^3 -allyl)dicarbonylmolybdenum complexes [16], the open face of the allyl is directed towards the two carbonyls. One of the sulfur atoms of dithiophosphate is *trans* to the allyl: S(1)–Mo–C(4), 161.7(1)°, while the other is *trans* to one carbonyl: S(2)–Mo–C(2), 167.9(1)°. The remaining carbonyl is *trans* to the nitrogen atom of the hydrazine: C(1)–Mo–N(1), 168.1(1)°. The small, but nevertheless significant assymetry of the coordination of the two sulfur atoms of dithiophosphate is noteworthy. For example, the Mo–S(1) distance of 2.552(1) Å (*trans* to allyl) is slightly shorter than Mo–S(2) of 2.642(1) Å (*trans* to CO). This can be attributed to the greater *trans* effect induced by the CO group when compared to that induced by the allyl. The N(1)–N(1') distance of 1.462(5) Å is close to that of free hydrazine (1.45 Å) and to those found in the reported structures containing hydrazine bridges, which range from 1.40(1) Å in $[\{\text{MoO}(\text{S}_2)_2\}_2(\mu_2\text{-S}_7)(\mu_2\text{-N}_2\text{H}_4)]$ [11], to 1.47(2) Å in $[\text{NEt}_4][\{(\text{Cl}_4\text{Cat})\text{MoFe}_3\text{S}_4\text{Cl}_3\}_2(\mu\text{-N}_2\text{H}_4)]$ [12].

3. Experimental details

Reactions and work-up were carried out under dinitrogen. IR spectra were recorded on a Perkin-Elmer FT 1720-X instrument. NMR spectra were recorded on a Bruker AC-300 spectrometer. Analyses were carried out on a Perkin-Elmer 240B analyzer. $\text{Na}[\text{S}_2\text{PPh}_2]$ was prepared according to literature procedures [17].

3.1. $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\{\text{S}_2\text{P}(\text{OEt})_2\}(\text{NCMe})]$ (**2a**)

3.1.1. Method A

A mixture of $[\text{Mo}(\text{CO})_6]$ (0.5 g, 1.89 mmol) and allyl bromide (175 μl , 2 mmol) in acetonitrile (15 ml) was heated at reflux for 3 h. After cooling to room temperature, the solvent was evaporated to afford $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCMe})_2\text{Br}]$ [13] as a yellow microcrystalline solid. This was dissolved in CH_2Cl_2 (20 ml) and then $\text{NH}_4[\text{S}_2\text{P}(\text{OEt})_2]$ (0.385 g, 1.89 mmol) was added. The mixture was stirred for 10 min and then filtered. Addition of hexane and slow evaporation in vacuo gave **2a** as a yellow–orange microcrystalline solid. Yield, 0.49 g; 65%. Anal. Calc. for $\text{C}_{11}\text{H}_{18}\text{MoNO}_4\text{PS}_2$: C, 31.51; H, 4.33; N 3.34%. Found: C, 31.22; H, 4.28; N, 3.30%.

3.1.2. Method B (one-pot synthesis)

A mixture of $[\text{Mo}(\text{CO})_6]$ (0.5 g, 1.89 mmol), $\text{NH}_4[\text{S}_2\text{P}(\text{OEt})_2]$ (0.385 g, 1.89 mmol) and allyl bromide (0.175 ml, 2 mmol)₄ was heated under reflux in MeCN (15 ml) for 3 h. The work-up was as described in method A above. Yield, 0.63 g; 79%. Anal. Calc. for $\text{C}_{11}\text{H}_{18}\text{MoNO}_4\text{PS}_2$: C, 31.51; H, 4.33; N, 3.34%. Found: C, 31.29; H, 4.15; N, 3.28%.

3.2. $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{PPh}_2)(\text{NCMe})]$ (**2b**)

A solution of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCMe})_2\text{Br}]$ [13] in CH_2Cl_2 was prepared from $[\text{Mo}(\text{CO})_6]$ (0.5 g, 1.89 mmol), and allyl bromide (175 μl , 2 mmol). To this was

Table 4

Atomic coordinates and equivalent isotropic displacement coefficients (\AA^2) for $[\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_2(\text{CO})_4\{\text{S}_2\text{P}(\text{OEt})_2\}_2(\mu\text{-NH}_2\text{NH}_2)]$ (**4a**)

Atom	x	y	z	$U_{\text{eq}} (\times 100)$
Mo(1)	0.24464(3)	0.15321(3)	0.40994(3)	2.27(1)
S(1)	0.2522(1)	–0.0122(1)	0.20241(9)	3.65(3)
S(2)	0.3327(1)	0.4030(1)	0.2987(1)	4.15(4)
N(1)	0.4823(3)	0.0923(4)	0.4971(3)	3.1(1)
C(1)	0.0400(4)	0.1712(5)	0.3049(4)	3.9(1)
O(1)	–0.0802(3)	0.1723(5)	0.2428(3)	6.7(1)
C(2)	0.1753(4)	–0.0585(4)	0.4571(4)	3.7(1)
O(2)	0.1286(4)	–0.1830(4)	0.4827(4)	6.9(2)
C(3)	0.1654(4)	0.3882(5)	0.4997(4)	4.1(2)
C(4)	0.2992(4)	0.3383(5)	0.5907(4)	4.1(2)
C(5)	0.3040(4)	0.1720(5)	0.6427(4)	4.5(2)
P(1)	0.33639(9)	0.2091(1)	0.16991(9)	3.41(3)
O(11)	0.4906(2)	0.1705(3)	0.1853(2)	3.9(1)
C(11)	0.5777(4)	0.3016(5)	0.1571(4)	4.1(1)
C(13)	0.5848(5)	0.2491(6)	0.0252(4)	5.4(2)
O(12)	0.2621(3)	0.2585(4)	0.0177(3)	5.1(1)
C(12)	0.1117(5)	0.298(1)	–0.0401(6)	10.3(3)
C(14)	0.0709(5)	0.3771(9)	–0.1590(6)	9.0(3)
H(1)	0.516(4)	0.137(4)	0.455(4)	3.0(1)
H(2)	0.539(4)	0.141(5)	0.584(4)	5.0(1)

^a U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

added $\text{Na}[\text{S}_2\text{PPh}_2]$ [17] (0.515 g, 1.89 mmol) and the mixture stirred for 10 min and filtered. The work-up was as described for **2a** (method A) to afford **2b** as yellow–orange microcrystals. Yield, 0.58 g; 63%. Anal. Calc. for $\text{C}_{19}\text{H}_{18}\text{MoNO}_2\text{PS}_2$: C, 47.21; H, 3.75; N, 2.90%. Found: C, 47.40; H, 3.68; N, 2.77%.

3.3. $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\{\text{S}_2\text{P}(\text{OEt})_2\}(4\text{-NH}_2\text{C}_6\text{H}_4\text{-Me})]$ (**3a**)

To a solution of **2a** (1.59 g, 3.79 mmol) in CH_2Cl_2 (25 ml) was added 4- $\text{NH}_2\text{C}_6\text{H}_4\text{Me}$ (0.406 g, 3.79 mmol) and the mixture stirred for 0.5 h and then evaporated to dryness. The residue was extracted with CH_2Cl_2 (2×10 ml). To the filtered extract was added hexane (15 ml) and the resulting mixture was left overnight in a fridge at -20°C to give orange crystals of **3a**. The mother liquor was decanted and the product dried in vacuo. Yield, 1.53 g; 83%. Anal. Calc. for $\text{C}_{16}\text{H}_{24}$

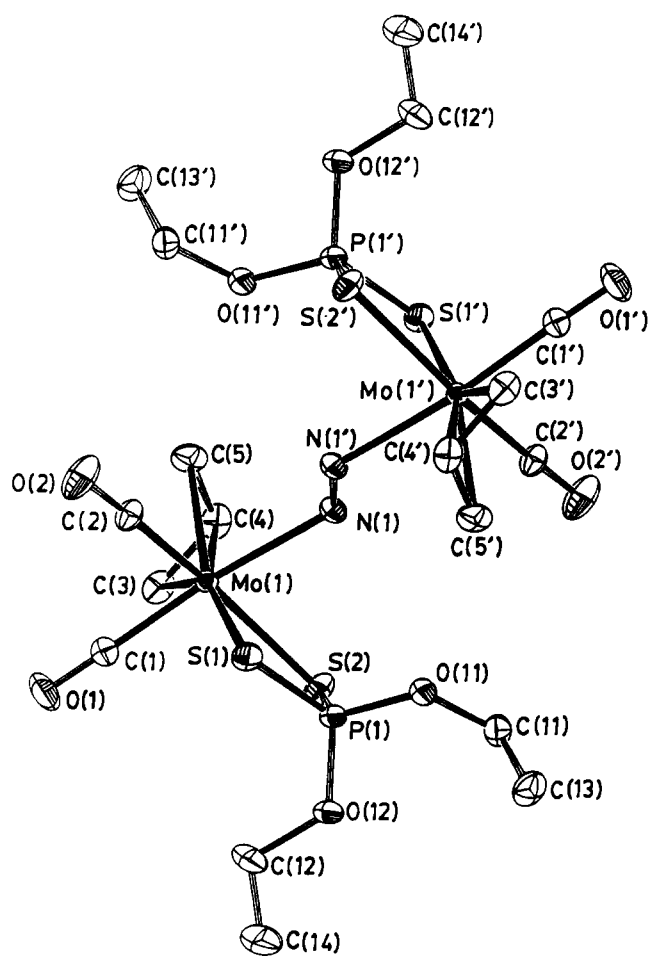


Fig. 1. Perspective view (EUCALID package) [21] of the structure of $[\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_2(\text{CO})_4(\text{S}_2\text{P}(\text{OEt})_2)_2(\mu\text{-NH}_2\text{NH}_2)]$ (**4a**), showing the atom numbering. Primed atoms are related to the corresponding unprimed ones by the inversion centre placed at the midpoint of the N–N' bond.

Table 5

Bond lengths (Å) and angles ($^\circ$) for $[\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_2(\text{CO})_4(\text{S}_2\text{P}(\text{OEt})_2)_2(\mu\text{-NH}_2\text{NH}_2)]$ (**4a**)

Mo(1)–S(1)	2.551(1)	Mo(1)–S(2)	2.642(1)
Mo(1)–N(1)	2.311(3)	Mo(1)–C(1)	1.957(3)
Mo(1)–C(2)	1.926(3)	Mo(1)–C(3)	2.317(3)
Mo(1)–C(4)	2.209(3)	Mo(1)–C(5)	2.331(4)
S(1)–P(1)	1.991(1)	S(2)–P(1)	1.988(1)
N(1)–N(1')	1.456(5)	C(1)–O(1)	1.143(4)
C(2)–O(2)	1.152(4)	C(3)–C(4)	1.401(5)
C(4)–C(5)	1.404(5)	P(1)–O(11)	1.574(2)
P(1)–O(12)	1.573(3)	O(11)–C(11)	1.458(4)
C(11)–C(13)	1.497(5)	O(12)–C(12)	1.463(5)
C(12)–C(14)	1.355(6)	N(1)–H(1)	0.77(4)
N(1)–H(2)	0.93(4)		
S(2)–Mo(1)–S(1)	77.32(5)	N(1)–Mo(1)–S(1)	80.0(1)
N(1)–Mo(1)–S(2)	81.6(1)	C(1)–Mo(1)–S(1)	88.4(1)
C(1)–Mo(1)–S(2)	98.1(1)	C(1)–Mo(1)–N(1)	168.2(1)
C(2)–Mo(1)–S(1)	90.7(1)	C(2)–Mo(1)–S(2)	167.9(1)
C(2)–Mo(1)–N(1)	97.9(1)	C(2)–Mo(1)–C(1)	79.9(2)
C(3)–Mo(1)–S(1)	148.8(1)	C(3)–Mo(1)–S(2)	83.6(1)
C(3)–Mo(1)–N(1)	121.5(1)	C(3)–Mo(1)–C(1)	70.0(1)
C(3)–Mo(1)–C(2)	106.6(1)	C(4)–Mo(1)–S(1)	161.8(1)
C(4)–Mo(1)–S(2)	88.1(1)	C(4)–Mo(1)–N(1)	87.2(1)
C(4)–Mo(1)–C(1)	104.6(1)	C(4)–Mo(1)–C(2)	103.9(1)
C(4)–Mo(1)–C(3)	36.0(1)	C(5)–Mo(1)–S(1)	149.4(1)
C(5)–Mo(1)–S(2)	120.7(1)	C(5)–Mo(1)–N(1)	78.9(1)
C(5)–Mo(1)–C(1)	110.9(1)	C(5)–Mo(1)–C(2)	70.7(2)
C(5)–Mo(1)–C(3)	61.7(1)	C(5)–Mo(1)–C(4)	35.9(1)
P(1)–S(1)–Mo(1)	87.61(6)	P(1)–S(2)–Mo(1)	85.18(7)
O(1)–C(1)–Mo(1)	176.4(3)	O(2)–C(2)–Mo(1)	177.3(3)
C(4)–C(3)–Mo(1)	67.8(2)	C(3)–C(4)–Mo(1)	76.2(2)
C(5)–C(4)–Mo(1)	76.8(2)	C(5)–C(4)–C(3)	116.4(4)
C(4)–C(5)–Mo(1)	67.3(2)	S(2)–P(1)–S(1)	109.3(1)
O(11)–P(1)–S(1)	107.5(1)	O(11)–P(1)–S(2)	113.4(1)
O(12)–P(1)–S(1)	112.7(1)	O(12)–P(1)–S(2)	112.0(1)
O(12)–P(1)–O(11)	101.8(1)	C(11)–O(11)–P(1)	121.6(2)
C(13)–C(11)–O(11)	109.7(3)	C(12)–O(12)–P(1)	119.3(3)
C(14)–C(12)–O(12)	112.6(4)	Mo(1)–N(1)–N(1')	117.6(2)
H(1)–N(1)–Mo(1)	108(3)	H(2)–N(1)–Mo(1)	116(2)
H(1)–N(1)–N(1')	108(3)	H(2)–N(1)–N(1')	104(2)
H(2)–N(1)–H(1)	102(3)		

MoNO_4PS_2 : C, 39.59; H, 4.98; N, 2.89%. Found: C, 39.30; H, 4.91; N, 2.66%.

3.4. $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{PPh}_2)(4\text{-NH}_2\text{C}_6\text{H}_4\text{Me})]$ (**3b**)

Compound **3b** was prepared as described above for **3a**, from **2b** (0.914 g, 1.89 mmol) and 4- $\text{NH}_2\text{C}_6\text{H}_4\text{Me}$ (0.203 g, 1.89 mmol). Yield, 0.64 g; 62%. Anal. Calc. for $\text{C}_{24}\text{H}_{24}\text{MoNO}_2\text{PS}_2$: C, 52.46; H, 4.40; N, 2.55%. Found: C, 52.27; H, 4.29; N, 2.54%.

3.5. $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\{\text{S}_2\text{P}(\text{OEt})_2\}(\text{py})]$ (**3c**)

To a solution of **2a** (0.3 g, 0.7 mmol) in CH_2Cl_2 (20 ml) was added pyridine (60 μl , 0.7 mmol) and the mixture stirred for 10 min and then evaporated to

dryness. The residue was extracted with a mixture of Et₂O/hexane (1:1, v:v; 3 × 10 ml). The filtered extract was concentrated in vacuo to ca. 10 ml and cooled overnight to –20°C to give orange crystals of **3c**. The mother liquor was decanted and the product dried in vacuo. Yield, 0.25 g; 78%. Anal. Calc. for C₁₄H₂₀MoNO₄PS₂: C, 36.77; H, 4.41; N, 3.06%. Found: C, 36.55; H, 4.41; N, 3.17%.

3.6. [Mo(η³-C₃H₅)(CO)₂(S₂PPh₂)(py)] (**3d**)

Compound **3d** was prepared as described above for **3c**, from **2b** (0.1 g, 0.2 mmol) and pyridine (17 μl, 0.2 mmol). Yield, 0.074 g; 71%. Anal. Calc. for C₂₂H₂₀MoNO₂PS₂: C, 50.68; H, 3.87; N, 2.69%. Found: C, 50.99; H, 3.91; N, 2.57%.

3.7. [Mo₂(η³-C₃H₅)₂(CO)₄{S₂P(OEt)₂}(μ-NH₂NH₂)] (**4a**)

To a solution of **2a** (0.3 g, 0.72 mmol) in CH₂Cl₂ (15 ml) was added hydrazine monohydrate (36 μl, 0.72 mmol). The mixture was stirred for 4 h and then evaporated to dryness. The residue was extracted with CH₂Cl₂ (2 × 10 ml). The filtered extract was concentrated in vacuo to ca. 10 ml. Addition of hexane and overnight cooling at –20°C afforded orange crystals of **4a**. The mother liquor was decanted and the product dried in vacuo. Yield, 0.19 g; 67%. Anal. Calc. for C₁₈H₃₄Mo₂N₂O₈P₂S₄: C, 27.41; H, 4.35; N, 3.55%. Found: C, 27.54; H, 4.12; N, 3.61%.

3.7.1. Structure determination of **4a**

Crystals suitable for X-ray determination were grown by slow diffusion of hexane into a concentrated solution of compound **4a** in CH₂Cl₂. Relevant crystallographic details are given in Table 3. Unit cell parameters were determined from the least-squares refinement of a set of 25 centred reflections. Three reflections were measured every hour as orientation and intensity control. Significant decay of the intensity was not observed. Heavy atoms were located from a Patterson synthesis and the remaining non-hydrogen atoms by DIRDIF [18]. Full matrix least-squares refinement was made with SHELX-76 [19]. After isotropic refinement, an absorption correction was applied with DIFFABS [20]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the hydrazine ligand were found in a difference map and were isotropically refined (*x*, *y*, *z*, *U*_{iso}). The remaining hydrogen atoms were geometrically positioned with a common isotropic temperature factor which was refined. After the final cycles of refinement the maximum difference electron density was 0.61 e Å⁻³ in the proximity of atom S(1). Full tables of bond lengths and angles, atomic coordinates and thermal parameters

have been deposited at the Cambridge Crystallographic Data Centre.

3.8. [Mo₂(η³-C₃H₅)₂(CO)₄{S₂P(OEt)₂}(μ-N₂C₄H₄)] (**4b**)

Compound **4b** was prepared as described above for **4a**, from **1a** (0.3 g, 0.72 mmol) and pyrazine (0.029 g, 0.36 mmol). The stirring time was 0.5 h. Yield, 0.25 g; 83%. Anal. Calc. for C₂₂H₃₄Mo₂N₂O₈P₂S₄: C, 31.59; H, 4.10; N, 3.35%. Found: C, 31.43; H, 3.81; N, 3.33%.

Acknowledgement

We thank DGICYT (Project PB 91-0678), FICYT and HUNOSA for financial support, and FICYT for the award of a grant (to G.B.). We also thank Prof. Gabino A. Carriedo for valuable discussions and help.

References

- [1] B.C. Gates, J.R. Katzer and G.C.A. Schuit, *Chemistry of Catalytic Processes*, McGraw-Hill, New York, 1979.
- [2] F.J. Derbyshire, *Catalysis in Coal Liquefaction: New Directions for Research*, IEA Coal Research, London, 1988.
- [3] D. Sellman, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 64.
- [4] (a) D. Miguel, V. Riera, J.A. Miguel, X. Soláns and M. Font-Altaba, *J. Chem. Soc., Chem. Commun.*, (1987) 472; (b) D. Miguel, V. Riera, J.A. Miguel, C. Bois, M. Philoche-Levisalles and Y. Jeannin, *J. Chem. Soc., Dalton Trans.*, (1987) 2875; (c) D. Miguel, V. Riera, J.A. Miguel and X. Soláns, *Angew. Chem., Int. Ed. Engl.*, **28** (1989) 1014; (d) D. Miguel, V. Riera, J.A. Miguel, F. Diego, C. Bois and Y. Jeannin, *J. Chem. Soc., Dalton Trans.*, (1990) 2719; (e) B. Alvarez, D. Miguel, V. Riera, J.A. Miguel and S. García-Granda, *Organometallics*, **10** (1991) 384; (f) D. Miguel, V. Riera, J.A. Miguel, M. Gómez and X. Soláns, *Organometallics*, **10** (1991) 1683; (g) B. Alvarez, S. García-Granda, Y. Jeannin, D. Miguel, J.A. Miguel and V. Riera, *Organometallics*, **10** (1991) 3005; (h) D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *Organometallics*, **12** (1993) 1394; (i) D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *Organometallics*, **12** (1993) 2888; (j) B. Alvarez, S. García-Granda, J. Li, D. Miguel and V. Riera, *Organometallics*, **13** (1994) 16; (k) D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *Organometallics*, **13** (1994) 1336.
- [5] (a) D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *Angew. Chem., Int. Ed. Engl.*, **31** (1992) 76. (b) G. Barrado, D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *J. Organomet. Chem.*, **463** (1993) 127; (c) G. Barrado, D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *J. Organomet. Chem.*, **466** (1993) 147.
- [6] B. Lastra, R. García, S.C. Mitchell, C.E. Snape, D. Miguel, G. Barrado and S.R. Moinelo, in K.H. Michaelian (ed.), *Proc. 7th Int. Conf. Coal Sci.*, Banff, Alberta, Canada, 1993, Vol. II, p. 261.
- [7] P. Sellmann, P. Kreutzer, G. Huttner and A. Frank, *Z. Naturforsch., Teil B*, **33** (1978) 1341.
- [8] L. Blum, I.D. Williams and R.R. Schrock, *J. Am. Chem. Soc.*, **106** (1984) 8316.

- [9] P.R. Challen, S.M. Koo, C.G. Kim, W.R. Dunham and D. Coucouvanis, *J. Am. Chem. Soc.*, **112** (1990) 8606.
- [10] M. Kawano, C. Hoshino and K. Matsumoto, *Inorg. Chem.*, **31** (1992) 5158.
- [11] N.Y. Zhu, S.W. Du, X.T. Wu and J.X. Lu, *Angew. Chem., Int. Ed. Engl.*, **31** (1992) 87.
- [12] P.E. Mosier, C.G. Kim and D. Coucouvanis, *Inorg. Chem.*, **12** (1993) 2620.
- [13] H.T. Dieck and H. Friedel, *J. Organomet. Chem.*, **14** (1968) 375.
- [14] (a) M.F. Perpiñan and A. Santos, *J. Organomet. Chem.*, **218** (1981) 185; (b) *ibid.*, **221** (1981) 163; (c) M.F. Perpiñan, L. Ballester and A. Santos, *J. Organomet. Chem.*, **241** (1983) 215.
- [15] K.B. Shiu, K.H. Yih, S.L. Wang and F.L. Liao, *J. Organomet. Chem.*, **420** (1991) 359.
- [16] For leading references, and an EHMO study on this and other features of complexes containing '(η^3 -allyl)Mo(CO)₂' fragments, see M.D. Curtis and O. Eisenstein, *Organometallics*, **3** (1984) 887.
- [17] W.A. Higgins, P.W. Vogel and W.G. Craig, *J. Am. Chem. Soc.*, **77** (1955) 1864; R.G. Cavell, W. Byers and E.D. Day, *Inorg. Chem.*, **10** (1971) 2710.
- [18] P.T. Beurskens, G. Admiraal, W.P. Bosman, G. Beurskens, H.M. Doesburg, S. García-Granda, R.O. Gould, J.M.M. Smits and C. Smikalla, *The DIRDIF Program System, Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands, 1982.
- [19] G.M. Sheldrick, *SHELX-76 Program for Crystal Structure Determinations*, University of Cambridge, 1976, Local version: F.J. Van der Maelen, *Ph.D. Thesis*, University of Oviedo, Oviedo, Spain, 1991.
- [20] N. Walker and D. Stuart, *Acta Crystallogr.*, **A39** (1983) 158.
- [21] A.L. Spek, The EUCLID Package, in E. Sayre (ed.), *Computational Crystallography*, Clarendon, Oxford, UK, 1982, p. 528.