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Organotransition-metal complexes of multidentate ligands

XVII *. Synthesis and characterization of some η^3-allylcarbonyl complexes of molybdenum containing dithiocarbamates as the uni-negative sulphur-bidentate ligands: crystal structure of $[Mo(\eta^2\text{-}S_2CNEt_2)(CO)(\eta^3\text{-allyl})\{\eta^2\text{-bis(diphenylphosphino)methane}\}]$

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Abstract

Complexes with a general formula of $[Mo\{\eta^2\text{-(S,S)}\}(CO)_2(\eta^3\text{-allyl})]$ ($(S,S)^-$ = *N,N*-diethyldithiocarbamato or pyrrolidine-1-carbodithioato) have been prepared by one of three preparative routes: (1) reaction of the anion, $[Mo\{\eta^2\text{-(S,S)}\}(CO)_4]^-$ with allyl bromide; (2) reaction of $[Mo(\eta^2\text{-}H_2CPz'_2)(CO)_2(\eta^3\text{-allyl})Br]$ (Pz′ = 3,5-dimethylpyrazol-1-yl) with $(S,S)^-$; and (3) the substitution reaction between $[Mo(MeCN)_2(CO)_2(\eta^3\text{-allyl})Br]$ and $(S,S)^-$. The complexes are probably mononuclear and diamagnetic, based on the relevant spectral data. These complexes can react with pyridine to give $[Mo\{\eta^2\text{-(S,S)}\}(CO)_2(\eta^3\text{-allyl})(py)]$ and with the phosphorus-bidentate ligand (P,P) to afford $[Mo\{\eta^2\text{-(S,S)}\}(CO)(\eta^3\text{-allyl})\{\eta^2\text{-(P,P)}\}]$ ((P,P) = bis(diphenylphosphino)methane (DPPM) or 1,2-bis(diphenylphosphino)ethane (DPPE)), which can also be prepared from the reaction of $[Mo\{\eta^2\text{-(P,P)}\}(CO)_2(\eta^3\text{-allyl})Br]$ with $(S,S)^-$. The new complexes were characterized by element analysis, IR and NMR spectroscopy. The crystal structure of $[Mo(\eta^2\text{-}S_2CNEt_2)(CO)(\eta^3\text{-allyl})(\eta^2\text{-DPPM})]$ was determined to confirm the di-hapticity of $(S,S)^-$ and of (P,P) in $[Mo\{\eta^2\text{-(S,S)}\}(CO)(\eta^3\text{-allyl})\{\eta^2\text{-(P,P)}\}]$: space group $P2_1/c$, $a = 16.028(4)$, $b = 8.867(2)$, $c = 23.459(4)$ Å, $\beta = 93.12(2)°$, $V = 3329.1(13)$ Å^3, $Z = 4$, $D_{calc} = 1.392$ g/cm^3, $R = 0.067$ and $R_w = 0.076$ on 3992 reflections with $I > 3.0\,\sigma(I)$.

Introduction

Since the preparation of the dialkyldithiocarbamate, $(S,S)^-$, derivatives of some metal carbonyl compounds in 1964 by Cotton and McCleverty [2], unusual struc-

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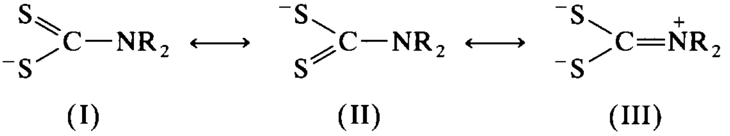
* For Part XVI see ref. 1.

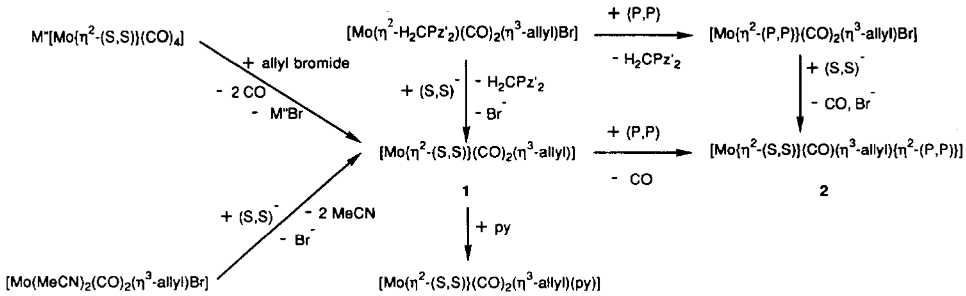
tures and/or reactions of the complexes have been described in many reports [3–19], probably due to the variable nature of the sigma donicity of $(S,S)^-$, implied by the three canonical forms, I–III. Following one of our recent research interests, having centered on exploration of the steric and electronic effects of substituents of multidentate ligands on the physical and chemical properties of the relevant metal carbonyl derivatives [20], we wish to report in this paper that both effects of $(S,S)^-$ are apparently responsible for the preparation of some new complexes including the diamagnetic, 16-electron compounds, $[Mo\{\eta^2\text{-}(S,S)\}(CO)_2(\eta^3\text{-allyl})]$, and the 18-electron derivatives, $[Mo\{\eta^2\text{-}(S,S)\}(CO)(\eta^3\text{-allyl})\{\eta^2\text{-}(P,P)\}]$ ($(S,S)^-$ = *N,N*-diethyldithiocarbamato or pyrrolidine-1-carbodithioato; (P,P) = bis(diphenylphosphino)methane (DPPM) or 1,2-bis(diphenylphosphino)ethane (DPPE)).



(I) (II) (III)

Results and discussion

The substitution reactions between $[Mo(MeCN)_2(CO)_2(\eta^3\text{-allyl})Br]$ and M′(S,S) (M′ = Na or K) in acetone were reported earlier by Perpinan and Santos to give $M'[Mo\{\eta^2\text{-}(S,S)\}\{\eta^1\text{-}(S,S)\}(CO)_2(\eta^3\text{-allyl})]$, which was formed independent of the molar ratio 1:1 or 1:2 ($[Mo(MeCN)_2(CO)_2(\eta^3\text{-allyl})Br]:(S,S)^-$) [12a]. Since M′(S,S) is an ionic solid [4] and slightly soluble in acetone [12a], we thought that the reaction product might be different using a more polar solvent to dissolve both compounds. Indeed, when equal amounts of $[Mo(MeCN)_2(CO)_2(\eta^3\text{-allyl})Br]$ and Na(S,S) or $NH_4(S,S)$ dissolved in MeCN, an orange-yellow precipitate formed after 10 min. This solid was later found to have a general formula of $[Mo\{\eta^2\text{-}(S,S)\}(CO)_2(\eta^3\text{-allyl})]$ (**1**). This compound can be prepared by two other alternative methods, either from the direct allylation of $[Mo\{\eta^2\text{-}(S,S)\}(CO)_4]^-$ in MeCN or from the substitution reaction between $[Mo(\eta^2\text{-}H_2CPz'_2)(CO)_2(\eta^3\text{-allyl})Br]$ (Pz′ = 3.5-dimethylpyrazol-1-yl) and $(S,S)^-$ in a mixed-solvent system of CH_2Cl_2 and MeOH. (Hence this reaction is similar to the one reported, involving the formation of $[Mo\{\eta^2\text{-}(P,P)\}(CO)_2(\eta^3\text{-allyl})Br]$ from the displacement reaction between $[Mo(\eta^2\text{-}H_2CPz'_2)(CO)_2(\eta^3\text{-allyl})Br]$ and (P,P) [21]). The neutral donors such as (P,P) or pyridine (PY) can react with **1** to give $[Mo\{\eta^2\text{-}(S,S)\}(CO)(\eta^3\text{-allyl})\{\eta^2\text{-}(P,P)\}]$ (**2**) or $[Mo\{\eta^2\text{-}(S,S)\}(CO)_2(\eta^3\text{-allyl})(PY)]$, respectively (Scheme 1). The latter compound was previously prepared from the reaction between $[Mo(PY)_2(CO)_2(\eta^3\text{-allyl})Br]$ and $(S,S)^-$ [12a]. Quite obviously, **1** can also react with M′(S,S) to give $M'[Mo\{\eta^2\text{-}(S,S)\}\{\eta^1\text{-}(S,S)\}(CO)_2(\eta^3\text{-allyl})]$. Probably, solvent dictates the reaction product. When equal amounts of $[Mo(MeCN)_2(CO)_2(\eta^3\text{-allyl})Br]$ (**3**) and M′(S,S) are in MeCN, the formation rate of **1** from **3** is faster than that of $M'[Mo\{\eta^2\text{-}(S,S)\}\{\eta^1\text{-}(S,S)\}(CO)_2(\eta^3\text{-allyl})]$ from **1** and a total conversion of **3** into **1** was observed in our laboratory. However, in acetone, the formation rate of **1** from **3** is much slower than that of $M'[Mo\{\eta^2\text{-}(S,S)\}\{\eta^1\text{-}(S,S)\}(CO)_2(\eta^3\text{-allyl})]$ from **1** and this compound is the only reaction product between **3** and M′(S,S) [12a].



Scheme 1.

In 1981, Perpinan and Santos also found that no reaction products were isolated from the reaction of $[\mathrm{Mo}(\eta^2\text{-DPPE})(\mathrm{CO})_2(\eta^3\text{-allyl})\mathrm{Br}]$ with alkyldithiocarbamates, $(\mathrm{S,S})'^-$, although this anionic bidentate ligand can react with $[\mathrm{Mo}(\eta^2\text{-BPY})(\mathrm{CO})_2(\eta^3\text{-allyl})\mathrm{Br}]$ to give $[\mathrm{Mo}\{\eta^1\text{-(S,S)}'\}(\mathrm{CO})_2(\eta^3\text{-allyl})(\eta^2\text{-BPY})]$ (BPY = 2,2′-bipyridine) [12b] while in the presence of PY, dialkyldithiocarbamates, $(\mathrm{S,S})^-$, can react with $[\mathrm{Mo}(\eta^2\text{-BPY})(\mathrm{CO})_2(\eta^3\text{-allyl})\mathrm{Br}]$ to afford $[\mathrm{Mo}\{\eta^2\text{-(S,S)}\}(\mathrm{CO})_2(\eta^3\text{-allyl})(\mathrm{PY})]$ [8]. Apparently, the more electron-releasing inductive effect of the alkyl group relative to that of the hydrogen atom increases the contribution of the canonical form III and makes $(\mathrm{S,S})^-$ a better sigma donor than $(\mathrm{S,S})'^-$. Accordingly, we found that $(\mathrm{S,S})^-$ can convert $[\mathrm{Mo}\{\eta^2\text{-(P,P)}\}(\mathrm{CO})_2(\eta^3\text{-allyl})\mathrm{Br}]$ into $[\mathrm{Mo}\{\eta^2\text{-(S,S)}\}(\mathrm{CO})(\eta^3\text{-allyl})\{\eta^2\text{-(P,P)}\}]$ (**2**). Probably, $[\mathrm{Mo}\{\eta^1\text{-(S,S)}\}(\mathrm{CO})_2(\eta^3\text{-allyl})\{\eta^2\text{-(P,P)}\}]$ is the intermediate leading to **2**. From the aforementioned results, it is true that the four- or five-membered chelate rings formed either in the $\mathrm{Mo}\{\eta^2\text{-(P–P)}\}$, $\mathrm{Mo}(\eta^2\text{-BPY})$, or $\mathrm{Mo}\{\eta^2\text{-(S,S)}\}$ fragment of the complexes are rather stable whereas the six-membered chelate ring of the $\mathrm{Mo}(\eta^2\text{-H}_2\mathrm{CPz}'_2)$ fragment is fragile. Based on the reported structures [20d,g,i,j,22] including the crystal structure described in Fig. 1, we believe that the nearly planar form of the chelate rings in the $\mathrm{Mo}\{\eta^2\text{-(P–P)}\}$, $\mathrm{Mo}(\eta^2\text{-BPY})$, or $\mathrm{Mo}\{\eta^2\text{-(S,S)}\}$ fragment and the boat form of the chelate ring in the $\mathrm{Mo}(\eta^2\text{-H}_2\mathrm{CPz}'_2)$ fragment, giving respectively neglibible and large nonbonded interactions in the complexes, are responsible for the observed substitution reactions (Scheme 1).

Following any one of the preparative methods mentioned above, both $[\mathrm{Mo}(\eta^2\text{-S}_2\mathrm{CNEt}_2)(\mathrm{CO})_2(\eta^3\text{-allyl})]$ (**1a**) and $[\mathrm{Mo}(\eta^2\text{-S}_2\mathrm{CNC}_4\mathrm{H}_8)(\mathrm{CO})_2(\eta^3\text{-allyl})]$ (**1b**) are very similar to each other in terms of IR and NMR data, but **1a** is more soluble than **1b** in organic solvents. Compound **1a** or **1b** shows four carbonyl stretching bands in the solid-state as a KBr disc, though exhibits only two broad bands in either $\mathrm{CH_2Cl_2}$ or $\mathrm{CH_3CN}$. Since the four bands appear as split from two broad bands and the average value of each split pair is very close to that of the corresponding solution band (e.g., **1a** displays 1952(s), 1922(s), 1860(s) and 1838(s) in the solid-state; the average value of 1937 for the first two bands is close to the first band, 1938(s) in $\mathrm{CH_3CN}$ or 1934(s) in $\mathrm{CH_2Cl_2}$ whereas that of 1849 for the latter two bands is close to the second band, 1842(s) in $\mathrm{CH_3CN}$ or 1840(s) $\mathrm{cm^{-1}}$ in $\mathrm{CH_2Cl_2}$) and no coordinated deuterated solvent such as acetonitrile-d_3 or dimethylsulfoxide-d_6 can be found in either $^1\mathrm{H}$ or $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra, recorded at room temperature, of **1a** and **1b** in the solvent, we believe that **1a** and **1b** are probably mononuclear and the four $\nu(\mathrm{CO})$ bands may be caused either by

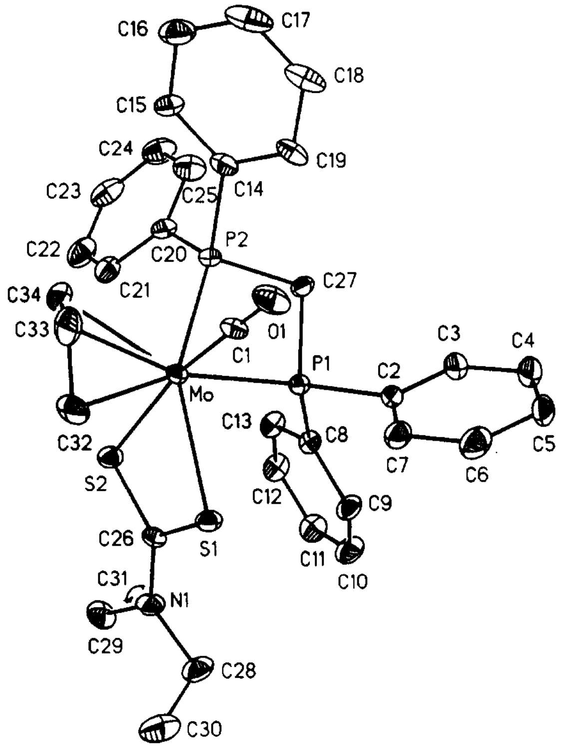


Fig. 1. Structure of [Mo(η^2-S_2CNEt_2)(CO)(η^3-allyl)(η^2-DPPM)] (**2a**) showing the atomic numbering scheme and 50% probability thermal ellipsoids.

intermolecular coupling between asymmetric (and symmetric) carbonyl oscillators in the unit cell of the compounds [23], or by the presence of two structural isomers in the solid state (i.e., a quick fluxional process converting one of the two isomers into the other occurs in solution in the NMR time scale at room temperature and the two compounds behave like "one" compound in solution). However, the poor solubility of either **1a** or **1b** in organic solvents at lower temperature prohibits any further confirmation by NMR. An A_2B_2X spectrum with a 2:2:1 intensity ratio is observed at room temperature for the five protons of the allyl group in the ^{1}H NMR spectrum of **1a** or **1b** and the group is coordinated with the metal atom in a common trihapto form [20a,f,h,l,m,21]. This spectral feature can further support that **1a** and **1b** are not paramagnetic but diamagnetic 16-electron species. If the molecular-orbital arguments [24] about the diamagnetic property of the six-coordinate, 16-electron complexes can be applied to **1a** and **1b** (the allyl group can be considered to occupy two coordination sites of the central metal atom in the compounds, because the η^3-allyl anion can donate four electrons to the metal atom [25]), the structures of **1a** and **1b**, like that of [Mo(η^2-$S_2CNPr^i_2$)$_2$(CO)$_2$] [11c], should deviate quite largely from ideal octahedral geometry. Unfortunately, after several trials we could not obtain single crystals with good quality suitable for structural analysis. However, upon addition of PY, **1a** can be converted into [Mo(η^2-S_2CNEt_2)(CO)$_2$(η^3-allyl)(PY)]. This reaction and the many others which have been reported previously in the literature [5,9–11] for [M(η^2-S_2CXR_2)$_2$(CO)$_2$]

(M = Mo or W; X = N or P) can support the electron-deficient nature of these compounds and **1**. Currently, exploration on complexes containg the M(η^2-S_2CR) fragment are under way and the related results will be reported in due course.

The four derivatives, [Mo{η^2-S_2CNEt_2}(CO)(η^3-allyl)(η^2-DPPM)] (**2a**), [Mo{η^2-S_2CNEt_2}(CO)(η^3-allyl)(η^2-DPPE)] (**2b**), [Mo{η^2-$S_2CNC_4H_8$}(CO)(η^3-allyl)(η^2-DPPM)] (**2c**), and [Mo{η^2-$S_2CNC_4H_8$}(CO)(η^3-allyl)(η^2-DPPE)] (**2d**), prepared either from the reaction of **1** with (P,P) or from the reaction of [Mo{η^2-(P,P)}$(CO)_2$(η^3-allyl)Br] with $(S,S)^-$ (Scheme 1) have similar NMR and IR features. The similarity led us to believe that the four structures are similar to each other. In the IR spectra, the carbonyl stretching frequency of **2a**, **2b**, **2c** or **2d** is found to be approx. 1800 cm^{-1}, which is much smaller than the average value of 1884 for **1a** and that of 1887 for **1b** measured in CH_2Cl_2. Apparently, the presence of the more electron donating (P,P) ligands than the CO ligands increases metal *d* to carbonyl π^* backbonding. Whether the (P,P) ligand (or the $(S,S)^-$ ligand) is monodentate or bidentate in the complexes cannot be known for sure based on the IR data. We thus performed the NMR measurements on these complexes. However, probably due to the coupling between most of protons of the allyl and $(S,S)^-$ and phosphorus nuclei of (P,P), all the ^1H NMR spectra contain many multiplets with some overlapped so that unambiguous assignment of the spectra is not possible, although two triplets at 0.76 and 1.03 ($J = 7.1$ Hz) are observed clearly for the two methyl groups of **2a** in $CDCl_3$ and two similar signals at 0.70 and 0.82 ppm ($J = 7.2$ Hz) are also found easily for the two methyl groups of **2b** in the same solvent. In order to more clearly characterize the structure of **2**, we have hence obtained single crystals of **2a** and determined its solid-state structure by X-ray crystallography. This structure (Fig. 1) confirms the di-hapticity of $(S,S)^-$ and of (P,P) in **2**. Thus, **2** is not another 16-electron compound like **1**, but an 18-electron species.

Crystal structure of [Mo(η^2-S_2CNEt_2)(CO)(η^3-allyl)(η^2-DPPM)] (2a)

Crystals of **2a** have four equivalent mononuclear units in a monoclinic cell. The molecular geometry, with numbering scheme, is depicted in the ORTEP drawing (Fig. 1). The pertinent crystallographic parameters are given in Tables 1–3.

As shown in Fig. 1, the structure consists of discrete units of **2a**, containing one bidentate diethyldithiocarbamate and one bidentate DPPM. If the η^3-allyl group is assumed to occupy one coordination site of the central metal atom, the whole geometry can be best viewed as a distorted pseudo-octahedron with one equatorial plane including approximately S(1), P(1), P(2) and the centroid position of the allyl group and one axial axis containing S(2) and C(1) (Fig. 2). Either two Mo–S or two Mo–P bond lengths are quite different from each other (Mo–S(1), 2.532(2); Mo–S(2), 2.612(2); Mo–P(1), 2.480(2); and Mo–P(2), 2.430(2) Å) probably indicating that the two groups *trans* to two ligating sulphur-(or phosphorus-) atoms have different *trans* influence [26]. Thus, when the bond angle of 168.6(2)° for S(2)–Mo–C(1) and that of 100.5(2)° for S(1)–Mo–C(1) are found, it is more appropriate to consider the carbonyl group, C(1)O(1), as the *trans* group to S(2) relative to S(1) and the Mo–S(2) bond length is thus longer than the Mo–S(1) bond, as expected. The lengthening of the Mo–S bond caused by the presence of the strong *trans* influence of other strong π-acid ligand such as nitrosyl was reported previously in [Mo(η^2-$S_2CN^nBu_2)_3$(NO)] [27]. Two bond lengths of 1.314(15) for

Table 1

Crystallographic data for [Mo(η^2-S_2CNEt_2)(CO)(η^3-allyl)(η^2-DPPM)] (**2a**)

Empirical formula	$C_{34}H_{37}MoNOP_2S_2$
Colour, habit	Orange-red, chunk
Crystal size (mm)	0.72×0.46×0.36
Space group	$P2_1/c$, monoclinic
Unit cell dimensions	$a = 16.028(4)$ Å
	$b = 8.867(2)$ Å; $\beta = 93.12(2)$°
	$c = 23.459(4)$ Å
No. reflections for indexing	15 (7.31° $\leqslant 2\theta \leqslant$ 25.34°)
Volume	3329.1(13) Å^3
Z	4
Formula weight	697.6
Density (calc.)	1.392 g/cm^3
Absorption coefficient	0.626 mm^{-1}
F(000)	1440
Diffractometer used	Siemens R3m/V
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)
Temperature (K)	295
Monochromator	Highly oriented graphite crystal
2θ range	2.5–48.0°
Scan type	$\theta/2\theta$
Scan speed	Variable, 3.66–14.65°/min in ω
Scan range (ω)	1.00° plus K_α-separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	3 measured every 50 reflections
Index ranges	$-18 \leqslant h \leqslant 18, 0 \leqslant k \leqslant 10, 0 \leqslant l \leqslant 24$
Reflections collected	6265 (4872 > 3.0$\sigma(I)$)
Independent reflections	5262 (3992 > 3.0$\sigma(I)$)
Min/max transmission	0.840/0.918
Extinction correction	$\chi = 0.00027(11)$, where $F = F\,[1+0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0050F^2$
Number of parameters refined	371
Final R indices (obs. data)	$R = 0.0668$, $R_w = 0.0758$
Goodness-of-fit	1.25
Data-to-parameter ratio	10.8:1
Largest difference peak/hole	2.25/−3.16 e Å^{-3}

C(32)–C(33) and 1.305(16) Å for C(33)–C(34) in **2a** are identical to each other within the experimental errors supporting the tri-hapticity of the allyl group. The distance of 2.366(9) for Mo–C(34) is significantly larger than those of 2.301(10) for Mo–C(32) and 2.295(11) Å for Mo–C(33) reflecting the presence of some bulky, sterically neighbouring, phenyl groups of DPPM (the nonbonded distances shorter than 4.6 Å between three allyl carbon atoms and 24 phenyl carbon atoms are 3.610 for C(34) ··· C(14), 3.755 for C(34) ··· C(15), 3.540 for C(34) ··· C(20), and 3.491 Å for C(34 ··· C(21)). The linear molybdenum carbonyl unit exhibits bond distances of 1.903(7) for Mo–C(1) and 1.185(9) Å for C(1)–O(1) typical of Mo^{II}

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients [a] ($\text{Å}^2 \times 10^3$) in **2a**

Atom	x	y	z	U_{eq}
Mo	7595(1)	2019(1)	3641(1)	33(1)
S(1)	6055(1)	2312(2)	3805(1)	42(1)
S(2)	6687(1)	56(2)	3055(1)	46(1)
P(1)	7471(1)	554(2)	4533(1)	35(1)
P(2)	8869(1)	651(2)	3913(1)	37(1)
O(1)	8321(3)	4656(6)	4372(3)	67(2)
N(1)	5070(4)	228(8)	3283(3)	54(2)
C(1)	8048(4)	3631(8)	4096(3)	41(2)
C(2)	7335(4)	1522(8)	5212(3)	40(2)
C(3)	7653(5)	880(10)	5722(3)	57(3)
C(4)	7574(6)	1646(13)	6228(4)	72(4)
C(5)	7191(6)	3047(11)	6248(4)	65(3)
C(6)	6874(6)	3647(12)	5741(4)	74(4)
C(7)	6940(5)	2941(9)	5222(3)	54(3)
C(8)	6809(4)	−1110(7)	4585(3)	37(2)
C(9)	6075(4)	−1058(9)	4865(3)	52(3)
C(10)	5548(5)	−2305(10)	4862(4)	65(3)
C(11)	5747(6)	−3587(9)	4581(4)	64(3)
C(12)	6478(5)	−3651(9)	4299(4)	61(3)
C(13)	6994(5)	−2414(8)	4298(3)	49(3)
C(14)	9822(4)	1736(8)	4077(3)	45(2)
C(15)	10447(5)	1801(10)	3696(4)	61(3)
C(16)	11156(6)	2721(12)	3821(5)	78(4)
C(17)	11223(6)	3498(11)	4319(6)	90(5)
C(18)	10610(6)	3445(10)	4698(5)	75(4)
C(19)	9909(5)	2573(10)	4575(4)	57(3)
C(20)	9255(4)	−1022(8)	3544(3)	44(2)
C(21)	8812(5)	−1619(10)	3075(3)	57(3)
C(22)	9056(7)	−2934(11)	2832(4)	75(4)
C(23)	9775(6)	−3642(11)	3044(5)	79(4)
C(24)	10234(6)	−3076(11)	3491(5)	79(4)
C(25)	9968(5)	−1778(10)	3753(5)	68(3)
C(26)	5840(4)	782(8)	3364(3)	41(2)
C(27)	8554(4)	−132(9)	4597(3)	46(2)
C(28)	4379(5)	747(11)	3611(4)	65(3)
C(29)	4881(5)	−967(10)	2880(4)	62(3)
C(30)	3844(7)	1920(16)	3341(6)	112(6)
C(31)	4959(7)	−2540(12)	3137(5)	82(4)
C(32)	7262(5)	3759(13)	2937(4)	83(4)
C(33)	8069(7)	3510(13)	2928(5)	86(4)
C(34)	8415(6)	2206(13)	2835(4)	72(4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

complexes [11c,20f,h,m,28]. The dithiocarbamato group exhibits C–S (1.73 and 1.70 Å, S_2–CNR_2) and C–N (1.33 Å, S_2C–NR_2) bond lengths that are nearly identical with those found in the Mo^0 complex, $[Et_4N][Mo(\eta^2\text{-}S_2CNEt_2)(CO)_4]$ [14b]. The short C–N bond length indicates considerable double-bond character as is typical for chelated 1,1-dithiolate ligands [4] and found consistent with the C–N stretching frequency of 1488 cm^{-1} in **2a** (the C–N single bond stretching frequencies in amines [29] fall in the region 1250–1350 cm^{-1} and the C=N stretching frequency in

Table 3

Selected bond lenghts and angles in **2a**

Bond lenghts (Å)			
Mo–S(1)	2.532 (2)	Mo–S(2)	2.612 (2)
Mo–P(1)	2.480 (2)	Mo–P(2)	2.430 (2)
Mo–C(1)	1.903 (7)	Mo–C(32)	2.301 (10)
Mo–C(33)	2.295 (11)	Mo–C(34)	2.366 (9)
S(1)–C(26)	1.730 (7)	S(2)–C(26)	1.702 (7)
P(1)–C(2)	1.833 (7)	P(1)–C(8)	1.826 (7)
P(1)–C(27)	1.838 (7)	P(2)–C(14)	1.828 (7)
P(2)–C(20)	1.841 (7)	P(2)–C(27)	1.844 (8)
O(1)–C(1)	1.185 (9)	N(1)–C(26)	1.332 (9)
N(1)–C(28)	1.458 (10)	N(1)–C(29)	1.440 (11)
C(2)–C(3)	1.396 (10)	C(2)–C(7)	1.409 (11)
C(3)–C(4)	1.379 (13)	C(4)–C(5)	1.387 (15)
C(5)–C(6)	1.376 (13)	C(6)–C(7)	1.377 (13)
C(8)–C(9)	1.379 (10)	C(8)–C(13)	1.378 (10)
C(9)–C(10)	1.390 (12)	C(10)–C(11)	1.361 (13)
C(11)–C(12)	1.379 (13)	C(12)–C(13)	1.373 (11)
C(14)–C(15)	1.381 (11)	C(14)–C(19)	1.385 (12)
C(15)–C(16)	1.416 (12)	C(16)–C(17)	1.356 (18)
C(17)–C(18)	1.326 (16)	C(18)–C(19)	1.381 (12)
C(20)–C(21)	1.382 (11)	C(20)–C(25)	1.390 (11)
C(21)–C(22)	1.364 (13)	C(22)–C(23)	1.382 (14)
C(23)–C(24)	1.345 (15)	C(24)–C(25)	1.382 (14)
C(28)–C(30)	1.469 (16)	C(29)–C(31)	1.522 (14)
C(32)–C(33)	1.314 (15)	C(33)–C(34)	1.305 (16)
Bond angles (°)			
S(1)–Mo–S(2)	68.2(1)	S(1)–Mo–P(1)	78.6(1)
S(2)–Mo–P(1)	91.6(1)	S(1)–Mo–P(2)	145.5(1)
S(2)–Mo–P(2)	104.0(1)	P(1)–Mo–P(2)	67.8(1)
S(1)–Mo–C(1)	100.5(2)	S(2)–Mo–C(1)	168.6(2)
P(1)–Mo–C(1)	88.1(2)	P(2)–Mo–C(1)	86.5(2)
S(1)–Mo–C(32)	81.4(2)	S(2)–Mo–C(32)	88.1(3)
P(1)–Mo–C(32)	158.5(2)	P(2)–Mo–C(32)	133.0(2)
C(1)–Mo–C(32)	88.0(3)	S(1)–Mo–C(33)	114.6(3)
S(2)–Mo–C(33)	101.3(3)	P(1)–Mo–C(33)	164.2(3)
P(2)–Mo–C(33)	99.9(3)	C(1)–Mo–C(33)	81.1(4)
C(32)–Mo–C(33)	33.2(4)	S(1)–Mo–C(34)	134.6(2)
S(2)–Mo–C(34)	86.7(2)	P(1)–Mo–C(34)	141.7(3)
P(2)–Mo–C(34)	75.5(2)	C(1)–Mo–C(34)	100.6(3)
C(32)–Mo–C(34)	59.8(3)	C(33)–Mo–C(34)	32.5(4)
Mo–S(1)–C(26)	89.6(2)	Mo–S(2)–C(26)	87.6(2)
Mo–P(1)–C(2)	120.5(2)	Mo–P(1)–C(8)	123.5(2)
C(2)–P(1)–C(8)	102.9(3)	Mo–P(1)–C(27)	97.1(2)
C(2)–P(1)–C(27)	104.0(3)	C(8)–P(1)–C(27)	106.1(3)
Mo–P(2)–C(14)	118.2(2)	Mo–P(2)–C(20)	125.4(2)
C(14)–P(2)–C(20)	103.0(3)	Mo–P(2)–C(27)	98.6(2)
C(14)–P(2)–C(27)	106.2(3)	C(20)–P(2)–C(27)	102.7(3)
C(26)–N(1)–C(28)	122.2(7)	C(26)–N(1)–C(29)	121.7(6)
C(28)–N(1)–C(29)	116.1(6)	Mo–C(1)–O(1)	178.6(6)
P(1)–C(2)–C(3)	119.9(6)	P(1)–C(2)–C(7)	120.5(5)
C(3)–C(2)–C(7)	119.6(7)	C(2)–C(3)–C(4)	119.3(8)
C(3)–C(4)–C(5)	122.1(8)	C(4)–C(5)–C(6)	117.4(8)
C(5)–C(6)–C(7)	123.1(9)	C(2)–C(7)–C(6)	118.4(7)

Table 3 (continued)

Bond angles (°)			
P(1)-C(8)-C(9)	121.3(5)	P(1)-C(8)-C(13)	120.3(5)
C(9)-C(8)-C(13)	118.2(6)	C(8)-C(9)-C(10)	120.3(7)
C(9)-C(10)-C(11)	120.5(8)	C(10)-C(11)-C(12)	119.7(8)
C(11)-C(12)-C(13)	199.7(8)	C(8)-C(13)-C(12)	121.6(7)
P(2)-C(14)-C(15)	120.9(6)	P(2)-C(14)-C(19)	120.3(6)
C(15)-C(14)-C(19)	118.8(7)	C(14)-C(15)-C(16)	119.5(9)
C(15)-C(16)-C(17)	119.8(10)	C(16)-C(17)-C(18)	121.3(9)
C(17)-C(18)-C(19)	119.4(10)	C(14)-C(19)-C(18)	121.3(8)
P(2)-C(20)-C(21)	120.7(5)	P(2)-C(20)-C(25)	121.0(6)
C(21)-C(20)-C(25)	118.2(7)	C(20)-C(21)-C(22)	120.9(8)
C(21)-C(22)-C(23)	119.4(9)	C(22)-C(23)-C(24)	121.4(9)
C(23)-C(24)-C(25)	119.2(9)	C(20)-C(25)-C(24)	120.9(9)
S(1)-C(26)-S(2)	114.4(4)	S(1)-C(26)-N(1)	121.9(5)
S(2)-C(26)-N(1)	123.7(6)	P(1)-C(27)-P(2)	96.1(3)
N(1)-C(28)-C(30)	116.0(8)	N(1)-C(29)-C(31)	113.9(7)
Mo-C(32)-C(33)	73.1(7)	Mo-C(33)-C(32)	73.7(7)
Mo-C(33)-C(34)	76.8(7)	C(32)-C(33)-C(34)	125.4(11)
Mo-C(34)-C(33)	70.7(6)		

the region 1640–1690 cm^{-1}). Clearly, the resonance form III, depicted in the Introduction, makes an appreciable contribution to the electronic structure of (S,S)$^-$ in the complex.

Experimental

All operations were performed by the usual Schlenk techniques [30], using deoxygenated, dry solvents and gases. IR spectra with abbreviation (s, strong; m, medium), calibrated with polystyrene, were recorded on a Hitachi Model 270-30 instrument; NMR spectra with abbreviation (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet) were obtained either on a Bruker WP-100 (^{1}H, 100 MHz) or Varian VXR-300 (^{1}H, 300 MHz; ^{13}C, 75.43 MHz) FT NMR spectrometer. Proton

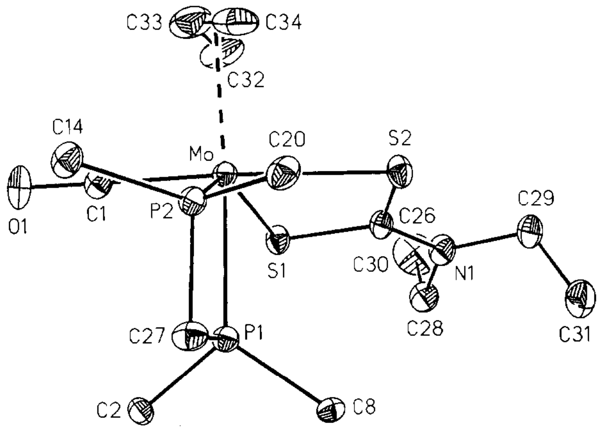


Fig. 2. Central part of the **2a** molecule.

chemical shifts (δ in ppm, J in Hz) are positive downfield or negative upfield relative to an internal trimethylsilane standard. Elemental analysis results were obtained by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University.

The complexes, [Mo(MeCN)$_2$(CO)$_2$(η^3-allyl)Br] [31], M″[Mo{η^2-(S,S)}(CO)$_4$] (M″ = Et$_4$N or bis(triphenylphosphoranylidene)ammonium (PPN)) [14b], [Mo(η^2-H$_2$CPz$'_2$)(CO)$_2$(η^3-allyl)Br] [20a], [Mo(η^2-DPPM)(CO)$_2$(η^3-allyl)Br] [21] and [Mo(η^2-DPPE)(CO)$_2$(η^3-allyl)Br] [21] were prepared by literature methods.

Preparation of [Mo{η^2-(S,S)}(CO)$_2$(η^3-allyl)] (1)

Method 1. A solution of 5 mmol of [Mo(MeCN)$_2$(CO)$_2$(η^3-allyl)Br] in 20 ml of MeCN was added to 5 mmol of $Na^+Et_2NCS_2^- \cdot 3\ H_2O$ or $NH_4^+C_4H_8NCS_2^-$ (Merck chemical). An orange-yellow precipitate formed after 10 min. The solid was collected, washed with 5 ml of cold MeOH, and dried under vacuum to give **1** in 85–91% yield.

Method 2. A solution of 1 mmol of M″[Mo{η^2-(S,S)}(CO)$_4$] in 30 ml of MeCN was treated with excess allyl bromide approx 0.5 ml). The mixture was stirred for 10 min. and the solution was concentrated to 5 ml. The orange-yellow solid formed upon addition of 10 ml of deaerated water was collected, washed with 5 ml of cold MeOH and dried under vacuum to give **1** in 90–95% yield.

Method 3. A solution of 1 mmol of [Mo(η^2-H$_2$CPz$'_2$)(CO)$_2$(η^3-allyl)Br] dissolved in 40 ml of CH_2Cl_2 was added to 1 mmol of $Na^+Et_2NCS_2^- \cdot 3\ H_2O$ or $NH_4^+C_4H_8NCS_2^-$ in 5 ml of MeOH. The mixture was stirred for 10 min and 20 ml of MeOH was then added. The volume of the solution was reduced to 15 ml forming an orange-yellow solid. The solid was collected, washed with 5 ml of cold MeOH and dried under vacuum to give 80–87% yield of **1**.

[Mo(η^2-S$_2$CNEt$_2$)(CO)$_2$(η^3-allyl)] (**1a**): Anal. Found: C, 34.95; H, 4.54; N, 4.13. $C_{10}H_{15}MoNO_2S_2$ calc.: C, 35.19; H, 4.43; N, 4.10%. IR: ν(CO), 1952(s), 1922(s), 1860(s), 1838(s) in KBr; 1938(s), 1842(s) in MeCN, 1928(s), 1840(s) in CH_2Cl_2 and ν(CN), 1500(m) cm^{-1} in KBr. ^{1}H NMR (CD$_3$CN, 296 K, 300 MHz): δ 1.16 (t, $J = 7.1$, 6H, CH$_3$); 1.23 (d, $J = 9.6$, 2H, H_{anti}); 3.21 (d, $J = 6.3$, 2H, H_{syn}); 3.70 (q, $J = 7.1$, 4H, -CH$_2$-); 4.06 (m, 1H, H_{cent}) ppm. ^{13}C{^{1}H} NMR (CD$_3$CN, 296 K, 75.43 MHz): δ 12.27 (2C, CH$_3$); 45.25 (2C, -CH$_2$-); 55.68 (2C, end-carbon atoms of the allyl group); 74.00 (1C, central carbon atom of the allyl group); 206.33 (1C, Et$_2$NCS$_2$); 228.50 (2C, CO) ppm.

[Mo(η^2-S$_2$CNC$_4$H$_8$)(CO)$_2$(η^3-allyl)] (**1b**): Anal. Found: C, 35.21; H, 3.85; N, 4.40. $C_{10}H_{13}MoNO_2S_2$ calc.: C, 35.40; H, 3.86; N, 4.13%. IR: ν(CO), 1952(s), 1924(s), 1866(s), 1848(s) in KBr; 1938(s), 1842(s) in MeCN; 1932(s), 1842(s) in CH_2Cl_2 and ν(CN), 1506(m) cm^{-1} in KBr. ^{1}H NMR (dimethylsulfoxide-d_6, 296 K, 100 MHz): δ 1.18 (d, $J = 9.8$, 2H, H_{anti}); 1.92 (m, 4H, four protons of $C_4H_8NCS_2$); 3.14 (d, $J = 6.5$, 2H, H_{syn}); 3.54 (m, 4H, four protons of $C_4H_8NCS_2$); 3.93 (m, 1H, H_{cent}) ppm.

Preparation of [Mo{η^2-(S,S)}(CO)(η^3-allyl){η^2-(P,P)}]

Method 1. One millimole of **1** and 1 mmol of (P,P) were stirred in 30 ml of MeCN for 2 h. The solvent was then removed under vacuum. Recrystallization from CH_2Cl_2/MeOH gave the orange-red product in 90–93% yield.

Method 2. A solution of 1 mmol of [Mo{η^2-(P,P)(CO)$_2$(η^3-allyl)Br] dissolved in 20 ml of CH_2Cl_2 was added to 1 mmol of $Na^+Et_2NCS_2^- \cdot 3\ H_2O$ or $NH_4^+C_4H_8NCS_2^-$ in 5 ml of MeOH. The mixture was stirred for 10 min and the solvents were removed under vacuum. Recrystallization from CH_2Cl_2/MeOH gave the orange-red product in 80–85% yield.

[Mo{η^2-S_2CNEt_2)(CO)(η^3-allyl)(η^2-DPPM)] (**2a**): Anal. Found: C, 58.06; H, 5.20; N, 2.01. $C_{34}H_{37}MoP_2NOS_2$ calc.: C, 58.53; H, 5.35; N, 2.01%. IR: ν(CO), 1806(s) in KBr, 1810(s) in CH_2Cl_2 and ν(CN), 1488(m) cm^{-1} in KBr.

[Mo{η^2-S_2CNEt_2)(CO)(η^3-allyl)(η^2-DPPE)] (**2b**): Anal. Found: C, 59.25; H, 5.52; N, 2.01. $C_{35}H_{39}MoP_2NOS_2$ calc.: C, 59.06; H, 5.52; N, 1.97%. IR: ν(CO), 1792(s) in KBr, 1788(s) in CH_2Cl_2, 1790(s) in MeCN and ν(CN), 1482(m) cm^{-1} in KBr.

[Mo{η^2-$S_2CNC_4H_8$)(CO)(η^3-allyl)(η^2-DPPM)] (**2c**): Anal. Found: C, 58.49; H, 5.08; N, 2.04. $C_{34}H_{35}MoP_2NOS_2$ calc.: C, 58.70; H, 5.07; N, 2.04%. IR: ν(CO), 1782(s) in KBr, 1784(s) in CH_2Cl_2 and ν(CN), 1485(m) cm^{-1} in KBr.

[Mo{η^2-$S_2CNC_4H_8$)(CO)(η^3-allyl)(η^2-DPPE)] (**2d**): Anal. Found: C, 58.68; H, 5.12; N, 1.77. $C_{35}H_{37}MoP_2NOS_2$ calc.: C, 59.23; H, 5.25; N, 1.97%. IR: ν(CO), 1788(s) in KBr, 1790(s) in CH_2Cl_2 and ν(CN), 1480(m) cm^{-1} in KBr.

Preparation of [Mo(η^2-S_2CNEt_2)(CO)$_2$(η^3-allyl)(PY)]

A solution of **1a** (0.34 g, 1.0 mmol) in 20 ml of CH_2Cl_2 was added with 0.1 ml of PY (approx. 1.2 mmol). The solution was stirred for 5 min and the solvent and unreacted PY were removed under vacuum. The orange-red product was then recrystallized from CH_2Cl_2/MeOH to give 0.34 g (80% yield). This product was identified as [Mo(η^2-S_2CNEt_2)(CO)$_2$(η^3-allyl)(PY)] by comparing IR and ^{1}H NMR data with those reported previously [12a].

X-Ray diffraction study of [Mo(η^2-S_2CNEt_2)(CO)(η^3-allyl)(η^2-DPPM)] (2a)

The crystals of **2a** were grown from CH_2Cl_2/hexane at room temperature. General procedures and listings of programs were previously given [20h]. Absorption correction was performed on this structure using ψ scans. Related crystal data (Table 1), final coordinates of the non-hydrogen atoms (Table 2), and selected bond lengths and bond angles (Table 3) are reported. The anisotropic displacement coefficients of the atoms, the H-atom coordinates and structural factors are available from the authors.

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