Journal of Organometallic Chemistry 658 (2002) 191–197

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Synthesis, reactivity and structures of diethyldithiophosphate molybdenum complexes: crystal structures of [Mo{η^2-$S_2P(OEt_2)\}_2(PhC{\equiv}CPh)_2$] and [Mo($\eta^3$-$C_3H_5$){$\eta^1$-$S_2P(OEt_2)$}(Phen)$(CO)_2$]

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Received 2 May 2002; received in revised form 28 May 2002; accepted 11 June 2002

Abstract

Treatment of [Mo(CH_3CN)(η^3-C_3H_5)$(CO)_2$\{η^2-$S_2P(OEt_2)$\}] (**1**) with diphenylacetylene, PhC≡CPh, in refluxing dichloromethane produced the bis(diphenylacetylene) complex [Mo\{η^2-$S_2P(OEt_2)$\}$_2$(PhC≡CPh)$_2$] (**2**). No similar bisalkyne product was obtained in the reaction of complexes [Mo(η^3-C_3H_5)$(CO)_2$(η^2-LL)(X)] (LL, X = Et_2NCS_2; $C_4H_8NCS_2$; $C_5H_{10}NCS_2$; H_2BPz_2; $C_5H_7O_2$, CH_3CN (**3**)) and PhC≡CPh, respectively, even under extreme experimental conditions. Complex [Mo(η^3-C_3H_5)\{η^1-$S_2P(OEt_2)$\}(Phen)$(CO)_2$] (**4**) are accessible by the reactions of **1** and phenanthroline at room temperature. The single crystal structures of complexes **2** and **4** were determined by X-ray diffraction analyses. Crystal data for **2**: space group, $P\bar{1}$ with $a = 10.874(4)$, $b = 11.745(4)$, $c = 16.052(11)$ Å, $\alpha = 90.44(4)$, $\beta = 94.45(4)$, $\gamma = 108.90(3)°$, $V = 1932.6(16)$ Å^3, $Z = 2$. The structure was refined to $R = 0.029$ and $R_w = 0.032$. Crystal data for **4**: space group, $P\bar{1}$ with $a = 7.9518(16)$, $b = 10.104(2)$, $c = 16.107(3)$ Å, $\alpha = 83.91(2)$, $\beta = 81.63(2)$, $\gamma = 66.55(2)°$, $V = 1172.9(4)$ Å^3, $Z = 2$. The structure was refined to $R = 0.062$ and $R_w = 0.154$. The coordination geometry about the molybdenum in **2** may be considered to be octahedral, with four sulfur atoms of the diethyldithiophosphato ligands and the two *cis* and parallel diphenylacetylene ligands. In complex **4**, pseudo-octahedral surrounding of the metal ion is formed by the coordination of two carbonyl ligands, of a phenanthroline ligand lying in the square plane of the molybdenum atom, and of a symmetrical η^3-allyl group and a η^1-diethyldithiophosphato ligand lying *trans* to one another in apical positions above and below the plane. No intramolecular trigonal twist behavior was found in solution state from 183 to 298 K of **4**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: bis(diPhenylacetylene); Phenanthroline; diEthyldithiophosphato ligand; Molybdenum; X-ray structure determination

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1. Introduction

A variety of alkyne complexes of Mo(II) and W(II) containing bidentate anionic sulfur donor ligands such as Dithiocarbamate have been described [1]. We are interested in the bisalkyne complexes of Mo(II) such as [Mo(HC≡CH)$_2$(S_2CNEt_2)$_2$] [2] which was prepared by treating [Mo$(CO)_2$(S_2CNMe_2)$_2$] and excess alkyne in dichloromethane. Complexes [Mo(RC≡CR)$_2$($S_2CNC_4H_4$)$_2$] [3] form spontaneously at room temperature cleanly from either [Mo$(CO)_3$($S_2CNC_4H_4$)$_2$] or [Et_4N][Mo$(CO)_2$I($S_2CNC_4H_4$)$_2$] and excess alkyne. Furthermore, several mixed bisalkyne Mo complexes [4] have been prepared by the reaction of [Mo(S_2CNMe_2)$_2$(CO)(RC≡CR)] and RC≡CR (R = Et, Ph, H). Till now, no bisalkyne complex of Mo(II) containing diethyldithiophosphate, $(EtO)_2PS_2^-$, ligand has been described.

As an extension of our recent work on the preparation of molybdenum complexes containing diethyldithiophosphate, $(EtO)_2PS_2^-$, ligand [5], we report in this paper the synthesis and structure of bis(diphenylacetylene) complex of molybdenum with $(EtO)_2PS_2^-$ ligand.

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PII: S0022-328X(02)01654-6

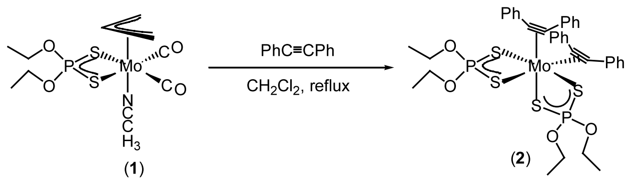
2. Result and discussion

2.1. Synthesis of bis(diphenylacetylene)bis(diethyldithiophosphate) complex [Mo{η^2-$S_2P(OEt_2)$}$_2$(PhC≡CPh)$_2$] (2)

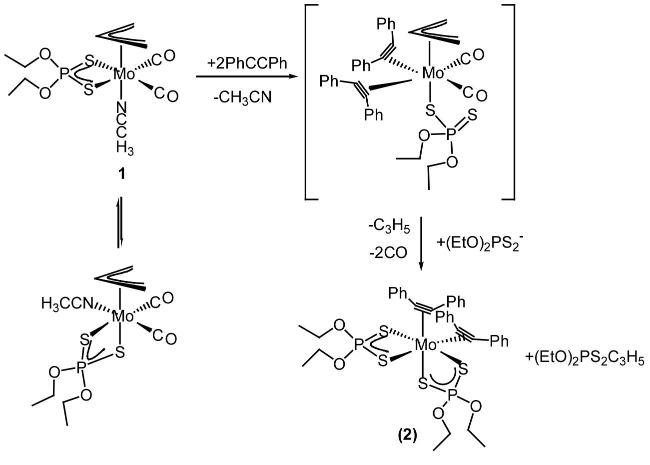
In our previous reports, we described the intramolecular trigonal twist behavior, free rotational energy calculation and crystal structure of the allyl diethyldithiophosphate complex [Mo(CH_3CN)(η^3-C_3H_5)(CO)$_2${η^2-$S_2P(OEt_2)$}] (**1**) [5a]. We have also recently reported the reaction of **1** and diphos forming endo and exo stereoisomers [5b]. To explore the reactivity of **1**, that was used to react with alkyne to form bisalkyne complex. Thus, treatment of complex **1** with diphenylacetylene in refluxing dichloromethane produces the two carbonyl, acetonitrile and allyl-displaced product [Mo{η^2-$S_2P(OEt_2)$}$_2$(PhC≡CPh)$_2$] (**2**) in 22% yield (see Scheme 1). The air-stable orange compound **2** is soluble in acetonitrile and slightly soluble in dichloromethane and diethyl ether, and insoluble in *n*-hexane. The analytical data of **2** are in agreement with the formulation. FAB mass spectrum of **2** shows a base peak with typical Mo isotope distribution corresponding to the [M^+] molecular mass. The IR spectrum of **2** shows two weak alkyne bands at 1588 and 1565 cm^{-1}, which as expected, is at considerably lower wavenumber compared with uncoordinated diphenylacetylene. The $^{13}C\{^1H\}$-NMR of **2** shows the expected features in accordance with the structure illustrated. Alkyne contact-carbon resonances were observed at δ 182.2 and 188.6. According to Templeton and Ward's [6] correlation, these values suggest that the alkynes are donating an average of three electrons each to the molybdenum. This allows the complex to conform to the effective atomic number rule.

In order to investigative the possible reactive mechanism, the ^1H- and $^{31}P\{^1H\}$-NMR tube experiments were carried out. During the detective period, the $^{31}P\{^1H\}$-NMR spectrum showed five resonances at δ 136.5, 109.1, 100.9, 97.9 and 94.2 ppm. The lowest downfield resonance is the free diethyldithiophosphato ligand. Another two resonances δ 100.9 and 97.9 are the starting compound **1** and the bisalkyne product **2**, respectively. The resonance δ 109.1 is the same as that was found in the complex [Mo(η^3-C_3H_5){η^1-$S_2P(OEt_2)$}(Phen)(CO)$_2$] (**4**) (describe below) in which the diethyldithiophosphato ligand coordinates to molybdenum through one sulfur atom. By comparison with the ^1H- and $^{31}P\{^1H\}$-NMR spectra, the highest up-field $^{31}P\{^1H\}$-NMR resonance δ 94.2 and the ^1H-NMR resonances δ 1.34 (t, 7.1 Hz, CH_3), 3.47, 3.48 (dd, 6.0, 8.9 Hz, SCH_2), 4.11, 4.18 (m, OCH_2), 5.11, 5.25 (dd, 10.0, 16.0 Hz, $=CH_2$) and 5.84 (m, $=CH$) with 6:1:1:2:2:1:1:1 ratio is consistent with organic compound $(EtO)_2P(S)S(C_3H_5)$ that can be produced by the reaction of $(EtO)_2P(S)SNH_4$ and BrC_3H_5. From the spectra of above-mentioned, we proposed a possible mechanism as shown in Scheme 2. Formation of the bisalkyne product **2** is believed to proceed CH_3CN substitution and a bond-rupture [7c] of Mo–S bond by two alkynes to form the η^1-diethyldithiophosphate intermediate, followed by the recoordination of the η^1 and free diethyldithiophosphato ligand with releasing of two carbonyl and allyl groups to give complex **2**. Indeed, the yield of **2** can be improved to 43% by the reaction of **1**, diphenylacetylene and diethyldithiophosphato ligand in a ratio of 1:2:1.

Interestingly, treatment of the analogous species [Mo(η^3-C_3H_5)(CO)$_2$(η^2-LL)(X)] (LL, X = Et_2NCS_2; $C_4H_8NCS_2$; $C_5H_{10}NCS_2$ [8a]; H_2BPz_2 [8b]; $C_5H_7O_2$, CH_3CN (**3**)) with PhC≡CPh, respectively, produced no bisalkyne complexes under extreme experimental conditions. The π-accepter ability of these anionic bidentate ligands is in this order: dithiocarbamato > dithiophosphato > dialkyldipyrazolylborato > β-diketonato. Only dithiophosphate derivative underwent the formation of the bisalkyne product may be due to the difficulty of the bond-rupture of the dithiocarbamato ligand from η^2 to η^1 coordination and weak recoordinative ability of the dialkyldipyrazolylborato and β-diketonato ligands from η^1 to η^2 coordination in competition of acetylene or carbon monoxide. Clearly, the preparation of the bisalkyne complexes using bisdithiocarbamate complexes [2–4] as starting material and in the reactions of [Mo(η^3-C_3H_5)(CO)$_2$(η^2-LL)(X)] (LL, X = H_2BPz_2; $C_5H_7O_2$, CH_3CN (**3**)) and dppm in



Scheme 1.



Scheme 2.

refluxing acetonitrile, respectively, no stereoisomers [5b] could be detected; instead, a bisdiphos complex [$Mo(CO)_2(\eta^2$-dppm$)_2$] [9] was isolated.

2.2. X-ray structure determination of [$Mo\{\eta^2$-$S_2P(OEt_2)\}_2(PhC{\equiv}CPh)_2$] (**2**)

Single crystals of complex **2** suitable for X-ray crystallography were grown from 20/1 diethyl ether–CH_3CN; its crystal data are listed in Table 1. The atomic coordinates of non-hydrogenic atoms and important bond parameters are displayed in Tables 2 and 3, respectively. Fig. 1 is an ORTEP drawing of **2** in which all hydrogen atoms are omitted. The molybdenum atom can be considered to have a six-coordinate octahedral environment being bonded to the sulfur atoms [Mo–S 2.556(2), 2.676(2), 2.551(1), 2.667(2) Å] of the two diethyldithiophosphato ligands, two diphenylacetylene ligands [Mo–C 2.063(4), 2.069(4), 2.062(3), 2.063(3) Å]. The molybdenum to alkyne contact-carbon bond lengths is in the range [1] for three-electron donor alkynes. The bend-back angles β [7a] are not equivalent [C(13)–C(9)–C(10) 37.7(4), C(19)–C(10)–C(9) 39.8(4), C(25)–C(11)–C(12) 39.9(4), C(31)–C(12)–C(11) 38.9(4)°].

Table 1
Crystal data and collection parameters for **2** and **4**

	2	**4**
Formula	$C_{36}H_{40}O_4P_2S_4Mo$	$C_{21}H_{23}N_2O_4PS_2Mo$
Formula weight	822.83	558.44
Crystal system	Triclinic	Triclinic
Crystal size (mm)	0.40 × 0.40 × 0.35	0.30 × 0.20 × 0.20
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.874(4)	7.9518(16)
b (Å)	11.745(4)	10.104(2)
c (Å)	16.052(11)	16.107(3)
α (°)	90.44(4)	83.91(2)
β (°)	94.45(4)	81.63(2)
γ (°)	108.90(3)	66.55(2)
V (Å^3)	1932.6(16)	1172.9(4)
Z	2	2
F(000)	846	568
Calculated density (g cm^{-3})	1.414	1.581
μ (Mo–K_α) (mm^{-1})	0.6549	0.835
2θ Range	18.70–24.06	
h, k, l	−11 to 11, 0 to 12, −17 to 17	−7 to 8, 0 to 10, −16 to 17
Reflections collected	5043	3069
Number of parameters	425	281
R [a]	0.029	0.062
R_w [b]	0.032	0.154
Transmission (min, max)	0.766, 0.821	0.8731, 0.7334
Number of atoms	87	54
Quality-of-fit [c]	1.61	1.042
Δ(D-map) max, min (e Å^{-3})	−0.22, 0.34	−0.691, 1.110

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

[c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{\text{reflections}} - N_{\text{parameters}})]^{1/2}$.

Table 2
Atomic parameters x, y, z and B_{eq} for important atoms of **2** [a]

Atom	x	y	z	B_{eq}
Mo	0.38803(3)	0.22041(3)	0.237024(20)	2.656(13)
S(1)	0.18020(9)	0.18158(8)	0.31214(6)	3.62(5)
S(2)	0.27424(9)	−0.01860(9)	0.22286(7)	3.86(5)
S(3)	0.58850(9)	0.16073(9)	0.21315(6)	3.50(5)
S(4)	0.46998(10)	0.18635(7)	0.38870(6)	3.89(5)
P(1)	0.12364(9)	0.01399(9)	0.26814(7)	3.52(5)
P(2)	0.62502(9)	0.16115(9)	0.33692(6)	3.45(5)
C(9)	0.2723(3)	0.2382(3)	0.13319(22)	3.10(18)
C(10)	0.3763(3)	0.2271(3)	0.10800(21)	2.89(17)
C(11)	0.5190(3)	0.3930(3)	0.24753(22)	3.12(17)
C(12)	0.4189(3)	0.3910(3)	0.28655(22)	3.20(17)

[a] Estimated S.D. values are in parentheses.

The average acetylene C–C bond length increased to 1.282(5) Å relative to the value of 1.21 Å for that in diphenylacetylene itself [7b] and the bond angles at the acetylene carbon atoms are decreased to 141.2(3) so that the diphenylacetylene molecules acquire a *cis* configuration. The average C_{ph}–C_{ph} distance in the phenyl rings is 1.374(6) Å with an average C_{ph}–C_{ph}–C_{ph} angle of 120.0(4)°. The molecular structure of the closely related complex [$Mo(S_2CNC_4H_4)_2(MeC{\equiv}CMe)_2$] has been previously described [3], and has the same basic arrangement of ligands around the molybdenum center.

2.3. Synthesis and X-ray structure determination of (η^3-allyl)(dicarbonyl) (η^1-diethyldithiophosphato)-(phenanthroline) molybdenum(II) (**4**)

Treatment of **1** with phenanthroline resulted in complex [$Mo(\eta^3$-$C_3H_5)\{\eta^1$-$S_2P(OEt_2)\}$(Phen)$(CO)_2$] (**4**) in 82% isolate yield. The solution IR spectra show the two carbonyls in equal intensity; this observation indicates that the two carbonyls are mutually *cis*. The $^{31}P\{^1H\}$ spectrum of **4** shows resonance at δ 109.1. From an AM_2X_2 pattern of the allyl group in the ^1H-NMR spectra and one equivalent resonance of the terminal carbon of the allyl group and one resonance of carbonyl group in the $^{13}C\{^1H\}$-NMR spectra, it looks as if the geometry of **4** with a mirror plane through the center carbon of allyl group, Mo, and coordinative S atom of the diethyldithiophosphato ligand; i.e. the phenanthroline ligand and the two carbonyls lie in a horizontal plane, whereas the allyl group and the diethyldithiophosphato ligand lie in *trans* positions above and below the plane, respectively (Scheme 3). Variable temperature (183–298 K) ^1H- and $^{13}P\{^1H\}$-NMR experiments were used to confirm no intramolecular trigonal twist behavior in complex **4** due to the steric hindrance of phenanthroline and diethyldithiophosphato ligands. Because the mentioned structure is

Table 3
Selected interatomic distances (Å) and angles (°) for **2**

Bond lengths			
Mo–S(1)	2.556(2)	Mo–C(10)	2.069(4)
Mo–S(2)	2.676(2)	Mo–C(11)	2.062(3)
Mo–S(3)	2.551(1)	Mo–C(12)	2.063(3)
Mo–S(4)	2.667(2)	C(9)–C(10)	1.275(5)
Mo–C(9)	2.063(4)	C(11)–C(12)	1.290(5)
Bond angles			
S(1)–Mo–S(2)	75.91(5)	Mo–C(9)–C(10)	72.26(22)
S(3)–Mo–S(4)	75.70(5)	Mo–C(11)–C(12)	71.81(21)
C(9)–Mo–C(10)	35.95(13)	Mo–C(12)–C(11)	71.74(21)
C(11)–Mo–C(12)	36.45(14)	C(13)–C(9)–C(10)	141.8(3)
C(9)–Mo–C(12)	95.22(14)	C(19)–C(10)–C(9)	141.1(3)
C(10)–Mo–C(11)	90.83(14)	C(25)–C(11)–C(12)	140.1(3)
Mo–C(10)–C(9)	71.79(22)	C(31)–C(12)–C(11)	141.7(3)

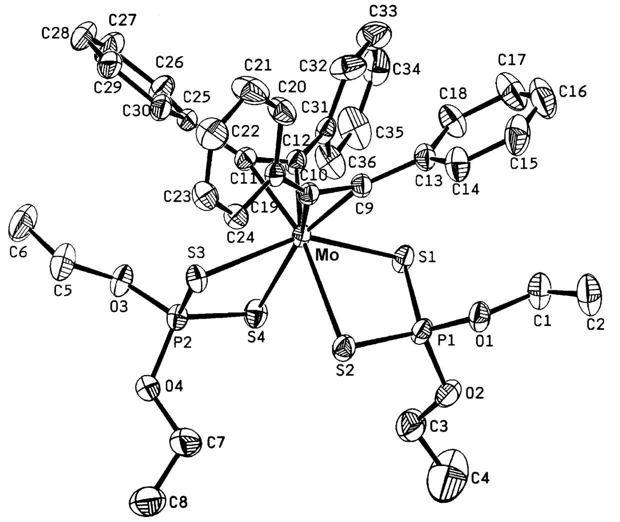
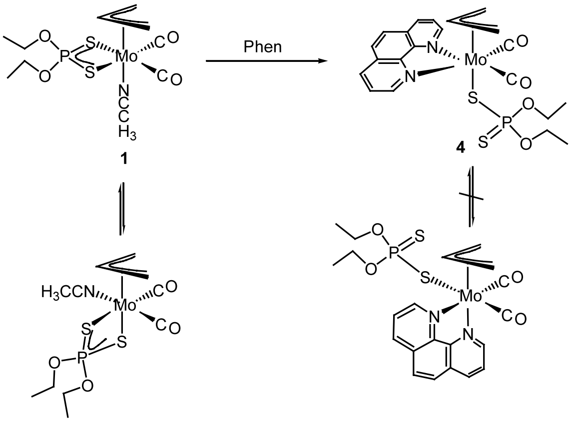


Fig. 1. ORTEP diagram of complex $[Mo\{\eta^2\text{-}S_2P(OEt_2)\}_2(PhC{\equiv}CPh)_2]$ (**2**).



Scheme 3.

incompatible with the complex $[Mo(\eta^3\text{-}C_3H_5)(\eta^1\text{-}O_2CCF_3)(Phen)(CO)_2]$ [10b] and $[Mo(CH_3CN)(\eta^3\text{-}C_5H_7)(Phen)(CO)_2][BF_4]$ [10a] and the structure still retain unknown, we have performed an X-ray diffraction study of **4** to elucidate the solid-state structure. An ORTEP plot of **4** is shown in Fig. 2. Table 5 shows the selected bond distances and bond angles of **4**. The coordination geometry around the molybdenum atom is a pseudo-octahedron with one dithiophosphato sulfur atom, phenanthroline, two carbonyls and the allyl group occupying the six coordination sites. The structure confirms an equivalent allyl group. The sulfur atom of dithiophosphato is *trans* to the allyl: S(1)–Mo–C(4), 159.3(3)°. The two carbonyl groups are *trans* to the two nitrogen atoms of the phenanthroline: C(1)–Mo–N(2), 172.4(4)° and C(2)–Mo–N(1), 168.5(4)°. The C(1)–Mo–C(2) angle of 80.3(5)° in **4** is similar to 82.0(3)° in **1** within the experimental errors. The Mo–C(3), C(4) and C(5) bond distances are 2.320(11), 2.424(10) and 2.326(10) Å, respectively. The bond distances and intercarbon angle of allyl group in **4** (1.384(15), 1.395(15) Å and 116.3(11)°) are insignificantly different in the region of related Mo(II)-allylic compounds (1.31–1.42 Å, 115–125°). Interestingly, the geometry of the complex $[Mo(\eta^3\text{-}C_3H_5)(\eta^1\text{-}O_2CCF_3)(1,2\text{-dimethoxyethane})(CO)_2]$ [12] is similar to **4** but different in the orientations of the η^1-anionic bidentate ligand. The η^1-anionic bidentate ligand approaches the neutral biden-

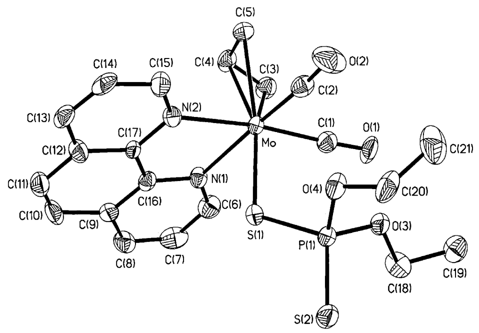


Fig. 2. ORTEP diagram of complex $[Mo(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}S_2P(OEt_2)\}(Phen)(CO)_2]$ (**4**).

tate ligand in former and opposite directions in latter that may be due to the more steric hindrance of diethyldithiophosphato ligand than trifluoroacetato ligand.

2.4. Conclusion

In various anionic bidentate ligands only diethyldithiophosphate allyl molybdenum(II) complex with alkyne produce the bisalkyne bisdiethyldithiophosphate molybdenum(II) complex. The formation of $[\mathrm{Mo}\{\eta^2\text{-}\mathrm{S_2P(OEt_2)}\}_2(\mathrm{PhC{\equiv}CPh})_2]$ (**2**) involves a dissociation and interconversion of the $\eta^1 \leftrightarrow \eta^2$ diethyldithiophosphato ligand. The geometry of $[\mathrm{Mo}(\eta^3\text{-}\mathrm{C_3H_5})\{\eta^1\text{-}\mathrm{S_2P(OEt_2)}\}(\mathrm{Phen})(\mathrm{CO})_2]$ (**4**) is a pseudo-octahedron that the phenanthroline ligand and the two carbonyls lie in a horizontal plane, whereas the allyl group and the diethyldithiophosphato ligand lie in *trans* positions above and below the plane.

3. Experimental

3.1. Materials

All manipulations were performed under nitrogen using vacuum-line and standard Schlenk techniques. NMR spectra were recorded on a Bruker AC-200 or a Bruker AM-300 WB FT-NMR spectrometer and are reported in units of δ (ppm) with residual protons in the solvent as an internal standard ($\mathrm{CDCl_3}$, δ 7.24; $\mathrm{CD_3CN}$, δ 1.93; $\mathrm{C_6D_6}$, δ 7.15; $\mathrm{C_2D_6CO}$, δ 2.04). IR spectra were measured on a Nicolet Avator-320 instrument and referenced to polystyrene standard, using cells equipped with calcium fluoride windows. Mass spectra were recorded on a JEOL SX-102A spectrometer. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. *n*-Hexane, diethyl ether, THF and benzene were distilled from sodium–benzophenone. Acetonitrile and dichloromethane were distilled from calcium hydride, and methanol from magnesium. All other solvents and reagents were of reagent grade and were used as received. $\mathrm{Et_2NCS_2Na}$, $\mathrm{C_4H_8NCS_2NH_4}$, $\mathrm{C_5H_7O_2Li}$, $\mathrm{PhC{\equiv}CPh}$, Phen, and dppm were purchased from Janssen. The compound $[\mathrm{Mo(CH_3CN)}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{CO})_2\{\eta^2\text{-}\mathrm{S_2P(OEt_2)}\}]$ (**1**) was prepared according to the literature method [5a,11]. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrumentation located at the National Taiwan University.

3.2. bis(η^2-diEthyldithiophosphato)bis(η^2-diphenylacetylene) molybdenum(II) (2)

$\mathrm{CH_2Cl_2}$ (20 ml) was added to a flask (100 ml) containing $[\mathrm{Mo(CH_3CN)}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{CO})_2\{\eta^2\text{-}\mathrm{S_2P(OEt_2)}\}]$ (**1**) (0.42 g, 1.0 mmol) and diphenylacetylene (0.178 g, 1.0 mmol). The solution was refluxed for 10 min, and an orange precipitate was formed. The precipitate was collected by filtration (G4) washed with *n*-hexane (2×10 ml) and then dried in vacuo yielding 0.40 g (22%) of $[\mathrm{Mo}\{\eta^2\text{-}\mathrm{S_2P(OEt_2)}\}_2(\mathrm{PhC{\equiv}CPh})_2]$ (**2**). Further purification was accomplished by recrystallization from 1/10 $\mathrm{CH_3CN}$–diethyl ether. Spectroscopic data for **2**: IR (KBr): υ(C≡C) 1588(m), 1565(m) $\mathrm{cm^{-1}}$; $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR (121 MHz, $\mathrm{CDCl_3}$, 298 K): δ 97.9; ^{1}H-NMR (200 MHz, $\mathrm{CDCl_3}$, 298 K): δ 0.72, 1.28 (t, *J*(HH) 7.0 Hz, 12H, C*H*$_3$), 3.25, 4.14 (m, 8H, OC*H*$_2$), 7.17–7.49 (m, 20H, Ph); $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR (50 MHz, $\mathrm{CDCl_3}$, 298 K): δ 15.3, 15.9 (d, ^3J(PC) 9.2 Hz, *C*H$_3$,), 62.5, 63.4 (d, ^2J(PC) 6.5 Hz, *C*H$_2$), 127.1–140.2 (m, C of Ph), 182.2, 188.6 (s, *C≡C*); MS (FAB, NBA) *m/z* 824 [$\mathrm{M^+}$], 646 [$\mathrm{M^+ - PhC_2Ph}$]. Anal. Calc. for $\mathrm{C_{36}H_{40}O_4P_2S_4Mo}$ (822.83): C, 52.54; H, 4.90. Found: C, 52.70; H, 5.12%.

3.3. Acetonitrile(η^3-allyl)(dicarbonyl)(η^2-acetylacetonato) molybdenum(II) (3)

$\mathrm{CH_3COCH_3}$ (30 ml) was added to a flask (100 ml) containing $[\mathrm{Mo(CH_3CN)_2}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{CO})_2\mathrm{Br}]$ (0.356 g, 1.0 mmol) and $\mathrm{C_5H_7O_2Li}$ (0.11 g, 1.0 mmol). The solution was stirred for 1 h, and a white precipitate was formed. The solution was filtered to remove the LiBr. Removal of the solvent in vacuo afforded a yellow solid **3** (0.32 g, 96%). Further purification was accomplished by recrystallization from 1/10 $\mathrm{CH_2Cl_2}$–*n*-hexane. Spectroscopic data for **3**: IR (KBr): υ(CN) 2310(m), 2281(m); υ(CO) 1932(vs), 1847(vs) $\mathrm{cm^{-1}}$; ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$, 298 K): δ 1.28 (br, 2H, H*anti* of allyl), 1.93 (s, 6H, C*H*$_3$), 2.04 (s, 3H, C*H*$_3$CN), 3.31 (br, 2H, H*syn* of allyl), 3.62 (s, 1H, C*H* of allyl), 5.24 (s, 1H, C*H*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR (75MHz, $\mathrm{CD_3COCD_3}$, 298 K): δ 1.1 (s, *C*H$_3$CN), 24.6, 27.6 (s, *C*H$_3$), 49.1, 53.4 (s, CH=*C*H$_2$), 75.3 (s, *C*H=CH$_2$), 100.9 (s, *C*HCCH$_3$), 117.1 (s, CH$_3$*C*N), 136.1, 136.4 (s, CH$_3$*C*CO), 204.1 (s, *C*O); MS (FAB, NBA) *m/z* 335 [$\mathrm{M^+}$], 294 [$\mathrm{M^+ - C_3H_5}$], 266 [$\mathrm{M^+ - C_3H_5 - CO}$], 238 [$\mathrm{M^+ - C_3H_5 - 2CO}$]. Anal. Calc. for $\mathrm{C_{12}H_{15}NO_4Mo}$ (333.14): C, 43.25; H, 4.54; N, 4.20. Found: C, 43.08; H, 4.65; N, 4.02%.

3.4. (η^3-Allyl)(dicarbonyl)(η^1-diethyldithiophosphato)-(η^2-phenanthroline) molybdenum(II) (4)

A solution of $\mathrm{C_{12}H_8N_2}$ (phenanthroline) (0.180 g, 1.0 mmol) in MeOH (20 ml) was added to a flask containing **1** (0.42 g, 1.0 mmol) in $\mathrm{CH_2Cl_2}$ (5 ml) in 2 min. A color change from yellow to red occurred immediately and a red precipitate formed. The precipitate was collected by filtration (G4), washed with *n*-hexane (2 × 10 ml) and then dried in vacuo to yield 0.46 g (82%) of **4**. IR (KBr) υ(CO) 1944(vs), 1870(vs) cm^{-1}; ^{31}P{^{1}H}-NMR (121 MHz, CDCl$_3$, 298 K): δ 109.1; ^{1}H-NMR (200 MHz, CD$_3$COCD$_3$, 298 K): δ 1.28 (t, *J*(HH) 7.0 Hz, 6H, OCH$_2$C*H*$_3$), 1.42 (d, *J*(HH) 8.4 Hz, 2H, H*anti* of allyl), 2.88 (m, 1H, C*H* of allyl), 3.30 (d, *J*(HH) 6.3 Hz, 2H, H*syn* of allyl), 3.94 (m, 4H, OC*H*$_2$), 7.99, 8.03 (dd, *J*(HH) 8.2 Hz, 2H, 3, 8H of Phen), 8.17 (s, 2H, 5, 6H of Phen), 8.75 (d, *J*(HH) 8.8 Hz, 2H, 4, 7H of Phen), 9.19 (d, *J*(HH) 4.3 Hz, 2H, 2, 9H of Phen); ^{13}C{^{1}H}-NMR (50 MHz, CD$_3$COCD$_3$, 298 K): δ 15.3 (s, OCH$_2$*C*H$_3$), 55.6 (s, =*C*H$_2$), 61.3 (s, O*C*H$_2$), 68.3 (s, =*C*H), 125.2 (s, 5, 6C of Phen), 127.3 (s, 3, 8C of Phen), 138.2 (s, 4, 7C of Phen), 152.7 (s, 2, 9C of Phen), 209.1 (s, *C*O); MS (FAB, NBA) *m/z* 560 [M^{+}], 519 [M$^{+}-$C$_3$H$_5$]. Anal. Calc. for $C_{21}H_{23}N_2O_4PS_2Mo$ (558.44): C, 45.16; H, 4.15; N, 5.02. Found: C, 45.30; H, 4.48; N, 5.47%.

3.5. *X-ray crystallography*

Single crystal of **2** suitable for X-ray diffraction analysis was grown by recrystallization from 20/1 diethyl ether–CH$_3$CN. The diffraction data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer equipped with graphite-monochromated Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) radiation. The raw intensity data were converted to structure factor amplitudes and their Estimated S.D.'s after corrections for scan speed, background, Lorentz, and polarization effects. An empirical absorption correction, based on the azimuthal scan data, was applied to the data. Crystallographic computations were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package [13].

Table 4
Atomic parameters *x*, *y*, *z* and B_{eq} for important atoms of **4** [a]

Atom	*x*	*y*	*z*	B_{eq}
Mo	1533(1)	14208(1)	2961(1)	36(1)
S(l)	1779(4)	16209(3)	1927(2)	42(1)
S(2)	1878(5)	19475(3)	1599(2)	58(1)
P(l)	2069(4)	17864(3)	2402(2)	38(1)
N(l)	−160(12)	14161(9)	1957(5)	39(2)
N(2)	3523(12)	12874(9)	1927(5)	37(2)
C(l)	−200(17)	15592(12)	3761(7)	50(3)
C(2)	3270(17)	14383(12)	3639(8)	48(3)
C(3)	−386(17)	13223(12)	3774(7)	51(3)
C(4)	1238(17)	12139(11)	3446(7)	48(3)
C(5)	2851(17)	12037(11)	3728(7)	50(3)
O(1)	−1156(12)	16391(9)	4255(5)	66(3)
O(2)	4320(16)	14402(12)	4041(7)	95(4)

[a] Estimated S.D. values are in parentheses.

A suitable single crystal of **2** was mounted on the top of a glass fiber with glue. Initial lattice parameters were determined from 24 accurately centered reflections with 2θ values in the range from 18.74 to 24.06°. Cell constants and other pertinent data were collected and are recorded in Table 1. Reflection data were collected using the $\theta-2\theta$ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2.06 to 8.24° min^{-1}. The θ scan angle was determined for each reflection according to the equation $0.70 \pm 0.35 \tan \theta$. Three check reflections were measure every 30 min throughout the data collection and showed no apparent decay. The merging of equivalent and duplicate reflections gave a total of 5059 unique measured data, of which 4092 reflections with $I > 2\sigma(I)$ were considered observed. The first step of the structure solution used the heavy-atom method (Patterson synthesis), which revealed the positions of metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The quantity minimized by the least-squares program was $w(|F_o|-|F_c|)^2$, where w is the weight of a given operation. The analytical forms of the scattering factor tables for the neutral atoms were used [14]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least-squares. The final residuals of this refinement were $R = 0.032$ and $R_w = 0.026$. Final values of all refined atomic positional parameters and selected bond distances and angles are listed in Tables 2 and 3, respectively.

Table 5
Selected interatomic distances (Å) and angles (°) for **4**

Bond lengths			
Mo–C(1)	1.961(12)	C(1)–O(1)	1.155(13)
Mo–C(2)	1.951(13)	C(2)–O(2)	1.135(13)
Mo–C(3)	2.320(11)	S(1)–P(1)	2.016(4)
Mo–C(4)	2.242(10)	S(2)–P(1)	1.939(4)
Mo–C(5)	2.326(10)	C(3)–C(4)	1.395(15)
Mo–S(1)	2.531(3)	C(4)–C(5)	1.384(15)
Mo–N(1)	2.265(8)	Mo–N(2)	2.261(8)
Bond angles			
C(1)–Mo–C(3)	69.3(4)	C(2)–Mo–S(1)	92.0(3)
C(1)–Mo–C(4)	102.5(4)	C(3)–Mo–C(5)	61.1(4)
C(1)–Mo–C(5)	106.6(4)	C(3)–Mo–S(1)	147.2(3)
C(1)–Mo–N(1)	105.6(4)	C(4)–Mo–C(3)	35.6(4)
C(1)–Mo–N(2)	172.4(4)	C(4)–Mo–C(5)	35.2(4)
C(1)–Mo–S(1)	92.2(3)	C(4)–Mo–S(1)	159.3(3)
C(2)–Mo–C(1)	80.3(5)	C(5)–Mo–S(1)	151.7(3)
C(2)–Mo–C(3)	110.4(5)	N(1)–Mo–S(1)	78.0(2)
C(2)–Mo–C(4)	104.7(5)	N(2)–Mo–N(1)	72.8(3)
C(2)–Mo–C(5)	71.2(4)	N(2)–Mo–S(1)	80.2(2)
C(2)–Mo–N(1)	168.5(4)	S(2)–P(1)–S(1)	113.95(18)
C(2)–Mo–N(2)	100.1(4)	O(3)–P(1)–O(4)	99.6(4)
P(1)–S(1)–Mo	116.81(14)	C(5)–C(4)–C(3)	116.3(11)

The procedures for **4** were similar to those for **2**. The unit cell constants were also determined from 24 accurately centered reflections. Cell constants and other pertinent data were collected in Table 1. The final residuals of this refinement were $R = 0.062$ and $R_w = 0.154$ for **4**. Final values of all refined atomic positional parameters and selected bond distances and angles are listed in Tables 4 and 5, respectively. Tables of thermal parameters are given in the supplementary material.

4. Supplementary material

Tables of complete atomic coordinates, bond lengths and angles, thermal parameters and listing of structure factors are available from the authors.

Acknowledgements

We thank the Hung Kuang Institute of Technology and National Science Council of the Republic of China for support.

References

[1] J.L. Templeton, Adv. Organomet. Chem. 29 (1989) 1 (and references therein).

[2] J.W. McDonald, W.E. Newton, C.T.C. Creedy, J.L. Corbin, J. Organomet. Chem. 92 (1975) C25.

[3] R.S. Herrick, S.J. Burgmayer, J.L. Templeton, Inorg. Chem. 22 (1983) 3275.

[4] R.S. Herrick, J.L. Templeton, Organometallics 1 (1982) 842.

[5] (a) K.H. Yih, G.H. Lee, Y. Wang, J. Organomet. Chem. 588 (1999) 125;
(b) K.H. Yih, G.H. Lee, Y. Wang, Inorg. Chem. Commun. 3 (2000) 458.

[6] J.L. Templeton, B.C. Ward, J. Am. Chem. Soc. 102 (1980) 3288.

[7] (a) B.W. Davies, N.C. Payne, Inorg. Chem. 13 (1974) 1848;
(b) L. Pauling, The Nature of the Chemical Bond, third ed., Cornell University Press, 1960, p. 230;
(c) H.M. Gau, R.C. Fay, Inorg. Chem. 29 (1990) 4974.

[8] (a) K.H. Yih, S.C. Chen, Y.C. Lin, M.C. Cheng, Y. Wang, J. Organomet. Chem. 494 (1995) 149;
(b) F.A. Cotton, A.G. Stanislowski, Inorg. Chem. 16 (1974) 5074.

[9] A.M. Bond, R. Colton, J.J. Jackowski, Inorg. Chem. 14 (1975) 274.

[10] (a) S.F. Lush, S.H. Wang, G.H. Lee, S.M. Peng, S.L. Wang, R.S. Liu, Organometallics 9 (1990) 1862;
(b) M.P.T. Sjogren, H. Frisell, B. Akermark, P.O. Norrby, L. Eriksson, A. Vitagliano, Organometallics 16 (1997) 942.

[11] G. Barrado, D. Miguel, V. Riera, S. Garcia-Granda, J. Organomet. Chem. 489 (1995) 129.

[12] F. Dawans, J. Dewailly, J. Menuier-piret, P. Piret, J. Organomet. Chem. 76 (1974) 53.

[13] E.J. Gabe, F.L. Lee, Y. Lepage, in: G.M. Shhelldrick, C. Kruger, R. Goddard (Eds.), Crystallographic Computing, vol. 3, Clarendon Press, Oxford, 1985, p. 167.

[14] (a) International Tables for X-ray Crystallography vol. IV, Reidel, Dordrecht, 1974.;
(b) Y. LePage, E. Gabe, J. Appl. Crystallogr. 23 (1990) 406.