Journal of Organometallic Chemistry, 215 (1981) 201—213
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

MOLYBDENUM AND TUNGSTEN COMPLEXES WITH THE HETEROALLYL-LIKE $Ph_2P(O)C(S)NR^-$ (R = Me, Ph) AS LIGAND. X-RAY STRUCTURAL ANALYSIS OF $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2 \cdot CH_2Cl_2$; A 4 : 3 PIANO-STOOL CONFIGURATION

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(Received January 8th, 1981)

Summary

$Ph_2P(O)C(S)N(H)R$ (R = Me, Ph) reacts with $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W) in the presence of Et_3N to give $M(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(O)C(S)NR)$. The deprotonated ligand coordinates in a bidentate manner through N and S to give a four-membered ring system. $M(CO)_3(PPh_3)_2Cl_2$ (M = Mo, W) reacts with $Ph_2P(O)C(S)N(H)R$ (R = Me, Ph) in the presence of Et_3N to give complexes in which the central metal atoms are seven coordinate through two ligands bonded via O and S to form five-membered ring systems, one PPh_3, and two CO groups. The complexes were characterised by elemental analyses, IR, ^1H NMR, and ^{31}P NMR spectroscopy, and an X-ray structural analysis of $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2 \cdot CH_2Cl_2$.

Introduction

Ph_2PH or $Ph_2P(Q)H$ (Q = S, O) can add to heteroallene molecules RN=C=X (X = S, O, NR) by nucleophilic attack at the central carbon atom to give $Ph_2PC(X)N(H)R$ and $Ph_2P(Q)C(X)N(H)R$, respectively [1]. These after deprotonation can act as heteroallyl-type ligands (Fig. 1) like xanthate, thioxan-

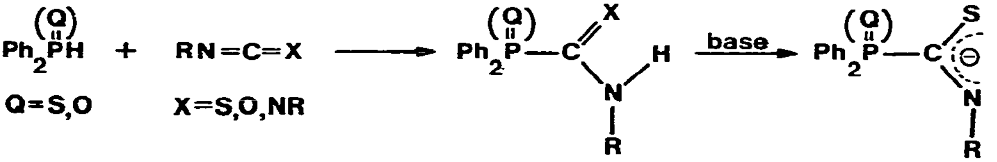

Fig. 1. Reactions of heteroallene molecules with $Ph_2P(Q)H$ (Q = O, S) or Ph_2PH.

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thate, and dithiocarbamate. A number of Mo and W complexes, in various coordination modes, of these ligands have been reported [2—4].

As a part of a study of the coordination properties of such ligands we describe here the reactions of $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W) and $M(CO)_3(PPh_3)_2Cl_2$ (M = Mo, W) with $Ph_2P(O)C(S)N(H)R$ (R = Me, Ph). Coordination via O and S in the deprotonated form of the ligands was found in Rh complexes by Gal et al. [5]. In the reaction of these ligands with Mo and W complexes another coordination mode is found.

Experimental

IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. ^1H NMR spectra were recorded on a Bruker WH-90 spectrometer at 90 MHz and $^{31}P\text{-}[^1H]$ NMR spectra were recorded on a Varian XL-100-FT spectrometer at 40.5 MHz or on a Bruker WH-90 spectrometer at 36.43 MHz. Elemental analyses were performed at the micro analytical department of this university.

Preparations

All preparations were carried out under nitrogen using Schlenk apparatus. $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W) [6], $M(CO)_3(PPh_3)_2Cl_2$ (M = Mo [7], W [8]) and $Ph_2P(O)C(S)N(H)R$ (R = Me, Ph) [9] were prepared as described in the literature.

$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(O)C(S)NR)$ (I, R = Ph; II R = Me). 1 mmol $Mo(CO)_3(\eta^5\text{-}C_5H_5)Cl$ and an equimolar amount of the appropriate ligand were refluxed in 15 ml benzene for two hours in the presence of Et_3N. Et_3NHCl was filtered off and after addition of n-hexane the product crystallized. Recrystallization from CH_2Cl_2/n-hexane gave orange-red crystals.

$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(O)C(S)NR)$ [III, R = Ph; IV, R = Me). 1 mmol $W(CO)_3(\eta^5\text{-}C_5H_5)Cl$ and an equimolar amount of the appropriate ligand were refluxed for 16 hours in 15 ml benzene in the presence of an excess of Et_3N. The Et_3NHCl was filtered off and after addition of n-hexane the product separated. Recrystallization from CH_2Cl_2/n-hexane gave the orange complex.

$Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NR)_2$ (V, R = Ph; VI, R = Me). To a suspension of $Mo(CO)_3(PPh_3)_2Cl_2$ (1 mmol) in 15 ml benzene $Ph_2P(O)C(S)N(H)R$ (2 mmol) and an excess of Et_3N were added. The mixture was stirred for several hours, then the Et_3NHCl was filtered off. The product was separated after addition of an equal volume of n-hexane. Recrystallization from CH_2Cl_2/ethanol gave red crystals.

$W(CO)_2(PPh_3)(Ph_2P(O)C(S)NR)_2$ (VII, R = Ph; VIII, R = Me). To a suspension of $W(CO)_3(PPh_3)_2Cl_2$ (1 mmol) in 15 ml benzene $Ph_2P(O)C(S)N(H)R$ (2 mmol) and an excess of Et_2N were added. The mixture was stirred for one night then the Et_3NHCl was filtered off. The product separated after addition of an equal volume of n-hexane. Recrystallization was from CH_2Cl_2/n-hexane.

Crystal structure determination of $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2 \cdot CH_2Cl_2$

$MoC_{58}H_{45}N_2O_4P_3S_2 \cdot CH_2Cl_2$. F.W. = 1202.45, triclinic, $P\bar{1}$, a = 13.176(4), b = 14.364(7), c = 18.230(9) Å, α = 110.84 (6), β = 72.44(4), γ = 115.24 (3)°, V = 2870.6 Å^3, D_x = 1.39 g/cm^3, Z = 2, $\mu(\text{Mo-}K_\alpha)$ = 4.8 cm^{-1}.

Unit cell dimensions were determined by least-squares fitting of the setting angles of 25 reflections measured on a CAD 4 diffractometer (Mo-K_α radiation, $\lambda = 0.71069$ Å).

For data collection a crystal of approximately 0.3 × 0.3 × 0.3 mm^3 sealed in a glass capillary was used, and 16625 independent reflections ($\sin 2\theta_{max} = 0.52$) were measured ($\omega$—$2\theta$ scan, Mo-K_α radiation, graphite crystal monochromator). Intensity control reflections were monitored every half hour; no significant loss of intensity during data collection was observed. Lorentz and polarization corrections were applied but absorption corrections were not.

The data were reduced to $|F_{obs}|$ values giving 10384 reflections with an $|F_{obs}|$ value above a preset threshold ($I > 3\sigma_I$, σ_I from counting statistics). The molybdenum, sulfur and phosphorus atoms were localized from a Patterson synthesis. The DIRDIF [10] procedure and difference Fourier syntheses showed the remaining non-hydrogen atoms and one CH_2Cl_2 molecule. The structure was refined by full matrix least-squares methods with anisotropic thermal parameters for the molybdenum, chlorine, sulfur and phosphorus atoms. The phenyl rings were constrained to an ideal model. The function minimized was $\Sigma W[|F_{obs}| - k|F_{calc}|]^2$ with $W = [\sigma(I)^2 - 0.005\ F_{obs}{}^2]^{-1}$. Hydrogen atoms were placed in calculated positions and used in the structure factor calculations but not refined. The final conventional R value was 0.077 for the 10384 "observed" reflections. The atom scattering factors were taken from the International Tables for X-ray Crystallography [11]. The anomalous dispersion of Mo was included in the structure-factor calculation using values listed in the International Tables for X-ray Crystallography [12]. The atomic coordinates are given in Table 5 and the thermal parameters in crystalline $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2 \cdot CH_2Cl_2$ in Table 6.

Results

Preparation and reactions

In the reactions of $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W) with $Ph_2P(O)C(S)N(H)R$ (R = Me, Ph) in the presence of Et_3N the chlorine and one carbonyl group are displaced by the deprotonated ligand (eq. 1) and compounds are obtained which give correct analyses for $M(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(O)C(S)NR)$ (Table 1).

TABLE 1

ELEMENTAL ANALYSES (THEORETICAL VALUES IN PARENTHESES)

Complex		C(%)	H(%)	N(%)
I	$Mo(CO)_2(Ph_2P(O)C(S)NPh)(\eta^5\text{-}C_5H_5)$	56.39(56.42)	3.80(3.64)	2.57(2.53)
II	$Mo(CO)_2(Ph_2P(O)C(S)NMe)(\eta^5\text{-}C_5H_5)$	50.84(51.33)	3.61(3.69)	3.05(2.85)
III	$W(CO)_2(Ph_2P(O)C(S)NPh)(\eta^5\text{-}C_5H_5)$	48.66(48.70)	3.12(3.14)	2.23(2.18)
IV	$W(CO)_2(Ph_2P(O)C(S)NMe)(\eta^5\text{-}C_5H_5)$	42.65(43.55)	3.13(3.13)	2.29(2.42)
V	$Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2 \cdot \frac{1}{2}\ CH_2Cl_2$ [a]	63.75(64.08)	4.15(4.17)	2.61(2.57)
VI	$Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NMe)_2 \cdot \frac{1}{2}\ CH_2Cl_2$	57.39(57.94)	4.08(4.21)	2.76(2.78)
VII	$W(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2 \cdot \frac{1}{2}\ CH_2Cl_2$	57.85(57.72)	3.72(3.81)	2.35(2.30)
VIII	$W(CO)_2(PPh_3)(Ph_2P(O)C(S)NMe)_2 \cdot \frac{1}{2}\ CH_2Cl_2$	53.32(53.28)	3.79(3.87)	2.34(2.56)

[a] The presence of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy.

No products were obtained in the absence of Et_3N.

$$\begin{array}{ll} M(CO)_3(\eta^5\text{-}C_5H_5)Cl + Ph_2P(O)C(S)N(H)R & \\ \quad (M = Mo, W) \qquad\qquad (R = Me, Ph) & \\ \xrightarrow{Et_3N} M(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(O)C(S)NR) + CO + Et_3NHCl & (1) \end{array}$$

Two equivalents of $Ph_2P(O)C(S)N(H)R$ react with $M(CO)_3(PPh_3)_2Cl_2$ (M = Mo, W) under the influence of Et_3N to give products in which two deprotonated ligands are coordinated to the metal atom (eq. 2a). The analyses of the products are consistent with the formula $M(CO)_2(PPh_3)(Ph_2P(O)C(S)NR)_2$ (Table 1).

Mo complexes can also be obtained from $Mo(CO)_4Cl_2$ (eq. 2b), and probably have the composition $Mo(CO)_3(Ph_2P(O)C(S)NR)_2$. However, these are very reactive and air-sensitive, and could not be obtained in analytically pure form. When PPh_3 is added to a solution of such a complex, gas evolution is observed and $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NR)_2$ is formed.

$$\begin{array}{ll} M(CO)_3(PPh_3)_2Cl_2 + 2\ Ph_2P(O)C(S)N(H)R & \\ \quad (M = Mo, W) \qquad\qquad (R = Me, Ph) & \\ \xrightarrow{Et_3N} M(CO)_2(PPh_3)(Ph_2P(O)C(S)NR)_2 + PPh_3 + CO + 2\ Et_3NHCl & (2a) \end{array}$$

$$\begin{array}{ll} Mo(CO)_4Cl_2 + 2\ Ph_2P(O)C(S)N(H)R & \\ \qquad\qquad\qquad (R = Me, Ph) & \\ \rightarrow Mo(CO)_3(Ph_2P(O)C(S)NR)_2 + CO + 2\ Et_3NHCl & \\ \qquad\qquad\qquad \downarrow PPh_3 & \\ \quad Mo(CO_2(PPh_3)(Ph_2P(O)C(S)NR)_2 + CO & (2b) \end{array}$$

IR spectra

In the infrared spectra of solutions of $M(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(O)C(S)NR)$ (M = Mo, W; R = Me, Ph) in CH_2Cl_2 two bands are found in the carbonyl stretching region. The band at highest wave number has the higher intensity, indicating that both CO groups are in *cis* positions [13]. Assignment of the ν(CN) is difficult because the $Ph_2P(O)$ vibration bands also lie in the 1400—1500 cm^{-1} region.

In the case of compound II we assigned a band found at 1505 cm^{-1} to the ν(CN). These low lying CN stretching bands indicate nitrogen coordination in these complexes. Oxygen coordination is excluded on the basis of the position of the ν(PO), which is found at about 1190 cm^{-1}, almost the same value as found in $Ph_2P(O)C(S)N(H)R$. From these results we conclude that the ligands in these cyclopentadienyl complexes are coordinated through nitrogen and sulfur.

In the infrared spectra of $M(CO)_2(PPh_3)(Ph_2P(O)C(S)NR)_2$ (M = Mo, W; R = Me, Ph) all the important ligand vibration bands are different from those of compounds I, II, III and IV. First of all the relatively high ν(CN) wave number

TABLE 2

INFRARED SPECTRAL DATA

Compound	ν(CO) [a]		Ligand vibrations [b]		
I	1965vs	1883s	—	1190vs	835m
II	1962vs	1879s	1505s	1198vs	820s
III	1953vs	1864s	—	1190vs	838m
IV	1952vs	1861s	—	1197vs	830m
V	1930vs	1845vs	1540vs	1125vs	950m
VI	1935vs	1854vs	1560vs	1130vs	946m
VII	1917vs	1822vs	1542vs	1120vs	954m
VIII	1917vs	1826vs	1562vs	1125vs	950m

[a] I—IV measured in CH_2Cl_2 solution and V—VIII measured in CsI pellets.
[b] Measured in CsI pellets.

(about 1550 cm^{-1}) indicates considerable more double bond character in the CN bond. This high ν(CN) is consistent with non-coordination of the nitrogen atom. The coordination of the oxygen atom can be seen in the IR-spectra by the position of the ν(PO) which is found at about 1130 cm^{-1}. This is about 60 cm^{-1} lower than ν(PO) in the free ligand and also lower than ν(PO) for the ligand in I, II, III and IV. The spectrum of the impure $Mo(CO)_3(Ph_2P(O)C(S)\text{-}NR)_2$ samples show one sharp and one broad band in the CO-stretching region. The ligand vibration bands found in the infrared spectrum of this complex are almost the same as those in the spectra of $M(CO)_2(PPh_3)(Ph_2P(O)C(S)NR)_2$, so we conclude that in this complex the ligands are again coordinated through oxygen and sulfur.

^{1}H *NMR and* $^{31}P[^1H]$ *NMR spectra*

In the proton NMR spectra (Table 3) of I, II, III and IV the cyclopentadienyl signal appears as a singlet at about 4.7 ppm. No N—H proton resonance signal could be found in the spectra of the complexes, indicating that the ligand is deprotonated. The methyl protons of $M(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(O)C(S)NMe)$ (M = Mo, W) give rise to a doublet in the proton NMR spectra. If *S,N*-coordination is assumed the doublet cannot arise from two stable rotamers. A phosphorus—proton coupling must be assumed. The temperature-dependent proton NMR measurements of $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NMe)_2$ show two doublets

TABLE 3

^{1}H NMR SPECTRAL DATA (IN ppm RELATIVE TO TMS AS INTERNAL STANDARD) [a]

Compound		
I	4.70	—
II	4.69	3.54(D) [b] (J = 1.46 Hz)
III	4.73	—
IV	4.75	3.60(D) (J = 2.05 Hz)
VI	—	3.93(D) 3.71(D) (J = 3.6 Hz)
VIII	—	3.92(D), 372(D) (J = 3.81 Hz)

[a] All spectra were taken in C_6D_6 solution
[b] D = doublet.

TABLE 4

^{31}P [^1H] NMR SPECTRAL DATA [a]

Compound	δ(PPh$_3$)	δ(ligand phosphorus)		Solvent
I	—	—14.68		C_6D_6
II	—	—15.80		C_6D_6
III	—	—19.30		C_6D_6
IV	—	—16.03		C_6D_6
V	—69.59(br) [c]	—29.63(S) [c]	—23.61(D: J = 7.93 Hz)	CD_2Cl_2
VI	—64.42(D: J = 6.61 Hz) [c]	—26.79(S)	—20.70(D: J = 6.50 Hz)	C_6D_6
VII	—36.97(D: J = 10.26 Hz) [b]	—31.27(S)	—23.28(D: J = 10.5 Hz)	CD_2Cl_2
VIII	—38.49(D: J = 10.08 Hz) [b]	—28.48(S)	—20.42(D: J = 9.96 Hz)	C_6D_6

[a] δ values in ppm relative to O = P(OMe)$_3$, using the solvent as internal lock; upfield is positive.
[b] $^1J(^{183}W—^{31}P)$ in both cases 250 Hz. [c] br = broad, D = doublet and S = singlet.

at room temperature which at higher temperatures become one doublet with the same coupling constant as that of the doublets at room temperature.

If $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NMe)_2$ has the same structure as we found by X-ray analysis for $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2$, both methyl groups are non-equivalent due to the low symmetry of the molecule. The ^1H NMR spectra can then be interpreted in terms of two different methyl groups giving two doublets by P—H coupling, possibly with some twist process giving a rapid interconversion of both methyl sites at higher temperature. Measurements at 300 MHz confirmed that the doublets must be assigned to the coupling of the methyl protons with the phosphorus atom of the same ligand. Interconversion of C=NMe rotamers seems a less likely explanation.

In the ^{31}P NMR spectra of I, II, III and IV (Table 4) only one signal is found, and this has almost the same chemical shift as the free ligand. This is again an indication for *N*,*S*-coordination of the ligand in these complexes. On the other hand a considerable downfield shift is found in the ^{31}P NMR spectra of the $M(CO)_2(PPh_3)(Ph_2P(O)C(S)NR)_2$ complexes as expected when P(O) is coordinated to the metal. All the spectra can be interpreted by assuming three differ-

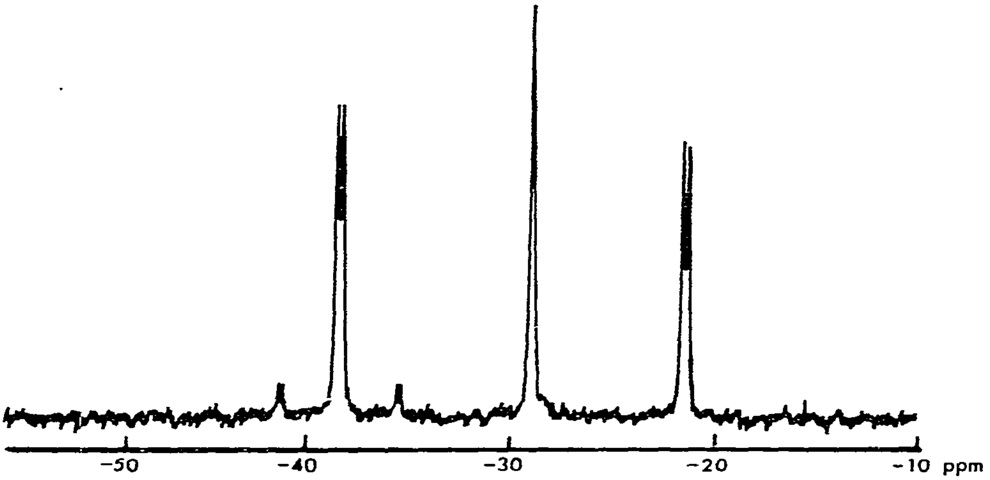


Fig. 2. ^{31}P[^1H] NMR spectrum of $W(CO)_2(PPh_3)(Ph_2P(O)C(S)NMe)_2$.

TABLE 5

FRACTIONAL ATOMIC COORDINATES ($\times 10^{-4}$)

Atom	x	y	z
Mo	3381.8(3)	7664.9(3)	7224.2(3)
S(1)	2325(2)	5701(1)	6678(1)
S(2)	3802(2)	9389(2)	8345(1)
P(1)	3524(2)	5898(1)	7899(1)
P(2)	1350(2)	8021(2)	8661(1)
P(3)	5470(2)	8600(1)	6807(1)
O(1)	4141(4)	6976(3)	7738(3)
O(2)	1941(3)	7227(3)	8197(3)
O(4)	3833(4)	7230(4)	5384(3)
O(5)	2331(5)	8856(5)	6719(4)
N(1)	1441(5)	4446(5)	7721(4)
N(2)	2063(5)	10152(5)	9171(4)
C(1)	2240(5)	5224(5)	7456(4)
C(2)	2419(5)	9383(5)	8771(4)
C(4)	3715(5)	7387(5)	6068(4)
C(5)	2699(5)	8403(5)	6924(4)
Cl(1)	9481(4)	9816(4)	4166(4)
Cl(2)	7880(4)	8484(4)	3110(3)
C(6)	9073(15)	9518(14)	3162(11)

ent phosphorus sites. Assuming the greatest chemical shift is for the phorphorus atom directly bonded to the metal, the signal at lowest field can be assigned to the PPh_3 phosphorus atom. In the spectra of the tungsten complexes this is confirmed by the appearance of a ^{31}P—^{183}W coupling constant of 250 Hz in the PPh_3 doublet (see Fig. 2). A coupling between the PPh_3 phosphorus and one of the ligand phosphorus atoms is also visible in the spectrum shown in Fig. 2.

A coupling of the other ligand phosphorus and the PPh_3 phosphorus is not observed in the case of R = Me, which means that this coupling is almost zero.

TABLE 6

THERMAL PARAMETERS IN CRYSTALLINE $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2 \cdot CH_2Cl_2$ ($Å^2 \times 10^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	2.87(3)	2.37(3)	2.98(3)	1.06(2)	−0.26(2)	0.87(2)
S(1)	4.38(8)	2.80(6)	3.21(7)	0.74(6)	−0.95(6)	0.75(5)
S(2)	3.38(7)	3.00(7)	4.63(8)	1.33(6)	−0.48(6)	0.39(6)
P(1)	3.39(7)	2.82(7)	3.65(7)	1.30(6)	−0.56(6)	1.01(6)
P(2)	3.35(7)	3.09(7)	3.34(7)	1.46(6)	0.02(6)	1.05(6)
P(3)	3.07(7)	2.71(6)	3.74(7)	0.99(5)	−0.35(6)	1.06(6)
Cl(1)	13.5(4)	12.9(4)	20.7(6)	2.0(3)	−6.5(4)	2.0(4)
Cl(2)	14.2(4)	14.5(4)	12.2(3)	5.2(3)	−4.3(3)	1.5(3)

Atom	U	Atom	U	Atom	U
O(1)	3.34(8)	N(1)	4.4(2)	C(4)	3.7(2)
O(2)	3.30(8)	N(2)	4.3(2)	C(5)	3.9(2)
O(4)	5.2(2)	C(1)	3.4(2)	C(6)	13.6(6)
O(5)	5.8(2)	C(2)	3.4(2)		

The anisotropic temperature factor is defined as $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + hka^*b^*U_{12} + ...)]$.

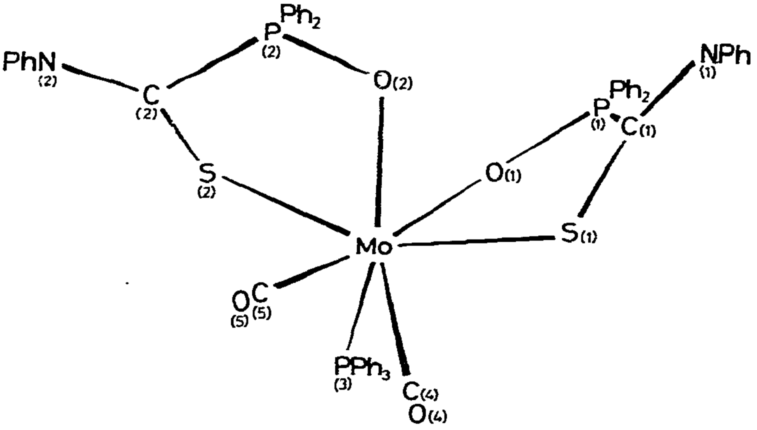


Fig. 3. Molecular structure of $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2$.

In the case of R = Ph this coupling is very small, as can be seen from the broadening of the PPh_3 doublet and the singlet of one of the ligand phosphorus atoms. A ^4J(P—P) coupling between the both ligand phosphorus atoms is not observed.

Description of the molecular structure of $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2 \cdot CH_2Cl_2$

The structure is illustrated in Figs. 3 and 4. Atomic positions and temperature parameters are given in Tables 5 and 6. Bond angles and distances of important intramolecular bonds are given in Table 7. The crystal structure analysis revealed the compound to be composed of seven-coordinate molybdenum atoms bonded to two bidentate (O, S) $Ph_2P(O)C(S)NPh^-$ ligands, one PPh_3 and two carbonyl groups.

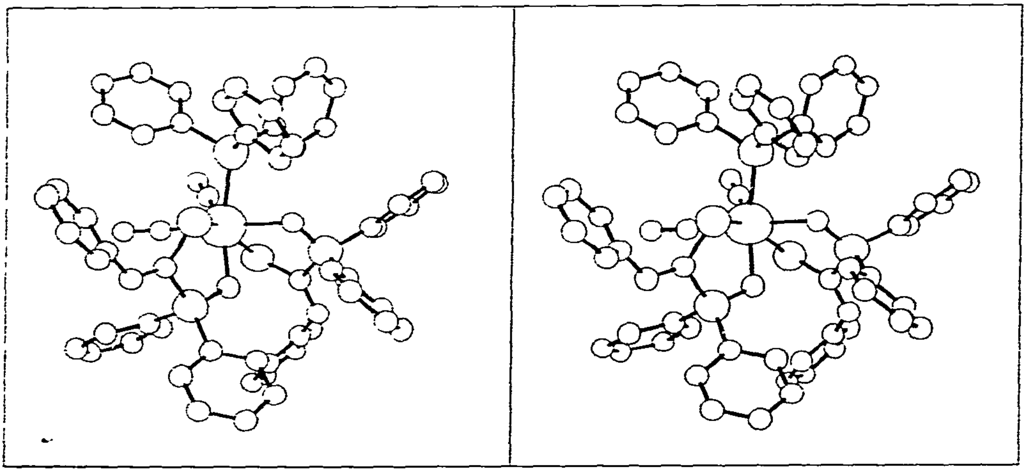


Fig. 4. Stereo plot of $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2$.

TABLE 7

IMPORTANT BOND ANGLES (°) AND BOND DISTANCES (Å)

Mo—L (L—Mo—L: see Table 10)					
Mo—S(1)	2.525(2)	Mo—O(2)	2.210(4)	Mo—C(4)	1.946(6)
Mo—S(2)	2.555(2)	Mo—P(3)	2.503(2)	Mo—C(5)	1.938(9)
Mo—O(1)	2.220(6)				
Carbonyl groups					
C(4)—O(4)	1.158(8)	Mo—C(4)—O(4)	174.7(7)		
C(5)—O(5)	1.163(11)	Mo—C(5)—O(5)	177.0(5)		
Bidentate $Ph_2P(O)C(S)NPh^-$ (1 and 2)					
S(1)—C(1)	1.740(8)	S(2)—C(2)	1.750(6)		
C(1)—P(1)	1.822(6)	C(2)—P(2)	1.842(5)		
C(1)—N(1)	1.290(8)	C(2)—N(2)	1.278(9)		
P(1)—O(1)	1.500(5)	P(2)—O(2)	1.516(5)		
Mo—O(1)—P(1)	122.5(3)	Mo—O(2)—P(2)	117.5(3)		
Mo—S(1)—C(1)	99.9(2)	Mo—S(2)—C(2)	100.5(2)		
S(1)—C(1)—P(1)	112.9(3)	S(2)—C(2)—P(2)	112.3(4)		
C(1)—P(1)—O(1)	109.1(3)	C(2)—P(2)—O(2)	109.0(2)		
P(1)—C(1)—N(1)	117.6(6)	P(2)—C(2)—N(2)	117.0(4)		
S(1)—C(1)—N(1)	129.3(5)	S(2)—C(2)—N(2)	130.6(4)		

The molybdenum—carbon distances are the same as those found in $[Mo(CO)_2(Ph_2PC(S)NMe)(\mu\text{-}Ph_2PC(S)NMe)]_2$ [3] where the CO groups are also in *cis* position. They are slightly shorter than the Mo-C distances in $Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2$ [14] where both CO groups are in *trans* positions. The average Mo—S distance of 2.54 Å is the same as found in other Mo complexes with bidentate sulfur-containing ligands [3,15]. The Mo—O distances are about 2.22 Å, which lies in the range of Mo—O distances in Mo^{IV} and Mo^{VI} complexes with phosphine oxides as ligands [16,17,18].

The geometry of both $Ph_2P(O)C(S)NPh^-$ ligands is roughly the same, the C, P, N and S atoms being coplanar (see Table 8). The P—O distances of 1.51 Å is slightly longer than the P=O distance found, for example, in Ph_3PO (1.46 Å) [19]. Considerable double bond character is reflected in the short C—N bond distance of 1.285 Å (the C—N single bond distance being 1.48 Å) [20].

The C—S bond distance of 1.74 Å is shorter than the C—S single bond distance of 1.81 Å [20], which means that the C—S bond also has considerable double bond character. The angles at the P atom of the ligand to the O and the 3 C atoms are close to 109°, revealing sp^3 hybridization of the P atom. Most of the previously studied compounds with a seven-coordinate central metal atom

TABLE 8

SOME LEAST SQUARE CALCULATIONS (Å)

Plane 1		Plane 2		Plane 3		Plane 4		Plane 5	
N(1)	−0.01(2)	N(2)	0.01(2)	O(2)	−0.01(2)	C(5)	0.04(5)	S(2)	−0.04(6)
C(1)	0.02(2)	C(2)	−0.02(2)	Mo	0.03(2)	Mo	−0.07(5)	Mo	0.09(6)
P(1)	−0.01(2)	P(2)	0.02(2)	C(4)	−0.01(2)	O(1)	0.03(5)	S(1)	−0.03(6)
S(1)	−0.01(2)	S(2)	0.01(2)	P(3)	−0.01(2)	S(1)	0.00(5)	C(4)	−0.02(6)

Angle between plane 1 and the plane Mo, O(1) and S(1) is 134.07°.
Angle between plane 2 and the plane Mo, O(2) and S(2) is 139.77°.

TABLE 9

DIHEDRAL ANGLE CALCULATIONS FOR THE SEVEN COORDINATE $Mo(CO)_2(PPh_3)(Ph_2P(O)C(S)NPh)_2$ IN VARIOUS TRIAL GEOMETRIES

	δ values (°)				δ values after normalization[a] (°)				"ideal" δ values[b] (°)			
Capped octahedron												
C(4): P(3) C(5) S(1): S(2) O(1) O(2)	5.06	26.72	37.19		8.82	26.45	31.84		24.2	24.2	24.2	
Capped trigonal prism												
S(2): C(5) O(2) O(1) P(3): C(4) S(1)	26.72	50.25	5.06	37.19	26.45	60.18	8.82	31.84	41.5	41.5	0	0
Pentagonal bipyramid												
O(1): O(2) S(1) S(2) C(4) P(3): C(5)	3.93	67.87			8.44	82.83			54.4	54.4		
4 : 3 piano/stool												
O(1) S(1) C(4) P(3): S(2) O(2) C(5)	12.28	11.07	13.97		4.64	8.75	0.35		0	0	0	0

[a] This means that the structure was projected on a sphere. [b] These values were taken from ref. 21.

TABLE 10

COMPARISON OF THE L—Mo—L BOND ANGLES (°) WITH THOSE OF "IDEAL" CTP, CO AND PB STRUCTURES

Angle	Value found	CTP	CO	PB
S(2)—Mo—C(5)	81.0(2)	82	76.6	90
S(2)—Mo—O(2)	77.9(1)	82	89.6	72
S(2)—Mo—O(1)	91.4(1)	82	89.6	90
S(2)—Mo—P(3)	77.94(6)	82	76.6	72
S(2)—Mo—C(4)	132.4(2)	144.2	125.5	144
S(2)—Mo—S(1)	153.09(6)	144.2	160.4	144
C(5)—Mo—O(2)	93.6(3)	99	76.6	90
P(3)—Mo—O(1)	78.3(1)	99	76.6	90
C(5)—Mo—P(3)	102.6(2)	78.7	112.8	90
O(1)—Mo—O(2)	82.0(2)	78.7	89.6	90
C(5)—Mo—O(1)	171.9(2)	164	160.4	180
P(3)—Mo—O(2)	148.2(2)	164	160.4	144
O(2)—Mo—S(1)	75.7(1)	75.1	76.6	72
O(1)—Mo—S(1)	80.0(1)	75.1	76.6	90
C(5)—Mo—C(4)	71.4(3)	75.1	74.1	90
P(3)—Mo—C(4)	71.5(2)	75.1	74.1	72
S(1)—Mo—C(5)	105.7(2)	118.9	112.8	90
S(1)—Mo—P(3)	124.16(5)	118.9	112.8	144
C(4)—Mo—O(1)	116.2(3)	118.9	125.5	90
C(4)—Mo—O(2)	140.1(2)	118.9	125.5	144
S(1)—Mo—C(4)	73.4(2)	71.5	74.1	72

Average angular deviation from CTP: 8.1; CO: 7.0; PB: 9.1.
We used the idealized angles of ref. 21.

could be described as a pentagonal bipyramide (PB), a capped trigonal prism (CTP) or as a capped octahedron (CO) [21]. Although not common, the alternative 4 : 3 piano-stool representation, in which a plane of 4 ligating atoms and a plane of the other 3 ligating atoms are coplanar, is a better description for some 7-coordinate complexes [21—23].

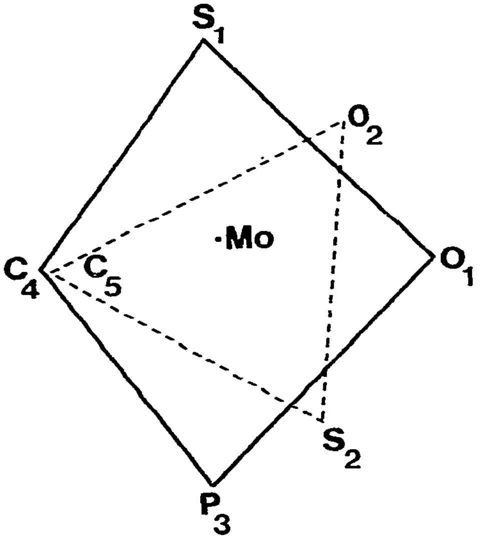
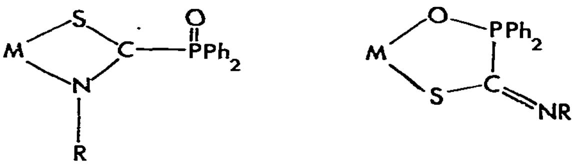


Fig. 5. Projection of C(5), O(2), S(2) and Mo on the best plane through S(1), O(1), P(3) and C(4).



bidentate by N and S

bidentate by O and S

Fig. 6. Modes of coordination of the $Ph_2P(O)C(S)NR^-$ ligands (R = Me, Ph).

The three polyhedra have been described in different ways [21—24]. From Tables 9 and 10, in which the results of calculations based on two of these descriptions are given, it can be concluded that the capped octahedron is the best description in terms of the polyhedra. Because of the poor agreement with the theoretical values for the capped octahedron, we think that the structure under consideration can best be described as a 4 : 3 piano stool (see Table 9). In Fig. 5 a projection is given of the triangle on the best plane through O(1), S(1), C(4) and P(3).

It is noteworthy that every point of the triangular face lies in a plane with Mo and two atoms of the quadrilateral face (see Table 8).

Conclusions

The reaction we have described of the ligands $Ph_2P(O)C(S)N(H)R$ with Mo and W complexes show that the uninegative heteroallyl-like ligand can coordinate in two ways, as shown in Fig. 6. The reason why the ligand coordinates through sulfur and nitrogen in the cyclopentadienyl complexes and through oxygen and sulfur in the other complexes containing two of these ligands is not at present clear, but differences in electron density on the metal atom may be involved.

The $Mo(CO)_3(Ph_2P(O)C(S)NR)_2$ complexes could not be isolated pure. They are very reactive, and further investigation of them is of interest.

Acknowledgements

The authors wish to thank Prof. Dr. Ir. J.J. Steggerda for stimulating discussions, Mr. J.H. Noordik for valuable assistance with the X-ray work, Mr. P.P.J. Schlebos, Mr. H.H.K. Brinkhof and Mr. J.W.M. van Kessel for recording the ^1H and ^{31}P NMR spectra, Mr. P.J.J. Koonen for performing the elemental analyses and the Institute for Organic Chemistry, TNO for measuring the 300 MHz ^1H NMR spectra on a Varian SC 300 spectrometer.

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