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Different Coordination Modes of Neutral and Deprotonated ZC(S)N(H)R Ligands (Z = PPh2, R = Ph, Me; Z = NMe2, R = Ph) in Molybdenum and Tungsten Complexes. X-ray Structure Analysis of [Mo(CO)2[Ph2PC(S)NMe][μ-Ph2PC(S)NMe]]2·CH2Cl2[1]

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The hetero allyl derivatives Ph2PC(S)N(H)R (R = Ph, Me) react with Mo(CO)4Cl2 and M(CO)3(PPh3)2Cl2 (M = Mo, W) to give two isomers of the formula M(CO)2[Ph2PC(S)N(H)R]2Cl2, e.g. one ionic complex with two P,S-bidentate ligands and one neutral complex with one P-monodentate and one P,S-bidentate ligand. For R = Me this isomeric mixture reacts with NH4+PF6− to give the ionic [M(CO)2Cl[Ph2PC(S)N(H)Me]2]+PF6− wherein both ligands are coordinated through P and S. The dichloride complexes react with Et3N, giving monomeric complexes M(CO)2[Ph2PC(S)NR]2 (M = Mo, W; R = Ph, Me). An X-ray structure analysis of the crystalline compound Mo(CO)2[Ph2PC(S)NMe2]2 (a = 18.958 (8) Å, b = 19.542 (8) Å, c = 18.879 (8) Å, β = 90.84 (5)°, space group C2/c, and Z = 4) revealed the compound to be dimeric [Mo(CO)2[Ph2PC(S)NMe][μ-Ph2PC(S)NMe]]2 in which one ligand acts as a bridge between the two Mo atoms and the other ligand coordinates in a bidentate manner through P and S. The thiourea derivative Me2NC(S)N(H)Ph reacts with Mo(CO)4Cl2 or M(CO)3(PPh3)2Cl2 (M = Mo, W) and Et3N to give complexes of the type M(CO)2(L)[Me2NC(S)NPh]2 (L = CO and PPh3, respectively). All compounds were characterized by means of elemental analyses, infrared spectroscopy, and 1H and 31P{H} NMR spectroscopy.

Introduction

The reaction of Ph2PH with a hetero allene molecule RN=C=X (X = S, O, NR) leads to compounds of formula Ph2PC(X)N(H)R, which can be deprotonated in the presence of a base. The deprotonated compounds such as the dithiocarbamato ion R2NC(S)S− and the thioureido ion Me2NC(S)NR− belong to the so-called class of hetero allyl anions because of their structural and electronic relationship with the allyl anion.

In this paper we describe the reaction of M(CO)3(PPh3)2Cl2 (M = Mo, W) and Mo(CO)4Cl2 with the hetero allyl derivatives Ph2PC(S)N(H)R (R = Ph, Me) and Me2NC(S)N-(H)Ph. Complexes of the neutral as well as of the deprotonated ligand are known.

The neutral ligand may coordinate in a monodentate manner like an ordinary tertiary phosphine[2,3] or as a bidentate through P and S.[2,4] The deprotonated ligand normally shows bidentate coordination through P and S.[2-7] The crystal structure of [Mo(CO)2[Ph2PC(S)NMe][μ-Ph2PC(S)NMe]]2 (Ib) shows that the ligand can act as a bridge between two Mo atoms, the N and S being coordinated to one Mo atom and the P to the other. All coordination modes described above are found in the newly prepared Mo and W compounds. The deprotonated thiourea derivatives, [Me2NC(S)NR]−, generally coordinate in a bidentate manner through N and S.[5-7] There are two examples of compounds in which the ligand is coordinated to more than one metal atom via sulfur bridges.[4,8,9] In this paper some thioureido complexes are reported in which the ligand coordinates in a bindentate manner through N and S.

Experimental Section

All preparations were carried out under a nitrogen atmosphere with use of Schlenk apparatus. Mo(CO)4Cl2,[10] Mo(CO)3(PPh3)2Cl2,[10] W(CO)3(PPh3)2Cl2,[11] Ph2PC(S)N(H)Ph,[12] Ph2PC(S)N(H)Me,[13] and Me2NC(S)N(H)Ph[14] were prepared as described in the literature.

Mo(CO)2Cl2[Ph2PC(S)N(H)R]2 (R = Ph, Ia; R = Me, IIa). A solution of Ph2PC(S)N(H)R (2 mmol) in 20 mL of CH2Cl2 was added to solid Mo(CO)4Cl2 (1 mmol). The color immediately turned to red, and gas was evolved. Red crystals of the products were obtained after addition of 20 mL of ethanol. The same products were obtained when a suspension of Mo(CO)3(PPh3)2Cl2 in benzene was used. The red products, separated from the reaction mixtures, were washed with ethanol; yield 60% analytically pure product.

W(CO)2Cl2[Ph2PC(S)N(H)R]2 (R = Ph, Ib; R = Me, IIb). To a suspension of W(CO)3(PPh3)2Cl2 in 20 mL of benzene was added 2 equiv of solid Ph2PC(S)N(H)R. After the mixture was stirred 20 h, the red product precipitated and was filtered off. The product was washed with ethanol and recrystallized from CH2Cl2/ethanol; yield 50%.

[M(CO)2Cl[Ph2PC(S)N(H)Me]2]+PF6− (M = Mo, IIIa; M = W, IIIb). To a solution of IIa or IIb in CH2Cl2 was added an equimolar quantity of NH4PF6. After the mixture was stirred for 4 h, the yellow hexafluorophosphate salts precipitated and were filtered and recrystallized from acetone/ethanol; yield 100%.

M(CO)2[Ph2PC(S)NR]2 (M = Mo, R = Ph, IVa; M = Mo, R = Me, Va; M = W, R = Ph, IVb; M = W, R = Me, Vb). These complexes are obtained from the reaction of M(CO)2Cl2[Ph2PC-(S)N(H)R]2 in CH2Cl2 solution with an excess of Et3N. Yellow needles are filtered off after addition of an equal volume of ethanol. The tungsten complexes could also be obtained from the reaction of W(CO)3(PPh3)2Cl2 with the appropriate ligand in the presence of Et3N; yield 70% for IVa and Va, 60% for IVb and Vb.

[Mo(CO)2[Ph2PC(S)NR][μ-Ph2PC(S)NR]]2 (R = Ph, VI; R = Me, VII). A solution of Ph2PC(S)N(H)R (2 mmol) and an excess of Et3N in CH2Cl2 was added to solid Mo(CO)4Cl2 (1 mmol). The color immediately turned to red, and carbon monoxide was evolved. Orange-red crystals were obtained after addition of an equal volume of ethanol. For R = Ph a mixture of IVa and VI was formed, which could be separated by slow recrystallization.

Mo(CO)3[Me2NC(S)NPh]2 (VIII). A solution of Me2NC(S)N-(H)Ph (2 mmol) and an excess of Et3N in 20 mL of CH2Cl2 was added to solid Mo(CO)4Cl2 (1 mmol). The color immediately turned to orange-red, and carbon monoxide was evolved. Orange-red crystals

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Table I. Elemental Analyses (Calculated Values in Parentheses)

no.	compd	% C	% H	% N
Ia	Mo(CO)$_2$(Ph$_2$PC(S)N(H)Ph)$_2$Cl$_2$·C$_6$H$_6$ ^{a}	58.2 (58.5)	4.0 (4.1)	2.8 (3.0)
Ib	W(CO)$_2$(Ph$_2$PC(S)N(H)Ph)$_2$Cl$_2$·C$_6$H$_6$ ^{a}	52.9 (53.6)	3.6 (3.7)	2.7 (2.7)
IIa	Mo(CO)$_2$(Ph$_2$PC(S)N(H)Me)$_2$Cl$_2$	49.1 (48.6)	3.8 (3.8)	3.2 (3.8)
IIb	W(CO)$_2$(Ph$_2$PC(S)N(H)Me)$_2$Cl$_2$·$^1/_6$C$_6$H$_6$ ^{a}	44.4 (44.2)	3.5 (3.5)	3.3 (3.3)
IIIa	[Mo(CO)$_2$(Ph$_2$PC(S)N(H)Me)$_2$Cl]$^+$PF$_6^-$	42.6 (42.3)	3.3 (3.3)	3.3 (3.3)
IIIb	[W(CO)$_2$(Ph$_2$PC(S)N(H)Me)$_2$Cl]$^+$PF$_6^-$	39.3 (39.7)	3.2 (3.1)	2.9 (3.1)
IVa	Mo(CO)$_2$(Ph$_2$PC(S)NPh)$_2$·Et$_3$N^a	61.0 (61.8)	5.3 (5.1)	4.5 (4.7)
IVb	W(CO)$_2$(Ph$_2$PC(S)NPh)$_2$·Et$_3$N·$^1/_2$CH$_2$Cl$_2$ ^{a}	54.3 (54.5)	4.5 (4.5)	4.1 (4.1)
Va	Mo(CO)$_2$(Ph$_2$PC(S)NMe)$_2$	53.0 (53.9)	4.1 (3.9)	4.1 (4.2)
Vb	W(CO)$_2$(Ph$_2$PC(S)NMe)$_2$·Et$_3$N·1$^1/_2$CH$_2$Cl$_2$ ^{a}	46.0 (45.7)	4.5 (4.5)	4.4 (4.3)
VI	[Mo(CO)$_2$(Ph$_2$PC(S)NPh)]$_2$ ^{b}			
VII	[Mo(CO)$_2$(Ph$_2$PC(S)NMe)]$_2$ ^{c}	53.7 (53.9)	4.2 (3.9)	4.2 (4.2)
VIII	Mo(CO)$_3$(Me$_2$NC(S)NPh)$_2$	46.8 (46.8)	4.6 (4.1)	10.5 (10.4)
IXa	Mo(CO)$_2$(PPh$_3$)(Me$_2$NC(S)NPh)$_2$	58.6 (57.0)	5.0 (4.8)	7.1 (7.2)
IXb	W(CO)$_2$(PPh$_3$)(Me$_2$NC(S)NPh)$_2$	52.7 (53.0)	4.3 (4.3)	6.5 (6.5)

^{a} The inclusion of the solvent molecules and/or Et$_3$N was confirmed by ^{1}H NMR spectroscopy. ^{b} No reproducible elemental analyses could be done owing to the inclusion of different amounts of solvent. ^{c} Molecular weight 1360 (1367), determined osmometrically under N$_2$ atmosphere in CHCl$_3$.

of VIII were obtained after addition of an equal volume of ethanol; yield 75%.

M(CO)$_2$(PPh$_3$)[Me$_2$NC(S)NPh]$_2$ (M = Mo, IXa; M = W, IXb). Me$_2$NC(S)N(H)Ph (2 mmol) and Et$_3$N (4 mmol) were added to a suspension of M(CO)$_3$(PPh$_3$)$_2$Cl$_2$ (1 mmol) in 20 mL of benzene. The mixture was stirred for 4 h; Et$_3$NHCl was filtered off. Orange-red crystals of IXa or IXb were obtained after addition of an equal volume of *n*-hexane. IXa could also be prepared from the reaction of VIII with PPh$_3$; yield 80%.

Elemental analyses are given in Table I.

Results and Discussion

a. Complexes of the Neutral Ph$_2$PC(S)N(H)R Ligands: Preparation and Characterization. Mo(CO)$_4$Cl$_2$ reacts with Ph$_2$PC(S)N(H)R (R = Ph, Me) to form Mo(CO)$_2$Cl$_2$-[Ph$_2$PC(S)N(H)R]$_2$. These compounds and the analogous tungsten complexes can also be prepared in the reaction of M(CO)$_3$(PPh$_3$)$_2$Cl$_2$ (M = Mo, W) with Ph$_2$PC(S)N(H)R (R = Ph, Me). Reaction of the Me compounds with NH$_4$PF$_6$ leads to [M(CO)$_2$Cl[Ph$_2$PC(S)N(H)Me]$_2$]$^+$PF$_6^-$, indicating that in the dichloro complex at least one chloride is coordinated to the metal whereas the other chloride may be a noncoordinating anion. The infrared spectra of all these complexes (Table II) show two carbonyl stretching frequencies. As usually found, the frequencies of the tungsten compounds are lower than those of the molybdenum complexes, which can be ascribed to the greater basicity of W.

The various bands in the ν(CN) region found in the spectra of the phenyl compounds (Ia and Ib) lead to the conclusion that the ligands have different coordination modes, one monodentate-coordinated ligand giving a ν(CN) at 1490 cm^{-1} and one bidentate-coordinated ligand leading to a ν(CN) at 1540 cm^{-1}. In the methyl compounds (IIa–IIIb) both ligands are most likely bidentate coordinated to the metal by P and S, giving a ν(CN) of very high intensity at 1570 cm^{-1}.

In Figure 1 two different isomers are given; although these isomers are not the only possibilities, they are illustrative and give an explanation for the spectra.

The different coordination modes of the ligands can easily be seen in the ^{31}P{^{1}H} NMR spectra of the molybdenum complexes (Table III), the chemical shifts of a coordinated phoshorus in the chelate ring system and of the phosphorus in the monodentate ligand being −35 and −60 ppm, respectively. The sharp signal at −39.90 ppm in the spectrum of the phenyl compound in CD$_2$Cl$_2$ solution is assigned to isomer i; the broad signals at −59, 78, and −36.07 ppm are most likely attributed to isomer ii, in which the monodentate- and bidentate-coordinated ligands are rapidly exchanged. This interconversion slows down at low temperatures, resulting in two doublets with a ^2J(P–P) of 16.5 Hz. In CD$_3$C(O)CD$_3$ solution
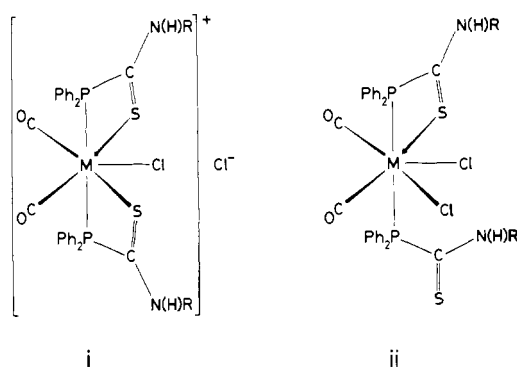

Figure 1. Two different isomers for M(CO)$_2$Cl$_2$[Ph$_2$PC(S)N(H)R]$_2$.

at room temperature, however, two sharp doublets are found at −59.47 and −34.70 ppm, indicating that only isomer ii is present. The spectra of the methyl compound show a similar pattern, but measured in CD$_2$Cl$_2$ the signal of isomer i is of much higher intensity compared to the broad signals of isomer ii than in the spectra of the phenyl compound.

The compounds W(CO)$_2$[Ph$_2$PC(S)N(H)R]$_2$Cl$_2$ (R = Ph, M) have complicated spectra, indicating that mixtures of isomers are present in solution. [M(CO)$_2$[Ph$_2$PC(S)N(H)-Me]$_2$Cl]$^+$PF$_6^-$ (M = W or Mo) show only one singlet in CD$_3$C(O)CD$_3$ (in CD$_2$Cl$_2$ they are insoluble) with a chemical shift typical for a coordinated phosphorus incorporated in a four-membered ring system (isomer i). Upon addition of 1 equiv of Bu$_4$N$^+$Cl$^-$ to a CD$_3$C(O)CD$_3$ solution of the Mo compound the singlet disappears and two doublets are found with the same chemical shift as those of IIa in acetone solution (isomer ii). Thus in acetone solutions of these dichloro complexes no ionic species are present, only isomer ii. The mono- and bidentate ligands are not rapidly exchanged; the solvation of the monodentate ligand by acetone molecules might be responsible for this slow interconversion and for the absence of the ionic isomer.

The proton NMR spectra (Table IV) measured in CD$_2$Cl$_2$ or CD$_3$C(O)CD$_3$ only show a N–H proton signal; the occasional absence of a N–H signal is unexplained.

The above-described reaction of Mo(CO)$_3$(PPh$_3$)$_2$Cl$_2$ with Ph$_2$PC(S)N(H)R (R = Ph, Me) can also be carried out with use of the blue Mo(CO)$_2$(PPh$_3$)$_2$Cl$_2$ as starting material. Although we did not succeed in preparing analytically pure compounds from these reactions, we have indications that not only are Ia and IIa formed in these reactions but also a considerable amount of a complex with PPh$_3$ as extra ligand. This PPh$_3$ ligand is readily lost in acetone solution, which can be observed in the ^{31}P NMR spectrum.
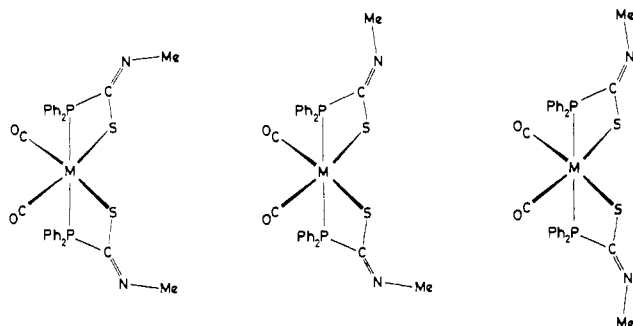
Figure 2. Different orientations of the methyl groups in $M(CO)_2$-$[Ph_2PC(S)NMe]_2$ (M = Mo, W).

b. Complexes of the Deprotonated $Ph_2PC(S)NR^-$ Ligands.

1. Preparation and Characterization. When Et_3N is added to the complexes $M(CO)_2Cl_2[Ph_2PC(S)N(H)R]_2$, abstraction of 2 mol of HCl takes place and the compounds with formula $M(CO)_2[Ph_2PC(S)NR]_2$ (M = Mo, R = Ph, IVa; M = Mo, R = Me, Va; M = W, R = Ph, IVb, M = W, R = Me, Vb) are formed. The presence of Et_3N in IVa, IVb, and Vb, designated by elemental analyses and by the proton NMR spectroscopy, must probably be assigned to coordination in the metal atom.

In the infrared spectra two carbonyl stretching frequencies are present, which are lower than those of complexes of the protonated ligands. A decreased PCS frequency and an increased $\nu(CN)$ frequency compared to those of the neutral ligand complexes indicate bidentate P,S-coordinated ligands.

The ^{31}P NMR spectra show only one singlet on a position typical for a coordinated phosphorus incorporated in a four-membered ring system.

The ^{31}P NMR spectra of the tungsten complexes show a $^1J(^{183}W-^{31}P)$ of 160 ± 5 Hz.

In the proton NMR of the methyl compounds (Va and Vb) two signals are found for the methyl protons, most likely attributed to different orientations of these methyl groups as given in Figure 2.

When $Mo(CO)_4Cl_2$ reacts with $Ph_2PC(S)N(H)R$ in the presence of Et_3N, a mixture of two products is obtained: the monomer as described above and a second complex with the same stoichiometry (for R = Me) but double the molecular weight. It was not possible to obtain pure samples of such a dimer for R = Ph. Once separated from the solution, the compound is insoluble in most solvents. The crystal structure of the methyl compound is described in the next section.

The same compounds were obtained when $Mo(CO)_3$-$(PPh_3)_2Cl_2$ was used as starting material.

From $W(CO)_3(PPh_3)_2Cl_2$ only the monomer could be obtained.

In the infrared spectra of the dimers there are two CN-stretching bands, which are attributed to two different coordinated ligands. The high $\nu(CN)$ can be ascribed to the bidentate P,S-coordinated ligand, and the low-lying CN frequency can be attributed to the bridging ligand.

In Figure 3 the ^{31}P NMR spectrum is given of VII (of VI no spectrum could be measured owing to the low solubility). In this spectrum two different phosphorus sites can be seen with a $^2J(P-P)$ of 107.3 Hz and a $^4J(P-P)$ of 4.3 Hz.

The reactions of the $Ph_2PC(S)N(H)R$ ligands in the presence of Et_3N can also be carried out with the blue $Mo(CO)_2(PPh_3)_2Cl_2$ as starting complex. Again we have indications for the formation of complexes with PPh_3 as an extra ligand. From ^{31}P NMR spectra of impure samples of this complex we conclude that in this complex the coordination around the molybdenum atom is the same as in the dimer, which leads to three different phosorus sites: one PPh_3, one P,S-coordinated ligand, and one S,N-coordinated ligand. A
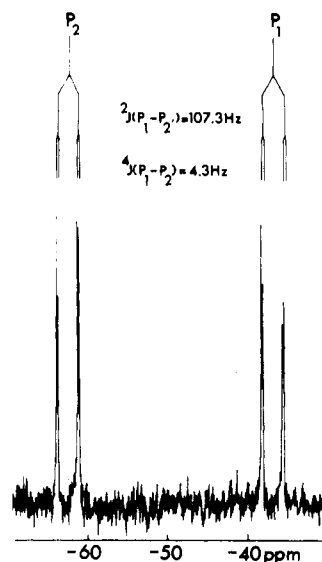

Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $[Mo(CO)_2[Ph_2PC(S)NMe]$-$[\mu\text{-}Ph_2PC(S)NMe]]_2$.
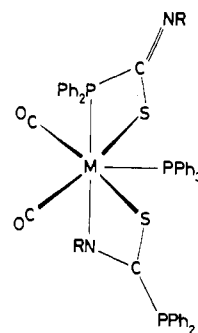
Figure 4. Possible structure for $M(CO)_2(PPh_3)[Ph_2PC(S)NR]_2$.
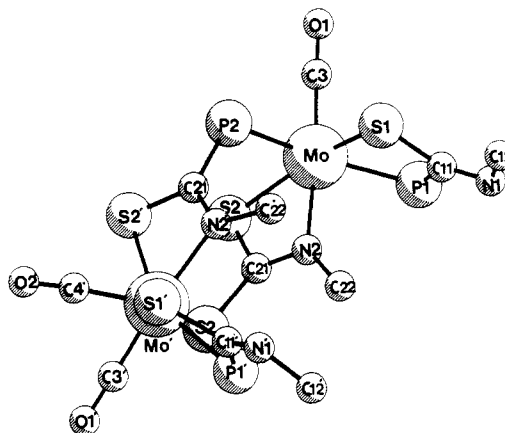
Figure 5. Molecular structure of $[Mo(CO)_2[Ph_2PC(S)NMe][\mu\text{-}Ph_2PC(S)NMe]]_2$. The phenyl groups are omitted; C4 and O2 are eclipsed by the Mo atom.

possible structure for these complexes is given in Figure 4.

2. Description of the Molecular Structure of $[Mo(CO)_2$-$[Ph_2PC(S)NMe][\mu\text{-}Ph_2PC(S)NMe]]_2$. The structure of VII is illustrated in Figure 5. The atomic coordinates and the most important bond angles and distances are given in Tables V and VI. Details about the experimental procedure and refinement can be found elsewhere.[1b] (Supplementary crystallographic materials are available on request.)

The crystal structure analysis revealed the compound to be composed of two seven-coordinated molybdenum atoms (viz. two carbonyl groups, the S and P atoms of the bidentate $Ph_2PC(S)NMe^-$ ligand, the S and N atoms of one bridging

Table II. Infrared Spectral Data[a] (cm⁻¹)

no.	compd	ν(CO)	ν(CN)	ν(PCS)	ν(PF)
Ia	$Mo(CO)_2(Ph_2PC(S)N(H)Ph)_2Cl_2$	1945 vs, 1855 vs	1543 s, 1388 s	948 m	
Ib	$W(CO)_2(Ph_2PC(S)N(H)Ph)_2Cl_2$	1928 vs, 1838 vs	1523 s, 1390 s	949 m	
IIa	$Mo(CO)_2(Ph_2PC(S)N(H)Me)_2Cl_2$	1950 vs, 1872 vs	1572 vs	948 m	
IIb	$W(CO)_2(Ph_2PC(S)N(H)Me)_2Cl_2$	1938 vs, 1857 vs	1570 vs	949 m	
IIIa	$[Mo(CO)_2(Ph_2PC(S)N(H)Me)_2Cl]^+PF_6^-$	1957 vs, 1878 vs	1580 s	912 m	837 vs
IIIb	$[W(CO)_2(Ph_2PC(S)N(H)Me)_2Cl]^+PF_6^-$	1940 vs, 1858 vs	1575 s	918 m	837 vs
IVa	$Mo(CO)_2(Ph_2PC(S)NPh)_2$	1924 vs, 1843 vs	1550 s, 1495 s	902 m	
IVb	$W(CO)_2(Ph_2PC(S)NPh)_2$	1916 vs, 1839 vs	1556 s, 1494 s	900 m	
Va	$Mo(CO)_2(Ph_2PC(S)NMe)_2$	1924 vs, 1840 vs	1575 s	928 m	
Vb	$W(CO)_2(Ph_2PC(S)NMe)_2$	1910 vs, 1820 vs	1582 s	897 m	
VI	$[Mo(CO)_2(Ph_2PC(S)NPh)_2]_2$	1953 vs, 1871 vs	1545 s, 1511 m, 1362 m, 1118 m	955 m, 920 m	
VII	$[Mo(CO)_2(Ph_2PC(S)NMe)_2]_2$	1935 vs, 1870 vs	1592 s, 1500 m, 1388 m, 1106 m	955 w, 788 m	
VIII	$Mo(CO)_3(Me_2NC(S)NPh)_2$	2008 vs, 1939 vs, 1912 vs	1542 s, 1351 s, 1198 m, 1110 m	958 w, 792 w, 798 w	
IXa	$Mo(CO)_2(PPh_3)(Me_2NC(S)NPh)_2$	1925 vs, 1824 vs	1544 s, 1358 s, 1202 m, 1108 m	785 w	
IXb	$W(CO)_2(PPh_3)(Me_2NC(S)NPh)_2$	1911 vs, 1794 vs	1550 s, 1362 s, 1206 m	790 m	

[a] Measured in CsI pellets. Abbreviations: vs = very strong, s = strong, m = medium, w = weak.
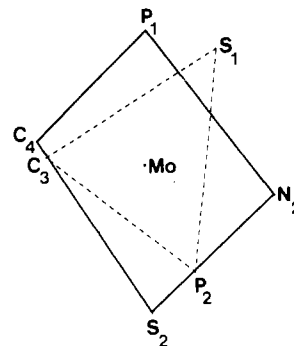
Figure 6. Projection of S(1), C(3), P(2), and Mo on the best plane through P(1), C(4), S(2), and N(2).

ligand, and the P atom of the other bridging ligand).

The Mo–C distances are the same as found for $Mo(CO)_2(PPh_3)[Ph_2P(O)C(S)NPh]_2$ in which the carbonyl groups are also in cis positions.[15] They are slightly shorter than the Mo–C distances in $Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2$ in which they are in trans positions.[16]

The average Mo–S bond distance of 2.518 Å lies in the range that is commonly found for Mo–S distances in other Mo complexes containing bidentate sulfur ligands.[15,17,18]

The Mo–P(1) distance of 2.453 Å is in the range that is commonly found for Mo(II)–P distances.[15,16,19-22] The other Mo–P distance is longer (2.607 Å), which is attributed to the repulsion between the two bridging ligands and the geometry of the eight-membered ring, where two four-membered rings are built in. The Mo–N distance of 2.25 Å lies in the range for Mo–N(sp²) bond distances. In the bidentate $Ph_2PC(S)NMe$ ligand the N, P, S, and C atoms are lying in a plane. The deviations from the least-squares plane through these atoms are as follows (in Å): 0.006 for N(1), 0.004 for S(1), 0.003 for P(1), and –0.013 for C(11). Molybdenum lies 0.58 Å from this plane. This in contrast with a Ni(II) complex in which two P- and S-coordinated $(C_6H_{11})_2PCS_2^-$ ligands are present.[23]

In this complex the Ni atom lies in the plane of the two sulfur atoms, the two phosphorus atoms, and the two carbon atoms. In the bridging ligand the Mo and P(2) atoms are 0.27 and 0.35 Å, respectively, above the plane through C(2), N(2), and S(2), which can be attributed to the repulsion caused by the other bridging ligand. The Mo–P(1)–C(11) angle is 93°, which means that the phosphorus atom P(1) has a considerably distorted tetrahedral geometry, which can be attributed to its incorporation in a four-membered ring system. For P(2) this distortion is somewhat less. The bite angle at molybdenum for the bidentate ligand is 68.2°, while the substitution of a PPh_2 group by an NMe group (which is the case for the bridging ligand) causes a decrease of this bite angle to 63.7°. This can also be seen in Rh(III) complexes of a dithiocarbamate ligand as compared with those of a thioureido ligand.[24,25]

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Table III. $^{31}P\{^{1}H\}$ NMR Spectral Data^a

no.	compd	T, K	δ^b			^2J(P-P)	$^1J(^{183}$W-^{31}P)	solvent
Ia	Mo(CO)₂(Ph₂PC(S)N(H)Ph)₂Cl₂	300	-59.78 (br)	-39.90 (S)	-36.07 (br)			CD₂Cl₂
		196	-58.68 (D)	-39.18 (S)	-35.62 (D)	16.5		CD₂Cl₂
		303	-59.47 (D)	-34.70 (D)		17.6		CD₃C(O)CD₃
Ib	W(CO)₂(Ph₂PC(S)N(H)Ph)₂Cl₂	303	-34.74 (D)	-10.84 (D)		16.1		CD₃C(O)CD₃
IIa	Mo(CO)₂(Ph₂PC(S)N(H)Me)₂Cl₂	303	-55.91 (br)	-37.32 (S)	-34.10 (br)			CD₂Cl₂
		203	-54.80 (D)	-37.07 (S)	-33.77 (D)	17.6		CD₂Cl₂
		303	-54.55 (D)	-33.38 (D)		19.0		CD₃C(O)CD₃
IIb	W(CO)₂(Ph₂PC(S)N(H)Me)₂Cl₂	303	-19.04 (D)	-18.33 (S)	-7.42 (D)	19.0	174.32	CD₂Cl₂
IIIa	[Mo(CO)₂(Ph₂PC(S)N(H)Me)₂Cl]⁺PF₆⁻	303	-35.30 (S)					CD₃C(O)CD₃
IIIb	[W(CO)₂(Ph₂PC(S)N(H)Me)₂Cl]⁺PF₆⁻	303	-23.30 (S)				175.8	CD₃C(O)CD₃
IVa	Mo(CO)₂(Ph₂PC(S)NPh)₂	303	-31.75 (S)					CD₂Cl₂
IVb	W(CO)₂(Ph₂PC(S)NPh)₂	303	-17.23 (S)				161.0	CD₂Cl₂
Va	Mo(CO)₂(Ph₂PC(S)NMe)₂	303	-30.64 (S)					CD₂Cl₂
Vb	W(CO)₂(Ph₂PC(S)NMe)₂	303	-16.30 (S)				160.5	CD₂Cl₂
VII	[Mo(CO)₂(Ph₂PC(S)NMe)₂]₂	303	-62.53 (DD)	-36.90 (DD)		107.3^c		CD₂Cl₂
IXa	Mo(CO)₂(PPh₃)(Me₂NC(S)NPh)₂	303	-51.80 (br)					CD₂Cl₂
IXb	W(CO)₂(PPh₃)(Me₂NC(S)NPh)₂	303	-32.27 (br)				d	CD₂Cl₂

^{a} δ values relative to O=P(OMe)₃, with the solvent as internal lock; upfield is positive. All J values are in Hz. ^{b} Abbreviations: br = broad, s = singlet, D = doublet, DD = doublet of doublets. ^{c} ^4J(P-P) = 4.3 Hz. ^{d} Not observed.

Table IV. ^{1}H NMR Spectral Data^a

no.	compd	δ(NMe)			δ(NH)	solvent
Ia	Mo(CO)₂(Ph₂PC(S)N(H)Ph)₂Cl₂				12.81 (br)	CD₂Cl₂
Ib	W(CO)₂(Ph₂PC(S)N(H)Ph)₂Cl₂					CD₂Cl₂
IIa	Mo(CO)₂(Ph₂PC(S)N(H)Me)₂Cl₂	3.06 (br)			12.33 (br)	CD₂Cl₂
IIb	W(CO)₂(Ph₂PC(S)N(H)Me)₂Cl₂	3.04 (br)			12.35 (br)	CD₂Cl₂
IIIa	[Mo(CO)₂(Ph₂PC(S)N(H)Me)₂Cl]⁺PF₆⁻	3.44 (S)				CD₃C(O)CD₃
IIIb	[W(CO)₂(Ph₂PC(S)N(H)Me)₂Cl]⁺PF₆⁻	3.42 (S)				CD₃C(O)CD₃
Va	Mo(CO)₂(Ph₂PC(S)NMe)₂	3.30 (S)	3.33 (S)			CD₂Cl₂
Vb	W(CO)₂(Ph₂PC(S)NMe)₂	3.30 (S)	3.22 (S)			CD₂Cl₂
VII	[Mo(CO)₂(Ph₂PC(S)NMe)₂]₂	3.25 (S)	3.23 (S)	2.68 (S)		CD₂Cl₂
VIII	Mo(CO)₃(Me₂NC(S)NPh)₂	2.66				CD₂Cl₂
IXa	Mo(CO)₂(PPh₃)(Me₂NC(S)NPh)₂	2.47 (br)				CD₂Cl₂
IXb	W(CO)₂(PPh₃)(Me₂NC(S)NPh)₂	2.62 (br D)				CD₂Cl₂

^{a} δ values relative to Me₄Si as internal standard. Abbreviations: br = broad, S = singlet, D = doublet.

Table V. Atomic Coordinates of [Mo(CO)₂[Ph₂PC(S)NMe][μ-Ph₂PC(S)NMe]]₂·CH₂Cl₂^a

	x/a (σ)	y/b (σ)	z/c (σ)		x/a (σ)	y/b (σ)	z/c (σ)
			Atomic Coordinates				
Mo	0.1496 (1)	0.2082 (1)	0.2192 (1)	N(2)	0.0458 (6)	0.1687 (6)	0.1770 (6)
S(1)	0.1769 (3)	0.0954 (2)	0.2772 (2)	C(11)	0.1936 (9)	0.0546 (9)	0.1959 (8)
S(2)	0.0599 (2)	0.2972 (2)	0.1825 (2)	C(12)	0.199 (1)	-0.057 (1)	0.242 (1)
P(1)	0.2014 (2)	0.1268 (2)	0.1359 (2)	C(21)	0.0091 (8)	0.2256 (7)	0.1682 (7)
P(2)	0.0883 (2)	0.2373 (2)	0.3382 (2)	C(22)	0.0142 (8)	0.1002 (8)	0.1657 (8)
O(1)	0.2852 (7)	0.2620 (7)	0.2951 (6)	C(3)	0.2326 (8)	0.2415 (8)	0.2673 (8)
O(2)	0.2304 (7)	0.3047 (7)	0.1174 (6)	C(4)	0.1983 (9)	0.2679 (9)	0.1533 (8)
N(1)	0.2012 (8)	-0.0087 (8)	0.1804 (8)				
			Atomic Coordinates Calculated from Refined Positional and Orientational Parameters of Constrained Groups				
C(111)	0.1605	0.1090	0.0516	C(214)	0.1024	0.4618	0.4140
C(112)	0.1296	0.1626	0.0129	C(215)	0.1338	0.4425	0.3504
C(113)	0.1010	0.1502	-0.0547	C(216)	0.1303	0.3744	0.3277
C(114)	0.1032	0.0843	-0.0836	C(221)	0.1176	0.1930	0.4185
C(115)	0.1340	0.0307	-0.0449	C(222)	0.1902	0.1868	0.4318
C(116)	0.1627	0.0431	0.0227	C(223)	0.2145	0.1590	0.4961
C(121)	0.2911	0.1330	0.1167	C(224)	0.1664	0.1376	0.5470
C(122)	0.3429	0.1327	0.1731	C(225)	0.0938	0.1438	0.5337
C(123)	0.4147	0.1425	0.1603	C(226)	0.0694	0.1711	0.4694
C(124)	0.4377	0.1529	0.0909	C(5)	0.3288	0.0445	0.3931
C(125)	0.3889	0.1532	0.0345	Cl(51)	0.3801	-0.0193	0.3660
C(126)	0.3172	0.1433	0.0474	Cl(52)	0.3671	0.1191	0.3699
C(211)	0.0951	0.3256	0.3684	C(6)	0.5341	0.3146	0.2193
C(212)	0.0636	0.3450	0.4320	Cl(61)	0.4619	0.2907	0.2745
C(213)	0.0672	0.4130	0.4548	Cl(62)	0.5292	0.4050	0.2253

^{a} The atoms C(111)-C(116) and C(121)-C(126) are the carbon atoms of the two phenyl groups attached to P(1), whereas C(211)-C(216) and C(221)-C(226) are those attached to P(2).

The two C–S distances are not signficantly different, and the average value of 1.74 Å witnesses to considerable dou-ble-bond character. Both central carbon–nitrogen distances show considerable double-bond character, while the N–Me

Table VI. Bond Distances (Å) and Angles (deg) in [Mo(CO)₂[Ph₂PC(S)NMe] [μ-Ph₂PC(S)NMe]]₂·CH₂Cl₂

Molybdenum Coordination

Mo–S(1)	2.512 (4)	Mo–S(2)	2.523 (4)	Mo–P(1)	2.453 (5)
Mo–P(2)	2.607 (4)	Mo–N(2)	2.25 (2)	Mo–C(3)	1.92 (2)
Mo–C(4)	1.95 (2)				

S(2)–Mo–C(4)	135.0 (5)	C(4)–Mo–P(2)	129.9 (5)	C(3)–Mo–P(1)	101.0 (5)
S(1)–Mo–C(3)	86.0 (5)	C(4)–Mo–S(2)	74.6 (5)	P(2)–Mo–S(2)	77.3 (2)
S(1)–Mo–P(2)	84.7 (2)	C(4)–Mo–N(2)	113.5 (6)	P(2)–Mo–N(2)	89.0 (3)
S(1)–Mo–S(2)	149.2 (2)	C(4)–Mo–P(1)	77.3 (5)	P(2)–Mo–P(1)	151.9 (2)
S(1)–Mo–N(2)	91.5 (3)	C(3)–Mo–P(2)	83.7 (5)	S(2)–Mo–N(2)	63.7 (3)
S(1)–Mo–P(1)	68.2 (2)	C(3)–Mo–S(2)	116.2 (5)	S(2)–Mo–P(1)	123.0 (2)
C(4)–Mo–C(3)	72.9 (7)	C(3)–Mo–N(2)	172.5 (6)	N(2)–Mo–P(1)	84.6 (3)

Bidentate [Ph₂PC(S)NMe]⁻ Ligand

S(1)–C(11)	1.76 (2)	P(1)–C(11)	1.82 (2)	N(1)–C(11)	1.28 (2)
N(1)–C(12)	1.49 (3)				

C(11)–N(1)–C(12)	115 (2)	Mo–S(1)–C(11)	93.2 (6)	Mo–P(1)–C(11)	93.8 (5)
P(1)–C(11)–N(1)	127 (2)	S(1)–C(11)–P(1)	102.0 (9)	S(1)–C(11)–N(1)	131 (2)

Bridging [Ph₂PC(S)NMe]⁻ Ligand

S(2)–C(21)	1.72 (2)	P(2)′–C(21)	1.86 (2)	N(2)–C(21)	1.32 (2)
N(2)–C(22)	1.48 (2)				

Mo–N(2)–C(21)	102.3 (9)	Mo–S(2)–C(21)	81.7 (5)	Mo′–P(2)′–C(21)	111.8 (5)
S(2)–C(21)–P(2)′	117.6 (8)	Mo–N(2)–C(22)	135.3 (9)	C(21)–N(2)–C(22)	122 (2)
		S(2)–C(21)–N(2)	112 (1)	P(2)′–C(21)–N(2)	129 (2)

Carbonyl Ligands

C(3)–O(1)	1.19 (2)	C(4)–O(2)	1.17 (2)
Mo–C(3)–O(1)	178 (2)	Mo–C(4)–O(2)	176 (2)
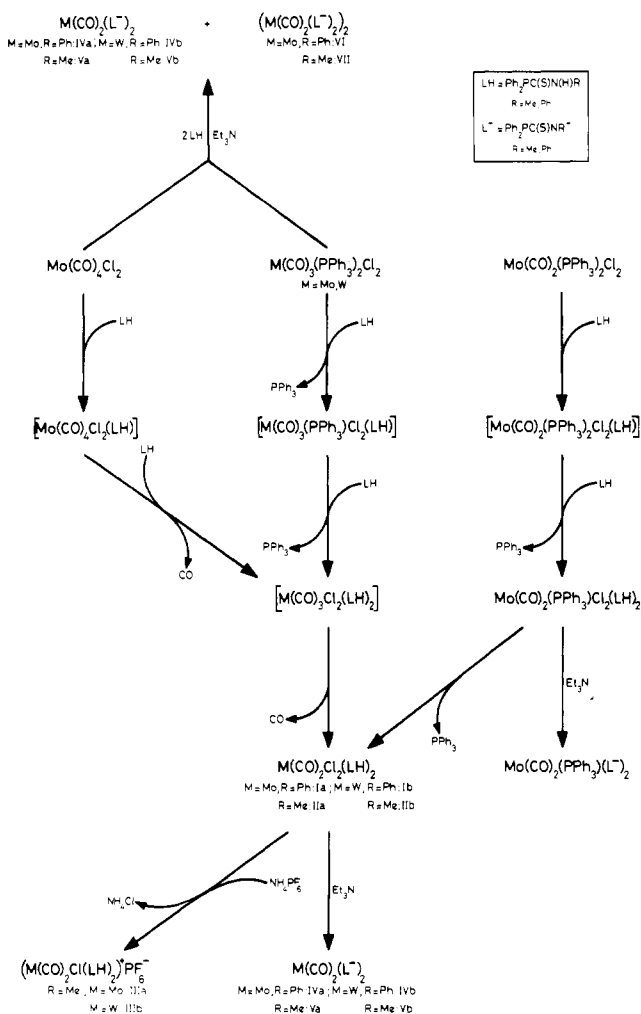
Figure 7. Formation of molybdenum and tungsten complexes with neutral and deprotonated Ph₂PC(S)N(H)R ligands.

distances are the same as one would expect for C–N single bonds.
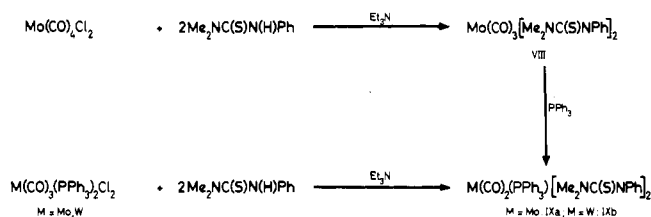
Figure 8. Preparation of [Me₂NC(S)NPh]⁻ complexes.

Because the P–C distances are the same as in Ni[(C₆-H₁₁)₂PCS₂]₂, we conclude that there is no π interaction between P(1)–C(11) and P(2)–C(21′). The geometry of the seven-coordinated centers can in a good approximation be described as a 4:3 piano-stool configuration (Figure 6).

c. Complexes of the Deprotonated Me₂NC(S)NPh⁻ Ligand: Preparation and Spectral Data. The reaction between Me₂NC(S)N(H)Ph and M(CO)₃(PPh₃)₂Cl₂ (M = Mo, W) and Et₃N produces M(CO)₂(PPh₃)[Me₂NC(S)NPh]₂ (M = Mo, IXa; M = W, IXb). From Mo(CO)₄Cl₂ the tricarbonyl complex Mo(CO)₃[Me₂NC(S)NPh]₂ is obtained. This complex reacts with PPh₃, giving Mo(CO)₂(PPh₃)[Me₂NC(S)-NPh]₂. Comparison of the infrared spectra with those of known Rh and Ir complexes of this ligand shows that in these complexes the ligands are also coordinated by sulfur and nitrogen, which means seven-coordinated M(II) complexes. The tricarbonyl molybdenum complex shows three and the dicarbonyl compounds two CO stretching bands. The ¹H NMR spectra show for VIII one sharp signal, for IXa a broad singlet, and for IXb a broad doublet for the methyl protons. These observations reveal an increasing hindered rotation around the C–NMe₂ bond on going from VIII to IXb. In the infrared spectra this is attended by an increasing value for ν(CN).

When Mo(CO)₃[Me₂NC(S)NPh]₂ in CD₂Cl₂ solution is treated with 1 equiv of PPh₃, the ³¹P NMR spectrum shows the presence of IXa. From the reactions without Et₃N no isolable products are formed. Chelate formation with neutral thiourea ligands is, in contrast to the case for the neutral
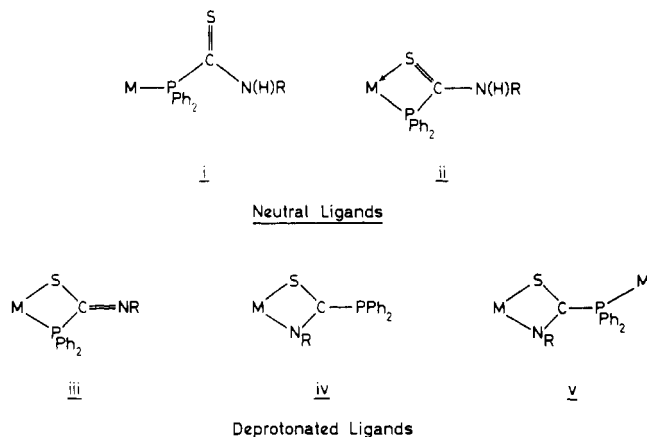
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Neutral Ligands

Deprotonated Ligands

Figure 9. Different coordination modes for the neutral and deprotonated Ph₂PC(S)N(H)R ligands.

Ph₂PC(S)N(H)R, not possible, which accounts for the absence of isolable products.

Conclusions

The reactions described are summarized in Figures 7 and 8. In this scheme the reactions of Mo(CO)₂(PPh₃)₂Cl₂ are also included. In the reaction of Mo(CO)₄Cl₂ and Mo-(CO)₂(PPh₃)₂Cl₂ with the neutral ligands the first step is probably an addition of a ligand to the six-coordinated (a 16-electron system) Mo complex, instead of a substitution of a PPh₃ group, which is probably the case in the reaction of the coordinatively saturated Mo(CO)₃(PPh₃)₂Cl₂ with these ligands. This reaction pattern gives an explanation why in the reaction with Mo(CO)₂(PPh₃)₂Cl₂ complexes with an extra PPh₃ ligand are found.

The different coordination modes found in the newly prepared compounds are summarized in Figure 9. Mo(CO)₂-(PPh₃)[Ph₂PC(S)NR]₂ and [Mo(CO)₂[Ph₂PC(S)NMe][μ-Ph₂PC(S)NMe]]₂ are the first examples in which coordination modes iv and v, respectively, are found. In the series of complexes Mo(CO)₂[Ph₂PC(S)NR]₂, Mo(CO)ₙ[R₂NC(S)S]₂ (n = 2 or 3), and Mo(CO)₃[Me₂NC(S)NPh]₂ an increasing affinity for a third CO group is manifested, indicating that the electron-donating properties of the thioureido ligand are better than those of a dithiocarbmate or Ph₂PC(S)NR⁻ ligand. The same effect is found in the CO stretching frequencies for Mo(CO)₂(η⁵-C₅H₅)(L⁻) and Rh(I)(CO)(PPh₃)(L⁻)³,⁷ (where L⁻ = Me₂NC(S)NPh⁻, Me₂NC(S)S⁻, and Ph₂PC(S)NPh⁻). The lowest CO frequencies are found for the thioureido complexes. Complexes of the neutral thiourea ligands could not be prepared. This can be ascribed to their poor chelate ability in contrast with that of the Ph₂PC(S)N(H)R ligands, from which isolable compounds are found.

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Preparation, Properties, and Structural Studies of Molybdenum and Tungsten Complexes with [Ph₂P(S)C(S)NR]⁻ (R = Me, Ph) or Ph₂PS⁻ Ligands. X-ray Structure Analysis of Mo(CO)₂(η⁵-C₅H₅)[Ph₂P(S)C(S)NPh]¹

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M(CO)₃(η⁵-C₅H₅)Cl (M = Mo, W) reacts with Ph₂P(S)C(S)N(H)R (R = Ph, Me) and a base to yield three different products depending on reaction time and temperature. At room temperature complexes of composition M(CO)₂(η⁵-C₅H₅)[Ph₂P(S)C(S)NR] are obtained, in which the ligands are coordinated by both sulfur atoms. At higher temperature mixtures are obtained of M(CO)₂(η⁵-C₅H₅)[Ph₂P(S)C(S)NR] (M = Mo, R = Ph, Me; M = W, R = Me), in which the ligand is coordinated through S(C) and N, and M(CO)₂(η⁵-C₅H₅)(η²-SPPh₂) (M = Mo, W). The last complexes can also be prepared from M(CO)₃(η⁵-C₅H₅)Cl in a direct reaction with SPPh₂H and Et₃N. M(CO)₃(PPh₃)₂Cl₂ (M = Mo, W) reacts with 2 equiv of Ph₂P(S)C(S)N(H)Ph in the presence of a base to form M(CO)₂(PPh₃)[Ph₂P(S)C(S)NPh]₂, in which the ligands show a dynamic behavior with respect to the coordinating mode. The starting complexes react with SPPh₂H and Et₃N to M(CO)₂(PPh₃)(η²-SPPh₂)₂. Under similar conditions Mo(CO)₄Cl₂ gives Mo(CO)₃(η²-SPPh₂)₂. The complexes are characterized by means of elemental analyses, infrared spectroscopy, and ¹H and ³¹P NMR spectroscopy. The X-ray structure analysis of Mo(CO)₂(η⁵-C₅H₅)[Ph₂P(S)C(S)NPh] is presented: a = 10.390 (4) Å, b = 14.328 (5) Å, c = 9.602 (3) Å, α = 73.02 (2)°, β = 108.49 (2)°, and γ = 112.39 (2)° in space group P1̄ and Z = 2.

Introduction

Sulfur-containing molecules coordinated to Mo and W are of interest because of their proposed similarity to enzymatic and catalytic systems. Unsaturated anions of the type SC-

(X)Y⁻ are called pseudo or hetero allyls because of their structural and electronic relation with the allyl anion. Also Ph₂P(X)C(S)NR⁻ (X = S, O) can be classified in this category. The preparation and coordination properties of these compounds toward Rh and Ir have been described.²,³ They

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