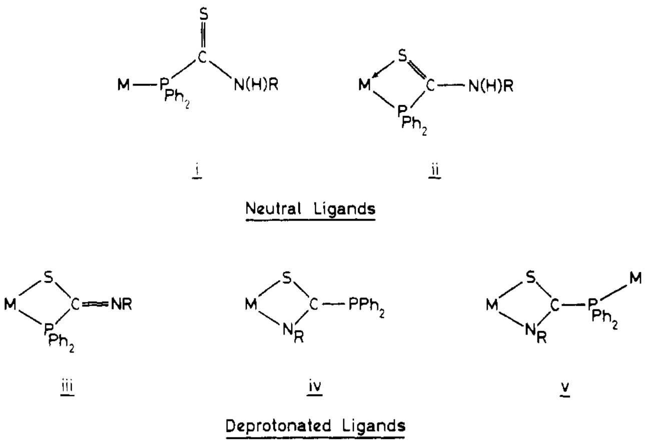

Figure 9. Different coordination modes for the neutral and deprotonated $Ph_2PC(S)N(H)R$ ligands.

$Ph_2PC(S)N(H)R$, 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 $Mo(CO)_2(PPh_3)_2Cl_2$ are also included. In the reaction of $Mo(CO)_4Cl_2$ and $Mo(CO)_2(PPh_3)_2Cl_2$ 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 PPh_3 group, which is probably the case in the reaction of the coordinatively saturated $Mo(CO)_3(PPh_3)_2Cl_2$ with these ligands. This reaction pattern gives an explanation why in the reaction with $Mo(CO)_2(PPh_3)_2Cl_2$ complexes with an extra PPh_3 ligand are found.

The different coordination modes found in the newly prepared compounds are summarized in Figure 9. $Mo(CO)_2(PPh_3)[Ph_2PC(S)NR]_2$ and $[Mo(CO)_2[Ph_2PC(S)NMe][\mu\text{-}Ph_2PC(S)NMe]]_2$ are the first examples in which coordination modes iv and v, respectively, are found. In the series of complexes $Mo(CO)_2[Ph_2PC(S)NR]_2$, $Mo(CO)_n[R_2NC(S)S]_2$ ($n = 2$ or 3), and $Mo(CO)_3[Me_2NC(S)NPh]_2$ 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 $Ph_2PC(S)NR^-$ ligand. The same effect is found in the CO stretching frequencies for $Mo(CO)_2(\eta^5\text{-}C_5H_5)(L^-)$ and $Rh(I)(CO)(PPh_3)(L^-)$[3,7] (where $L^- = Me_2NC(S)NPh^-$, $Me_2NC(S)S^-$, and $Ph_2PC(S)NPh^-$). 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 $Ph_2PC(S)N(H)R$ ligands, from which isolable compounds are found.

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Registry No. Ia, 74594-46-0; Ib, 90839-24-0; IIa, 90839-25-1; IIb, 90839-26-2; IIIa, 90839-28-4; IIIb, 90839-30-8; IVa, 90839-31-9; IVb, 90839-32-0; Va, 90839-33-1; Vb, 90839-34-2; VI, 90839-35-3; VII, 90839-37-5; VIII, 90839-38-6; IXa, 90839-39-7; IXb, 90839-40-0; $Mo(CO)_4Cl_2$, 15712-13-7; $Mo(CO)_3(PPh_3)_2Cl_2$, 17250-39-4; $W(CO)_3(PPh_3)_2Cl_2$, 18130-04-6.

Supplementary Material Available: Listings of structure factors and thermal parameters and derived coordinates for hydrogen atoms and a stereoview for $Mo(CO)_2[Ph_2PC(S)NMe][\mu\text{-}Ph_2PC(S)NMe]]_2 \cdot CH_2Cl_2$ (28 pages). Ordering information is given on any current masthead page.

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Preparation, Properties, and Structural Studies of Molybdenum and Tungsten Complexes with $[Ph_2P(S)C(S)NR]^-$ (R = Me, Ph) or Ph_2PS^- Ligands. X-ray Structure Analysis of $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$[1]

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$M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W) reacts with $Ph_2P(S)C(S)N(H)R$ (R = Ph, Me) and a base to yield three different products depending on reaction time and temperature. At room temperature complexes of composition $M(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NR]$ are obtained, in which the ligands are coordinated by both sulfur atoms. At higher temperature mixtures are obtained of $M(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NR]$ (M = Mo, R = Ph, Me; M = W, R = Me), in which the ligand is coordinated through S(C) and N, and $M(CO)_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}SPPh_2)$ (M = Mo, W). The last complexes can also be prepared from $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ in a direct reaction with $SPPh_2H$ and Et_3N. $M(CO)_3(PPh_3)_2Cl_2$ (M = Mo, W) reacts with 2 equiv of $Ph_2P(S)C(S)N(H)Ph$ in the presence of a base to form $M(CO)_2(PPh_3)[Ph_2P(S)C(S)NPh]_2$, in which the ligands show a dynamic behavior with respect to the coordinating mode. The starting complexes react with $SPPh_2H$ and Et_3N to $M(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2$. Under similar conditions $Mo(CO)_4Cl_2$ gives $Mo(CO)_3(\eta^2\text{-}SPPh_2)_2$. The complexes are characterized by means of elemental analyses, infrared spectroscopy, and ^1H and ^{31}P NMR spectroscopy. The X-ray structure analysis of $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ is presented: $a = 10.390$ (4) Å, $b = 14.328$ (5) Å, $c = 9.602$ (3) Å, $\alpha = 73.02$ (2)°, $\beta = 108.49$ (2)°, and $\gamma = 112.39$ (2)° in space group $P\bar{1}$ 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 $Ph_2P(X)C(S)NR^-$ (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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(1) Preliminary results have been published: Ambrosius, H. P. M. M.; Noordik, J. H.; Ariaans, G. J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 832.

(2) Thewissen, D. H. M. W.; Ambrosius, H. P. M. M.; van Gaal, H. L. M.; Steggerda, J. J. *J. Organomet. Chem.* **1980**, *192*, 101.

0020-1669/84/1323-2678$01.50/0

Table I. Elemental Analyses and Molecular Weight Determinations (Calculated Values in Parentheses)

no.	compd	% C	% H	% N	% S	% P	mol wt
Ia	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NPh)$	54.5 (54.8)	3.7 (3.5)	2.6 (2.5)			
Ib	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NPh)$	54.8 (54.8)	3.6 (3.5)	2.5 (2.5)			556 (574)[a]
IIa	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NMe)$	49.9 (49.7)	3.6 (3.6)	2.8 (2.8)			
IIb	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NMe)$	49.5 (49.7)	3.6 (3.6)	2.8 (2.8)			
III	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NPh)$	47.2 (47.5)	3.1 (3.1)	2.2 (2.1)			
IVa	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NMe)$	42.3 (42.4)	3.1 (3.1)	2.4 (2.4)			
IVb	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NMe)$	42.4 (42.4)	3.1 (3.1)	2.4 (2.4)			
V	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(SPPh_2)$	52.7 (52.6)	3.4 (3.5)	...			449 (434)[b]
VI	$W(CO)_2(\eta^5\text{-}C_5H_5)(SPPh_2)$	44.0 (43.7)	2.9 (2.9)	...			
VII	$Mo(CO)_2(PPh_3)(Ph_2P(S)C(S)NPh)_2\cdot CH_2Cl_2$[c]	58.9 (58.9)	4.0 (3.9)	2.5 (2.3)			
VIII	$W(CO)_2(PPh_3)(Ph_2P(S)C(SONPh)_2\cdot CH_2Cl_2$[c]	54.7 (54.9)	3.7 (3.7)	2.2 (2.2)			
IX	$Mo(CO)_2(PPh_3)(SPPh_2)_2\cdot CH_2Cl_2$[c]	57.8 (57.9)	3.9 (4.0)	...	7.4 (6.9)	10.8 (10.0)	820 (821)[a]
X	$W(CO)_2(PPh_3)(SPPh_2)_2$	56.2 (56.4)	3.9 (3.8)	...			
XI	$Mo(CO)_3(SPPh_2)_2\cdot C_6H_6$	57.0 (57.2)	3.8 (3.8)	...	9.3 (9.3)	8.9 (9.0)	680 (692)

[a] Determined osmometrically in CH_2Cl_2. [b] Determined osmometrically in toluene. [c] The presence of CH_2Cl_2 in these complexes was confirmed by ^1H NMR.

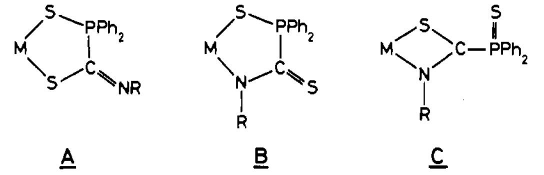

Figure 1. Different coordination possibilities for $Ph_2P(S)C(S)NR^-$.

are ambidentate; their different coordination modes are given in Figure 1 for $Ph_2P(S)C(S)NR^-$.

The preparation and properties of Mo and W complexes of the latter anion are described in this paper. Complexes of this ligand might lose RNCS, leaving Ph_2PS bonded to the metal. Only a few examples are known of this interesting small ligand bonded to a metal. It is known to coordinate end-on in Rh and Ir complexes[4] or to bridge between two metal atoms via sulfur and phosphorus.[5-8] Recently the first examples of side-on-bonded $SPPh_2^-$ were reported for some Rh complexes,[3] and Lindner assumes a side-on-bonded $SPMe_2^-$ as an intermediate in the reaction of $[(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}SPMe_2)]_2$ with acetylenes.[8]

The $SPPh_2$ complexes described in this paper all have side-on-bonded $SPPh_2^-$ ligands.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer. The ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WH-90-FT spectrometer. Elemental analyses were performed in the microanalytical department of this university (C, H, and N) or by Prof. Dipl. Ing. Dr. H. Malissa G. Reuter, Analytische Laboratorien, Elbach über Engelskirchen, West Germany, who also performed the molecular weight determinations.

Preparations. All preparations were carried out under a pure nitrogen atmosphere with use of standard Schlenk techniques.

$Mo(CO)_3(PPh_3)_2Cl_2$,[9] $W(CO)_3(PPh_3)_2Cl_2$,[10] $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ (M = Mo, W),[11] $Ph_2P(S)C(S)N(H)R$ (R = Ph, Me),[12] and $SPPh_2H$[13] were prepared as described in the literature.

$M(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ (M = Mo, Ia; M = W, III). One millimole of $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$, 1 mmol of $Ph_2P(S)C(S)N(H)Ph$, and 1.2 mmol of KOH were dissolved in 100% ethanol. After a few hours the mixture was evaporated to dryness under reduced pressure. The residue was chromatographed on a silica column (width 1.5 cm, length 75 cm) with CH_2Cl_2/*n*-hexane as eluent. ((6–3):1). Recrystallization from CH_2Cl_2/*n*-hexane gave very dark red crystals, yield 60%.

$Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ (Ib). One millimole of $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ (Ia) was refluxed for $1^1/_2$ h in 25 mL of benzene. After cooling of the solution to room temperature and evaporation of the solvent under reduced pressure the mixture was chromatographed on a silica column with CH_2Cl_2/*n*-hexane ((4–1):1) as eluent. The first fraction was the red $Mo(CO)_2(\eta^5\text{-}C_5H_5)(SPPh_2)$ (V), the second was the red starting material (Ia), and the last was orange $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ (Ib) in 20% yield. Suitable crystals for the X-ray structure analysis were obtained from a CH_2Cl_2/*n*-hexane solution of the last compound.

$M(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NMe]$ (M = Mo, IIa; M = W, IVa). One millimole of $M(CO)_3(\eta^5\text{-}C_5H_5Cl)$, 1 mmol of the ligand, and 1.2 mmol of KOH were dissolved in 100% ethanol. The mixture was stirred for 20 h. The product precipitated together with a small amount of KCl. The product was dissolved in CH_2Cl_2, and KCl was filtered off. After *n*-hexane was added to the solution, the product crystallized in dark red needles, yield 70%.

$M(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NMe]$ (M = Mo, IIb; M = W, IVb). One millimole of $M(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NMe]$ (M = Mo, IIa; M = W, IVa) was refluxed for 2 h in benzene. After cooling of the solution to room temperature and evaporation of the solvent under reduced pressure the mixture was chromatographed on a silica column with CH_2Cl_2/hexane (3:1) as eluent. Two fractions could be collected. The first was the red $M(CO)_2(\eta^5\text{-}C_5H_5)(SPPh_2)$ (M = Mo, V; M = W, VI), the second was IIb and IVb, respectively. The yields were 20% for IIb and 40% for IVb.

$M(CO)_2(\eta^5\text{-}C_5H_5)(SPPh_2)$ (M = Mo, V; M = W, VI). $SPPh_2H$ (1 mmol) and $M(CO_3(\eta^5\text{-}C_5H_5)Cl$ (1 mmol) were refluxed with an excess of Et_3N in benzene for 4 h. Et_3NHCl was filtered off, and the red products were separated with *n*-hexane; yield 75%.

$M(CO)_2(PPh_3)[Ph_2P(S)C(S)NPh]_2$ (M = Mo, VII; M = W, VIII). To a suspension of 1 mmol of $M(CO)_3(PPh_3)_2Cl_2$ in benzene were added 2 mmol of $Ph_2P(S)C(S)N(H)Ph$ and an excess of Et_3N. The color changed slowly from yellow to red-brown. After 20 h the Et_3NHCl was filtered off and the product was precipitated by addition of *n*-hexane. Recrystallization from CH_2Cl_2/*n*-hexane gave red crystals, yield 75%.

$M(CO)_2(PPh_3)(SPPh_2)_2$ (M = Mo, IX; M = W, X). A suspension of $M(CO)_3(PPh_3)_2Cl_2$ in benzene was stirred with 2 equiv of $SPPh_2H$ and an excess of Et_3N for 4 h. The Et_3NHCl was filtered off, the solution evaporated to dryness, and the product recrystallized from CH_2Cl_2/*n*-hexane; yield 80%.

$Mo(CO)_3(SPPh_2)_2$ (XI). A solution of $SPPh_2H$ (2 mmol) in C_6H_6 was added to solid $Mo(CO)_4Cl_2$ (1 mmol). The color turned to brown-red, and carbon monoxide was evolved. Two millimoles of Et_3N was added to the reaction mixture, and Et_3NHCl precipitated. After the Et_3NHCl was filtered off and *n*-hexane was added to the solution, orange crystals of the product was obtained; yield about 40%.

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Table II. Infrared Spectral Data (Absorptions Given in cm^{-1})[a]

no.	compd	$\nu(CO)$[b]		$\nu(CN)$[c]		$\nu(PCS)$[c]	$\nu(PS)$[c]	$\nu(MS)$[c]
Ia	$\mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(\mathit{S})C(\mathit{S})NPh)}$	1958 vs	1866 s	1508 s		948 m	568 s	
Ib	$\mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(\mathit{S})\mathit{N}Ph)}$	1960 vs	1878 s	1490 s		...	635 s	
IIa	$\mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(\mathit{S})C(\mathit{S})NMe)}$	1954 vs	1862 s	1535 s		948 m	519 s	
IIb	$\mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(\mathit{S})\mathit{N}Me)}$	1960 vs	1876 s	1502 m		...	658 s	
III	$\mathrm{W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(\mathit{S})C(\mathit{S})NPh)}$	1943 vs	1846 s	1507 s		947 m	565 m	
IVa	$\mathrm{W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(\mathit{S})C(\mathit{S})NMe)}$	1940 vs	1842 s	1535 s		949 m	518 s	
IVb	$\mathrm{W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(\mathit{S})\mathit{N}Me)}$	1950 vs	1859 s	1492 m		...	662 s	
V	$\mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)(SPPh_2)}$	1954 vs	1870 s				514 s	
VI	$\mathrm{W(CO)_2(\eta^5\text{-}C_5H_5)(SPPh_2)}$	1942 vs	1852 s				520 s	
VII	$\mathrm{Mo(CO)_2(PPh_3)(Ph_2P(S)C(S)NPh)_2}$	1948 s	1865 vs	1536 m	1494 m	936 w	514 s	
VIII	$\mathrm{W(CO)_2(PPh_3)(Ph_2P(S)C(S)NPh)_2}$	1938 s	1850 vs	1540 m	1492 m	935 w	514 s	
IX	$\mathrm{Mo(CO)_2(PPh_3)(SPPh_2)_2}$	1947 m	1871 vs				532 s	372 m
X	$\mathrm{W(CO)_2(PPh_3)(SPPh_2)_2}$	1923 w	1852 vs				530 s	384 m
XI	$\mathrm{Mo(CO)_3(SPPh_2)_2}$	2030 w	1932 vs				552 s	341 s

[a] Abbreviations: vs = very strong, s = strong, m = medium, w = weak. [b] Measured in CH_2Cl_2 solution except for VII and VIII, which were measured in CsI pellets. [c] Measured in CsI pellets.

Table III. ^1H NMR Spectral Data[a]

no.	compd	$\delta(C_5H_5)$	$\delta(CH_3)$	solvent
Ia	$\mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(\mathit{S})C(\mathit{S})NPh)}$	4.68		C_7D_8
Ib	$\mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(\mathit{S})\mathit{N}Ph)}$	4.78		C_7D_8
IIa	$\mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(\mathit{S})C(\mathit{S})NMe)}$	4.72	3.60 (D)[b]	C_7D_8
IIb	$\mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(\mathit{S})\mathit{N}Me)}$	4.74	3.43 (D)[c]	C_7D_8
III	$\mathrm{W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(\mathit{S})C(\mathit{S})NPh)}$	5.28		CD_2Cl_2
IVa	$\mathrm{W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(\mathit{S})C(\mathit{S})NMe)}$	4.81	3.59 (D)[b]	C_7D_8
IVb	$\mathrm{W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(\mathit{S})\mathit{N}Me)}$	4.78	3.49 (D)[c]	C_7D_8
V	$\mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)(SPPh_2)}$	4.77		C_7D_8
VI	$\mathrm{W(CO)_2(\eta^5\text{-}C_5H_5)(SPPh_2)}$	4.79		C_7D_8

[a] δ values relative to Me_4Si as internal standard; D = doublet. [b] $^4J(^1H-^{31}P) = 3.90$ Hz. [c] $^4J(^1H-^{31}P) = 1.47$ Hz.

Products V and VI can also be prepared by the reaction of $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ with $Ph_2P(S)C(S)N(H)R$ in the presence of Et_3N at 80 °C. The yields are about 50%.

Elemental analyses and molecular weight determinations are given in Table I.

Crystal Structure Determinations of $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ (Ib) and $Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPH_2)_2\cdot CH_2Cl_2$ (IX). The experimental details of the crystal structure determination and refinement of IX can be found elsewhere;[1] those of Ib are given below.

(a) Collection and Reduction of Crystallographic Data. Crystallographic data of a crystal of 0.3 × 0.25 × 0.3 mm were collected on a single-crystal CAD4 diffractometer using Mo Kα radiation ($\lambda = 0.71069$ Å) monochromated with a graphite-crystal monochromator. The unit cell dimensions were calculated from the setting angles of 25 reflections having $30° < 2\theta < 40°$. The lattice constants are $a = 10.390$ (4) Å, $b = 14.328$ (5) Å, $c = 9.602$ (3) Å, $\alpha = 73.02$ (2)°, $\beta = 108.49$ (2)°, $\gamma = 112.39$ (2)°, and $V = 1229.5$ Å^3 in space group $P\bar{1}$, with $\rho_{calcd} = 1.54$ g cm^{-3}, $Z = 2$, and linear absorption coefficient $\mu(Mo) = 7.8$ cm^{-1}. The data were collected with use of the ω–2θ scan mode with a variable scan speed, with a maximum of 40 s/reflection. A total of 5287 reflections with $2° < \theta < 21°$ were recorded ($\pm h,\pm k,+l$). Three standard reflections were measured after every 1800 s of X-ray exposure time. Their intensities remained constant within 1%. After equivalent reflections were averaged (R_{av} [=[$\sum||I|$ − $|\bar{I}||]/|\sum|I|]$] = 0.012, including all reflections), 2645 reflections remained, of which 2356 had $I > 3\sigma(I)$ ($\sigma(I)$ based on counting statistics). The intensity data of the remaining 2356 reflections were corrected for Lorentz and polarization effects and then reduced to $|F_o|$ values. Correction of the data for absorption was not considered to be necessary.

(b) Solution and Refinement of the Structure. The structure was solved with use of a Patterson synthesis to find the position of the molybdenum atom. The remaining non-hydrogen atoms were positioned by the DIRDIF procedure.[14]

All 2356 observed reflections were used in the refinement by the full-matrix least-squares method, allowing anisotropic temperature factors for the molybdenum, sulfur, and phosphorus atoms. The positional parameters of the hydrogen atoms were calculated. All hydrogen atoms were assigned a fixed isotropic temperature factor of 5 Å^2.

The weight for each reflection was calculated according to the formula $w = [\sigma^2(I) + 0.004F^2]^{-1}$ ($\sigma(I)$ based on counting statistics). The refinement converged to a conventional R value ($=\sum(|F_o| - |F_c|)^2/|\sum|F_o|$) of 0.048 and $R_w(=[\sum w(|F_o| - |F_c|)^2/|w|F_o|^2]^{1/2}) = 0.069$, based on 153 variables. A final difference Fourier map showed a residual electron density of 0.89 e/Å^3 near the cyclopentadienyl ligand. Other peaks were below 0.5 e/Å^3. The atomic scattering factors were taken from ref 15. All crystallographic calculations were performed with use of the X-RAY-76 program.[16] Positional parameters are listed in Table V and bond distances and angles in Table VI. The numbering of the atoms is shown in Figure 10. Observed and calculated structure factors are available. Temperature factors of the non-hydrogen atoms are listed in supplementary material.

Results and Discussion

(a) $M(CO)_2(C_5H_5)[Ph_2P(S)C(S)NR]$. The reaction of $M(CO)_3(C_5H_5)Cl$ (M = Mo, W) with $Ph_2P(S)C(S)N(H)R$ (R = Ph, Me) and KOH at room temperature in ethanol yields products that give analysis corresponding to $M(CO)_2(C_5H_5)[Ph_2P(S)C(S)NR]$ (M = Mo, R = Ph, Ia; M = Mo, R = Me, IIa; M = W, R = Ph, III; M = W, R = Me, IVa).

In the infrared spectra (Table II) of all compounds two absorption bands are found in the carbonyl stretching region; the band at lowest frequency is also of lowest intensity, which means that both carbonyl groups are coordinated in cis positions.[17]

In the spectra of the $Ph_2P(S)C(S)NR^-$ complexes three ligand vibration bands can give an indication about the mode

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Table IV. $^{31}P\{^1H\}$ NMR Spectral Data[a]

no.	compd	δ(ligand)		δ(PPh$_3$)	$^1J(^{183}W-^{31}P)$	solvent
Ia	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NPh)$	−38.21				CH_2Cl_2
Ib	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NPh)$	−35.39				CD_2Cl_2
IIa	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NMe)$	−34.91				CH_2Cl_2
IIb	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NMe)$	−32.18				CH_2Cl_2
III	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NPh)$	−36.85				CH_2Cl_2
IVa	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NMe)$	−33.34				CH_2Cl_2
IVb	$W(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(S)C(S)NMe)$	−38.14				CH_2Cl_2
V	$Mo(CO)_2(\eta^5\text{-}C_5H_5)(SPPh_2)$	−46.40				C_6D_6
VI	$W(CO)_2(\eta^5\text{-}C_5H_5)(SPPh_2)$	−10.92			233.6	C_6D_6
VII	$Mo(CO)_2(PPh_3)(Ph_2P(S)C(S)NPh)_2$	−36.23	−34.02 (br)[b]	−72.72 (br)[b]		CD_2Cl_2
VIII	$W(CO)_2(PPh_3)(Ph_2P(S)C(S)NPh)_2$	−38.40	−33.98	−39.65		CD_2Cl_2
IX	$Mo(CO)_2(PPh_3)(SPPh_2)_2$	−64.46 (D)[b,c]		−42.65 (T)[b,c]		C_6D_6
X	$W(CO)_2(PPh_3)(SPPh_2)_2$	−34.04		−24.40	195 resp 265	C_6D_6
XI	$Mo(CO)_3(SPPh_2)_2$	−58.10[d]				C_6H_6

[a] δ values relative to $O{=}P(OMe)_3$ (TMP), with external ^{19}F lock or the deuterated solvent as internal lock. All J values are in Hz. [c] Abbreviations: br = broad, D = doublet, T = triplet. [c] $^2J(^{31}P-^{31}P) = 3.75$ Hz. [d] Measured on a Varian XL-100 spectrometer with ^{19}F external lock.

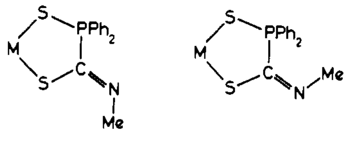
Table V. Positional Parameters with Esd's in Parentheses

	x	y	z
Mo	0.29873 (6)	0.30707 (5)	0.72547 (7)
S(1)	0.0769 (2)	0.1569 (2)	0.6905 (2)
S(2)	−0.2374 (2)	0.3107 (2)	0.3387 (3)
P	−0.1447 (2)	0.2055 (2)	0.4010 (2)
N	0.1392 (6)	0.3273 (4)	0.5192 (6)
O(1)	0.4424 (8)	0.1361 (6)	0.8131 (8)
O(2)	0.4971 (7)	0.3809 (5)	0.5039 (8)
C	0.0324 (7)	0.2404 (5)	0.5284 (7)
C(1)	0.3832 (9)	0.1999 (7)	0.7771 (9)
C(2)	0.4221 (9)	0.3549 (6)	0.5871 (9)
C(111)	0.1416 (7)	0.4115 (5)	0.3923 (7)
C(112)	0.1380 (8)	0.5023 (6)	0.4082 (8)
C(113)	−0.1437 (9)	0.4162 (7)	−0.287 (1)
C(114)	−0.1529 (9)	0.4252 (7)	−0.153 (1)
C(115)	−0.1603 (9)	0.5152 (7)	−0.140 (1)
C(116)	0.1551 (8)	0.4019 (6)	0.2599 (8)
C(121)	0.227 (1)	0.3350 (7)	0.917 (1)
C(122)	0.2491 (9)	0.4254 (7)	0.816 (1)
C(123)	0.389 (1)	0.4614 (7)	0.806 (1)
C(124)	0.456 (2)	0.3898 (9)	0.910 (2)
C(125)	0.349 (2)	0.3117 (8)	0.975 (2)
C(211)	−0.2408 (7)	0.0856 (5)	0.5072 (7)
C(212)	−0.3087 (8)	0.0904 (6)	0.6073 (8)
C(213)	−0.6128 (9)	0.0010 (6)	0.3128 (9)
C(214)	−0.6017 (9)	0.0927 (6)	0.3342 (9)
C(215)	−0.3322 (9)	−0.0977 (6)	0.5651 (9)
C(216)	−0.2522 (8)	−0.0087 (6)	0.4861 (8)
C(221)	−0.1221 (7)	0.1680 (5)	0.2486 (7)
C(222)	−0.0087 (8)	0.1348 (6)	0.2637 (8)
C(223)	0.0009 (8)	0.1031 (6)	0.1447 (9)
C(224)	−0.1017 (9)	0.1043 (7)	0.0138 (9)
C(225)	−0.213 (1)	0.1368 (7)	−0.002 (1)
C(226)	−0.2254 (8)	0.1690 (6)	0.1148 (8)

of coordination of the ligands. A high ν(CN) indicates a considerable double-bond character in the CNR bond, which is expected when the nitrogen atom is not coordinated to the central metal atom. In Rh(I), Rh(III), and Ir(I) complexes of these ligands, in which S,S coordination is assumed, ν(CN) is 1509–1529 cm^{-1} compared with 1533 cm^{-1} for the free ligand. In these complexes a band at about 950 cm^{-1} is assigned to ν(PCS). Finally the P═S stretching frequency could give an indication about the coordination mode, but this band is often difficult to assign. In the free ligand this band is found at 639 cm^{-1} and in the Rh and Ir complexes at about 510 cm^{-1}.

When the ligand vibration bands, given in Table II, are compared with those of the known Rh and Ir complexes, it is clear that in Ia, IIa, III, and IVa a S,S coordination must be assumed.

In the proton NMR spectra of IIa and IVa the methyl signal appears as a doublet. Measurements of the spectra of 90 and 200 MHz showed that the doublet arises from a $^1H-^{31}P$ coupling. Temperature-dependent measurements from −90 to +80 °C show no broadening of the doublet, indicating that in this temperature range only one of the two rotamers i and ii exists in solution. (see Figure 2). For reasons of steric hindrance we think that rotamer i is the most stable one.



i ii

Figure 2. Different orientations of the methyl group for a S,S-coordinated $Ph_2P(S)C(S)NMe^-$ ligand.

(b) Elimination of RNCS from $M(CO)_2(C_5H_5)[Ph_2P(S)C(S)NR]$ To Give $SPPh_2$ Complexes. When the reaction of $M(CO)_3(C_5H_5)Cl$ with $Ph_2P(S)C(S)N(H)R$ and KOH is performed at 80 °C, other products are obtained, which have the composition $M(CO)_2(C_5H_5)(SPPh_2)$ (M = Mo, V; M = W, VI). For R = Me the heating also yields a product with the same analysis as IIa and IVa, respectively, but with different properties (M = Mo, IIb; M = W, IVb). These kinds of products can also be obtained for R = Ph when the reaction mixture is cooled down after $1^1/_2$ h and only in the case of M = Mo (Ib).

Refluxing a solution of Ia, IIa, or Ib for about 6 h results in the case of Ia and Ib in the formation of V and in the case of IIa in the formation of a mixture of V and IIb. Compound IB is stable at 80 °C. Refluxing of a solution of III gives VI and some unidentified products, and refluxing a solution of IVa yields a mixture of VI and IVb. The $SPPh_2$ complexes can also be prepared in a direct reaction of $SPPh_2H$, Et_3N, and $M(CO)_3(\eta^5\text{-}C_5H_5)Cl$ in refluxing benzene. The above-described reactions are summarized in Figure 3. The $SPPh_2$ complexes are stable and do not react with RNCS. This is in contrast with Rh(I)–$SPPh_2$ complexes, which insert PhNCS in $Rh[Ph_2P(S)C(S)NPh]$ compounds.[2]

In the infrared spectra of Ib, IIb, and IVb low CN-stretching frequencies, no PCS band at 950 cm^{-1}, and a high ν(PS) are found. These observations lead to the conclusion that N and S(C) must be coordinated to the central atom.

In the proton NMR spectra of IIb and IVb a doublet is found that must be ascribed to a proton–phosphorus coupling that is much smaller than in the case of IIa and IVa. This coupling has the same value as $^4J(^1H-^{31}P)$ of $M(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(O)C(S)NMe]$, in which the ligand is also assumed to be coordinated through N and S in a four-membered ring system.[18]

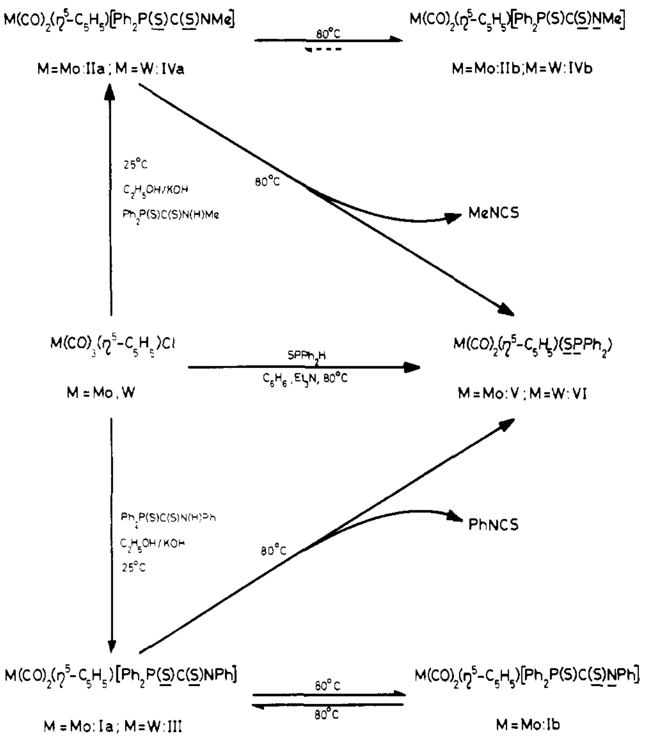


Figure 3. Preparation and reactivity of cyclopentadienyl-containing complexes of molybdenum and tungsten with $Ph_2P(S)C(S)NR^-$ and $SPPh_2^-$ ligands (assumed coordinating atoms are underlined).

The reaction pathway from compound Ia, in which the ligand is S,S coordinated, or from Ib, in which the ligand is S,N coordinated in a four-membered ring system, to the final product V can both be followed by means of ^{31}P or ^{1}H NMR spectroscopy at 80 °C. In Figure 4 an example is given of a series of ^{31}P NMR spectra taken at different moments after the start at 80 °C of the reaction of Ia to Ib and V. Starting from pure Ib the first new signal that appears in the ^{31}P NMR spectra at 80 °C is that of Ia. The conversion of Ia to Ib is reversible at this temperature. Both reactions were followed by means of proton NMR spectroscopy. Each 2 min a spectrum was taken and the concentrations of the three different complexes were calculated from the integrated cyclopentadienyl signals, as these were sufficiently separated. In Figures 5 and 6 plots are given of the concentrations of the three complexes vs. the reaction time.

The plots of the concentrations vs. the reaction time were simulated, and the best fits are given by the solid lines in Figures 5 and 6. These simulations were made on the basis of the reaction scheme of Figure 7, assuming first-order reactions. Excellent fits for the reaction of pure Ia as well as for the reaction starting with pure Ib are obtained with $k_1 = 3.5 \times 10^{-5}\ s^{-1}$, $k_2 = 7.6 \times 10^{-5}\ s^{-1}$, $k_3 = 2 \times 10^{-5}\ s^{-1}$, and k_4, k_5, $k_6 = 0$.

From these kinetic data the following conclusions can be drawn.

(i) The reaction from Ia to Ib is reversible with an equilibrium constant $K_{12} = 0.46$. The free energy difference between coordination modes A and C, as calculated from $\Delta G = -RT \ln K_{12}$, is 2.3 kJ mol^{-1}. As ΔS is expected to be small, this result points to a small energy difference between Ia and Ib, which, considering their structural differences, is rather surprising.

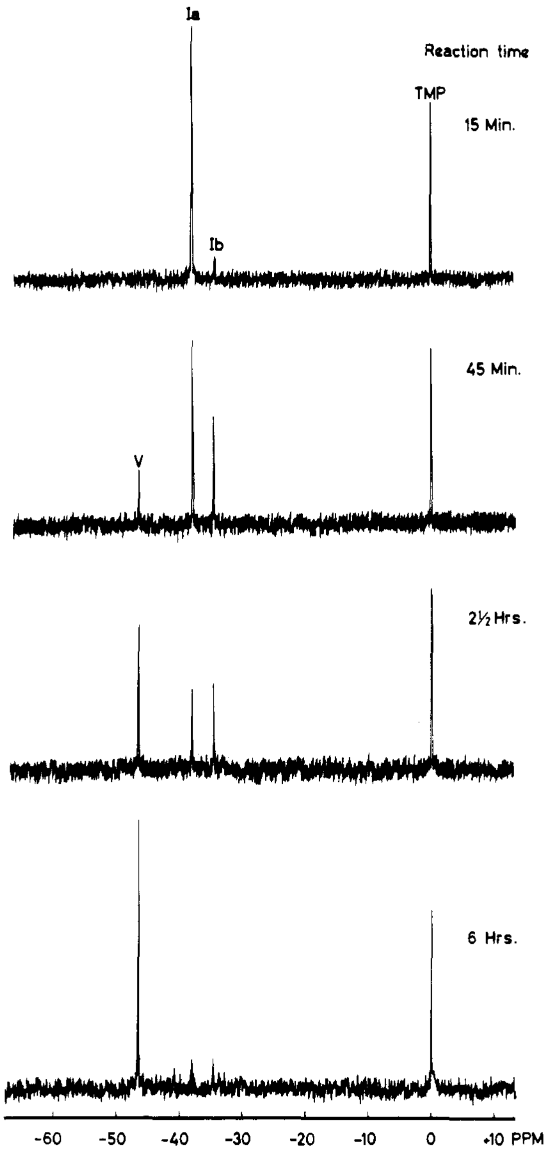


Figure 4. Series of ^{31}P NMR spectra taken at different moments after the start at 80 °C of the reaction of Ia to form Ib and V.

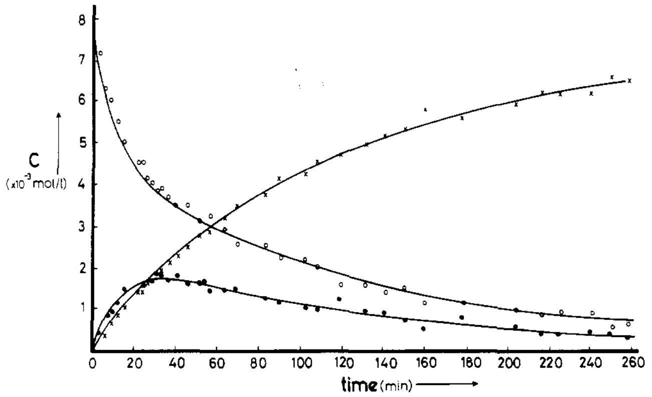


Figure 5. Plot of the concentration of Ia, Ib, and V vs. reaction time (reaction temperature 80 °C), starting from pure Ia: (○) experimental concentration of Ia at time *t*; (●) experimental concentration of Ib at time *t*; (×) experimental concentration of V at time *t*. The simulated plots are given by the solid lines.

(ii) The conversion of Ib to V is very slow. PhNCS elimination probably was only take place from an intermediate compound in which the S(P) atom is coordinated to the central metal atom; only then does an intramolecular mechanism as

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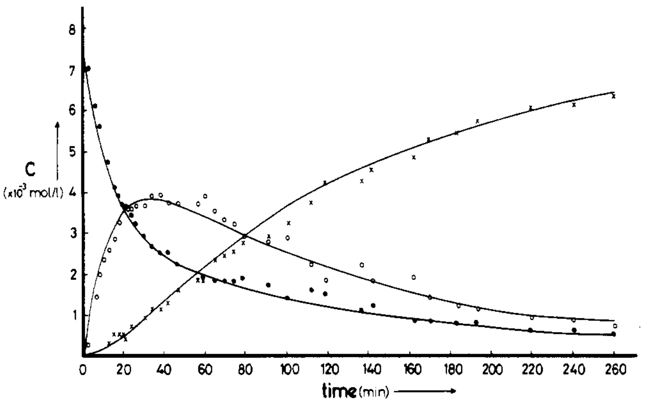

Figure 6. Plot of the concentration of Ia, Ib, and V vs. reaction time (reaction temperature 80 °C), starting from pure Ib: (○) experimental concentration of Ia at time *t*; (●) experimental concentration of Ib at time *t*; (×) experimental concentration of V at time *t*. The simulated plots are given by the solid lines.

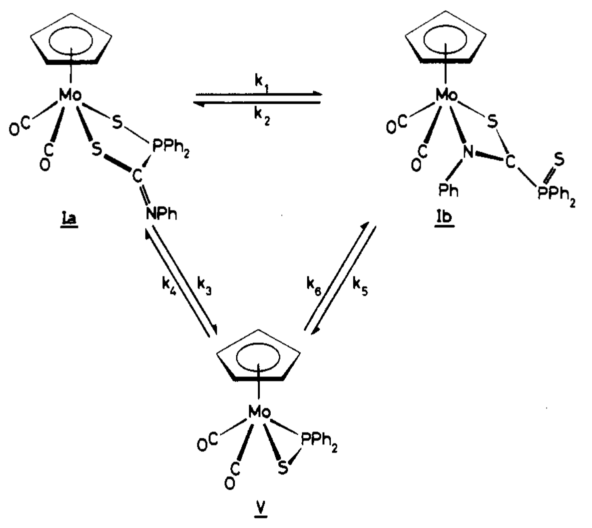

Figure 7. Reaction scheme for the reaction of Ia and/or Ib to form V.

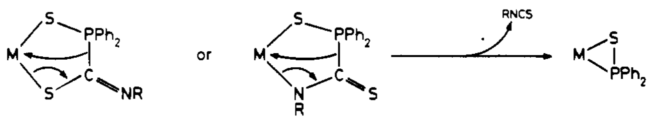

Figure 8. Mechanism of the RNCS-deinsertion reaction.

given in Figure 8 seem to be possible.

When a solution of $W(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ (III) was refluxed, about 35% was converted to VI, a considerable amount was decomposed at 80 °C, and no S(C)N-coordinated $Ph_2P(S)C(S)NPh^-$ complex could be isolated.

For the reaction of IIa to IIb and V and of IVa to IVb and VI the reaction scheme can be given as for Ia, Ib, and V in Figure 8. These reactions were also followed by means of ^1H and ^{31}P NMR spectroscopy. From these results it was clear that k_2 is very small. k_1 has almost the same value as observed in the former case. This means that the free energy difference between IIa and IIb (or IVa and IVb) is greater than 2.3 kJ mol^{-1}.

The stability difference between the methyl-substituted compound (IIb) and Ib is probably due to the more electron-donating properties of the methyl group making a stronger metal to nitrogen bond. The elimination of MeNCS is faster than in the case of PhNCS (k_3 increased).

(c) $[Ph_2P(S)C(S)NR]_2$ and $(SPPh_2)_2$ Complexes. Reaction of $M(CO)_3(PPh_3)_2Cl_2$ (M = Mo, W) with 2 equiv of $Ph_2P(S)C(S)N(H)Ph$ leads to $M(CO)_2(PPh_3)[Ph_2P(S)C(S)NPh]_2$ (M = Mo, VII; M = W, VIII). The RNCS elimination described above for the cyclopentadienyl complexes (Ia–IVb) (Figure 3) could not be observed, when benzene solutions of VII or VIII were refluxed for several hours. Instead, decomposition to unidentified products takes place. To obtain $M(CO)_2(PPh_3)(SPPh_2)_2$, the reaction of $M(CO)_3(PPh_3)_2Cl_2$ with 2 $SPPh_2H$ and Et_3N seems to be the only preparative method (Figure 9).

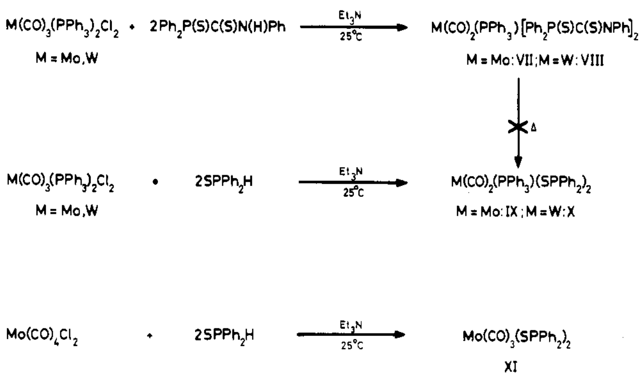

Figure 9. Preparation of the $[Ph_2P(S)C(S)NPh]^-{}_2$ and $[SPPh_2]^-{}_2$ complexes.

The spectra of VII and VIII show two CN absorption bands at 1540 and about 1490 cm^{-1}, indicating that the two ligands have different coordination modes. The comparable $M(CO)_2(PPh_3)[Ph_2P(O)C(S)NR]_2$ (M = Mo, W; R = Ph, Me) was only one CN-stretching band of very strong intensity at 1550 cm^{-1}. A crystal structure determination of $Mo(CO)_2(PPh_3)[Ph_2P(O)C(S)NPh]_2$ showed that the ligands are both coordinated by sulfur and oxygen.[18] In VII and VIII we therefore assume that one ligand is coordinated by both sulfur atoms, resulting in a ν(CN) band of medium intensity at 1540 cm^{-1}, and the other ligand is coordinated by N and one of the sulfur atoms, giving ν(CN) at 1490 cm^{-1}. We assign the very intense band at 514 cm^{-1} to ν(PS) (coordination mode B of Figure 1).

The ^{31}P NMR spectra of the $[Ph_2P(S)C(S)NPh]^-{}_2$ complexes (VII and VIII) show a complicated pattern. For the Mo complex one sharp and two broad signals are found in the spectrum at room temperature. At low temperatures these broad bands become sharp and they show no P–P coupling in contrast to the comparable $Mo(CO)_2(PPh_3)[Ph_2P(O)C(S)NPh]_2$.[18] The dynamic process at room temperature is not influenced by an excess of PPh_3. It is possible that in solution one or both ligands are dynamic with respect to their coordination mode. At low temperatures this interconversion is very slow or only one isomer is present in solution, giving the three sharp signals.

The tungsten complex shows almost the same pattern. In this spectrum it is difficult to assign the signal that is attributed to the PPh_3, because no ^{31}P–^{183}W coupling satellites can be seen. In the spectrum of the comparable $W(CO)_2(PPh_3)[Ph_2P(O)C(S)NPh]_2$,[18] the signal at lowest field showed a ^{31}P–^{183}W coupling. On this basis we assigned the lowest field signal to the PPh_3 ligand.

The $(\eta^2\text{-}SPPh_2)_2$ complexes (IX and X) show a ^{31}P NMR spectrum in which only two different phosphorus sites can be recognized. In the spectrum of IX one doublet (from the two equivalent $SPPh_2$ ligands) and one triplet (from the PPh_3 ligand) are found ($^2J(^{31}P\text{–}^{31}P)$ = 3.75 Hz). This coupling pattern is not observed in the spectrum of X. The ^{31}P–^{183}W coupling constants are 195 Hz for the $SPPh_2$ signal and 265 Hz for the PPh_3 signal.

$Mo(CO)_3(SPPh_2)_2$ can be obtained from the reaction of $Mo(CO)_4Cl_2$ with $SPPh_2H$ and Et_3N. It reacts with extra $SPPh_2H$ and Et_3N to give a compound that has most likely

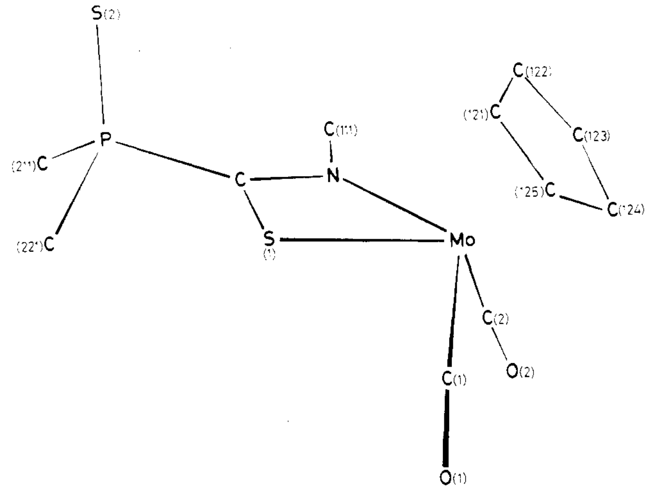

Figure 10. Molecular structure of $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$.

Table VI. Bond Angles (deg) and Distances (Å) in $Mo(\eta^5\text{-}C_5H_5)(CO)_2(Ph_2P(S)C(S)NPh)$

	Molybdenum Coordination		
Mo–S(1)	2.490 (2)	Mo–C(121)	2.38 (2)
Mo–N	2.175 (5)	Mo–C(122)	2.40 (2)
Mo–C(1)	1.92 (2)	Mo–C(123)	2.31 (2)
Mo–C(2)	1.94 (2)	Mo–C(124)	2.27 (2)
		Mo–C(125)	2.31 (2)
S(1)–Mo–N	64.3 (2)	C(1)–Mo–C(2)	78.0 (5)
S(1)–Mo–C(1)	80.4 (2)	C(2)–Mo–N	81.6 (4)
	$[Ph_2P(S)C(S)NPh]^-$ Ligand		
C–S(1)	1.709 (7)	P–C(221)	1.806 (10)
C–N	1.321 (5)	P–C(211)	1.820 (7)
C–P	1.838 (6)	P–S(2)	1.942 (2)
N–C(111)	1.430 (9)		
Mo–S(1)–C	81.4 (2)	Mo–N–C(111)	131.0 (4)
S(1)–C–N	110.4 (5)	N–C–P	128.4 (5)
C–N–Mo	103.8 (4)	S–C–P	121.1 (7)
C–N–C(111)	125.2 (6)	C–P–S(2)	114.1 (6)
	Cyclopentadienyl Ring		
C(121)–C(122)	1.40 (2)	C(124)–C(125)	1.44 (2)
C(122)–C(123)	1.39 (2)	C(125)–C(121)	1.34 (2)
C(123)–C(124)	1.47 (2)		
C(121)–C(122)–C(123)	109 (1)	C(124)–C(125)–C(121)	109 (1)
C(122)–C(123)–C(124)	106.2 (9)	C(125)–C(121)–C(122)	109 (1)
C(123)–C(124)–C(125)	106 (1)		
	CO Groups		
C(1)–O(1)	1.19 (2)	C(2)–O(2)	1.18 (2)
Mo–C(1)–O(1)	176.6 (7)	Mo–C(2)–O(2)	178 (1)

the composition $Et_3NH^+[Mo(CO)_3(SPPh_2)_3]^-$. The true nature of this compound is still under investigation and will not be discussed further here. It is also often found as a side product in the preparation of $Mo(CO)_3(SPPh_2)_2$.

(d) Crystal Structures of $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ (Ib) and $Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2\cdot CH_2Cl_2$ (IX). In Figure 10 the structure of $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ is illustrated. The important bond angles and distances are given in Table VI. The Mo–carbonyl distances are somewhat shorter than those in IX owing to the cis positions of the carbonyl groups as in $Mo(CO)_2(PPh_3)[Ph_2P(O)C(S)NPh]_2$ and $Mo(CO)_2[Ph_2PC(S)NMe][\mu\text{-}Ph_2PC(S)NMe]]_2$.[18,20] The Mo–S distance of 2.490 Å is in the range

Table VII. Bond Angles (deg) and Distances (Å) in $Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2\cdot CH_2Cl_2$

	Molybdenum Coordination		
Mo–S(1)	2.613 (2)	Mo–P(3)	2.382 (2)
Mo–S(2)	2.630 (2)	Mo–C(1)	2.007 (7)
Mo–P(1)	2.401 (2)	Mo–C(2)	2.027 (7)
Mo–P(2)	2.542 (2)		
P(1)–Mo–S(1)	47.11 (5)	C(1)–Mo–P(3)	88.1 (2)
S(1)–Mo–P(2)	87.90 (5)	C(1)–Mo–S(1)	92.9 (2)
P(2)–Mo–S(2)	81.49 (5)	C(1)–Mo–S(2)	88.3 (2)
S(2)–Mo–P(3)	46.91 (5)	C(2)–Mo–P(1)	89.5 (2)
P(1)–Mo–P(3)	96.74 (6)	C(2)–Mo–P(2)	89.1 (2)
C(1)–Mo–C(2)	176.5 (5)	C(2)–Mo–P(3)	92.1 (2)
C(1)–Mo–P(1)	87.1 (2)	C(2)–Mo–S(1)	84.9 (2)
C(1)–Mo–P(2)	93.5 (2)	C(2)–Mo–S(2)	94.4 (2)
	η^2-$SPPh_2$ Ligands		
P(1)–S(1)	2.013 (2)	P(3)–S(2)	2.008 (2)
P(1)–C(3)	1.824 (8)	P(3)–C(33)	1.806 (8)
P(1)–C(9)	1.814 (8)	P(3)–C(39)	1.816 (8)
Mo–S(1)–P(1)	60.91 (6)	Mo–P(3)–C(39)	123.1 (2)
Mo–P(1)–S(1)	71.98 (7)	C(3)–P(1)–C(9)	104.2 (5)
Mo–P(1)–C(3)	124.5 (2)	S(1)–P(1)–C(3)	110.6 (2)
Mo–P(1)–C(9)	126.0 (2)	S(1)–P(1)–C(9)	113.9 (2)
Mo–S(2)–P(3)	60.04 (7)	C(33)–P(3)–C(39)	103.9 (5)
Mo–P(3)–S(2)	73.04 (7)	S(2)–P(3)–C(33)	114.1 (2)
Mo–P(3)–C(33)	125.9 (2)	S(2)–P(3)–C(39)	112.8 (2)
	CO Ligands		
C(1)–O(1)	1.137 (9)	C(2)–O(1)	1.130 (9)
Mo–C(1)–O(2)	175.9 (6)	Mo–C(2)–O(1)	177.3 (7)

that would be expected for Mo(II) complexes with sulfur-containing ligands.[18,20–22]

The Mo–N distance is about the same as in other Mo(II) complexes with an sp^2 nitrogen atom.[20,23] The molybdenum atom lies in the plane of N, S(1), C, and P. The deviations from the least-squares plane through these atoms are as follows (in Å): 0.05 for Mo, 0.04 for N, 0.03 for C, 0.03 for S(1), and 0.05 for P. The geometry of the four-membered ring is almost the same as found in $[Mo(CO)_2[Ph_2PC(S)NMe][\mu\text{-}Ph_2PC(S)NMe]]_2$.[20] The coordination around the molybdenum atom can be regarded as tetragonal pyramidal, when the cyclopentadienyl ring is considered as one coordination point to the molybdenum. The C(1), C(2), S(1), and N atoms are almost lying in a plane (the deviations from the least-squares plane through these atoms are as follows (in Å): 0.06 for C(1), –0.07 for C(2), 0.06 for N, and –0.06 for S(1). The molybdenum atom is situated at 1.02 Å above this plane.

The main bond angles and distances of $Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2\cdot CH_2Cl_2$ are given in Table VII.

The molybdenum atom is seven-coordinated by two CO groups, three phosphorus atoms, and two sulfur atoms. The Mo–C distances are somewhat longer than those in complexes in which the CO groups are coordinated in cis positions (see ref 18 and 20 and complex Ib). The Mo–S distances are longer than those in other Mo(II) complexes containing sulfur donor ligands.[18,20–22] The Mo–P($SPPh_2$) distances are shorter (2.39 Å) than the Mo–P(PPh_3) distance of 2.542 Å. The last one is normal for Mo–P distances in which the ligands are trialkyl- or triarylphosphines.[18,24,25]

The average value of 2.01 Å for the P–S distances is closer to the P═S vond length of 1.95 Å than to the P—S bond length of 2.28 Å. These P–S bond distances are almost the

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same as found in R_2PS^- complexes, in which the ligand forms a $MP(R_2)SM$ bridge between two metal atoms.[5,9] The coordination around the molybdenum atom can be regarded as a pentagonal bipyramid with both CO groups on the axial positions and the three P atoms and the two S atoms in the equatorial plane. The deviations from the least-squares plane through Mo, P(1), P(2), P(3), S(1), and S(2) are as follows: (in Å): 0.003 for Mo, 0.07 for P(1), 0.007 for P(2), −0.06 for P(3), −0.06 for S(1), and 0.04 for S(2).

In this compound the oxidation state of Mo is II, when both $SPPh_2^-$ ligands are considered to be uninegative 4-electron donors. The complex obeys the 18-electron rule. It is interesting to note the structural similarity between IX and the 18-electron compounds like $IrCl(PPh_3)_2(\eta^2\text{-}C_2H_4)_2$ and $IrCl(PPh_3)_2(\eta^2\text{-}O_2)(\eta^2\text{-}C_2H_4)$.[26,27] To stress this point, an alternative description of this complex as having a Mo(−II) center (d^8 as with Ir(I)) with two unipositive 2-electron-donor $SPPh_2$ ligands is possible. Although this alternative description is illustrative, we prefer Mo(II) rather than a Mo(−II), because we think that II is a more realistic indication of the electron density distribution.

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Registry No. Ia, 90967-97-8; Ib, 90967-98-9; IIA, 90967-99-0; IIB, 90968-00-6; III, 90968-01-7; IVa, 90968-02-8; IVb, 91002-34-5; V, 76380-95-5; VI, 76374-51-1; VII, 90990-39-9; VIII, 90990-40-2; IX, 76375-06-9; X, 76374-49-7; XI, 90968-03-9; $Mo(CO)_3(\eta^5\text{-}C_5H_5)Cl$, 12128-23-3; $W(CO)_3(\eta^5\text{-}C_5H_5)Cl$, 12128-24-4; $Ph_2P(S)C(S)N(H)Ph$, 7067-81-4; $Ph_2P(S)C(S)N(H)Me$, 14825-33-3; $SPPh_2H$, 6591-07-7; $Mo(CO)_3(PPh_3)_2Cl_2$, 17250-39-4; $W(CO)_3(PPh_3)_2Cl_2$, 18130-04-6; $Mo(CO)_4Cl_2$, 15712-13-7.

Supplementary Material Available: Listings for $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ of structure factors, thermal parameters of the non-hydrogen atoms, and the fractional coordinates of the hydrogen atoms attached to the phenyl carbon atoms, stereo plots of $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ and $Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2\cdot CH_2Cl_2$, and a plot of the molecular structure of $Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2$ (26 pages). Ordering information is given on any current masthead page.

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Ruthenium Complexes with Diazabutadienes. 3.[1] Trans and Cis Isomers of Dichlorobis(diazabutadiene)ruthenium, $(RN{=}CR'{-}CR'{=}NR)_2RuCl_2$

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The preparation of a series of (diazabutadiene)ruthenium complexes, $(dad)_2RuCl_2$ (dad = $RN{=}CR'{-}CR'{=}NR$ (R' = H, CH_3; R = C_6H_5, substituted phenyl group)), is described. In a thermal reaction starting from tetrakis(benzonitrile)dichlororuthenium, blue or green *trans*-$(dad)_2RuCl_2$ are formed first, which isomerize above 130 °C to the violet cis complexes. Electron spectroscopic, ^1H NMR, and electrochemical data are discussed with respect to symmetry and conformation of the complexes formed. Cis complexes with ligands derived from biacetyl (R' = CH_3) show unusual chemical shifts for aromatic ortho protons, indicating a rigid *N*-phenyl conformation. Two rotational barriers for symmetry-independent aromatic substituents are detected. While the Ru(II)–Ru(III) redox process is fully reversible for both stereochemistries, the reduction is irreversible. The trans → cis isomerization can be achieved catalytically by electron transfer. The otherwise very inert chloro ligands can easily be substituted at potentials below the irreversible reduction step to give, for example, in the presence of free dad and after reoxidation complexes $[Ru(dad)_3]^{2+}$.

Introduction

The coordination chemistry of 2,2'-bipyridine (bpy) has been, by far, more extensively investigated than the coordination chemistry of the related diazabutadiene (dad) ligand system; this is especially true for ruthenium, since research interests focused on the potential applications of tris(bipyridine)ruthenium ions in the photochemical water-splitting reaction.[2] It has only recently become clear that the diazadienes show a much wider range of coordination modes and reaction types[3,4] than bpy. Other advantages that can be ascribed to the diazadiene system are (i) simple synthesis from inexpensive starting materials,[5a,b] (ii) broad variability of substituents including chiral groups,[6] (iii) simple theoretical description of the small $-N{=}C{-}C{=}N-$ system,[7] and (iv) enhanced solubilities as compared to many analogous bpy complexes.

The stereochemistry of the important starting materials bis(bipyridine)$(L)_2$ruthenium(II) was reinvestigated recently, and the trans isomer $(bpy)_2RuCl_2$ is still a poorly characterized material because of its extreme insolubility.[8] Despite the fact that there is no literature evidence for octahedral complexes with two trans dad ligands, we knew, from our stereochemical studies with other coordination geometries, that these should be accessible with relatively small N substituents.[5b] We report here on the synthesis of bis(diazabutadiene)dichlororuthenium complexes with N aromatic substituents, on their trans–cis

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