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Synthesis and Properties of Nitrosyl Complexes of Molybdenum and Tungsten Containing Halide and PMe_3 Ligands. Crystal and Molecular Structures of $MoCl_3(NO)(PMe_3)_3$ and $MoCl(NO)(S_2CPMe_3\text{-}S,S',C)(PMe_3)_2$

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The low-temperature reaction of $MCl_3(PMe_3)_3$ (M = Mo, W) complexes with NO affords the 18-electron species $MCl_3(NO)(PMe_3)_3$ (M = Mo, **1a**; M = W, **1b**), which display ^{31}P NMR features indicative of well-resolved coupling between the ^{31}P and the ^{14}N nuclei. Sodium amalgam reduction of **1** in the presence of PMe_3 gives the M(0) mononitrosyl derivatives $MCl(NO)(PMe_3)_4$ (**2a,b**). Complex **2a** reacts with NaS_2CX to afford $Mo(S_2CX)(NO)(PMe_3)_3$ (X = NMe_2, **3**; X = OMe, **4**). Compounds **2** react with $CNCMe_3$ in a stepwise manner with production of mono- and bis(isocyanide) derivatives, $MCl(NO)(CNCMe_3)_n(PMe_3)_{4-n}$ (n = 1, **8a,b**; n = 2, **9a,b**), but the reaction of **2a** with CO yields only $MoCl(CO)(NO)(PMe_3)_3$ (**5**). Addition of CS_2 to solutions of **2a** furnishes $MoCl(NO)(S_2CPMe_3)(PMe_3)_2$ (**11**), which contains a phosphonium dithiocarboxylate group, $Me_3P^+CS_2^-$, acting formally as a four-electron, η^3 S,S′,C pseudo-allylic ligand. The structures of **1a** and **11**·$CHCl_3$ have been determined by X-ray crystallography. **1a** is monoclinic, $P2_1/c$, with unit cell constants a = 14.796 (4) Å, b = 11.461 (2) Å, c = 11.461 (2) Å, β = 92.49 (4)°, and D(calcd) = 1.56 g cm^{-3} for Z = 4. The molybdenum atom is in a seven-coordinate capped-octahedral environment, with the NO ligand capping the P_3 face. **11**·$CHCl_3$ is also monoclinic, $P2_1/n$, with unit cell constants a = 11.536 (7) Å, b = 28.42 (2) Å, c = 9.84 (2) Å, β = 92.42 (4)°, and D(calcd) = 1.56 g cm^{-3} for Z = 4. The complex contains a zwitterionic ligand, $Me_3P^+CS_2^-$, bonded to molybdenum through the two sulfur atoms and the C atom of the CS_2 group. The PCS_2 fragment is planar, and the angles around the central carbon atom are close to the ideal 120° value expected for sp^2 hybridization.

Introduction

The coordination chemistry of nitric oxide has considerably expanded in the last few decades.[1] Current important aspects of transition-metal nitrosyl chemistry involve the structural characteristics of NO complexes, the chemical reactivity of the coordinated nitrosyl ligand, and the study of the effect of the coordination of NO in the reactivity of organometallic species.[2]

Nitric oxide complexes of molybdenum are very numerous,[3] but most of the complexes known contain in addition the η^5-cyclopentadienyl ligand. Some of these Cp–Mo–NO derivatives exhibit unusual chemical properties. For instance, the $M(\eta^5\text{-}C_5H_5)(NO)R_2$ (M = Mo, W) compounds prepared by Legzdins and co-workers display novel reactivity toward oxygen and sulfur.[4-6] Nitrosyl complexes of molybdenum that contain only halides and tertiary phosphine ligands are comparatively few in number, and this probably reflects the experimental difficulties commonly encountered in the preparation of such compounds. Direct reactions of halo phosphine complexes of molybdenum with NO often lead to intractable mixtures or to complexes containing oxo or phosphine oxide ligands.[7]

During some of our previous investigations on the coordination and organometallic chemistry of molybdenum in low oxidation states, we had the opportunity to characterize a number of trimethylphosphine complexes containing π-acceptor ligands such as CO, N_2, CO_2, C_2H_4, and related species.[8] We have more recently turned our attention to nitric oxide, and herein we wish to report the results of these studies. Formally Mo(II) and Mo(0) compounds of composition $MoCl_3(NO)(PMe_3)_3$ (**1a**) and $MoCl(NO)(PMe_3)_4$ (**2a**) have been prepared and their chemical properties investigated. Particular attention has been devoted to the monochloro species **2a**, whose substitution chemistry with anionic bidentate ligands and with neutral monodentate ligands is described. Prior to the start of this work, complexes related to **1a** and **2a** had been characterized by other groups. For instance, the dimethylphenylphosphine analogue of **1a**, $MoCl_3(NO)(PMe_2Ph)_3$, had been reported by Leigh in 1977, but yields were rather low and the synthetic methodology cumbersome.[7] Subsequently, $MoX(NO)(dppe)_2$ compounds (X = halide or similar ligand; dppe = $Ph_2PCH_2CH_2PPh_2$) were prepared by Richards,[9] and very recently, the iodide analogue of **2a**, $MoI(NO)(PMe_3)_4$, was reported by Legzdins.[10] In this paper we provide clean and straightforward syntheses of **1a**, **2a**, and related derivatives, using the readily available[11a] $MoCl_3(PMe_3)_3$ as the starting material. In addition, the preparation and properties of some analogous tungsten complexes are reported for comparative purposes. The reactions leading to the new compounds are summarized in Scheme I; spectroscopic data are collected in Tables IV and V.

Results and Discussion

Preparation and Properties of $MCl_3(NO)(PMe_3)_3$ Compounds (M = Mo, 1a; M = W, 1b). Crystal and Molecular Structure of 1a. On the somewhat arbitrary, although commonly accepted, assumption that coordinated nitric oxide is NO^+ and acts as a three-electron donor, the 15-electron species $MoCl_3(PMe_3)_3$ can be expected to react with NO to furnish the seven-coordinate, 18-electron compound $MoCl_3(NO)(PMe_3)_3$ (**1a**). However, when nitric oxide is bubbled through a thf solution (thf = tetrahydrofuran) of $MoCl_3(PMe_3)_3$ for ca. 30 min, an intractable mixture of several insoluble species is produced. Small amounts of **1a** are also formed, but they can only be separated with considerable difficulty from other reaction products. As has been previously noted by Leigh,[7] reactions of this type do not often proceed clearly due to (i) the high affinity of molybdenum for oxygen, which frequently gives rise to the formation of oxo–molybdenum products, (ii) the propensity of the phosphine ligands to convert into phosphine oxides, and (iii) the tendency of nitrosyl complexes to

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(1) For an early review on the subject see for example: Connely, N. G. *Inorg. Chim. Acta, Rev.* **1972**, 47.

(2) Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Guillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 2, Chapter 13.3.

(3) Leigh, G. J.; Richards, R. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Guillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 3, Chapter 36.2.

(4) Legzdins, P.; Rettig, S. J.; Sánchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 1411.

(5) Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* **1985**, *4*, 1470.

(6) Legzdins, P.; Sánchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525.

(7) King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1977**, 429.

(8) For a general reference on this work see: Carmona, E. *J. Organomet. Chem.* **1988**, *358*, 283.

(9) Kan, C. T.; Hitchcock, P. B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1982**, 79.

(10) Christensen, N. J.; Hunter, A. D.; Legzdins, P.; Sánchez, L. *Inorg. Chem.* **1987**, *26*, 3344.

(11) (a) Wilkinson, G.; Carmona, E. *J. Chem. Soc., Dalton Trans.* **1978**, 1139. (b) Sharp, P. R. *Organometallics* **1984**, *3*, 1217.

Table I. Crystallographic Data for Compounds **1a** and **11**·$CHCl_3$

	1a	**11**·$CHCl_3$
chem formula	$C_9Cl_3H_{27}MoNOP_3$	$C_{11}Cl_4H_{28}MoNOP_3S_2$
a, Å	14.796 (4)	11.536 (7)
b, Å	11.461 (2)	28.42 (2)
c, Å	11.574 (8)	9.84 (2)
α, deg	90.00 (0)	90.00 (0)
β, deg	92.49 (4)	113.63 (8)
γ, deg	90.00 (0)	90.00 (0)
V, $Å^3$	1941 (1)	2955 (6)
Z	4	4
fw	460.5	585
space group	$P2_1/c$	$P2_1/n$
T, °C	22	22
λ, Å	0.71069	0.71069
ρ(calcd), g cm^{-3}	1.56	1.31
μ, cm^{-1}	12.99	10.96
transmissn coeff	0–60	0–50
$R(F_o)$	0.028	0.12
$R_w(F_o)$	0.030	0.155

form polynitrosyls. The above inconveniences can be overcome by carrying out the reaction of $MoCl_3(PMe_3)_3$ with NO at low temperatures (−10 to 0 °C) for short periods of time (2–5 min), so as to avoid overexposure to NO. In this way, yellow microcrystalline **1a** precipitates out of the solution in 70% yield. A similar procedure (eq 1) provides the tungsten analogue $WCl_3(NO)(PMe_3)_3$ (**1b**), with $WCl_3(PMe_3)_3$[11b] as the starting material.

$$MCl_3(PMe_3)_3 + NO \xrightarrow{\text{THF, 0 °C}} \underset{\mathbf{1}}{MCl_3(NO)(PMe_3)_3} \quad (1)$$

Compounds **1** are moderately air-stable solids, but their solutions in organic solvents decompose rapidly upon exposure to air. A strong IR absorption in the 1600-cm^{-1} region (1620 and 1590 cm^{-1} for **1a** and **1b**, respectively) suggests linear M–N–O systems. The lower energy of ν(N–O) observed for the tungsten derivative **1b** may reflect well-known differences in metal basicity.[12]

^1H and ^{13}C NMR spectra for compounds **1** are not very informative, although they seem to indicate equivalence of the three phosphine ligands. Thus, a filled-in doublet, i.e. a doublet with a broad central resonance, is observed in the ^1H NMR spectra and a four-line multiplet in the $^{13}C\{^1H\}$ spectra. These results suggest a facial configuration of the phosphine ligands and the existence of only one isomer in solution. Since fluxionality is commonly encountered in seven-coordinate complexes of this type, compounds **1** may be fluxional but, as discussed below, the observed changes in the $^{31}P\{^1H\}$ NMR spectrum of **1a** with temperature cannot be attributed to fluxionality.

The $^{31}P\{^1H\}$ NMR spectra of nitrosyls **1** are somewhat more informative and exhibit some interesting and rather unusual features, which deserve some comment. Indeed, the most notable spectrosopic property of these compounds is the appearance of a 1:1:1 triplet (J = 15 Hz (**1a**), 12 Hz (**1b**)) in the $^{31}P\{^1H\}$ NMR spectrum. The outermost peaks are of somewhat smaller intensity due to appreciable line width, but this effect becomes less evident above room temperature. Upon cooling, however, the triplet structure is lost, and at −30 °C (data for **1a** in CH_2Cl_2 solution) a broad singlet, flanked by two small shoulders, is observed. Below this temperature, the spectrum is a broad singlet centered at about 31 ppm. On the basis of these data, the triplet structure can be attributed to well-resolved ^{14}N–^{31}P coupling, whose observation is made possible by a slow relaxation of the ^{14}N nuclei. The broadening at low temperatures can be explained by faster quadrupole relaxation, which produces unresolved coupling. A related situation has recently been found by Gilbert and Bergman in the compounds $(C_5Me_5)IrH_2(SiMe_3)Li(pmdeta)$ and $(C_5Me_5)IrH_3Li(pmdeta)$, which have provided the first direct observation[13] of scalar spin–spin coupling between ^7Li and ^1H. Resolution of ^{14}N–^{31}P coupling, although a rare observation, is not unprecedented and was first demonstrated[14] in compounds of composition *cis*-$Pt(NCS)_2(P(OPh)_3)_2$ and subsequently in other related platinum complexes.[15] Although information on the magnitude of such coupling is very scarce, the 12–15-Hz value found for $^2J_{PN}$ in compounds **1** suggests that the three PMe_3 ligands are cis to the NO group.[14] A possible structure of these complexes, in accord with these data, is the capped-octahedral geometry

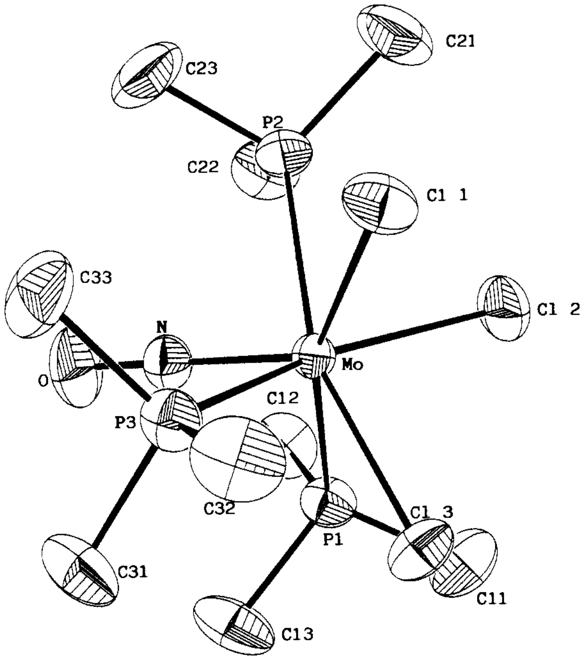
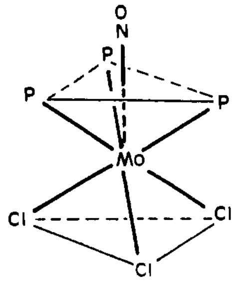


Figure 1. Structure determined by X-ray diffraction of the complex $MoCl_3(NO)(PMe_3)_3$.

Table II. Bond Distances (Å) and Principal Angles (deg) in **1a**

Mo–P1	2.5149 (9)	P1–C11	1.812 (5)
Mo–P2	2.5130 (9)	P1–C12	1.811 (4)
Mo–P3	2.504 (1)	P1–C13	1.811 (4)
Mo–Cl1	2.5115 (9)	P2–C21	1.804 (4)
Mo–Cl2	2.487 (2)	P2–C22	1.813 (4)
Mo–Cl3	2.535 (1)	P2–C23	1.815 (5)
Mo–N	1.774 (3)	P3–C31	1.815 (4)
N–O	1.192 (3)	P3–C32	1.807 (4)
		P3–C33	1.803 (4)
P1–Mo–P2	111.71 (3)	P3–Mo–Cl1	73.79 (4)
P1–Mo–P3	115.76 (5)	P3–Mo–Cl2	152.48 (4)
P1–Mo–Cl1	160.09 (6)	P3–Mo–Cl3	73.90 (4)
P1–Mo–Cl2	77.35 (4)	P3–Mo–N	75.22 (9)
P1–Mo–Cl3	74.50 (4)	Cl1–Mo–Cl2	87.07 (5)
P1–Mo–N	76.80 (9)	Cl1–Mo–Cl3	92.80 (4)
P2–Mo–P3	116.38 (5)	Cl1–Mo–N	123.11 (10)
P2–Mo–Cl1	75.75 (4)	Cl2–Mo–Cl3	87.81 (5)
P2–Mo–Cl2	74.24 (5)	Cl2–Mo–N	132.29 (9)
P2–Mo–Cl3	160.65 (6)	Cl3–Mo–N	122.15 (10)
P2–Mo–N	77.13 (9)		



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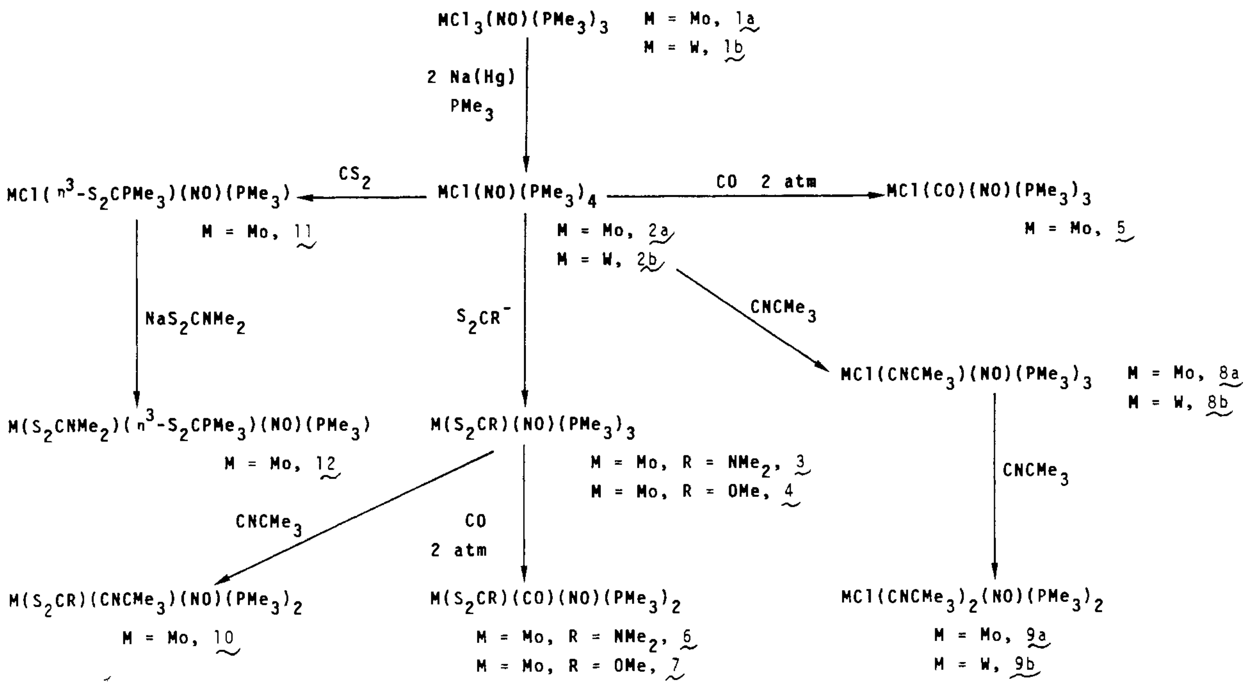
(12) Shriver, D. F. *Acc. Chem. Res.* **1970**, 231.

(13) Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6391.

(14) Goggin, P. L.; Goodfellow, R. J.; Haddock, S. R. *J. Chem. Soc., Chem. Commun.* **1975**, 176.

(15) (a) Anderson, S. J.; Goggin, P. L.; Goodfellow, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1959. (b) Anderson, S. J.; Goodfellow, R. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1683.

Scheme I



A single-crystal X-ray diffraction study, carried out with **1a**, demonstrates that this is also the solid-state structure. High-quality crystals of **1a** can be obtained from CH_2Cl_2 or $CHCl_3$ solutions, but they rapidly lose crystallinity and crumble into powder under vacuum. Suitable crystals for the X-ray investigation were obtained from dilute thf solutions. The structure consists of discrete monomeric molecules in the solid state. Figure 1 shows an ORTEP perspective view, including the atom-numbering scheme; structural data and selected bond distances and angles are collected in Tables I and II. The molybdenum center is in a seven-coordinate environment, and the coordination polyhedron can be approximately described as a capped octahedron, with the chloride and phosphine ligands in facial distribution, i.e. occupying the vertices of two triangular faces. The nitrosyl group can be considered to cap the P_3 face, and its location at this position causes the main distortions in the structure. Thus, the three Cl–Mo–Cl angles have similar values (87.1 (5), 92.8 (4), and 87.8 (5)°) that are close to the ideal 90° value, while the P–Mo–P angles open up to accommodate the NO ligand in the capping position (corresponding values are 111.7 (3), 115.8 (5), and 116.4 (5)°; see Table II). The NO ligand is therefore transoid to the chlorides (N–Mo–Cl angles of 123.1 (10), 132.3 (9), and 122.1 (10)°) but occupies a cisoid position with respect to the PMe_3 groups (N–Mo–P angles of 76.8 (9), 77.1 (9) and 75.2 (9)°). This is in good agreement with the low value found for $^2J(^{31}P-^{14}N)$ (see above). The Mo–P distances in **1a** vary from 2.504 to 2.515 Å and can therefore be considered normal since Mo–P bond lengths usually span over the large range of 2.3–2.6 Å. Similarly, the Mo–Cl lengths, which vary between 2.487 and 2.535 Å, also appear normal. They are shorter than the distance calculated from covalent radii[16] (1.58 (Mo) + 1.00 (Cl) = 2.58 Å) but compare well with those found in other PMe_3 complexes of Mo(II) (e.g. 2.550 (1) Å in $MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3$[17]). The nitrosyl ligand is linear (M–N–O angle 178.6 (2)°), and the Mo–N and N–O separations of 1.774 (3) and 1.192 (3) Å, respectively, are also in reasonable agreement with corresponding values previously found in other mononitrosyl complexes.[9,18]

Synthesis and Chemical Properties of $MCl(NO)(PMe_3)_4$ (M = Mo, 2a; M = W, 2b). At variance with the relatively large number of known compounds of composition $ML_2(PR_3)_4$, where L stands for a π-acceptor ligand such as CO, N_2, or CNR,[3,19] information on the formally isoelectronic nitrosyl complexes, $MCl(NO)(PR_3)_4$, is limited to a few such derivatives. For example, a molybdenum compound of diphenylphosphine, $MoCl(NO)(PPh_2H)_4$, has been prepared by the magnesium reduction[7] of $MoCl_5(NO)^{2-}$ in the presence of the phosphine ligand, while treatment of the dinitrogen species *trans*-$Mo(N_2)_2(dppe)_2$ with $MeN(NO)C(O)NH_2$ or Et_2NNO, under appropriate conditions, provides the nitrosyls *trans*-$MoX(NO)(dppe)_2$ (X = NCO, H, OH). Analogous halide derivatives can be prepared by metathesis and have trans X and NO ligands, as demonstrated by X-ray studies[9] on the hydroxide complex (X = OH). More recently, the preparation of the iodides $MI(NO)(PMe_3)_4$ (M = Mo, W), by direct action of PMe_3 on the dimers $[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2$, has been reported.[10]

The ready availability of $MCl_3(NO)(PMe_3)_3$ compounds on a several-gram scale has prompted us to attempt their reduction to the corresponding M(0) derivatives. Addition of a thf solution of $MCl_3(NO)(PMe_3)_3$ to a suspension of Na–Hg in the same solvent, in the presence of 1 equiv of PMe_3, affords yellow crystalline solids of the expected composition, as depicted in eq 2. The chloride ligand in compounds **2** can be readily displaced by other halides, and, for instance, interaction of **2a** with KI affords the known[10] $MoI(NO)(PMe_3)_4$ (eq 3).

$$\underset{\mathbf{1}}{MCl_3(NO)(PMe_3)_3} + PMe_3 \xrightarrow{\text{Na-Hg}} \underset{\mathbf{2}}{trans\text{-}MCl(NO)(PMe_3)_4} \qquad (2)$$

$$\underset{\mathbf{2a}}{MoCl(NO)(PMe_3)_4} + KI \rightarrow MoI(NO)(PMe_3)_4 + KCl \qquad (3)$$

The metathetical replacement of the chloride ligand in **2a** by the chelating, three-electron-donor dithiocarbamate and xanthate ligands results in addition in the displacement of one of the PMe_3 groups, with formation of the corresponding red (dithiocarbamate) or green (xanthate) Mo(0) complexes in high yields (eq 4).

Spectroscopic data, particularly NMR data (see below), uniquely define the molecular geometry of compounds **2**–**4**. IR studies show the presence of a strong absorption in the region 1540–1520

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(16) Slater, J. C. *J. Chem. Phys.* **1964**, *41*, 3199.

(17) Carmona, E.; Sánchez, L.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Priester, P. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214.

(18) Hunter, A. D.; Legzdins, P. *J. Am. Chem. Soc.* **1984**, *108*, 3843.

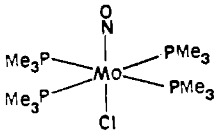
(19) Kirtley, S. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 3, Chapter 26.1.

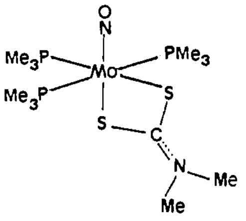
(20) Hillhouse, G. L.; Haymore, B. L. *Inorg. Chem.* **1987**, *26*, 1876.

$$\underset{\mathbf{2a}}{\mathrm{MoCl(NO)(PMe_3)_4}} + \mathrm{NaS_2CX} \rightarrow \mathrm{Mo(S_2CX)(NO)(PMe_3)_3} + \mathrm{NaCl} + \mathrm{PMe_3} \quad (4)$$
$$\mathrm{X} = \mathrm{NMe_2}\ (\mathbf{3}),\ \mathrm{OMe}\ (\mathbf{4})$$

cm^{-1} (Nujol mulls) due to the N–O stretching vibration of the coordinated nitrosyl ligand. Although this frequency is close to the range found for bent N–O, the propensity of Mo and W to achieve an 18-electron configuration in complexes of this type strongly argues in favor of the proposed linear coordination. The low nitrosyl frequencies found for compounds **2**–**4** compare well with those observed by others in related mononitrosyls (e.g. Mo(NCO)(NO)(dppe)$_2$,[9] 1550 cm^{-1}; MoI(NO)(PMe$_3$)$_4$,[10] 1540 cm^{-1}).

Compounds **2** exhibit deceptively simple NMR features. For instance, a singlet is observed in the ^{31}P{^{1}H} NMR spectrum of **2a**, while the ^{1}H and ^{13}C{^{1}H} NMR spectra consist of unique, albeit complex, resonances (a pseudotriplet and a pseudoquintet, respectively). This is consistent with the equivalence of the four phosphine ligands. The three coordinated phosphine ligands of the dithiocarbamate and xanthate complexes, **3** and **4**, give rise to a doublet and a triplet in the ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra, in accord with a meridional distribution of these groups. The dithiocarbamate methyl groups in **3** give separate ^{1}H and ^{13}C resonances, indicating restricted rotation around the N–C bond. The spectroscopic properties of compounds **2**–**4** are in agreement with their possessing six-coordinate structures of the type exemplified for **2a** and **3**:


2a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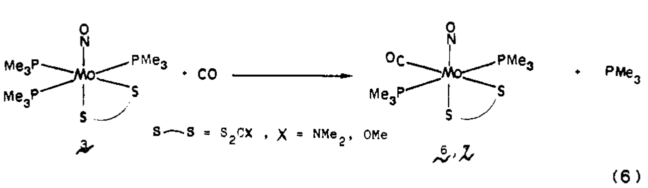
Reactions with CO and CNBu^t. The interaction of compounds **2**, and in some cases of **3** and **4**, with the neutral molecules CO, CNBu^t, and CS$_2$ has been studied. We now describe reactions with CO and CNBu^t; the discussion of the reaction with CS$_2$ will be deferred until the following section.

Tetrahydrofuran solutions of **2a** slowly react with carbon monoxide, with displacement of one of the PMe$_3$ ligands and formation of *mer*-MoCl(NO)(CO)(PMe$_3$)$_3$ (**5**) (eq 5). The proposed meridional geometry finds support in the observation of a virtually coupled triplet and a doublet in the ^{1}H and ^{13}C{^{1}H} NMR spectra and of a characteristic AX$_2$ pattern (δ_A −16.7 ppm; δ_X −9.6 ppm; $^2J_{AX}$ = 28 Hz) in the ^{31}P NMR spectrum. Compounds **3** and **4** also undergo phosphine replacement by carbon monoxide with formation of the monocarbonyl derivatives M(S$_2$CX)(NO)(CO)(PMe$_3$)$_2$ (M = Mo; X = NMe$_2$ (**6**), X = OMe (**7**)). The analogous reaction of **3** with CNCMe$_3$ affords Mo(S$_2$CNMe$_2$)(NO)(CNCMe$_3$)(PMe$_3$)$_2$ (**10**). As for **5**, NMR data unambiguously define the distribution of the ligands in the molecules of these compounds. For instance, the ^{31}P{^{1}H} spectra of **6** and **7** show singlets while the ^{1}H spectrum shows a virtually coupled triplet for the trimethylphosphine protons. This is indicative of a trans distribution of the PMe$_3$ ligands in these species, whose formation can be represented as in eq 6.

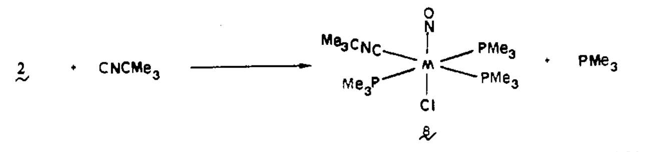
(5)

Not surprisingly, a significant shift to higher energy is observed in the value of the N–O stretching frequency upon substitution of PMe$_3$ by CO. Thus, ν(N–O) moves from 1535 cm^{-1} in MoCl(NO)(PMe$_3$)$_4$ (**2a**) or 1530 cm^{-1} in **3** to 1580 and 1590 cm^{-1} in the corresponding monocarbonyls **5** and Mo(S$_2$CNMe$_2$)(NO)CO(PMe$_3$)$_2$ (**6**), respectively. Correspondingly, ν(C–O) has relatively low values (1930 cm^{-1} in **5** and 1930 cm^{-1} in **6**).

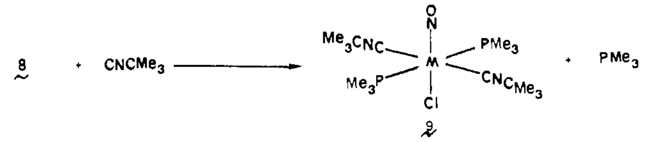


(6)

The reaction of **2a** with carbon monoxide under pressure (2–3 atm), at 60 °C, leads only to the monocarbonyl **5**, and substitution of a second PMe$_3$ ligand by CO is not observed. This contrasts with the facile, stepwise substitution of PMe$_3$ undergone by compounds **2** in the presence of CNBu^t. As shown in eq 7 and 8, formation of both mono- and bis(isocyanide) derivatives is readily achieved. The proposed formulation for **8** and **9** is based upon arguments similar to those used for other related compounds reported in this paper, and therefore, they will not be discussed any further. A brief comment regarding the differences in the reactivity of **2a** toward CO and CNR is, however, pertinent at this moment. It is likely that a dicarbonyl analogue of **9**, MoCl(NO)(CO)$_2$(PMe$_3$)$_2$, is formed when **2a** and CO are reacted under the above conditions, but it is also probable that the displaced PMe$_3$, which has not been removed from the reaction system, reacts back with the dicarbonyl, reversing the reaction[21] to the formation of the monocarbonyl 5. In accord with this, when CO is bubbled through a thf solution of **2a**, at 60 °C, for several hours (see Experimental Section), a ca. 2:1 mixture of **5** and the dicarbonyl MoCl(NO)(CO)$_2$(PMe$_3$)$_2$ is obtained. For the isocyanide system, the reverse conversion of **9** → **8** seems to be less favored. The observed differences may therefore reflect the relative trans effects of the CNR and CO ligands. Note finally that most compounds of this type known[22] contain a square-planar "*trans*-MX(NO)(PR$_3$)$_2$" fragment that would force the two additional CNR or CO ligands to occupy mutually trans positions, as in *trans,trans*-MoCl(NO)(CNBu^t)$_2$(PMe$_3$)$_2$ (**9**) or *trans,trans*-WX(NO)(CO)$_2$(PPh$_3$)$_2$.[20] In fact the latter tungsten complexes are more stable than the corresponding cis,cis isomers, which contain cis carbonyl and phosphine ligands.[20]



(7)



(8)

Reactions with CS$_2$. X-ray Structure of MoCl(NO)(S$_2$CPMe$_3$)(PMe$_3$)$_2$ (11). Addition of CS$_2$ to a solution of compound **2a** in thf (1:1 molar ratio) produces, after several changes in color, a pale orange solution and an off-white precipitate. Evaporation of the solvent from this reaction mixture and crystallization of the resulting residue from CHCl$_3$ afford pale yellow crystals of **11**. Analytical data and a Signer molecular weight determination indicate compound **11** is monomeric and has incorporated one molecule of CS$_2$ with loss of one of the original phosphine ligands. Its IR spectrum shows, in addition to a strong absorption at 1450 cm^{-1}, attributed to ν(N–O) of a linear nitrosyl, two bands at 990 and 945 cm^{-1}, which are due to

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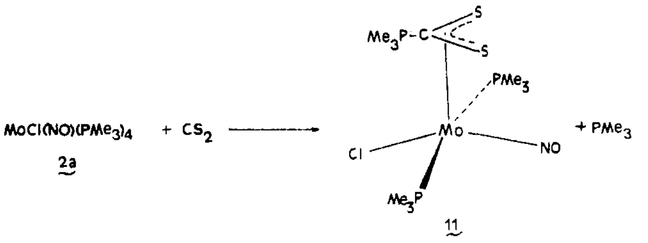
(21) Hill, M. M.; Hillhouse, G. C.; Folting, K.; Huffman, J. C. *Organometallics* **1987**, *6*, 1522.

(22) See for example the nitrosyls reported in this paper, with the exception of **11** (which contains two chelating ligands), and many of the PPh$_3$ derivatives reported by Hillhouse and co-workers.[20,21]

the PMe_3 groups. The band at 945 cm^{-1} appears invariably in compounds that contain coodinated PMe_3, but the somewhat higher energy of the other absorption (990 cm^{-1}) suggests the existence of a phosphonium group. The formation of complex **11** can be represented as depicted in eq 9. Support for the proposed formulation comes from NMR studies. The $^{31}P\{^1H\}$ NMR spectrum consists of two broad singlets at 2.3 and 35.5 ppm (intensity ratio ca. 2:1). The former has a chemical shift in the range found for coordinated PMe_3 in other Mo^0–NO compounds prepared in this work (+20 to −20 ppm) and can therefore be assigned to the molybdenum-bound PMe_3 ligands, while the latter is at considerably lower field than expected for molybdenum-bound PMe_3 and is well in the region corresponding to quaternary phosphorus atoms bearing a formal positive charge (e.g. 32.9 ppm in $Ni(C_2S_4PMe_3)(PMe_3)$[23] and 44–54 ppm in $MO[S_2C(PMe_3)OR](S_2COR)$ complexes, M = Mo and W[24]). The singlet at 35.5 ppm splits into a singlet and a doublet, resembling a ca. 1:2:1 triplet ($^1J_{PC}$ = 82.5 Hz) in the spectrum of a sample of **11*** (approximately 50% enriched in $^{13}CS_2$). In the $^{13}C\{^1H\}$ NMR spectrum the trimethylphosphonium group affords a characteristic, relatively high field doublet (11.2 ppm) with a large coupling constant ($^2J_{PC}$ = 58 Hz), while the CS_2 carbon atom of **11*** provides a doublet of triplets ($^1J_{PC}$ = 82.5 Hz, $^2J_{PC}$ = 5.2 Hz). This not only demonstrates the formation of a phosphonium dithiocarboxylate ligand, S_2CPMe_3, but also suggests the existence of some bonding interaction between the S_2CPMe_3 carbon atom and the molybdenum center, which has been demonstrated by X-ray studies (see below). Finally, two doublets with intensity ratio 2:1 are observed for the PMe_3 protons in the ^1H NMR spectrum of **11**. The first, at δ 1.5 ppm, has $^2J_{PH}$ = 9 Hz, i.e. in the 5–10-Hz range associated with metal-bound PMe_3, but the second (1.6 ppm) has a larger coupling constant of 13 Hz, characteristic of phosphonium salts.[23]



(9)

In order to unequivocally establish the bonding mode of the $Me_3P^+CS_2^-$ ligand, a single-crystal X-ray structural determination of **11**·$CHCl_3$ has been undertaken. Crystals of this complex are very unstable toward loss of $CHCl_3$ molecules of crystallization and crumble into powder in the absence of solvent, even when kept under N_2. For the structural determination, a very unstable crystal of dimensions 0.3 × 0.3 × 0.4 nm was coated with an epoxy resin and mounted in the diffractometer. The already mentioned instability of the crystal, which in addition became damaged by radiation, and above all the existence of a very important nonresolvable positional disorder prevented anisotropic refinement of the structure. The final refinement with fixed isotropic temperature factors and coordinates for H atoms gave R = 0.12. Nevertheless, the positions of all the atoms could be fixed and sufficiently accurate bonding parameters obtained. These should, however, be regarded and used with caution when attempting to stablish precise comparisons.

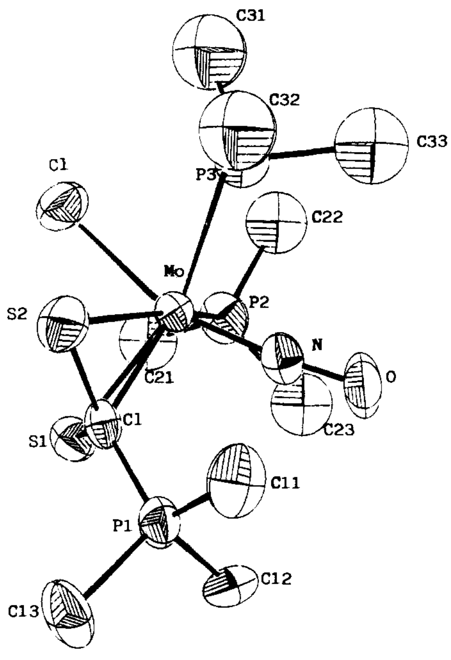


Figure 2. Perspective ORTEP drawing and atom-labeling scheme for the complex $MoCl(S_2CPMe_3$-*S*,*S'*,*C*$)(NO)(PMe_3)_2$.

Table III. Bond Distances (Å) and Angles (deg) in **11**·$CHCl_3$

Mo–S1	2.492 (8)	P1–C11	1.81 (3)
Mo–S2	2.500 (11)	P1–C12	1.77 (4)
Mo–Cl1	2.573 (8)	P1–C13	1.81 (4)
Mo–P2	2.474 (11)	P2–C21	1.75 (4)
Mo–P3	2.514 (10)	P2–C22	1.87 (6)
Mo–N	1.76 (2)	P2–C23	1.84 (6)
Mo–C1	2.14 (3)	P3–C31	1.74 (7)
S1–C1	1.75 (2)	P3–C32	1.63 (7)
S2–C1	1.76 (3)	P3–C33	1.82 (7)
C1–P1	1.74 (3)	N–O	1.24 (3)
S1–Mo–S2	76.5 (3)	Cl1–Mo–P2	80.5 (3)
S1–Mo–Cl1	87.9 (3)	Cl1–Mo–P3	82.9 (3)
S1–Mo–P2	86.8 (3)	Cl1–Mo–N	158.6 (8)
S1–Mo–P3	164.5 (4)	P2–Mo–P3	103.8 (4)
S1–Mo–N	108.2 (8)	P2–Mo–N	86.3 (8)
S2–Mo–Cl1	88.2 (3)	P3–Mo–N	84.1 (8)
S2–Mo–P2	160.2 (4)	O–N–Mo	174 (2)
S2–Mo–P3	90.7 (3)	S1–C1–C2	123 (2)
S2–Mo–N	108.9 (8)	S1–C1–P1	117 (2)
		S2–C1–P1	118 (2)

Figure 2 shows an ORTEP view of the molecule of **11**; structural data and selected bond distances and angles are collected in Tables I and III. Due to the low quality of the X-ray data available, the discussion of the structure is restricted to the overall geometry of the Mo–CS_2PMe_3 linkage, which is in fact the most salient structural feature of **11**. If the phosphonium dithiocarboxylate ligand is considered to occupy two coordination sites, the formally molybdenum(0) center is in a six-coordinated distorted-octahedral geometry. An alternative and otherwise useful structural representation derives from a square pyramid, with the Me_3PCS_2 ligand formally occupying a single apical coordination position, as shown in eq 9. The Mo–S separations (2.492 (8) and 2.500 (11) Å) are normal and compare well with those found in related complexes, e.g. ca. 2.5 Å in $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$,[25] but the central carbon atom is well within bonding distance to molybdenum (2.14 (3) Å; to be compared with the distance calculated from covalent radii,[16] 1.58 (Mo) + 0.70 (C) = 2.28 Å). Therefore, the Me_3PCS_2 groups acts formally as a four-electron, η^3 S,S′,C pseudo-allylic ligand. The P–C1–S1–S2 fragment is planar, and the angles around C1 within this unit are very close to the ideal value of 120° expected for sp^2 hybridization. The bonding mode found for the Me_3PCS_2 group in complex **11** is unusual in monomeric species, although it has been previously established in some binuclear compounds.[25,26] It is also reminiscent of the pseudo-allylic η^3 S,S′,C coordination that we have described recently for xanthate ($ROCS_2^-$) and thioxanthate ($RSCS_2^-$) ligands in some oxo complexes of Mo(IV) and W(IV).[24,27]

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(23) Mason, M. G.; Swepston, P. N.; Ibers, J. S. *Inorg. Chem.* **1983**, *22*, 411.

(24) Carmona, E.; Galindo, A.; Gutiérrez-Puebla, E.; Monge, A. *Inorg. Chem.* **1986**, *25*, 3806.

(25) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *Organometallics* **1986**, *1*, 778.

(26) Miguel, D.; Riera, V.; Miguel, J. A.; Solana, X.; Font-Altaba, M. *J. Chem. Soc., Chem. Commun.* **1987**, 472.

Table IV. Spectroscopic Data for Complexes **1–12**

	NMR data[a]				IR data[b]		
	PMe$_3$		S$_2$CR	CNBu^t			
	^{31}P ($^2J_{PP}$)	^1H ($^2J_{PH}$) [J_{appPH}]	^1H ($^2J_{PH}$)	^1H	ν(NO)	ν(CO)	ν(CN)
1a	25.2 t[c]	1.5 pt[d] [6.2]			1620		
1b	19.4 t[c]	1.49 pt [2.5]			1590		
2a	−2.3 s	1.29 pt			1535		
2b	−23.1 s	1.62 br s			1520		
3	−2.8 d (16)	1.28 d (6.64)	2.75 s		1530		
	17.7 t	1.42 pt [2.71]	2.87 s				
4	3.0 d (16.9)	1.18 d (6.7)	3.64 s		1540		
	16.0 t	1.31 pt [2.8]					
5	−16.7 t (28)	1.06 d (6.34)			1580	1930	
	−9.6 d	1.25 pt [3.12]					
6	−7.8 s	1.30 pt [3.24]	2.74 s		1590	1930	
			2.63 s				
7	−7.4 s	1.17 pt [3.55]	3.54 s		1610	1890	
8a	−7.8 t (23.5)	1.28 d (6.1)		1.06 s	1540		2120
	−5.5 d	1.40 pt [2.78]					
8b	−26.5 t (14.1)	1.38 d (6.59)		1.09 s	1545		2080
	−25.5 d	1.59 pt [3.25]					
9a	−0.19 s	1.43 pt [3.13]		1.50 s	1550		2060
9b	−24.02 s	1.55 pt [3.51]		1.44 s	1540		2060
10	−6.15 s	1.47 pt [3.12]	2.9 s	1.25 s	1560		1920
			2.8 s				1870
11	2.31 br s	1.5 d (9.17)	1.6 d[f]		1540		
	35.49 br s[e]						
12	7.16 s	1.51 d (9.2)	1.75 d[f]		1550		
	40.33 s[e]		3.19 s				
			3.33 s				

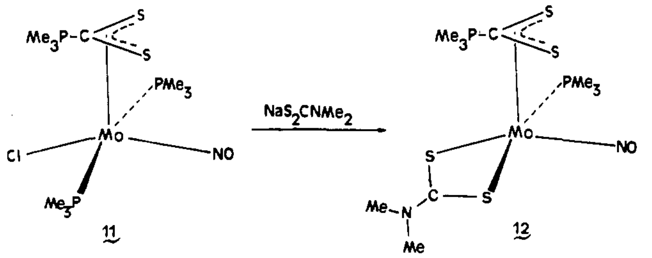
[a] δ in ppm; J in Hz. Deuterated solvents used: C_6D_6 for **2a,b**, **3–7**, **8a,b**, **9a,b**, and **10**; CD_2Cl_2 for **1a,b** and **11**; $CDCl_3$ for **12**. [b] Nujol mulls; in cm^{-1}. [c] $^2J(^{14}N-^{31}P)$ = 15 Hz (**1b**). [d] pt = pseudotriplet. [e] S_2CPMe_3 resonance. [f] S_2CPMe_3 resonance; $^2J_{PH}$ = 13 Hz (**11**), 13.5 Hz (**12**).

Table V. $^{13}C\{^1H\}$ NMR[a] Data for Complexes **1–12**

	PMe$_3$ (J_{PC})[b] [J_{appPC}]	S$_2$CR (Me)	CNC*Me*$_3$	CN*C*Me$_3$
1a	13.02 m			
1b	11.74 m			
2a	19.00 pq [5.5]			
2b	19.85 br s			
3	17.52 pt [9.1]	39.26 s		
	21.67 d (20.2)			
4	17.65 pt [9.7]	56.90 s		
	21.43 d (21.7)			
5	17.50 pt [11.1]			
	16.94 d (18.4)			
6	15.31 pt [11]	39.13 s		
		39.41 s		
7	15.36 pt [11.7]	57.30 s		
8a	18.33 pt [9.4]		30.23 s	55.71 s
	18.85 d (18.6)			
9a	17.10 pt [10.6]		30.73 s	59.02 s
9b	17.67 pt [13.3]		30.96 s	56.36 s
10	15.74 pt [10.05]	39.54 s	31.70 s	58.10 s
		39.23 s		
11[d]	11.25 d[c] (58)			
	16.15 d (12)			
12[e]	11.00 d[c] (58.4)			
	14.54 d (26.3)			

[a] δ in ppm. Deuterated solvents used: C_6D_6 for **2a,b, 3–7, 8a,b, 9a,b,** and **10**; CD_2Cl_2 for **1a,b** and **11**; $CDCl_3$ for **12**. [b] J in Hz. [c] S_2CPMe_3 resonance. [d] Resonance of a sample enriched 50% in $^{13}CS_2$: 82.75 dt; $^1J_{PC}$ = 82.5 Hz; $^2J_{PC}$ = 5.2 Hz. [e] Resonance of a sample enriched 50% in $^{13}CS_2$: 82.9 dd; $^1J_{PC}$ = 84.4 Hz; $^2J_{PC}$ = 4.1 Hz.

Compound **11** reacts with a thf suspension of NaS_2CNMe_2, with formation of yellow $Mo(S_2CNMe_2)(NO)(S_2CPMe_3)(PMe_3)$ (**12**) (eq 10). Spectroscopic data for **12** are in accord with the proposed formulation. For instance, the molybdenum-bound PMe_3 ligand gives a doublet at 14.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum, with a normal $^1J_{PC}$ coupling constant of 26 Hz, while the phosphonium group affords a second doublet at somewhat higher field (11 ppm) with a larger coupling of 58.5 Hz. The bonding mode of the S_2CPMe_3 unit is retained as evidenced by the observation of a doublet of doublets centered at 82.9 ppm ($^1J_{PC}$ = 84.8 Hz, $^2J_{PC}$ = 4.1 Hz) in the $^{13}C\{^1H\}$ NMR spectrum of a sample of **12** ca. 50% enriched in $^{13}CS_2$. These and other data are consistent with the structure shown in eq 10.



(10)

Experimental Section

Microanalyses were carried out by the Analytical Service of the University of Sevilla. All new compounds gave satisfactory elemental analyses.

IR spectra were recorded as Nujol mulls, or in an appropriate solvent, on Perkin-Elmer Models 577 and 684 instruments. ^1H, ^{13}C, and ^{31}P NMR spectra were run on a Varian XL-200 instrument. ^{31}P NMR shifts were referenced to external 85% H_3PO_4, while ^1H and ^{13}C NMR shifts were referenced to the residual signals of the deuterated solvent employed, and all data are reported in ppm downfield from Me_4Si.

All preparations and manipulations were carried out under oxygen-free nitrogen or argon, by following the conventional Schlenk techniques. Solvents were dried and degassed before use. All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was checked by elemental analyses, NMR techniques, and/or other suitable methods.

The experimental procedures, with the molybdenum complexes as representative examples throughout, were as follows.

Preparation of $MCl_3(NO)(PMe_3)_3$ (M = Mo, 1a; M = W, 1b) Complexes. Through a stirred suspension of $MoCl_3(PMe_3)_3$ (1.6 g, ca. 3.7 mmol) in 40 mL of thf, nitric oxide was slowly bubbled at 0 °C until there was formation of a yellow microcrystalline precipitate (ca. 2–5 min). Longer reaction times have deleterious effects and considerably diminish the yield. The solvent was then partially removed under vacuum

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(27) Carmona, E.; Galindo, A.; Guille-Photin, C.; Lai, R.; Monge, A.; Ruiz, C.; Sänchez, L. *Inorg. Chem.* **1988**, *27*, 488.

Table VI. Atomic Coordinates for $MoCl_3(NO)(PMe_3)$ (**1a**)

atom	*x/a*	*y/b*	*z/c*
H111	0.112 40 (0)	−0.165 50 (0)	1.011 60 (0)
H112	0.012 30 (0)	−0.178 60 (0)	0.947 90 (0)
H113	0.059 50 (0)	−0.048 50 (0)	0.960 00 (0)
H121	0.083 40 (0)	−0.339 20 (0)	0.787 20 (0)
H122	0.183 60 (0)	−0.326 00 (0)	0.850 90 (0)
H123	0.169 60 (0)	−0.297 10 (0)	0.711 60 (0)
H131	0.001 60 (0)	−0.032 30 (0)	0.717 10 (0)
H132	−0.018 80 (0)	−0.172 10 (0)	0.708 60 (0)
H133	0.057 00 (0)	−0.113 30 (0)	0.626 60 (0)
H211	0.545 60 (0)	−0.157 40 (0)	0.857 70 (0)
H212	0.471 00 (0)	−0.135 60 (0)	0.955 40 (0)
H213	0.503 10 (0)	−0.025 90 (0)	0.874 80 (0)
H221	0.357 60 (0)	−0.311 80 (0)	0.850 50 (0)
H222	0.432 10 (0)	−0.333 60 (0)	0.752 80 (0)
H223	0.327 40 (0)	−0.298 50 (0)	0.711 40 (0)
H231	0.506 10 (0)	−0.171 00 (0)	0.624 30 (0)
H232	0.484 50 (0)	−0.031 30 (0)	0.628 10 (0)
H233	0.407 70 (0)	−0.121 80 (0)	0.574 40 (0)
H311	0.126 00 (0)	0.171 40 (0)	0.467 60 (0)
H312	0.075 50 (0)	0.141 50 (0)	0.586 80 (0)
H313	0.128 00 (0)	0.037 10 (0)	0.518 50 (0)
H321	0.182 60 (0)	0.315 20 (0)	0.706 90 (0)
H322	0.233 10 (0)	0.345 10 (0)	0.587 70 (0)
H323	0.293 60 (0)	0.306 20 (0)	0.704 30 (0)
H331	0.310 30 (0)	0.194 80 (0)	0.453 30 (0)
H332	0.317 00 (0)	0.053 90 (0)	0.473 30 (0)
H333	0.377 80 (0)	0.142 40 (0)	0.557 70 (0)
Mo	0.257 20 (1)	−0.012 60 (2)	0.774 10 (2)
P1	0.121 80 (5)	−0.138 60 (7)	0.808 30 (7)
P2	0.399 80 (5)	−0.131 10 (7)	0.767 80 (7)
P3	0.235 10 (6)	0.141 30 (7)	0.621 90 (7)
Cl1	0.381 80 (5)	0.133 40 (7)	0.810 40 (8)
Cl2	0.285 10 (6)	−0.077 00 (9)	0.977 70 (7)
Cl3	0.137 70 (6)	0.124 70 (7)	0.846 20 (7)
N	0.241 90 (17)	−0.091 00 (22)	0.642 50 (20)
O	0.230 90 (20)	−0.145 70 (23)	0.555 40 (20)
C11	0.070 20 (27)	−0.133 70 (39)	0.947 40 (37)
C12	0.140 90 (27)	−0.293 30 (31)	0.789 10 (34)
C13	0.029 30 (24)	−0.110 70 (37)	0.704 30 (39)
C21	0.489 80 (26)	−0.111 80 (41)	0.876 30 (40)
C22	0.378 10 (27)	−0.286 70 (32)	0.772 20 (36)
C23	0.457 60 (27)	−0.111 10 (42)	0.634 10 (38)
C31	0.128 80 (27)	0.122 20 (35)	0.539 90 (33)
C32	0.235 20 (27)	0.294 60 (30)	0.658 40 (36)
C33	0.318 40 (30)	0.131 60 (38)	0.513 10 (32)

Table VII. Atomic Coordinates for **11**·$CHCl_3$

atom	*x/a*	*y/b*	*z/c*
H111	0.354 20 (0)	0.053 50 (0)	1.223 80 (0)
H112	0.426 00 (0)	0.059 50 (0)	1.111 70 (0)
H113	0.443 60 (0)	0.011 30 (0)	1.207 80 (0)
H121	0.335 20 (0)	−0.001 80 (0)	0.832 70 (0)
H122	0.217 00 (0)	−0.037 70 (0)	0.803 60 (0)
H123	0.354 40 (0)	−0.048 40 (0)	0.935 60 (0)
H131	0.094 30 (0)	−0.043 70 (0)	0.999 80 (0)
H132	0.141 20 (0)	−0.012 40 (0)	1.151 60 (0)
H211	−0.047 70 (0)	0.119 50 (0)	0.406 90 (0)
H212	−0.009 80 (0)	0.063 80 (0)	0.426 20 (0)
H213	0.005 30 (0)	0.094 40 (0)	0.295 50 (0)
H221	0.297 50 (0)	0.172 20 (0)	0.512 60 (0)
H222	0.151 80 (0)	0.190 90 (0)	0.455 70 (0)
H223	0.199 20 (0)	0.163 60 (0)	0.344 00 (0)
H231	0.239 70 (0)	0.031 90 (0)	0.525 60 (0)
H232	0.355 40 (0)	0.069 70 (0)	0.566 10 (0)
H233	0.257 10 (0)	0.062 10 (0)	0.394 80 (0)
H311	0.290 10 (0)	0.270 20 (0)	0.845 50 (0)
H312	0.154 10 (0)	0.252 40 (0)	0.841 30 (0)
H313	0.194 20 (0)	0.239 50 (0)	0.702 80 (0)
H321	0.276 40 (0)	0.205 40 (0)	1.103 40 (0)
H322	0.412 40 (0)	0.223 20 (0)	1.107 60 (0)
H323	0.386 50 (0)	0.166 50 (0)	1.117 20 (0)
H331	0.500 70 (0)	0.224 60 (0)	0.945 50 (0)
H332	0.447 10 (0)	0.201 80 (0)	0.779 20 (0)
H333	0.492 20 (0)	0.166 50 (0)	0.925 60 (0)
H2	0.912 10 (0)	0.172 40 (0)	0.893 50 (0)
H3	0.757 00 (0)	0.110 50 (0)	0.617 50 (0)
Mo	0.183 00 (21)	0.112 40 (9)	0.791 20 (26)
S1	0.033 90 (67)	0.044 50 (27)	0.725 40 (84)
S2	0.126 00 (72)	0.105 10 (30)	1.010 10 (81)
Cl1	−0.010 20 (72)	0.166 50 (29)	0.670 70 (95)
C1	0.139 40 (221)	0.056 30 (94)	0.907 80 (263)
P1	0.245 30 (67)	0.012 00 (28)	1.001 70 (86)
C11	0.036 30 (291)	0.036 30 (132)	1.151 10 (347)
C12	0.293 50 (301)	−0.022 50 (105)	0.884 10 (385)
C13	0.169 80 (296)	−0.029 10 (130)	1.081 40 (357)
P2	0.163 20 (79)	0.110 30 (37)	0.531 40 (85)
C21	0.012 80 (364)	0.096 20 (139)	0.399 60 (431)
C22	0.209 10 (471)	0.162 70 (186)	0.450 10 (567)
C23	0.265 80 (440)	0.065 90 (169)	0.500 80 (528)
P3	0.294 60 (84)	0.188 90 (35)	0.889 40 (103)
C31	0.229 70 (625)	0.242 30 (245)	0.808 90 (759)
C32	0.354 30 (636)	0.195 50 (237)	1.069 40 (747)
C33	0.447 20 (567)	0.197 60 (220)	0.879 10 (666)
N	0.336 60 (204)	0.090 50 (79)	0.839 20 (238)
O	0.447 10 (188)	0.078 70 (87)	0.864 50 (260)
Cl2	0.766 30 (169)	0.228 20 (68)	0.829 90 (203)
Cl3	0.794 10 (193)	0.153 60 (77)	1.028 50 (236)
Cl4	0.985 20 (224)	0.216 90 (89)	1.085 10 (267)
C2	0.872 40 (386)	0.190 40 (156)	0.949 80 (468)
Cl5	0.669 90 (199)	0.125 80 (77)	0.330 10 (238)
Cl6	0.665 40 (210)	0.053 80 (86)	0.494 60 (252)
Cl7	0.584 90 (322)	0.155 50 (126)	0.503 20 (383)
C3	0.684 80 (598)	0.110 30 (271)	0.514 70 (717)

to eliminate the unreacted NO and the resulting mixture cooled overnight at −30 °C. Yellow crystals of $MoCl_3(NO)(PMe_3)_3$ were collected, washed with cold thf, and recrystallized from CH_2Cl_2; yield 75%.

The complex $WCl_3(NO)(PMe_3)_3$ was also similarly obtained as yellow crystals in ca. 65% yield.

Preparation of $MCl(NO)(PMe_3)_4$ (M = Mo, 2a; M = W, 2b) Complexes. $MoCl_3(NO)(PMe_3)_3$ (1.8 g, ca. 3.8 mmol) was added to a stirred suspension of 1% sodium amalgam (0.2 g Na, ca. 8.7 mmol) in thf (40 mL) containing PMe_3 (0.4 mL, ca. 4 mmol). Stirring was continued for 6 h at room temperature to ensure completion of the reaction. The final supernatant solution was cannulated away from the mercury-containing residue, centrifuged, and evaporated to dryness under reduced pressure. The residue was washed with petroleum ether (2 × 10 mL) and extracted with thf (30 mL); further centrifuging and cooling at −30 °C overnight produced $MoCl(NO)(PMe_3)_4$ as yellow crystals in ca. 80% yield. The complex $WCl(NO)(PMe_3)_4$ was also obtained as yellow crystals in similar yields by using an analogous procedure.

Preparation of $Mo(\eta^2\text{-}S_2CX)(NO)(PMe_3)_3$ (X = NMe_2, 3; X = OMe, 4) Complexes. Forty milliliters of thf was syringed onto a mixture of $MoCl(NO)(PMe_3)_4$ (0.46 g, ca. 1 mmol) and anhydrous NaS_2CNMe_2 (1 mmol). The reaction mixture was stirred at room temperature for 2 h. The solvent was then removed in vacuo and the residue extracted with a 2:1 petroleum ether–diethyl ether mixture. Complex **3** was obtained as red crystals in 80% yield upon cooling at −30 °C for several hours.

From the same chloro nitrosyl compound and anhydrous KS_2COMe the complex $Mo(\eta^2\text{-}S_2COMe)(NO)(PMe_3)_3$ (green crystals in 80% yield) has been obtained by the same procedure.

Preparation of $MoCl(CO)(NO)(PMe_3)_3$ (5). $MoCl(NO)(PMe_3)_4$ (0.46 g, ca. 1 mmol) was dissolved with stirring in thf (30 mL) and the solution transferred into a 300-mL Fisher–Porter vessel, which was subsequently pressurized to 2 atm of CO. After a reaction time of 12 h, the pressure in the vessel was relieved, the solvent evaporated in vacuo, and the residue extracted with 20 mL of a 4:1 petroleum ether–diethyl ether mixture. Further centrifuging and cooling at −30 °C overnight afforded yellow crystals of $MoCl(CO)(NO)(PMe_3)_3$ in 65% yield.

CO was bubbled through a thf solution of **2a**, at 60 °C for 8 h, in an attempt to obtain the dicarbonyl $MoCl(CO)_2(NO)(PMe_3)_2$. The solvent was evaporated in vacuo and the residue extracted with 20 mL of a 1:1 petroleum ether–diethyl ether mixture. Cooling at −30 °C overnight afforded yellow crystals of a 2:1 mixture of **5** and the expected dicarbonyl complex as inferred from IR (ν(C–O) 1960, 1920 cm^{-1}) and NMR studies ($^{31}P\{^1H\}$, δ −9.4 s).

Preparation of $Mo(\eta^2\text{-}S_2CX)(CO)(NO)(PMe_3)_2$ (X = NMe_2, 6; X = OMe, 7) Complexes. These compounds were prepared by combining the corresponding $Mo(\eta^2\text{-}S_2CX)(NO)(PMe_3)_3$ complexes and CO as described above for the synthesis of **5** but using Et_2O as the reaction solvent and letting the reactions proceed for 6 h at room temperature. The complexes $Mo(\eta^2\text{-}S_2CNMe_2)(CO)(NO)(PMe_3)_2$ (**6**) and $Mo(\eta^2\text{-}S_2COMe)(CO)(NO)(PMe_3)_2$ (**7**) were isolated as orange crystals from Et_2O.

Preparation of $MCl(CNCMe_3)(NO)(PMe_3)_3$ (M = Mo, 8a; M = W, 8b) Complexes. To a stirred solution of **2a** (0.46 g, ca. 1 mmol) in thf

(40 mL) was added 1 equiv of $CNCMe_3$, and the mixture was stirred for 8 h at room temperature. The resulting solution was evaporated to dryness and the residue extracted with Et_2O (15 mL). Centrifuging and cooling at −30 °C afforded $MoCl(CNCMe_3)(NO)(PMe_3)_3$ as yellow crystals in 80% yield.

If **2b** is used, $WCl(CNCMe_3)(NO)(PMe_3)_3$ can be obtained as yellow crystals in similar yield, by using an analogous procedure.

Preparation of $MCl(CNCMe_3)_2(NO)(PMe_3)_2$ (M = Mo, 9a; M = W, 9b) Complexes. To a stirred solution of **2a** (0.46 g, ca. 1 mmol) in thf (40 mL) was added 2 mL of a 1 M solution of $CNCMe_3$ in thf and the mixture stirred for 24 h at room temperature. The initial yellow solution gradually became dark yellow. Removal of volatiles in vacuo and crystallization of the residue from thf at −30 °C produced yellow crystals of $MoCl(CNCMe_3)_2(NO)(PMe_3)_2$ in ca. 70% yield.

$WCl(CNCMe_3)_2(NO)(PMe_3)_2$ can be obtained in similar yield by using an analogous procedure. Higher temperatures (50 °C for 6 h) are required, however.

Preparation of $Mo(\eta^2\text{-}S_2CNMe_2)(CNCMe_3)(NO)(PMe_3)_2$ (10). This compound was prepared by reaction of $Mo(\eta^2\text{-}S_2CNMe_2)(NO)(PMe_3)_3$ with 1 equiv of $CNCMe_3$, as described for the preparation of **8a** and **8b**. This resulted in the formation of complex **10**, which was crystallized, as red crystals, from a 4:1 petroleum ether–diethyl ether mixture at −30 °C; yield ca. 75%.

Preparation of $MoCl(\eta^3\text{-}S_2CPMe_3)(NO)(PMe_3)_2$ (11). To a solution of **2a** (0.65 g, ca. 1.4 mmol) in thf (35 mL) was added 1.4 equiv of CS_2 (1.4 mL of a 1 M solution in thf) and the resulting mixture stirred for 24 h at room temperature. This resulted in an almost colorless solution and a pale brown precipitate. The solid was collected by filtration, washed with Et_2O, and crystallized, as off-white crystals, from $CHCl_3$ at −30 °C; yield ca. 75%.

An enriched sample of **11** was prepared by using a ca. 1 M solution of CS_2 in thf, 50% enriched in $^{13}CS_2$.

Preparation of $Mo(\eta^3\text{-}S_2CPMe_3)(S_2CNMe_2)(NO)(PMe_3)$ (12). This compound was prepared by reacting **11** with 1 equiv of anhydrous NaS_2CNMe_2, as described for **6**, but letting the reaction proceed for 12 h. The title product was obtained, as yellow crystals, from a toluene solution at −30 °C in ca. 50% yield.

X-ray Structure Determination of 1a. A yellow prismatic crystal of size 0.2 × 0.4 × 0.4 mm was mounted in an Enraf-Nonius CAD4-F automatic diffractometer. The cell dimensions were refined by least-squares fitting of values of 25 reflections. The intensities of all 5691 unique reflections with $1 < \theta < 30°$ and the range from (−20,0,0) to (20,16,16) were measured at 295 K with monochromatic Mo Kα radiation (λ = 0.71069 Å) and an $\omega/2\theta$ scan technique. There was no appreciable change in the periodically monitored standard reflection. The intensities were corrected for Lorentz and polarization effects, and 4466 of these were considered as observed with $I > 2\sigma(I)$.

Scattering factors for neutral atoms and anomalous dispersion corrections for Mo, P, and Cl were taken from ref 28.

The structure was solved by Patterson and Fourier methods.

An empirical absorption correction[29] was applied at the end of the isotropic refinement. Anisotropic full-matrix least-squares refinement with unit weights, minimizing $\sum[|F_o| - |F_c|]^2$, led to $R = 0.034$. No trend in ΔF vs F_o and $(\sin\theta)/\lambda$ was observed.

Final refinement with fixed isotropic temperature factors and coordinates for H atoms gave $R = 0.028$ and $R_w = 0.030$. Maximum and average shift/error values were 0.018 and 0.004, respectively.

Most of the calculations were carried out with XRAY80.[30]

X-ray Structure Determination of 11·$CHCl_3$. A very unstable crystal (0.3 × 0.3 × 0.4 mm) was epoxy resin coated and mounted in an Enraf-Nonius CAD4-F automatic diffractometer. The cell dimensions were refined by least-squares fitting of the values of 25 reflections. The intensities of all 3587 unique reflections with $1 < \theta < 25°$ and the range from (−13,0,0) to (13,33,11) were measured at 295 K with monochromatic Mo Kα radiation (λ = 0.71069 Å) and an $\omega/2\theta$ scan technique. The crystal became damaged by radiation. The intensities were scaled from the variation of three standard reflections whose intensities fell to 50% at the end of the data collection. The intensities were corrected for Lorentz and polarization effects, and 2543 of these were considered as observed with $I > 2\sigma(I)$.

Scattering factors for neutral atoms and anomalous dispersion corrections for Mo, P, Cl, and S were taken from ref 28.

The structure was solved by Patterson and Fourier methods.

An empirical absorption correction[29] was applied at the end of the isotropic refinement. A very important nonresolvable positional disorder was found around the Cl_3CH molecules of crystallization.

Mixed full-matrix least-squares refinement with unit weights, minimizing $\sum[|F_o| - |F_c|]^2$, led to $R = 0.129$. Final refinement with fixed isotropic temperature factors and coordinates for H atoms gave $R = 0.12$. The average shift/error was 0.83.

Most of the calculations were carried out with XRAY80.[30]

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Registry No. **1a**, 119998-04-8; **1b**, 119998-16-2; **2a**, 119998-05-9; **2b**, 119998-17-3; **3**, 119998-06-0; **4**, 119998-07-1; **5**, 119998-08-2; **6**, 119998-09-3; **7**, 119998-10-6; **8a**, 119998-11-7; **8b**, 119998-18-4; **9a**, 119998-12-8; **9b**, 120032-86-2; **10**, 119998-13-9; **11**, 119998-14-0; **11**·$CHCl_3$, 120056-16-8; **12**, 119998-15-1; $MoCl_3(PMe_3)_3$, 73534-30-2; $WCl_3(PMe_3)_3$, 85798-78-3; $MoCl(CO)_2(NO)(PMe_3)_2$, 119998-19-5; CS_2, 75-15-0; PMe_3, 594-09-2.

Supplementary Material Available: Table SI, giving analytical data for complexes **1**–**12**, Tables SII–SV, listing bond distances and angles for **1a** and **11**, and Tables SVI and SVIII, listing thermal parameters for **1a** and **11** (9 pages); Tables SVII and SIX, listing observed and calculated structure factors for **1a** and **11** (73 pages). Ordering information is given on any current masthead page.

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(28) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(29) Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A* **1983**, *A39*, 158.

(30) Stewart, J. M. "The X-ray System"; Computer Science Center, University of Maryland: College Park, MD, 1985.