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# Seven-Coordinate Halo and Dithiocarbamate Trimethylphosphine Derivatives of Molybdenum(II) and Tungsten(II)

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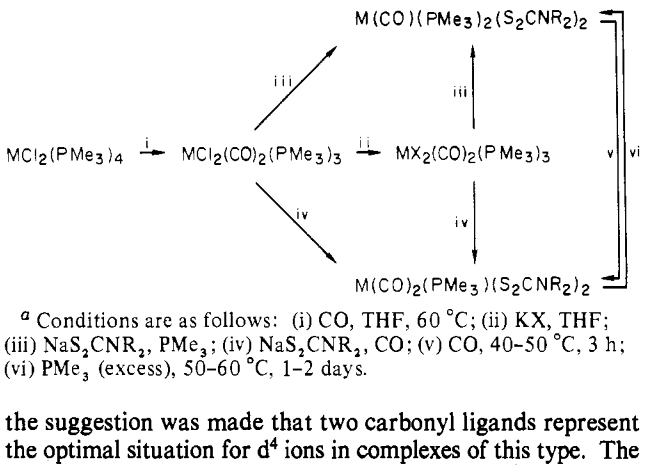
The seven-coordinate complexes $MCl_2(CO)_2(PMe_3)_3$ (M = Mo, W) have been prepared by interaction of the 16-electron paramagnetic species $MCl_2(PMe_3)_4$ (M = Mo, W) with carbon monoxide in boiling tetrahydrofuran. Metathesis with the appropriate potassium salts, KX, yields $MX_2(CO)_2(PMe_3)_3$ (X = Br, I, NCO, NCS), while reaction with $NaS_2CNR_2$ (R = Me, Et, *i*-Pr) gives a mixture of complexes $M(CO)_n(PMe_3)_{3-n}(S_2CNR_2)_2$ ($n$ = 1, 2). The monocarbonyl derivatives ($n$ = 1) have unusually low C–O stretching frequencies for terminal carbonyl groups (1760–1735 $cm^{-1}$) and transform readily into the corresponding dicarbonyl complexes by interaction with carbon monoxide. The reverse reactions require prolonged heating (50–60 °C) in the presence of a 3–4 molar excess of $PMe_3$ and in general, even under these conditions, do not go to completion. Variable-temperature $^1H$ and $^{31}P$ NMR spectra have been recorded for the new compounds. The proton spectra are very complex and show marked temperature dependence, providing relatively little information with regard to the stereochemistry of the complexes. For most of the halo derivatives $MX_2(CO)_2(PMe_3)_3$, the $^{31}P\{^1H\}$ NMR spectrum consists of an $AX_2$ pattern with some additional lines of smaller intensity being present at low temperatures (−60 °C). On the basis of IR and NMR data, structures are proposed for some of the complexes and are discussed in terms of those known for other related species.

## Introduction

Although the halo carbonyl complexes of Mo(II) and W(II) containing other additional ligands constitute one of the largest classes of seven-coordinate (7C) derivatives of these elements, compounds of composition $MX_2(CO)_2L_3$ are relatively rare, and for L = tertiary phosphine, are limited to the $PMe_2Ph$ derivatives.[2] The bulkier phosphines $PEt_3$, $PPh_3$, etc., also form 7C compounds, but they are usually of the $MX_2(CO)_3L_2$ type. Another important group of 7C derivatives of these elements is that formed by complexes in which the metal sites have mixed tertiary phosphine and sulfur chelating ligand environments. Among these, the dithiocarbamate complexes have received considerable attention since some of them are known to act as reversible CO carriers,[3] to display a versatile substitution reaction chemistry, and to bind carbon monoxide and other $\pi$-acid ligands at different oxidation states.[4,5]

Recent work in our laboratories and in those of others[6,7] has led to convenient, large-scale synthetic procedures for the preparations of $MCl_2(PMe_3)_4$ (M = Mo, W[7]) complexes. Since (i) these compounds are open-shell electron-deficient (i.e. 16-electron) species and (ii) on the basis of the steric requirements of the $PMe_3$ ligands, the compounds $MCl_2(CO)_2(PMe_3)_3$ are expected to be stable under normal conditions, we attempted their preparation by reaction of the 6C complexes $MCl_2(PMe_3)_4$ with carbon monoxide. The facility with which these conversions take place stimulated our interest in investigating their reaction chemistry, particularly the substitution of the chlorine atoms by the powerful chelating dithiocarbamate ligands. This interest was further enhanced by two literature reports. The first was concerned with the synthesis[5] of $W(CO)_2L(S_2CNR_2)_2$ complexes (L = phosphine or phosphite) by addition of the ligand to $W(CO)_3(S_2CNR_2)_2$. Failure to substitute a second carbonyl group by another phosphine molecule was explained on electronic grounds, and the suggestion was made that two carbonyl ligands represent the optimal situation for $d^4$ ions in complexes of this type. The second dealt with the preparation of the monocarbonyls $Mo(CO)L_2(S_2CNEt_2)_2$ (L = $PMe_2Ph$, $PMePh_2$) from the reaction of $MoCl_2(CO)_2L_n$ (L = $PMe_2Ph$, $n$ = 3; L = $PMePh_2$, $n$ = 2) with $NaS_2CNEt_2$. Formation of the dicarbonyl derivatives $Mo(CO)_2L(S_2CNEt_2)_2$ was not observed.[4]

Scheme I[a]



[a] Conditions are as follows: (i) CO, THF, 60 °C; (ii) KX, THF; (iii) $NaS_2CNR_2$, $PMe_3$; (iv) $NaS_2CNR_2$, CO; (v) CO, 40–50 °C, 3 h; (vi) $PMe_3$ (excess), 50–60 °C, 1–2 days.

In order to further ascertain the factors governing the formation of the mono- and dicarbonyl derivatives $M(CO)_nL_{3-n}(S_2CNR_2)_2$ ($n$ = 1,2), we have investigated the interaction of $MCl_2(CO)_2(PMe_3)_3$ (Mo = Mo, W) complexes with dithiocarbamate salts. In addition to the synthesis of a series of complexes of composition $MX_2(CO)_2(PMe_3)_3$ (M = Mo, W; X = Cl, Br, I, NCO, NCS), we report in this paper their reactions with $NaS_2CNR_2$, to yield the mono- and dicarbonyl derivatives $M(CO)(PMe_3)_2(S_2CNR_2)_2$ and $M(CO)_2(PMe_3)(S_2CNR_2)_2$ (M = Mo, W; R = Me, Et, *i*-Pr). The reactions leading to the new complexes are summarized in Scheme I. While this paper was in preparation, some $MX_2(CO)_2(PMe_3)_3$ complexes (M = Mo, W; X = Cl, Br, I) have been reported.[17]

## Results and Discussion

**$MoX_2(PMe_3)_4$ and $MX_2(CO)_2(PMe_3)_3$ Complexes.** We have recently shown[6] that the reduction of $MoCl_3(PMe_3)_3$[8] with Zn powder in tetrahydrofuran (THF), in the presence of a slight excess of trimethylphosphine, gives $MoCl_2(PMe_3)_4$

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(1) (a) Universidad de Sevilla. (b) Instituto Venezolano de Investigaciones Científicas.

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**Table I.** Analytical and Spectroscopic Data for $MX_2(CO)_2(PMe_3)_3$ Compounds

| compd | anal.[a] % C | % H | % other | mol wt[b] | IR data $\nu$(CO), cm$^{-1}$ | $K_{CO}$[c] | $K_i$[c] |
|---|---|---|---|---|---|---|---|
| $MoCl_2(CO)_2(PMe_3)_3$ | 29.4<br>(29.3) | 5.9<br>(6.0) | Cl 15.1<br>(15.7) | 476<br>(451) | 1920,[d] 1820 | 14.13 | 0.76 |
| $MoBr_2(CO)_2(PMe_3)_3$ | 24.5<br>(24.4) | 5.1<br>(5.0) | | 537<br>(540) | 1930,[e] 1825 | 14.25 | 0.79 |
| $MoI_2(CO)_2(PMe_3)_3$ | 21.1<br>(20.8) | 4.3<br>(4.3) | | | 1940,[e] 1840 | 14.43 | 0.76 |
| $Mo(NCO)_2(CO)_2(PMe_3)_3$ | 32.9<br>(33.6) | 5.7<br>(5.8) | N 5.8<br>(6.0) | 433<br>(464) | 1920,[d] 1825[f] | 14.17 | 0.72 |
| $Mo(NCS)_2(CO)_2(PMe_3)_3$ | 30.6<br>(31.4) | 5.3<br>(5.4) | N 5.6<br>(5.6) | | 1950,[e] 1860[g] | 14.66 | 0.69 |
| $WCl_2(CO)_2(PMe_3)_3$ | 24.1<br>(24.5) | 5.0<br>(5.0) | Cl 13.0<br>(13.2) | 483<br>(539) | 1910,[d] 1805 | 13.94 | 0.79 |
| $WI_2(CO)_2(PMe_3)_3$ | 18.4<br>(18.3) | 3.7<br>(3.7) | P 14.6<br>(13.9) | | 1930,[e] 1830 | 14.28 | 0.76 |
| $W(NCO)_2(CO)_2(PMe_3)_3$ | 28.3<br>(28.3) | 5.0<br>(4.9) | N 5.1<br>(5.1) | 539<br>(552) | 1905,[d] 1810[f] | 13.94 | 0.71 |
| $W(NCS)_2(CO)_2(PMe_3)_3$ | 26.7<br>(26.7) | 4.7<br>(4.6) | N 4.7<br>(4.8) | | 1935,[e] 1845[g] | 14.43 | 0.69 |

[a] Calculated values are given in parentheses. [b] Cryoscopically determined in benzene. [c] In mdyn·Å$^{-1}$. [d] Benzene solution. [e] Nujol mull. [f] $\nu$(NCO) 2220, 2200 cm$^{-1}$. [g] $\nu$(NCS) 2060 cm$^{-1}$.

**Table II.** $^{31}P\{^1H\}$ NMR Data for $MX_2(CO)_2(PMe_3)_3$ Complexes

| complex | *T*, K | $\delta(P_X)$ (d)[a] | $\delta(P_A)$ (t) | $J_{PP}$, Hz | solvent |
|---|---|---|---|---|---|
| $MoCl_2(CO)_2(PMe_3)_3$ | 308 | 22.5 | −14.8 | 17 | $CD_2Cl_2$ |
| $MoBr_2(CO)_2(PMe_3)_3$ | 303 | 16.3<br>13.3 | −20.7<br>−25.3 | 18 | $CD_3COCD_3$ |
| $MoI_2(CO)_2(PMe_3)_3$ | 308 | 8.0 | −37.2 | 19 | $CD_2Cl_2$ |
| $Mo(NCO)_2(CO)_2(PMe_3)_3$ | 273 | 27.6 | −5.0 | 15 | $CD_3COCD_3$ |
| $WCl_2(CO)_2(PMe_3)_3$[b] | 308 | −4.3 | −23.2 | 13 | $CD_3COCD_3$ |
| $WI_2(CO)_2(PMe_3)_3$[c] | 308 | −21.7 | −55.4 | 16 | $CD_3COCD_3$ |
| $W(NCO)_2(CO)_2(PMe_3)_3$[d] | 308 | −2.0 | −21.8 | 11 | $CD_3COCD_3$ |

[a] 85% $H_3PO_4$ as external reference. [b] Spectrum dominated by a singlet at $\delta$ −36.3, $J_{WP}$ = 108 Hz (see text). [c] $J_{WP}$ = 78 Hz. [d] $J_{WP}$ = 66 Hz.

in good yields. For large-scale preparations (ca. 20 mmol or larger), the reduction is best carried out with use of sodium amalgam as reductant. Metathesis reactions of $MoCl_2(PMe_3)_4$ with KX (X = Br, I) in boiling THF give the corresponding $MoX_2(PMe_3)_4$ derivatives as crystalline, moderately air-stable materials. The IR spectra of all these compounds are very similar and are dominated by the absorptions due to the $PMe_3$ ligands. As expected, these 16-electron species are paramagnetic, with magnetic moments (measured in solution by the Evans method) close to 2.80 $\mu_B$. However, in spite of their paramagnetism, they give observable albeit broad NMR signals between $\delta$ −7.5 and −9.0. Although the spectra are not very informative, the observation of a single resonance for each compound suggests a trans arrangement of halogen atoms. This has been confirmed for the chlorine derivative by X-ray crystallography.[6]

Since 6C $d^4$ metal complexes are electron-deficient species that have only 16 metal valence electrons, they usually display reactivity patterns characteristic of coordinatively unsaturated metal compounds. To test the electrophilicity of the open-shell $MX_2(PMe_3)_4$ complexes (M = Mo, W[7]), we have carried out their reaction with carbon monoxide. At room temperature, THF solutions of $MX_2(PMe_3)_4$ complexes react only very slowly with CO, but at temperatures near reflux (50–60 °C), the reactions go to completion in ca. 3–6 h (eq 1).

$$MX_2(PMe_3)_4 + 2CO \rightarrow MX_2(CO)_2(PMe_3)_3 + PMe_3 \quad (1)$$
$$M = Mo;\ X = Cl, Br, I$$
$$M = W;\ X = Cl$$

Further metathesis in acetone or THF with an excess of the appropriate potassium salts leads to the remaining $MX_2(CO)_2(PMe_3)_3$ complexes studied in this work (M = Mo, X = NCO, NCS; M = W, X = I, NCO, NCS). All the compounds are crystalline materials, moderately stable to air in the solid state, although they decompose quickly in solution in the presence of small amounts of oxygen and water. Molecular weight determinations, cryoscopically in benzene, for some of the compounds show they are monomeric. Inasmuch as the remaining derivatives have similar properties, they can be assumed to be monomeric.

IR studies for the complexes (Table I) show the presence of two strong bands between 1950 and 1800 cm$^{-1}$ due to the C–O stretching vibrations of the two coordinated CO groups. From the relative intensities of the bands observed in solution for $MoCl_2(CO)_2(PMe_3)_3$, an approximate value of 82° can be computed for the OC–Mo–CO angle in this compound. This compares well with 71.4°, found for $MoCl_2(CO)_2(PMe_2Ph)_3$ by X-ray crystallography.[9]

Qualitative differences in the extent of $\pi$ back-donation from the metal to the carbon monoxide $\pi^*$ orbitals can be obtained from a comparison of the observed vibrational frequencies or of the values of the approximate carbon monoxide force constants, computed by the Cotton–Kraihanzel method[10] assuming $C_{2v}$ symmetry for the $M(CO)_2$ moieties. From the data in Table I, the following can be concluded: (i) A small but systematic shift to lower values for the C–O stretching frequencies and force constants is observed for the tungsten complexes with respect to their molybdenum analogues. This indicates greater $\pi$ back-donation for the tungsten complexes, which is possibly a consequence of the increase in metal basicity on going from molybdenum to tungsten.[12] (ii) In these complexes the extent of the metal-to-carbonyl backbonding shows some dependence on the basicity of the P-donor ligands. The shift in the value of $K_{CO}$ on going from the $PMe_3$ to the $PMe_2Ph$ derivatives, although in the proper direction, is of little significance owing to its small magnitude and to the uncertainties, but the expected decrease observed on going from the $P(OMe)_3$[11] to the $PMe_3$ complexes is large enough to allow a qualitative differentiation.

The room-temperature $^1H$ and $^{31}P$ NMR spectra of the complexes $MX_2(CO)_2(PMe_3)_3$ are rather complex and do not allow any conclusive stereochemical assignments. Since the

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(11) Calculated values of $K_{CO}$ for $MoX_2(CO)_2(P(OMe)_3)_3$ (X = Cl, Br)[16] are 15.08 (X = Cl) and 15.07 (X = Br) mdyn·Å$^{-1}$.

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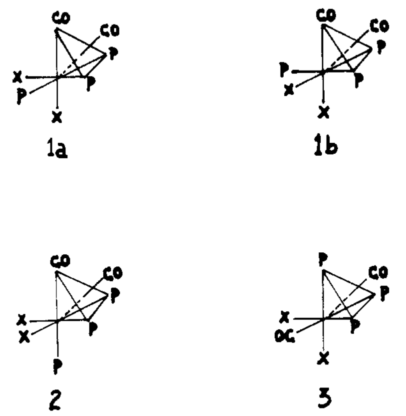

1a 1b 2 3

**Figure 1.** Configurations for the seven-coordinate (7C) complexes.

spectra are temperature dependent, variable-temperature (from −60 to +60 °C) NMR studies have been carried out for some of these complexes (M = Mo, X = Cl, Br, I, CNO; M = W, X = Cl, I, CNO). Selected $^{31}P\{^1H\}$ NMR data are collected in Table II ($^1H$ and $^{31}P$ variable-temperature spectra are available as supplementary material). With some exceptions that are discussed below, the low-temperature $^1H$ NMR spectra are very complex and do not provide any additional information. The complexity arises because of the similarities in the chemical shifts of the phosphine methyl protons, the virtual coupling effects between the $PMe_3$ ligands, and possibly the presence in solution of more than one isomer. The $^{31}P\{^1H\}$ NMR spectra are however considerably simpler and display, in most of the cases studied, a neat $AX_2$ pattern in the above temperature range. Some other lines of smaller intensity, placed between the doublet and the triplet, are in some instances observed, and their presence can be related to isomerization processes that generate comparatively minor concentrations of other species. There are two exceptions to this general behavior. The first corresponds to the complex $MoBr_2(CO)_2(PMe_3)_3$, which gives rise to two $AX_2$ patterns of relative intensity 1:2, indicating the presence of two isomers. In the second, viz. $WCl_2(CO)_2(PMe_3)_3$, the spectrum is dominated from +50 to −60 °C by a singlet at $\delta$ −36.3 ($^1J_{WP}$ = 107 Hz). An $AX_2$ pattern ($\delta$ −4.3 d, −23.2 t, $^2J_{PP}$ = 13 Hz) of very little total intensity can also be observed. This clearly suggests that the major species present in solution is fluxional in this temperature range.

The cyanate derivatives $M(NCO)_2(CO)_2(PMe_3)_3$ deserve more detailed comment, since an unambiguous structural assignment can be made for these complexes on the basis of IR and $^1H$ and $^{31}P$ NMR spectroscopic studies. Assuming a capped octahedron geometry for our $MX_2(CO)_2(PMe_3)_3$ complexes as it has been found in other structurally characterized 7C complexes of molybdenum and tungsten with halide, carbonyl, and phosphine ligands, four possible configurations can be envisaged (Figure 1). The enantiomeric pair **1a**–**1b** corresponds to an AMX spin system for the phosphorus nuclei and can therefore be discarded on the basis of the available $^{31}P$ NMR data. The geometries **2** and **3** correspond to $AX_2$ systems and are compatible with both $^1H$ and $^{31}P\{^1H\}$ NMR data. For instance, the $^1H$ NMR spectrum of $W(NCO)_2(CO)_2(PMe_3)_3$ consists of a filled-in doublet ($\delta$ 1.65) for the two symmetry-related $PMe_3$ molecules, indicative of a small or intermediate coupling between the phosphorus nuclei, and of a doublet ($\delta$ 1.29) for the third $PMe_3$ group, at all temperatures between −60 and 30 °C. This supports a cis (facial) distribution of the three phosphine molecules, and this assumption is further supported by the low value of $J_{PP}$ (see Table II) measured for these compounds. A unique assignment is not however possible on the sole basis of NMR data, and further discrimination between these two geometries requires the use of IR data. For each of the two $C_s$ geometries **2** and **3**, two C–N (A′ + A″) and two C–O (2 A′) stretching bands are expected for the cyanate and carbonyl groups, and indeed the IR spectra of the $M(NCO)_2(CO)_2(PMe_3)_3$ complexes agree well with these expectations (Table I). In **2** the two carbonyl groups display a cisoid configuration, while in **3** they occupy transoid positions. Thus, a distinction between **2** and **3** can in principle be made from the approximate values of the CO–Mo–CO angles as calculated from the relative intensities of the two carbonyl bands. Benzene solutions of the complexes $M(NCO)_2(CO)_2(PMe_3)_3$ display two carbonyl bands at 1920 and 1825 $cm^{-1}$ (M = Mo) and 1905 and 1810 $cm^{-1}$ (M = W) whose intensity ratios remain largely invariant and from which CO–M–CO angles of 80° (Mo) and 85° (W) can be computed. This is therefore in support of geometry **2**, which is also the more favorable on electronic grounds.[13]

**Dithiocarbamate Derivatives.** Seven-coordinate dialkyldithiocarbamate complexes of the type $M(CO)_2L(S_2CNR_2)_2$ (L = phosphine ligand) have been known for many years.[12,14] More recently, Templeton has reported[5] the synthesis of a series of compounds of the type $W(CO)_2L(S_2CNR_2)_2$ (R = Me, Et; L = tertiary phosphine or phosphite), from the reaction of $W(CO)_3(S_2CNR_2)_2$ with the appropriate ligand, while Pickett and Chatt[4] have prepared the monocarbonyl derivatives $Mo(CO)L_2(S_2CNEt_2)_2$ (L = $PMe_2Ph$, $PMePh_2$; $L_2$ = $Ph_2P(CH_2)_2PPh_2$). The interaction of THF or acetone solutions of $MX_2(CO)_2(PMe_3)_3$ with $NaS_2CNEt_2$ affords usually the corresponding dicarbonyl complexes (eq 2), only

$$MCl_2(CO)_2(PMe_3)_3 + NaS_2CNEt_2 \rightarrow M(CO)_2(PMe_3)(S_2CNEt_2)_2 + NaCl + PMe_3 \quad (2)$$

minor amounts of the monocarbonyl derivatives being isolated. For the $S_2CNMe_2^-$ and $S_2CN\text{-}i\text{-}Pr_2^-$ derivatives, variable proportions of the two types of complexes are usually obtained. Interconversion of these compounds can be achieved under appropriate conditions. Thus, the bis(phosphine) derivatives are transformed into the corresponding dicarbonyl complexes by interaction with carbon monoxide at ca. 50 °C for about 4 h. The reverse reactions take place less readily, and for some of the complexes studied, they require heating at 50–60 °C for 1–2 days in the presence of an excess (3–4 equiv) of $PMe_3$. The importance of electronic effects is therefore clear, and as already suggested[5] the presence of two carbonyl ligands may represent the optimal situation for $d^4$ ions in this type of complex. However, under rather forcing conditions, substitution of a second carbonyl group by the relatively small phosphine $PMe_3$ takes place, clearly illustrating the importance of the steric effects at the metal site. These bis(phosphine) complexes are electron-rich species, and this property is clearly shown not only by the ease of substitution of one of the $PMe_3$ molecules by a carbonyl group but also by the low value of the C–O stretching frequency (1760–1735 $cm^{-1}$) observed in these complexes (vide infra).

The IR spectra of the $M(CO)_2(PMe_3)(S_2CNR_2)_2$ derivatives (Table III) show two C–O stretching frequencies in the range 1925–1800 $cm^{-1}$. As for the $MX_2(CO)_2(PMe_3)_3$ complexes, lower $K_{CO}$ values and CO stretching frequencies are systematically observed for the tungsten derivatives. No significant differences can however be detected in the values of $K_{CO}$ for $M(CO)_2L(S_2CNR_2)_2$ compounds (L = $PMe_3$, $PPh_3$, $P(OEt)_3$, $PEt_3$). On the basis of the similarities in the carbonyl region of the IR spectra, the complexes $M(CO)_2(PMe_3)(S_2CNR_2)_2$ seem to have structures similar to that of $W(CO)_2(PPh_3)(S_2CNEt_2)_2$, which has been described as a tetragonal-base trigonal-base (4:3 "piano stool") geometry,

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(13) See, for instance: Burdett, J. K.; Albright, T. A. *Inorg. Chem.* **1979**, *18*, 2112.

(14) Colton, R.; Rose, G. G. *Aust. J. Chem.* **1970**, *23*, 1111.

Table III. Analytical and Spectroscopic Data for $M(CO)_n(PMe_3)_{3-n}(S_2CNR_2)_2$ ($n$ = 1, 2) Complexes

| | anal.[a] | | | IR data,[b] $cm^{-1}$ | | $^1H$ NMR data, $\delta$ | | | $^{31}P$ NMR data[c] | |
|---|---|---|---|---|---|---|---|---|---|---|
| compd | % C | % H | % N | $\nu$(CO) | $\nu$(CN) | Me-P[d] | Me-dtc | $-CH_n$-dtc | $\delta$[e] | $J_{PW}$, Hz |
| $Mo(CO)_2(PMe_3)(S_2CNMe_2)_2$ | 27.6<br>(28.2) | 4.4<br>(4.5) | 5.8<br>(6.0) | 1920<br>1830 | 1515 | 1.62 d | 2.87 s | | | |
| $Mo(CO)_2(PMe_3)(S_2CNEt_2)_2$ | 35.2<br>(34.4) | 5.0<br>(5.5) | 6.0<br>(5.3) | 1925<br>1835 | 1500 | 1.47 d | 1.02 t | 3.51 q | | |
| $Mo(CO)_2(PMe_3)(S_2CN\text{-}i\text{-}Pr_2)_2$ | *f* | | | 1915<br>1830 | 1475 | 1.62 d | 1.43 d | 4.67 m | | |
| $Mo(CO)(PMe_3)_2(S_2CNMe_2)_2$ | 30.3<br>(30.2) | 5.7<br>(5.8) | 5.5<br>(5.4) | 1760 | 1505 | 1.46 d[g] | 3.25 s | | 22.7 | |
| $Mo(CO)(PMe_3)_2(S_2CNEt_2)_2$ | 35.6<br>(35.7) | 6.7<br>(6.6) | 4.7<br>(4.9) | 1755 | 1490 | 1.67 d[g] | 1.02 t | 3.63 q | | |
| $Mo(CO)(PMe_3)_2(S_2CN\text{-}i\text{-}Pr_2)_2$ | 39.9<br>(40.1) | 7.1<br>(7.3) | 4.4<br>(4.5) | 1755 | 1480 | 1.59 d[g] | 1.17 d | 4.50 m | 22.0 | |
| $W(CO)_2(PMe_3)(S_2CNMe_2)_2$ | 23.9<br>(23.7) | 3.8<br>(3.8) | 5.1<br>(5.0) | 1900<br>1805 | 1520 | 1.61 d | 3.25 s | | −10.9 | 210 |
| $W(CO)_2(PMe_3)(S_2CNEt_2)_2$ | 29.6<br>(29.4) | 4.8<br>(4.7) | 4.5<br>(4.6) | 1910<br>1820 | 1490 | 1.56 d | 0.97 t | 3.37 q | | |
| $W(CO)_2(PMe_3)(S_2(CN\text{-}i\text{-}Pr_2)_2$ | 34.0<br>(34.1) | 5.6<br>(5.5) | 4.3<br>(4.2) | 1915<br>1825 | 1505 | 1.40 d | 1.10 d | 4.40 m | −11.8 | 208 |
| $W(CO)(PMe_3)_2(S_2CNMe_2)_2$ | 25.7<br>(25.8) | 4.8<br>(5.0) | 4.5<br>(4.6) | 1735 | 1500 | 1.68 d[g] | 2.60 s | | −4.3 | 202 |
| $W(CO)(PMe_3)_2(S_2CNEt_2)_2$ | 29.4<br>(30.9) | 5.8<br>(5.8) | 4.1<br>(4.2) | 1740 | 1495 | 1.85 d[g] | 1.37 t | 3.47 q | | |
| $W(CO)(PMe_3)_2(S_2CN\text{-}i\text{-}Pr_2)_2$ | 35.2<br>(35.2) | 6.5<br>(6.4) | 3.9<br>(3.9) | 1740 | 1485 | 1.70 d[g] | 1.16 d | 4.50 m | −4.5 | 200 |

[a] Calculated values are given in parentheses. [b] Nujol mull. [c] In $CD_3COCD_3$. [d] $J_{HP}$ = 8.0–9.5 Hz. [e] 85% $H_3PO_4$ as external reference. [f] No satisfactory analytical data were obtained. [g] Doublet with some central intensity.

with CPSS:CSS distribution of the donor atoms. In this respect, the approximate value of ca. 85° computed for the CO–M–CO angle in the $M(CO)_2(PMe_3)(S_2CNR_2)_2$ complexes, from intensity measurements of the solution C–O stretching bands, compares favorably with that of 71.6° found for the $PPh_3$ complex by X-ray crystallography.[5] The monocarbonyl derivatives show a single C–O band at a rather unusually low frequency (1760–1735 $cm^{-1}$), in the range normally associated with bridging carbonyl groups. This is obviously indicative of intense $\pi$ back-donation from the metal to the CO $\pi^*$ orbitals. Comparison with the lower energy band in the dicarbonyl analogues shows a shift of ca. 75–80 $cm^{-1}$ to lower energy. Although this is to be expected from qualitative theory of the M–CO bond upon substitution of the $\pi$-acid CO molecule by the strongly electron-releasing $PMe_3$ ligand, the order of magnitude is uncommon and may be indicative of a change of stereochemistry, with the single carbonyl group now occupying a position trans to one of the $PMe_3$ ligands.

As expected the $^1H$ NMR spectra of the dithiocarbamate complexes (Table III) show at room temperature equivalence of all the alkyl groups. Thus, a singlet is for instance observed for the $S_2CNMe_2$ derivatives, and a triplet and a doublet are observed for the $S_2CNEt_2$ complexes. The phosphine methyl protons give rise to a neat doublet in the compounds $M(CO)_2(PMe_3)(S_2CNR_2)_2$ and a doublet with some central intensity in the $M(CO)(PMe_3)_2(S_2CNR_2)_2$ derivatives suggesting in the latter a cis distribution of the phosphine ligands. These features remain unchanged in the temperature range from −60 to +60 °C. A single resonance is observed in the $^{31}P\{^1H\}$ NMR spectra for all the complexes; inasmuch as no changes are observed upon lowering the temperature down to −60 °C, it can be concluded that there is only one isomer present in solution in appreciable concentration. For the tungsten complexes, the one-bond $^1J_{WP}$ coupling constants ($^{183}W$, 14.42%) have normal values (ca. 200–210 Hz), and since the coupling is maintained between −60 and +60 °C, the fluxional process responsible for the equilibration of the $S_2CNR_2$ alkyl groups does not involve phosphine dissociation. This is in agreement with the results of detailed $^{13}C$ and $^{31}P$ NMR studies carried out by Templeton[5] on the related complexes $W(CO)_2L(S_2CNR_2)_2$ (L = $PPh_3$, $PEt_3$, $P(OEt)_3$).

## Experimental Section

Microanalyses were performed by Butterworth Microanalytical Consultancy Ltd. and Pascher Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer Model 577. NMR spectra were taken at 60 MHz ($^1H$) and 28.289 MHz ($^{31}P$) on a Bruker WP60 instrument, operating in the Fourier transform mode, and on a Perkin-Elmer R-12B ($^1H$). All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Molecular weights were measured cryoscopically in benzene under nitrogen. Magnetic susceptibilities were determined by the Evans method. Solvents were dried and degassed before use. The compounds $MoCl_2(PMe_3)_4$[6] and $WCl_2(PMe_3)_4$[7] were prepared as described in the literature. The ligand $PMe_3$ was obtained by the method of Wolfsberger and Schmidbaur.[15] Sodium dialkyldithiocarbamate salts were dried by heating at 100 °C for 7 days under vacuum. $MoBr_2(PMe_3)_4$ and $MoI_2(PMe_3)_4$ were obtained in ca. 80% yield by metathesis of $MoCl_2(PMe_3)_4$ with KBr and KI, respectively, in tetrahydrofuran, at 60 °C over a period of 10 h.

**A. Synthesis of $MX_2(CO)_2(PMe_3)_3$ Complexes. Dichlorodicarbonyltris(trimethylphosphine)molybdenum(II), $MoCl_2(CO)_2(PMe_3)_3$.** Carbon monoxide is bubbled through a solution of $MoCl_2(PMe_3)_4$ (1.88 g, ca. 4 mmol) in THF (60 mL), at 65–70 °C for 3 h. The solvent is then removed under vacuum and a yellow product precipitated by addition of 30–40 mL of diethyl ether. This solid is filtered off, washed with 30 mL of $Et_2O$, and dissolved in 45 mL of petroleum ether–$CH_2Cl_2$ (3:1); the resultant solution is then centrifuged. The resulting yellow–orange solution is concentrated under vacuum and cooled at −30 °C overnight, yielding 1.40 g (3.1 mmol) of the product (75%).

The dibromo $MoBr_2(CO)_2(PMe_3)_3$ and diiodo $MoI_2(CO)_2(PMe_3)_3$ analogues can be prepared in high yields by a procedure entirely similar to that described above for the chlorine analogue or by metathesis of this latter compound with KBr or KI in THF at reflux for ca. 3–4 h. Crystallization is achieved from $Et_2O$ at −30 °C.

The thiocyanate, $Mo(NCS)_2(CO)_2(PMe_3)_3$, and cyanate, $Mo(NCO)_2(CO)_2(PMe_3)_3$, analogues are also prepared by metathesis with the corresponding potassium salts in THF at room temperature for about 4 h in ca. 70% yield. The NCO complex is relatively soluble

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in diethyl ether, while the NCS derivative requires a mixture of $EtOH-CH_2Cl_2$ to crystallize.

By carbonylation of $WCl_2(PMe_3)_4$ in a way similar to that described for $MoCl_2(PMe_3)_4$ for a period of 6–8 h, the complex dichlorodicarbonyltris(trimethylphosphine)tungsten(II), $WCl_2(CO)_2(PMe_3)_3$, can be obtained. Crystallization is achieved from petroleum ether–$CH_2Cl_2$ (3:1) at −30 °C (70% yield).

Metathesis with the appropriate potassium salts in acetone at room temperature affords the I, NCS, and NCO derivatives in ca. 40–50% yield.

**B. Synthesis of $M(CO)(PMe_3)_2(S_2CNR_2)_2$ Complexes. Carbonylbis(trimethylphosphine)bis(dimethyldithiocarbamato)molybdenum(II), $Mo(CO)(PMe_3)_2(S_2CNMe_2)_2$.** To a mixture of $MoCl_2(CO)_2(PMe_3)_3$ (0.45 g, ca. 1 mmol) and $NaS_2CNMe_2$ (ca. 4 mmol) is added 40 mL of acetone or THF via syringe. The suspension is stirred for ca. 4 h while a red color develops. Excess of $PMe_3$ (0.3 mL, ca. 3 mmol) is then added and the stirring continued for 12–18 h, at 40–50 °C. The solvent is stripped off in vacuo and the residue extracted with a diethyl ether–acetone mixture. Centrifugation and cooling at −30 °C give the product as red crystals in ca. 60% yield.

The compounds $Mo(CO)(PMe_3)_2(S_2CNR_2)_2$ (R = Et, *i*-Pr) were obtained as red crystals from $Et_2O$, in similar yields by an analogous procedure.

Starting with the chlorocarbonyltungsten(II) complex, $WCl_2(CO)_2(PMe_3)_3$, the corresponding tungsten compounds were prepared: $W(CO)(PMe_3)_2(S_2CNMe_2)_2$, red crystals from $CH_2Cl_2$–acetone; $W(CO)(PMe_3)_2(S_2CNEt_2)_2$, red crystals from $Et_2O$; $W(CO)(PMe_3)_2(S_2CN\text{-}i\text{-}Pr_2)_2$, red crystals from $Et_2O$–acetone.

**C. Synthesis of $M(CO)_2(PMe_3)_2(S_2CNR_2)_2$ Complexes. Dicarbonyl(trimethylphosphine)bis(dimethyldithiocarbamato)molybdenum(II), $Mo(CO)_2(PMe_3)(S_2CNMe_2)_2$.** $MoCl_2(CO)_2(PMe_3)_3$ (0.45 g, ca. 1 mmol) and $NaS_2CNMe_2$ (ca. 4 mmol) are mixed together, and 40 mL of THF or acetone is added. After it was stirred at room temperature for 4 h, the resulting dark red mixture is reacted at 50–60 °C with carbon monoxide at atmospheric pressure until the IR spectrum shows complete disappearance of the absorptions due to the monocarbonyl derivative $Mo(CO)(PMe_3)_2(S_2CNMe_2)_2$ (approximately 4 h). The suspension is then evaporated to dryness and the residue crystallized from $Et_2O$ to give red crystals of the title compound.

The following complexes can be obtained by similar procedures: $Mo(CO)_2(PMe_3)(S_2CN\text{-}i\text{-}Pr_2)_2$, red crystals from $Et_2O$–acetone; $W(CO)_2(PMe_3)(S_2CNR_2)_2$, red crystals from $Et_2O$–acetone for R = Me and orange crystals from $Et_2O$ for R = *i*-Pr. The $S_2CNEt_2$ derivatives can be obtained similarly, although they are usually obtained directly (red crystals from $Et_2O$) from the reactions of $NaS_2CNEt_2$ with the corresponding $MCl_2(CO)_2(PMe_3)_3$ (M = Mo, W) complexes. Yields are about 50–60%.

**Registry No.** $MoCl_2(CO)_2(PMe_3)_3$, 83828-53-9; $MoBr_2(CO)_2(PMe_3)_3$, 83828-52-8; $MoI_2(CO)_2(PMe_3)_3$, 83828-51-7; $Mo(NCO)_2(CO)_2(PMe_3)_3$, 88393-32-2; $Mo(NCS)_2(CO)_2(PMe_3)_3$, 88393-33-3; $WCl_2(CO)_2(PMe_3)_3$, 83828-56-2; $WI_2(CO)_2(PMe_3)_3$, 83828-54-0; $W(NCO)_2(CO)_2(PMe_3)_3$, 88393-34-4; $W(NCS)_2(CO)_2(PMe_3)_3$, 88393-35-5; $Mo(CO)_2(PMe_3)(S_2CNMe_2)_2$, 88393-36-6; $Mo(CO)_2(PMe_3)(S_2CNEt_2)_2$, 88393-37-7; $Mo(CO)_2(PMe_3)(S_2CN\text{-}i\text{-}Pr_2)_2$, 88393-38-8; $Mo(CO)(PMe_3)_2(S_2CNMe_2)_2$, 88393-39-9; $Mo(CO)(PMe_3)_2(S_2CNEt_2)_2$, 88393-40-2; $Mo(CO)(PMe_3)_2(S_2CN\text{-}i\text{-}Pr_2)_2$, 88393-41-3; $W(CO)_2(PMe_3)(S_2CNMe_2)_2$, 88393-42-4; $W(CO)_2(PMe_3)(S_2CNEt_2)_2$, 88393-43-5; $W(CO)_2(PMe_3)(S_2CN\text{-}i\text{-}Pr_2)_2$, 88393-44-6; $W(CO)(PMe_3)_2(S_2CNMe_2)_2$, 88393-45-7; $W(CO)(PMe_3)_2(S_2CNEt_2)_2$, 88393-46-8; $W(CO)(PMe_3)_2(S_2CN\text{-}i\text{-}Pr_2)_2$, 88393-47-9; $MoCl_2(PMe_3)_4$, 85185-53-1; $MoBr_2(PMe_3)_4$, 85185-54-2; $MoI_2(PMe_3)_4$, 85248-74-4; $WCl_2(PMe_3)_4$, 85798-76-1.

**Supplementary Material Available:** $^1H$ and $^{31}P\{^1H\}$ NMR spectra (13 pages). Ordering information is given on any current masthead page.

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# The $[VO(O_2)_2Cl]^{2-}$–$[V(O_2)_3Cl]^{2-}$ Pair in Peroxyvanadium(V) Chemistry: Synthesis of the First Chloroperoxyvanadate(V) Compounds and Evidence for Diperoxyvanadate(V)–Triperoxyvanadate(V) Interconversion

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Alkali-metal and ammonium salts of yellow oxydiperoxychlorovanadates(V), $A_2[VO(O_2)_2Cl]$, and blue triperoxychlorovanadates(V), $A_2[V(O_2)_3Cl]$ (A = Na, K, or $NH_4$), have been synthesized, for the first time, by reacting $V_2O_5$ with alkali chloride, ACl, and hydrogen peroxide in varying concentrations of alkaline media. The three salts of the anion $[VO(O_2)_2Cl]^{2-}$ are comparatively more stable than those of the complex anion $[V(O_2)_3Cl]^{2-}$. Characterization of the compounds has been made from the results of elemental analyses, magnetic susceptibility measurements, and IR spectroscopic studies. The IR spectra suggest that the peroxy groups are bonded to vanadium(V) in a triangular bidentate manner and that the O–O bond order of peroxy ligands decreases with the increase in the number of peroxy ligands coordinated to the metal center. The conversion of $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$ and the reverse provide good evidence for the facile diperoxyvanadate(V)–triperoxyvanadate(V) interconversion.

Studies of peroxyvanadium chemistry have generated considerable current interest[1–7] probably owing to the special biochemical significance[8,9] of peroxy–transition-metal complexes. Whereas most of the recent reports on peroxyvanadium chemistry deal with the studies in solutions,[2–7] the synthesis and structural assessment of such compounds have received only scant attention. Moreover, only a few heteroligand peroxy complexes of vanadium are known, in contrast to many such reported examples for the other transition metals.[9–11] Our interest in this area involving the synthesis, characterization, structural assessment, and study of the chemistry of peroxyvanadium compounds[12,13] has led to the synthesis of chloro-

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