intermediate-spin, and low-spin complexes. While the theoretical results for the intermediate-spin complexes are controversial, remarkably good agreement with the extended Hückel results is obtained in this study, the exception being the relative ordering of the $d_{x^2-y^2}$ and d_{z^2} populations. The effect of σ-donation by the ligands is observed in all complexes studied so far. It leads to peaks along the x and y directions in the high-spin iron(II) porphyrin FeTPP(THF)$_2$ and reduces the asymmetry of the electron distribution around iron in the low-spin complex analyzed in this study.

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Registry No. Fe(TPP), 16591-56-3; Fe(py)$_2$TPP, 16999-25-0.

Supplementary Material Available: Figure S1, showing the definition of the local coordinate system used in the multipole refinement, and tables of maximum and minimum intensity corrections, least-squares planes, electron population parameters, hydrogen atom coordinates, and bond lengths and angles involving hydrogen atoms (16 pages); a listing of observed and calculated structure factors for crystal 2, refinement IV (51 pages). Ordering information is given on any current masthead page.

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Oxo-Molybdenum(IV) and -Tungsten(IV) Complexes with Dithio Acid Ligands. Synthesis and Structural Investigation of MoO[S$_2$C(PMe$_3$)S-*i*-Pr-*S*,*S*′](S$_2$CS-*i*-Pr-*S*,*S*′,*C*)

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The title compound has been synthesized by the reaction of MoOCl$_2$(PMe$_3$)$_3$ with the potassium salt of the isopropyl thioxanthate ligand, in the presence of CS$_2$. The analogous reactions of the oxo complexes MOCl$_2$(PMe$_3$)$_3$ (M = Mo, W) with this and other thioxanthate ligands $^-$S$_2$CSR (R = *i*-Pr, *t*-Bu) afford related products displaying similar IR spectral properties, but only for M = Mo and R = *i*-Pr have analytically pure crystals been isolated. The formation of the related dimethylphenylphosphine–xanthate complexes MO[S$_2$C(PMe$_2$Ph)O-*i*-Pr](S$_2$CO-*i*-Pr) (M = Mo, W) is also reported. The molecular structure of MoO[S$_2$C(PMe$_3$)S-*i*-Pr](S$_2$CS-*i*-Pr) has been determined by X-ray studies, which confirm that one of the thioxanthate ligands has suffered a nucleophilic attack of PMe$_3$ on the carbon atom of the CS$_2$ moiety, with formation of the zwitterionic ligand $^-$S$_2$C$^-$($^+$PMe$_3$)SR, S,S′-bonded to the molybdenum atom, while the other acts as an η^3, S,S′,C ligand. The crystals are triclinic, $P\bar{1}$, with unit cell constants a = 6.355 (3) Å, b = 12.252 (2) Å, c = 13.061 (2) Å, α = 92.96 (1)°, β = 93.65 (2)°, γ = 85.16 (3)°, and D_{calcd} = 1.61 g cm^{-3} for Z = 2. The structure was refined to an R value of 0.032 by using 3488 independent observed reflections.

Introduction

The chemistry of group 6B (6[21]) metal complexes of dithio acid ligands has attracted considerable attention in the last few decades, in view of the possible relevance of some of these compounds to metalloenzymes, as examples of complexes with high coordination number in various oxidation states, and because of their ability to produce unique structural types of carbon- and sulfur-containing ligands, through ligand dissociation, coupling, fragmentation, or rearrangement.[1] Fruits of these studies are a very large number of complexes containing these ligands or others, thereof derived, such as thiocarboxamide, thiocarbonyl, and related groups.[2]

We have recently reported[3] that the reaction of the oxo complexes MOCl$_2$(PMe$_3$)$_3$ (M = Mo, W) with potassium *O*-alkyl xanthates KS$_2$COR (R = Me, Et, *i*-Pr) occurs, as in eq 1, with

$$\mathrm{MOCl_2(PMe_3)_3 + 2KS_2COR \xrightarrow{THF} MO[S_2C(PMe_3)OR](S_2COR) + 2PMe_3 + 2KCl} \quad (1)$$

formation of oxo complexes that contain two different xanthate ligands: a zwitterionic ligand, $^-$S$_2$C$^-$($^+$PMe$_3$)OR, S,S′-bonded to the metal atom, formed by nucleophilic attack of PMe$_3$ on the carbon atom of the CS$_2$ moiety, and an η^3-S$_2$COR ligand, bonded through the two sulfur atoms and the carbon atom of the CS$_2$ group. As a continuation of these studies, we have attempted to extend the above results to related complexes of other dithio acid ligands, particularly to the thioxanthate ligand, $^-$S$_2$CSR. This choice was partly dictated by the previous isolation[4] of the complex MoO(S$_2$CS-*i*-Pr)$_2$, which has been shown by X-ray crystallography to contain a thioxanthate group exhibiting the usual bidentate geometry and a second acting as a nonclassical η^3 S,S′,C ligand, and by the isolation of its PPh$_3$ adduct, MoO(S$_2$CS-*i*-Pr)$_2$(PPh$_3$), from the reaction of the dinuclear complex Mo$_2$O$_3$(S$_2$CS-*i*-Pr)$_4$ with an excess of PPh$_3$.[4] In this paper, we report the synthesis of the new dithio acid complex MoO[S$_2$C(PMe$_3$)S-*i*-Pr](S$_2$CS-*i*-Pr) and compare its structural properties, ascertained by NMR and X-ray studies, with those found for the xanthate complex analogue.[3] The ability of other phosphines to form analogous zwitterionic ligands has been demonstrated with the synthesis of the related compounds MO[S$_2$C(PMe$_2$Ph)O-*i*-Pr](S$_2$CO-*i*-Pr) (M = Mo, W).

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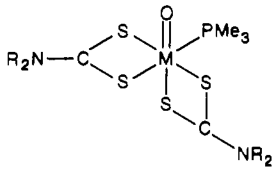
Table I. NMR Data for $MO[S_2C(PR_3)X$-*i*-Pr](S_2CX-*i*-Pr) (X = S, O)

complex	^{31}P, δ PR$_3$	^1H, δ: P–Me ($^2J_{HP}$, Hz)	^1H, δ: *i*-Pr ($^4J_{HP}$, Hz)	^{13}C, δ: P–Me ($^1J_{CP}$, Hz)	^{13}C, δ: *i*-Pr ($^3J_{CP}$, Hz)
$MoO[S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr)	45.41 s[c]	2.27 d (12.7)[d]	1.20 d (CH_3)	8.15 d (35.4)[c]	23.17 s (CH_3)
			1.30 dd (1.1)[a] (CH_3)		25.34 s (CH_3)
			3.08 dh (1.6) (CH)		37.51 d (5.3) (CH)
			3.31 h (CH)		42.88 s (CH)
$MoO[S_2C(PMe_2Ph)O$-*i*-Pr](S_2CO-*i*-Pr)	35.47 s[c]	2.51 d (13.1)[c]	0.98 d (CH_3)	6.77 d (57.6)[c]	22.16 s (CH_3)
			1.20 d (CH_3)		24.00 s (CH_3)
			3.93 dh (2.0) (CH)		68.23 d (10.6) (CH)
			4.48 h (CH)		75.92 s (CH)
$WO[S_2C(PMe_2Ph)O$-*i*-Pr](S_2CO-*i*-Pr)	41.57 s[d]	2.58 d (13.1)[d]	1.04 d (CH_3)	6.40 d (57.3)[d]	22.34 s (CH_3)
			1.19 d (CH_3)		23.83 s (CH_3)
			4.03 dh (2.0) (CH)		68.86 d (10.7) (CH)
			4.31 h (CH)		75.71 s (CH)

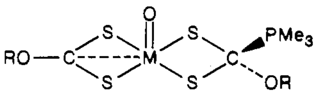
[a] Value of $^5J_{HP}$ in Hz. [b] 85% H_3PO_4 as external reference. [c] In $CDCl_3$. [d] In CD_2Cl_2.

Results and Discussion

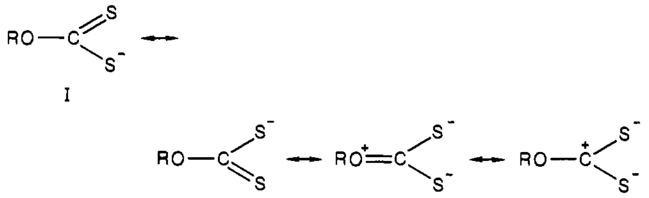
Synthesis of $MoO[S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr) and Related Complexes. The oxo compounds $MOCl_2(PMe_3)_3$ have been shown to react with the sodium or potassium salts of various dithiocarbamate and xanthate ligands, with formation of crystalline complexes of analytical composition $MO(S_2CX)_2(PMe_3)$ (X = NR_2, OR). The two types of complexes, namely dithiocarbamate and xanthate, display different structural and chemical behavior. The former are six-coordinate complexes, with a structure of type A and with tendency toward loss of PMe_3, to afford the five-coordinate species $MO(S_2CNR_2)_2$.[6] As for the xanthates, they are in fact five-coordinate complexes that contain an η^3, S,S′,C xanthate ligand and a zwitterionic $^-S_2C^-(^+PMe_3)OR$ group, S,S′-bonded to the metal atom, as shown in B. The formation of this ligand, by nucleophilic attack of PMe_3 on the carbon atom of the CS_2 group, suggests a significant contribution of resonance structure IV to the total structure of the xanthate group in this type of complex. This suggestion could reasonably be extended to the related thioxanthate complexes, and we therefore anticipated that the interaction of $MOCl_2(PMe_3)_3$ compounds with KS_2CSR would yield the analogous $MO[S_2C(PMe_3)SR](S_2CSR)$ complexes containing a phosphonium betainic thioxanthate ligand. The reactions of these oxo compounds with KS_2CSR (R = *i*-Pr, CMe_3) were therefore carried out, and although IR studies indicated formation of the above complexes to some extent, we were not able to isolate the desired products in pure form, due to extensive decomposition to species that were not further investigated. Since CS_2 elimination is a commonly observed process for thioxanthate complexes,[1] the above reactions were carried out in the presence of added CS_2. In this way, the molybdenum complex $MoO[S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr) could be isolated in ca. 40% yield as shown in eq 2. The remaining complexes of this type could not however be obtained as analytically pure materials.



A



B



I

II III IV

$$MoOCl_2(PMe_3)_3 + 2KS_2CS\text{-}i\text{-}Pr \xrightarrow{THF} MoO[S_2C(PMe_3)S\text{-}i\text{-}Pr](S_2CS\text{-}i\text{-}Pr) + 2PMe_3 + 2KCl \quad (2)$$

The complex $MoO[S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr) is a yellow crystalline material, moderately stable to air in the solid state, although it decomposes rapidly in solution in the presence of oxygen or moisture. Its IR spectrum shows several absorptions in the region 1170–900 cm^{-1} that indicate the presence of thioxanthate,[7-9] PMe_3, and oxo ligands.[3] The formation of the zwitterionic group $^-S_2C^-(^+PMe_3)S$-*i*-Pr is indicated by NMR studies. Thus, the $^{31}P\{^1H\}$ spectrum is a singlet at 45.4 ppm, i.e. in the region expected for quaternary phosphorus atoms bearing a formal positive charge (e.g. 32.9 ppm in $Ni(C_2S_4PMe_3)(PMe_3)$[10] and 46–51 ppm in $MoO[S_2C(PMe_3)OR](S_2COR)$ complexes[3]). At variance with the behavior found for the xanthate complex analogues,[3] only one isomer seems to exist in the temperature range 20–75 °C, as shown variable-temperature ^{31}P NMR studies. This may likely be a consequence of the higher steric requirements of the bulkier –S-*i*-Pr group, and in accord with that, the observable isomer contains *i*-Pr in an *anti* position with respect to the Mo=O linkage (see below). The ^1H and ^{13}C NMR spectrum are also indicative of the formation of a zwitterionic ligand. Thus, the two thioxanthate ligands give rise to two sets of ^1H and ^{13}C reasonances, those of one set being split by coupling to phosphorus, as shown in Figure 1 for the methyne protons of the isopropyl

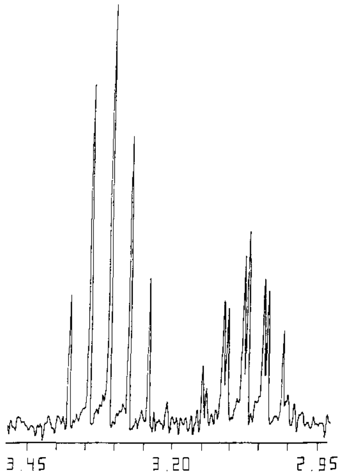


Figure 1. ^1H NMR spectrum (200 MHz, CD_2Cl_2) of $MoO[S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr) showing the CH resonances of the isopropyl thioxanthate groups.

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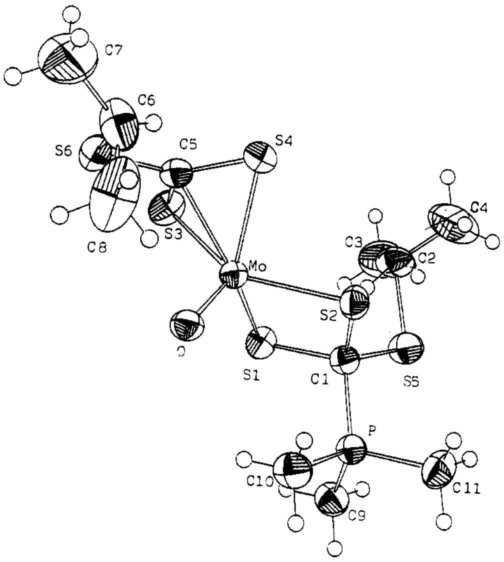

Figure 2. Molecular structure and atom-labeling scheme for $MoO[S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr).

Table II. Bond Distances (Å) and Angles (deg) in $MoO[S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr)

Mo–S1	2.389 (1)	S2–C1	1.839 (4)
Mo–S2	2.393 (1)	S3–C5	1.722 (4)
Mo–S3	2.381 (2)	S4–C5	1.726 (5)
Mo–S4	2.371 (1)	S5–C1	1.820 (4)
Mo–O	1.679 (3)	S5–C2	1.838 (6)
Mo–C5	2.222 (4)	S6–C5	1.774 (5)
P–C1	1.816 (4)	S6–C6	1.828 (6)
P–C9	1.781 (5)	C2–C3	1.496 (9)
P–C10	1.782 (5)	C2–C4	1.484 (11)
P–C11	1.797 (6)	C6–C7	1.512 (12)
S1–C1	1.822 (4)	C6–C8	1.501 (11)
O–Mo–C5	100.87 (16)	Mo–S3–C5	63.21 (16)
S4–Mo–C5	44.00 (11)	Mo–S4–C5	63.40 (15)
S4–Mo–O	114.67 (12)	C1–S5–C2	101.72 (22)
S3–Mo–C5	43.76 (12)	C5–S6–C6	105.69 (25)
S3–Mo–O	114.87 (13)	S2–C1–S5	114.35 (23)
S3–Mo–S4	78.16 (6)	S1–C1–S5	113.86 (25)
S2–Mo–C5	131.53 (12)	S1–C1S2	103.25 (21)
S2–Mo–O	108.27 (13)	P–C1–S5	106.30 (21)
S2–Mo–S4	88.21 (5)	P–C1–S2	109.27 (23)
S2–Mo–S3	136.63 (6)	P–C1–S1	109.76 (22)
S1–Mo–C5	131.74 (14)	S5–C2–C4	110.35 (49)
S1–Mo–O	108.08 (11)	S5–C2–C3	109.10 (40)
S1–Mo–S4	136.98 (6)	C3–C2–C4	111.33 (60)
S1–Mo–S3	88.59 (7)	S4–C5–S6	123.91 (28)
S1–Mo–S2	73.78 (5)	S3–C5–S6	115.44 (27)
C10–P–C11	108.22 (26)	S3–C5–S4	120.65 (27)
C9–P–C11	108.98 (25)	Mo–C5–S6	127.06 (22)
C9–P–C10	109.43 (24)	Mo–C5–S4	72.60 (15)
C1–P–C11	109.96 (23)	Mo–C5–S3	73.03 (16)
C1–P–C10	110.50 (22)	S6–C6–C8	108.23 (54)
C1–P–C9	109.71 (23)	S6–C6–C7	109.46 (54)
Mo–S1–C1	91.21 (15)	C7–C6–C8	114.02 (61)
Mo–S2–C1	90.66 (15)		

Table III. Crystal Data of $MoO[S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr)

empirical formula	$C_{11}H_{23}PS_6OMo$
color	yellow
mol wt	490.6
space group	$P\bar{1}$
cell constants	
a, Å	6.355 (3)
b, Å	12.252 (2)
c, Å	13.061 (2)
α, deg	92.96 (1)
β, deg	93.65 (2)
γ, deg	85.16 (3)
cell vol, $Å^3$	1010.2
molecules/unit cell	2
calcd density, g cm^{-3}	1.61
linear abs coeff, cm^{-1}	13.02
radiation	Mo Kα (0.71069 Å)
rflns measd	4869
rflns collcd	3488
R	3.2
R_w	4.7

Table IV. Final Fractional Coordinates for $MoO[S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr)

atom	*x/a*	*y/b*	*z/c*	10^4U_{eq}, $Å^2$
Mo	0.12295 (5)	0.05415 (3)	0.23089 (3)	305 (1)
P	0.21253 (17)	0.24734 (9)	−0.01242 (8)	359 (3)
S1	−0.10085 (16)	0.17189 (9)	0.12267 (8)	405 (3)
S2	0.31374 (17)	0.21098 (9)	0.20994 (8)	405 (3)
S3	−0.18139 (18)	0.016116 (11)	0.31589 (10)	484 (4)
S4	0.25272 (20)	0.05644 (10)	0.40525 (8)	453 (3)
S5	0.02338 (23)	0.40771 (9)	0.13398 (10)	513 (4)
S6	0.09267 (19)	−0.17539 (10)	0.38694 (9)	472 (4)
O	0.22694 (49)	−0.05055 (25)	0.15722 (22)	403 (9)
C1	0.10924 (63)	0.26300 (33)	0.11450 (31)	352 (11)
C2	−0.06930 (96)	0.41236 (45)	0.26474 (39)	566 (17)
C3	−0.29322 (115)	0.461227 (68)	0.26302 (55)	821 (27)
C4	0.07043 (149)	0.47603 (86)	0.33622 (60)	1053 (37)
C5	0.06054 (68)	−0.03209 (36)	0.37002 (31)	388 (12)
C6	0.37125 (96)	−0.20539 (46)	0.42755 (52)	663 (20)
C7	0.49580 (114)	−0.238.81 (64)	0.33446 (85)	1022 (37)
C8	0.38496 (172)	−0.29048 (70)	0.50677 (67)	1119 (38)
C9	0.00635 (81)	0.28089 (41)	−0.10713 (38)	491 (15)
C10	0.31984 (86)	0.10998 (40)	−0.03678 (39)	516 (16)
C11	0.41954 (81)	0.33714 (46)	−0.02096 (42)	540 (17)

thioxanthate grops. On the other hand, the PMe_3 group yields ^1H and ^{13}C doublets, with separation $^2J_{PH}$ = 12.8 Hz and $^1J_{PC}$ = 55.4 Hz, respectively. The magnitude of these couplings is clearly in accord with the quaternization of PMe_3 with the thioxanthate ligand.[10] Due to low solubility, the CS_2 carbon resonances cannot be unequivocally assigned. Other ^1H and ^{13}C resonances are included in Table I and require no further comments.

Crystal Structure of $MoO[S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr). Figure 2 shows the molecular structure and atom-labeling scheme for this complex. Relevant intramolecular bond distances and angles are collected in Table II. Table III shows crystal data; the atomic positional parameters with standard deviations are presented in Table IV. The structure consists of monomeric molecules of $MoO[S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr), in which the molybdenum atom is coordinated to the oxo group, to the two sulfur atoms of the CS_2 group of the phosphonium betainic thioxanthate ligand, and to the two sulfur atoms and the carbon atom of the CS_2 group of the other thioxanthate. The coordination sphere around the metal is therefore analogous to that found in $MoO(S_2CS$-*i*-$Pr)_2$[4] and in the related xanthate complex $MoO[S_2C(PMe_3)O$-*i*-Pr](S_2CO-*i*-Pr).[3] The overall geometry of the O and S atoms around the metal is that of a distorted square pyramid. The Mo–S bond lengths are similar to those observed for other molybdenum xanthate and thioxanthate complexes. There are two types of Mo–S bonds, with lengths averaging 2.375 (4) Å (Mo–S3 and Mo–S4) and 2.391 (2) Å (Mo–S1 and Mo–S2), which correspond to the two chemically different thioxanthate ligands. The Mo–S average distance for the η^3-thioxanthate (2.375 (4) Å) is slightly longer than that found in $MoO(S_2CS$-*i*-$Pr)_2$ (2.370 (4) Å) and essentially identical with that corresponding to the analogous bonds in $MoO[S_2C(PMe_3)O$-*i*-Pr](S_2CO-*i*-Pr) (2.375 (4) Å). The Mo–C5 separation at 2.222 (4) Å is shorter than that found in the above-mentioned thioxanthate and xanthate complexes (2.25 (1) and 2.274 (5) Å, respectively) and in the related $Mo_2(S_2COC_2H_5)_4I_2$ (2.302 (6) Å[2a]). This is indicative of a strong Mo–C bonding interaction (in the molybdenum(IV) alkyl complex $Mo(CH_2SiMe_3)_3Cl(PMe_3)$ the Mo–C bond lengths average 2.110 (16) Å[11]).

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The formation of the zwitterionic ligand $^{-}S_2C^{-}(^{+}PMe_3)S$-*i*-Pr, by nucleophilic attack of PMe_3 on the carbon atom of the CS_2 group of the second thioxanthate ligand, takes place with the expected variation in bond lengths and angles, not only within the CS_3 grouping but also in the Mo–thioxanthate linkage. Thus, as indicated above, the Mo–S bond separation for this ligand averages 2.391 (2) Å, as compared with the value of 2.375 (4) Å found for the average Mo–S distance in the Mo–η^3--thioxanthate linkage. On the other hand, the average C–S bond distance in the zwitterionic ligand, 1.83 Å, is the expected value for a single C–S bond (typically 1.82 Å) but is significantly longer than the corresponding distances for the other thioxanthate ligand in this molecule (1.74 Å average) and for the two thioxanthate groups in the complex $MoO(S_2CS$-*i*-$Pr)_2$.[4] The angles around C1 are approximately tetrahedral, and the C1–P distances at 1.816 (4) Å is somewhat longer that the P–CH_3 bonds (1.79 (1) Å average) and shorter than the analogous distance in the xanthate complex $MoO[S_2C(PMe_3)O$-*i*-$Pr](S_2CO$-*i*-$Pr)$ (1.839 (4) Å). As shown in Figure 2, the –S-*i*-Pr group is anti with respect to the oxo group.

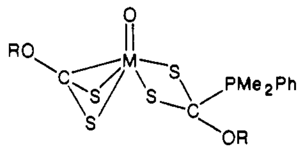
Synthesis and Properties of $MO[S_2C(PMe_2Ph)O$-*i*-$Pr](S_2CO$-*i*-$Pr)$ (M = Mo, W) Complexes. The above results regarding the formation of the trimethylphosphonium thioxanthate ligand, and those previously reported for the xanthate derivative analogs, suggest the possibility of forming similar zwitterionic ligands for phosphines other than PMe_3. We now report results on the dimethylphenylphosphine–*O*-isopropyl xanthate system; those concerning other phosphines and/or other dithio acid ligands are currently being investigated and will be the subject of future publications.

When the oxo complex $MoOCl_2(PMe_2Ph)_3$ is stirred with a slight excess of KS_2CO-*i*-Pr, the initial green color rapidly disappears, and after 1.5–2 h of stirring at room temperature, the new complex $MoO[S_2C(PMe_2Ph)O$-*i*-$Pr](S_2CO$-*i*-$Pr)$ is formed in ca. 80% isolated yield, as depicted in eq 3. A similar reaction,

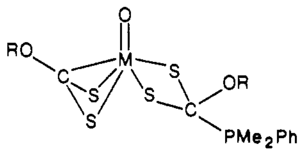
$$MoOCl_2(PMe_2Ph)_3 + 2KS_2CO\text{-}i\text{-}Pr \xrightarrow{THF} MoO[S_2C(PMe_2Ph)O\text{-}i\text{-}Pr](S_2CO\text{-}i\text{-}Pr) + 2PMe_2Ph + 2KCl \quad (3)$$

carried out with $WOCl_2(PMe_2Ph)_3$, provides the tungsten analogue $WO[S_2C(PMe_2Ph)O$-*i*-$Pr](S_2CO$-*i*-$Pr)$. Both complexes are yellow crystalline solids, sparingly soluble in nonpolar organic solvents. Their IR spectra display absorptions characteristic of the xanthate ligand and of the oxo and the PMe_2Ph groups, but due to the complexity of the spectrum in the 1200–850 cm^{-1} region, no specific assignments can be made. The existence of the zwitterionic ligand in the molecules of these complexes is demonstrated by ^1H, ^{13}C, and ^{31}P NMR studies, whose results are summarized in Table I. The $^{31}P\{^1H\}$ NMR spectra are low-field singlets, that of the tungsten complex showing no phosphorus to tungsten coupling, while the ^1H and ^{13}C resonances of the PMe_2Ph methyl groups are doublets with separations of 13 Hz ($^2J_{PH}$) and 57 Hz ($^1J_{PC}$). Other relevant NMR data are included in Table I.

In contrast with the behavior found for the thioxanthate complex $MoO[S_2C(PMe_3)S$-*i*-$Pr](S_2CS$-*i*-$Pr)$, the NMR spectra of the complexes indicate the presence of two isomers in solution, in an approximate ratio of 1:3. The minor component also contains different xanthate ligands and displays ^1H, ^{13}C, and ^{31}P resonances due to the PMe_2Ph group, which are indicative of the presence of the zwitterionic ligand $^{-}S_2C^{-}(^{+}PMe_2Ph)O$-*i*-Pr. By similarity with the PMe_3 complex analogues, the isomers are proposed to differ in the orientation of the PMe_2Ph and O-*i*-Pr groups with respect to the M=O group, as shown in C and D. It is likely that isomer C, which is the only one found to exist in the solid state for $MoO[S_2C(PMe_3)X](S_2CX)$ complexes (X = O-*i*-Pr, S-*i*-Pr), is the major component in solution.

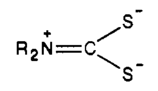


C

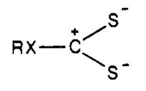


D

Concluding Remarks. Some final comments on the formation of the zwitterionic ligands $^{-}S_2C^{-}(^{+}PR_3')X$ (X = OR, SR) are in order at this point. In this and in previous publications,[3,6] we have characterized a number of oxo–molybdenum and tungsten complexes derived from various dithio acid ligands (dithiocarbamates, xanthates, and thioxanthates) by the same general reaction, namely the interaction of the oxo complexes $MOCl_2(PR_3')_3$ (R_3' = Me_3, Me_2Ph) with the sodium or potassium salt of the dithio acid ligand $^{-}S_2CX$ (X = NR_2, OR, SR). Striking differences are observed between the dithiocarbamate complexes on one side and the xanthate and thioxanthate complexes on the other. The latter are formulated as $MO[S_2C(PR_3')X](S_2CX)$ (X = OR, SR) and contain two different dithio acid ligands: a nonclassical $^{-}S_2CX$ ligand, S,S′,C-bonded to the metal atom, and a zwitterionic ligand, $^{-}S_2C^{-}(^{+}PR_3')X$, formed by nucleophilic attack of PR_3' on the carbon atom of the CS_2 group of the xanthate or thioxanthate ligand. No tendency toward the formation of such a ligand is observed for the dithiocarbamate complexes, and thus, the reaction of $WOCl_2(PMe_3)_3$ with NaS_2CNMe_2 yields[6b] the six-coordinate complex $WO(S_2CNMe_2)PMe_3$, containing a PMe_3 group directly bonded to tungsten ($^1J_{WP}$ = 422 Hz). Furthermore, the analogous molybdenum complex $MoO(S_2CNEt_2)_2PMe_3$ readily dissociates PMe_3 to form not a zwitterionic complex but the phosphine-free oxo species[6a] $MoO(S_2CNEt_2)_2$. We believe these differences reflect the different contributions of resonance structures V and VI to the total structure of the dithio acid ligand in this type of complex.



V



VI

As is well-documented,[1] resonance form V plays a significant role in the chemistry of dithiocarbamate complexes, while it is of little importance for the analogous xanthate and thioxanthate complexes. Our results not only are in accord with these observations but also emphasize the importance of resonance form VI in the chemistry of xanthate and thioxanthate complexes of the type we have studied.

The isolation of $MO[S_2C(PMe_2Ph)O$-*i*-$Pr](S_2CO$-*i*-$Pr)$ compounds shows that the nucleophilic attack at the CS_2 carbon atom is not restricted to the small, basic PMe_3 ligand. Work aimed at ascertaining the applicability of this reaction to other phosphine ligands and other xanthate complexes of molybdenum and tungsten, in different oxidation states, is in progress. As for the applicability to complexes of other transition metals, it seems reasonable that complexes which are known to undergo nucleophilic attack at the CS_2 carbon atom by amines (e.g. $Co_2(SEt)_2(S_2CSEt)_4$,[8] $[Ni(SR)(S_2CSR)]_2$[9]) or other nucleophiles (for instance $Mn(S_2CH)(CO)_3(dppm)$[15]) are in principle good candidates to form zwitterionic ligands of the type found for our molybdenum and tungsten complexes.

Experimental Section

Microanalyses were carried out by Pascher Microanalytical Laboratory, Bonn, West Germany. Infrared spectra were recorded as Nujol mulls on Perkin-Elmer Model 577 and 684 instruments. ^1H, ^{13}C, and ^{31}P NMR spectra were run on a Varian XL-200 instrument. ^{31}P NMR shifts are referenced to external 85% H_3PO_4.

All preparations and operations were carried out under oxygen-free nitrogen or argon, by following the conventional Schlenk techniques. Solvents were dried by standard techniques and degassed before use. The compounds $MOCl_2(PMe_3)_3$ (M = Mo, W) were prepared according to

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(13) Reference deleted in revision.

(14) Reference deleted in revision.

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the literature procedures.[6] The potassium salts of S_2CO-*i*-Pr and S_2CSR (R = *i*-Pr, CMe_3) were obtained by slow addition of CS_2 to solutions of KOH in the corresponding alcohol or thiol. KS_2CSR compounds were recrystallized from EtOH–Et_2O mixtures at −35 °C. The PMe_3 ligand is prepared according to the literature procedure.[16]

Preparation of MoO[$S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr). A solution of $MoOCl_2(PMe_3)_3$ (ca. 1 mmol) in THF (35 mL) was treated with KS_2CS-*i*-Pr (0.382 g, 2 mmol). To the resulting solution was added a few drops of CS_2, and the reaction mixture was stirred at room temperature over a period of 6–8 h. The color of the solution changed from the initial green or blue to yellow, and a white, finely divided solid resulted. The solution was filtered, the solvent removed under reduced pressure, and the resulting yellow gum washed several times with Et_2O. The residual yellow solid was dissolved in acetone (20 mL), the volume reduced in vacuo, and the solution cooled at −35 °C to give the yellow complex in ca. 40–50% yield. IR (Nujol mull): 1200, 1270, 1110, 1070, 1030, 970, 950, 935, 815 cm^{-1}. Crystals of the compound MoO[$S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr) suitable for X-ray analysis were obtained by slow evaporation of CH_2Cl_2 solutions at 0 °C.

Attempts to prepare the tungsten complex analogue WO[$S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr) and the *tert*-butyl thioxanthate derivatives MO[$S_2C(PMe_3)S$-*t*-Bu](S_2CS-*t*-Bu) (M = Mo, W), by a similar procedure, were unsuccessful. The salts KS_2CSR did react with the oxo-dichloride complexes $MOCl_2(PMe_3)_3$, and solids displaying IR spectra similar to that recorded for MoO[$S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr) were obtained. We have been unable to isolate pure crystalline materials from these reactions.

Preparation of MO[$S_2C(PMe_2Ph)O$-*i*-Pr](S_2CO-*i*-Pr) Compounds (M = Mo, W). These complexes can be obtained by reacting the oxo derivatives $MOCl_2(PMe_2Ph)_3$ with KS_2CO-*i*-Pr, by following the procedure previously described for the analogous trimethylphosphine derivatives[3] MO[$S_2C(PMe_3)O$-*i*-Pr](S_2CO-*i*-Pr). The starting $MOCl_2(PMe_2Ph)_3$ was obtained from $MoCl_4(THF)_2$ or $WCl_4(PMe_2Ph)_3$,[6b] as exemplified below for the molybdenum complex: $MoCl_4(THF)_2$ (3.6 g, ca. 10 mmol) was stirred in 50 mL of THF with a slight excess of water (ca. 12 mmol) and 5 equiv of PMe_2Ph at 60 °C for 3 h. The resulting green solution was filtered, the solvent evaporated in vacuo, and the desired complex $MoOCl_2(PMe_2Ph)_3$[12] crystallized from THF; yield 79%.

MoO[$S_2C(PMe_2Ph)O$-*i*-Pr](S_2CO-*i*-Pr). Anal. Calcd for $C_{16}H_{25}PS_4O_3Mo$: C, 36.9; H, 4.8. Found: C, 37.1; H, 4.8. IR (Nujol mull): 3080, 1405, 1365, 1150, 1115, 1090, 1040, 960, 940, 870, 740, 690 cm^{-1}. The NMR data of the main isomer are given in Table I. ^1H NMR ($CDCl_3$; minor isomer): δ 5.27 (hd, 1 H, $^3J_{HH}$ = 6.2 Hz, $^4J_{HP}$ = 2.0 Hz, C*H*($CH_3)_2$), 4.45 (h, 1 H, $^3J_{HH}$ = 6.2 Hz, C*H*($CH_3)_2$), 1.78 (d, 6 H, $^2J_{HP}$ = 13.1 Hz, P*Me*$_2$Ph), 1.39 (d, 6 H, CH(C*H*$_3)_2$), 1.18 (d, 6 H, CH(C*H*$_3)_2$). $^{31}P\{^1H\}$ NMR (Cl_3CD; minor isomer): δ 29.0 s.

WO[$S_2C(PMe_2Ph)O$-*i*-Pr](S_2CO-*i*-Pr). IR (Nujol mull): 1405, 1365, 1140, 1115, 1090, 1040, 955, 940, 930, 910, 880, 740, 685 cm^{-1} (see Table I). ^1H NMR (CD_2Cl_2 minor isomer): δ 5.31 (hd, 1 H, $^3J_{HH}$ = 6.2 Hz, $^4J_{HP}$ = 1.8 Hz, C*H*($CH_3)_2$) 4.56 (h, 1 H, C*H*($CH_3)_2$), 1.88 (d, 6 H, $^2J_{HP}$ = 13.0 Hz, P*Me*$_2$Ph), 1.41 (d, 6 H, CH(C*H*$_3)_2$), 1.18 (d, 6 H, CH(C*H*$_3)_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; minor isomer): δ 35.2 $^{13}C\{^1H\}$ NMR (CD_2Cl_2; minor isomer): δ 75.8 (s, *C*H($CH_3)_2$), 70.8 (d, $^3J_{CP}$ = 10.0 Hz, *C*H($CH_3)_2$), 24.2 (s, CH(*C*H$_3)_2$), 22.4 (s, CH(*C*H$_3)_2$), 5.7 (d, $^1J_{CP}$ = 58.6 Hz, P*Me*$_2$Ph). The attempted recrystallization of this complex produced extensive decomposition. Slow decomposition of the solid is also observed, even in the absence of air. This precludes us from obtaining accurate analytical data.

X-ray Data Collection, Structure Determination, and Refinement. A yellow single crystal, of size 0.7 × 0.4 × 0.3 mm, of MoO[$S_2C(PMe_3)$-S-*i*-Pr](S_2CS-*i*-Pr) was sealed under N_2 in a thin-walled glass capillary. The crystal was mounted on a Nonius CAD 4-F automatic diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections.

Intensities were collected by $\omega/2\theta$ scan. There was no appreciable drop in intensity of three standard reflections, checked every 1 h. A total 5297 reflections within $1° < \theta < 28°$ and *hkl* range from (−8,−16,0) to (8,16,17) were collected, resulting in 4896 unique reflections.

The intensities were corrected for Lorentz and polarization effects, and 3488 were considered observed by the criterion $I > 3\sigma(I)$.

Scattering factors for neutral atoms and anomalous dispersion corrections for Mo, P, and S were taken from ref 17.

The crystal structure was solved by three-dimensional Patterson and Fourier synthesis, allowing the location of all non-hydrogen atoms. An empirical absorption correction[18] was applied at the end of the isotropic refinements. Anisotropic full-matrix least-squares refinement with unit weights led to $R = 0.033$; H atoms were fixed at calculated positions. In order to prevent bias on $\langle\Delta^2F\rangle$ vs $\langle F_o\rangle$ and $(\sin\theta)/\lambda$, the last steps of the refinement were carried out with weights $w = 1/(a + b|F_o|)^2$, where $a = 3.015$ and $b = -0.216$ if $|F_o| < 11.5$ and $a = 0.320$ and $b = 0.019$ if $|F_o| > 11.5$; a and b are calculated by PESOS.[19] Final refinement with fixed isotropic temperature factors and coordinates for H atoms gave $R = 0.032$ and $R_w = 0.047$. Maximum and average shift/error are 0.91 and 0.04, respectively. Most of the calculations were carried out with XRAY80.[20]

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Registry No. C (M = Mo, R = *i*-Pr), 111820-49-6; C (M = W, R = *i*-Pr), 111717-78-3; D (M = Mo, R = *i*-Pr), 111717-79-4; D (M = W, R = *i*-Pr), 111819-56-8; $MoOCl_2(PMe_3)_3$, 90397-97-0; MoO[$S_2C(PMe_3)S$-*i*-Pr](S_2CS-*i*-Pr), 111717-77-2; $MoOCl_2(PMe_2Ph)_3$, 30134-06-6; $WOCl_2(PMe_2Ph)_3$, 36216-84-9; $MoCl_4(THF)_2$, 16998-75-7; $WCl_4(PMe_2Ph)_3$, 47690-18-6; KS_2CS-*i*-Pr, 52207-49-5.

Supplementary Material Available: Tables of final anisotropic thermal parameters and calculated hydrogen atom positions (2 pages); a table of calculated and observed structure factors (33 pages). Ordering information is given on any current masthead page.

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(21) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III → 3 and 13.)