is scattered with rocking modes. The vibrations of the bridge, however, are situated in a part that is much cleaner. Some very useful rules thus may be added (see Figure 5):

(4) $\nu_{\mathrm{Al-Me^b}} > \nu_{\mathrm{Al-Cl^b}}$. This relation is valid for all the four bridging modes separately. The mass change is evidently responsible for the trend.

(5) $\nu_{17}(\mathrm{Al-Cl^b}) = 320 \pm 10\ \mathrm{cm^{-1}}$ and $\nu_2(\mathrm{Al-Cl^b}) = 340 \pm 10\ \mathrm{cm^{-1}}$. The first of these bands is always strong in the IR region and the second is dominant in the Raman region. Note that the AlCC bend may be present in the same spectral region.

(6) ν_6 and ν_{13} increase gradually when terminal methyl groups are substituted by chlorine, i.e. in the series $\mathrm{Me_{6-\mathit{n}}Al_2Cl_\mathit{n}}$ (n = 2–6), clearly showing the inductive effect of the alkyl group.

In conclusion, the systematic variations of the skeletal frequencies and the force fields build a strong case for the interpretation of the high-temperature reactions in terms of successive chlorine substitution.

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Supplementary Material Available: Tables of the structure, symmetry, and normal-coordinate representation of the skeletal modes for $\mathrm{(CH_3)_{6-\mathit{n}}Al_2Cl_\mathit{n}}$, applied geometrical parameters for methylaluminum chlorides, simplified valence force fields for monomeric alkylaluminum chlorides, and symmetry coordinates for a double-bridged $\mathrm{A_2X_3YZ_3}$ model, figures showing valence coordinates for the $\mathrm{AX_2Y}$ and double-bridged $\mathrm{A_2X_2YZ_3}$ models, and a correlation diagram for symmetry reductions from D_{2h} to C_{2h} and C_s (5 pages). Ordering information is given on any current masthead page.

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Formation of Zwitterionic Ligands, $\mathrm{ROC^-(^+PMe_3)S^-{}_2}$, by Nucleophilic Attack of $\mathrm{PMe_3}$ on Coordinated Xanthates. X-ray Structure of $\mathrm{MoO[S_2C(PMe_3)O\text{-}\mathit{i}\text{-}Pr\text{-}\mathit{S,S'}](CS_2CO\text{-}\mathit{i}\text{-}Pr\text{-}\mathit{S,S',C})}$[†]

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New oxo complexes of composition $\mathrm{MO(S_2COR)_2(PMe_3)}$ (M = Mo, W; R = Me, Et, *i*-Pr) have been synthesized by the reactions of $\mathrm{MOCl_2(PMe_3)_3}$ with the potassium salts of the xanthate ligands. NMR studies (^{1}H, ^{13}C, ^{31}P) show the existence in the molecules of these complexes of the zwitterionic ligands $\mathrm{^-S_2C^-(^+PMe_3)OR}$, formed by nucleophilic attack of trimethylphosphine on the carbon atom of the $\mathrm{CS_2}$ moiety. This has been confirmed by an X-ray study, carried out on the molybdenum isopropyl derivative, which shows in addition that the second xanthate group displays an unusual coordination, acting as an η^3 ligand, bonded to molybdenum through the two sulfur atoms and the carbon atom of the $\mathrm{CS_2}$ group. The crystals are orthohombic, *Pbca*, with unit cell constants a = 13.168 (7) Å, b = 13.622 (9) Å, c = 21.732 (6) Å, and $D_{\mathrm{calcd}} = 1.57\ \mathrm{g\ cm^{-3}}$ for Z = 8. The structure was refined to an R value of 0.034 by using 2446 independent observed reflections. The molybdenum atom is in a distorted-square-pyramidal environment, with a Mo–O separation of 1.668 (3) Å, lying 0.83 Å above the basal plane formed by the four sulfur atoms of the xanthate ligands.

Introduction

The interest in the bioinorganic chemistry of molybdenum and the implication of Mo–S bonding in the active site of the iron–molybdenum protein of nitrogenase have originated numerous studies on molybdenum complexes of dithio acid ligands.[1] In the course of the past few years, we have become interested in the synthesis and properties of molybdenum and tungsten complexes containing this type of ligand[2,3] and reported recently that the interaction of the oxo derivatives $\mathrm{MOCl_2(PMe_3)_3}$ with various dialkyldithiocarbamates, $\mathrm{^-S_2CNR_2}$, yields the new complexes $\mathrm{MO(S_2CNR_2)_2(PMe_3)}$ (R = Me, Et) as shown in eq 1. As an

$$\mathrm{MOCl_2(PMe_3)_3 + 2NaS_2CNR_2 \rightarrow MO(S_2CNR_2)_2(PMe_3) + 2PMe_3 + 2NaCl} \quad (1)$$

extension of these studies, the preparation of the alkyl xanthate ($\mathrm{^-S_2COR}$) analogues by a similar procedure has been attempted, and the results are reported in this paper. While the reactions of the oxo complexes with $\mathrm{KS_2COR}$ (R = Me, Et, *i*-Pr) afford monomeric compounds of the expected analytical composition, namely $\mathrm{MO(S_2COR)_2(PMe_3)}$, NMR studies (^{1}H, ^{13}C, and ^{31}P) and an X-ray analysis carried out on the molybdenum isopropyl derivative reveal that (i) the $\mathrm{PMe_3}$ ligand is not bonded directly to the metal atom but instead forms a bidentate zwitterionic ligand, $\mathrm{^-S_2C^-(^+PMe_3)OR}$, and (ii) the second xanthate group is acting as a tridentate ligand, bonded to molybdenum through the two sulfur atoms and the carbon atom of the $\mathrm{CS_2}$ unit, in a way that resembles a π-allyl–metal interaction.

Results and Discussion

Synthesis of the Complexes $\mathrm{MO[S_2C(PMe_3)OR](S_2COR)}$ (M = Mo, W; R = Me, Et, *i*-Pr). Interaction of the oxo compounds $\mathrm{MOCl_2(PMe_3)_3}$ with potassium *O*-alkyl xanthates, $\mathrm{KS_2COR}$ (R = Me, Et, *i*-Pr), in tetrahydrofuran (THF), at room temperature, gives yellow crystalline complexes of analytical composition

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Table I. Analytical and NMR Data for $MO[S_2C(PMe_3)OR](S_2COR)$ Complexes

		anal. data[a]			^{1}H NMR data, δ		^{13}C NMR data, δ		
M	R	% C	% H	^{31}P NMR data,[b] δ	PMe$_3$ ($^2J_{PH}$, Hz)	–OR ($^4J_{PH}$, Hz)	PMe$_3$ ($^2J_{PC}$, Hz)	–OR ($^3J_{PC}$, Hz)	S$_2$C-OR ($^1J_{PC}$, Hz)
Mo	Me	21.2	3.8	46.1 s[c]	2.2 d (13.4)[c]	3.2 d (1.4) [CH_3]	7.3 d (54)[c]	50.4 d (11.3) [CH_3]	
		(20.9)	(3.7)			3.6 s [CH_3]		59.1 s [CH_3]	
	Et	25.1	4.5	44.0 s[d]	2.1 d (13)[d]	1.1 t [CH_3]	6.7 d (53)[d]	14.3 s [CH_3]	110.5 d (84)
		(25.1)	(4.5)			1.2 t [CH_3]		14.7 s [CH_3]	139.2 s
						3.5 dc (1) [CH_2]		59.0 d (10) [CH_2]	
						3.9 c [CH_2]		68.0 s [CH_2]	
	i-Pr			51.0 s	1.3 d (13.3)[e]	1.0 d [CH_3]	7.1 d (54)[d]	22.2 s [CH_3]	110.4 d (89)
						1.2 d [CH_3]		24.1 s [CH_3]	139.3 s
						4.2 dh (1.8) [CH]		68.2 d (10.5) [CH]	
						4.7 h [CH]		76.0 s [CH]	
W	Me	17.3	3.1	53.8 s	2.3 d (14)	3.2 d (1) [CH_3]	7.4 d (54)	51.0 d (11) [CH_3]	
		(17.1)	(3.1)			3.4 s [CH_3]		58.9 s [CH_3]	
	Et			55.1 s	2.3 d (14)	1.0 t [CH_3]	6.4 d (54)	14.7 s [CH_3]	111.5 d (86)
						1.1 t [CH_3]		15.0 s [CH_3]	122.6 s
						3.5 dc (1.3) [CH_2]		59.7 d (10) [CH_2]	
						3.8 c [CH_2]		67.6 s [CH_2]	
	i-Pr	24.2	4.2	54.4 s	1.4 d (13.5)[e]	1.0 d [CH_3]	6.4 d (54)	22.5 s [CH_3]	
		(24.2)	(4.2)			1.2 d [CH_3]		24.0 s [CH_3]	
						4.2 dh (1.2) [CH]		68.6 d (10) [CH]	
						4.6 h [CH]		75.4 s [CH]	

[a] Calculated values are given in parentheses. [b] 85% H_3PO_4 as external reference. Recorded in acetone-d_6 unless noted otherwise. [c] In Cl_2CD_2. [d] In Cl_3CD. [e] In C_6D_6.

$MO(S_2COR)_2(PMe_3)$. Initially, a six-coordinate structure similar to that found for the related dithiocarbamate complexes,[3] was considered for these derivatives, but the differences in color, the decreased solubility of the xanthates, and above all NMR data suggested a different formulation. Room-temperature NMR studies (vide infra) indicate that the two xanthate ligands are in different chemical environments, one of them being coupled to the phosphorus nucleus, and that the PMe_3 group is not bonded to the metal but is rather involved in a bentainic phosphonium $^{-}S_2C^{-}(^{+}PMe_3)OR$ interaction. Therefore, the new oxo complexes should be formulated as indicated in eq 2. These compounds are

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

yellow crystalline materials, moderately air stable in the solid state (crystals can be handled in air for several hours without noticeable decomposition) although they decompose rapidly in solution in the presence of air. This moderate stability, although less pronounced, is similar to that found for the related $MoO(S_2CSR)_2$ complexes[4a] and contrasts with the instability of the dithiocarbamate analogues $MoO(S_2CNR_2)_2PMe_3$ toward oxidation to Mo(V) and Mo(VI).

Since $MoO(S_2CNR_2)_2(PMe_3)$ complexes[3] easily lose the coordinated PMe_3 ligand, it is reasonable to assume that the initial metathetical reaction leading to the xanthate complexes is accompanied, or followed, by trimethylphosphine dissociation and then by nucleophilic attack of the phosphine at the $^{-}S_2C(OR)$ carbon. Nucleophilic attack on xanthate and related ligands is not unprecedented. For instance, conversion of coordinated thioxanthate, $^{-}S_2CSR$, into coordinated dithiocarbamate, $^{-}S_2CNR_2$, by nucleophilic attack by secondary amines, HNR_2, has been reported,[5] as has been the formation of a tridentate ligand, $Ph_2PCH_2P(Ph)_2C(H)SS$, by nucleophilic attack of one of the P atoms of the dppm ligand ($Ph_2PCH_2PPh_2$) at the HCS_2 carbon in the complex[6] $Mn(S_2CH)(CO)_3(dppm)$.

The IR spectra of the new complexes are very similar and show three strong absorptions in the region 1200–1000 cm^{-1}, which are due to vibrations arising from the xanthate ligands. This is in agreement with data reported for related complexes, since the $ROCS_2$ group is characterized[7] by three bands in the region 1250–1000 cm^{-1} and a fourth absorption at ca. 550 cm^{-1}, each of these bands arising from combinations of the $\nu(C{=}S)$, $\nu(C{-}O)$, $\nu(C{-}S)$, and $\nu(R{-}O)$ modes.[7] In addition, two strong, characteristic absorptions are found at ca. 980 and 950 cm^{-1}, which are due to the PMe_3 and the oxo group. Since CH_2Cl_2 solutions of the complexes display IR spectra in the region 1200–900 cm^{-1}, essentially identical with those recorded for the solid samples (matched cells; 1160, 1100, 1040, 980, and 950 cm^{-1} for $MoO[S_2C(PMe_3)O\text{-}i\text{-}Pr](S_2CO\text{-}i\text{-}Pr)$; CH_2Cl_2 solution), it seems likely that the solid-state structure persists in solution.

The presence of a zwitterionic ligand, $^{-}S_2C^{-}(P^{+}Me_3)OR$, in these complexes is suggested by ^1H, ^{13}C, and ^{31}P NMR studies (Table I). The $^{31}P\{^1H\}$ spectra are singlets in the region 44–54 ppm, i.e. at considerably lower field than expected for coordinated PMe_3 (e.g. −19.8 ppm for $WO(S_2CNMe_2)_2(PMe_3)$[3]) and in the region corresponding to quaternary phosphorus atoms bearing a formal positive charge (e.g. 32.9 ppm in $Ni(C_2S_4PMe_3)(PMe_3)$[8]). In addition, no phosphorus to tungsten coupling is observed for the tungsten derivatives $WO[S_2C(PMe_3)OR](S_2COR)$, while in $WO(S_2CNMe_2)_2(PMe_3)$ a value of 211 Hz was found[3] for the one-bond P–W coupling constant. Further support comes from ^1H NMR studies, since (i) the two xanthate ligands give rise to two sets of resonances, those of one set being split by coupling to phosphorus, and (ii) the PMe_3 ligand yields a doublet, with $^2J_{PH}$ = 13–14 Hz. As pointed out recently by Ibers,[8] this is consistent with complete use of the phosphorus atom lone pair of electrons, i.e. formation of a dative P–C bond: the value of $^2J_{PH}$ changes from 2.7 Hz in free PMe_3 to 5–10 Hz in coordinated PMe_3 and >13 Hz in phosphonium salts, $R_3P^{+-}CS_2$ complexes, $Ni(C_2S_4PMe_3)(PMe_3)$,[8] $Ni[C(PMe_3)(Ph)C(H)(COCH_2CMe_2Ph)]Cl(PMe_3)$,[9] and related compounds.

^{13}C NMR studies are also in accord with the formation of the zwitterionic ligand. Although due to low solubility observation of the CS_2 carbon resonance has not been possible for all the complexes studied, in some cases (Table I) two separate resonances at ca. 110–113 and 122–140 ppm, respectively, have been observed. The first is a doublet of separation ~85 Hz, clearly demonstrating that formation of a P–C bond has taken place. Again, this value of $^1J_{PC}$ is very similar to that of 73.3 Hz found in the nickel

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Table II. Bond Distances (Å) and Angles (deg) in MoO[$S_2C(PMe_3)O$-*i*-Pr](S_2CO-*i*-Pr)

Mo–S1	2.390 (2)	C1–P1	1.839 (4)
Mo–S2	2.388 (2)	O1–C2	1.462 (6)
Mo–S3	2.375 (2)	C2–C3	1.512 (9)
Mo–S4	2.375 (2)	C2–C4	1.487 (9)
Mo–C5	2.274 (5)	C5–O2	1.341 (6)
Mo–O3	1.668 (3)	O2–C6	1.450 (6)
S1–C1	1.819 (4)	C6–C7	1.496 (9)
S2–C1	1.830 (4)	C6–C8	1.495 (11)
S3–C5	1.726 (5)	P1–C9	1.767 (6)
S4–C5	1.709 (6)	P1–C10	1.783 (6)
C1–O1	1.396 (5)	P1–C11	1.786 (6)
C5–Mo–O3	98.2 (2)	S1–C1–P1	111.3 (2)
S4–Mo–O3	113.0 (1)	S1–C1–O1	116.3 (3)
S4–Mo–C5	43.1 (1)	O1–C1–P1	100.9 (3)
S3–Mo–O3	112.3 (1)	C1–O1–C2	116.7 (3)
S3–Mo–C5	43.5 (1)	O1–C2–C4	106.6 (4)
S3–Mo–S4	77.26 (6)	O1–C2–C3	106.9 (4)
S2–Mo–O3	107.9 (1)	S3–C5–S4	119.4 (3)
S2–Mo–C5	132.4 (1)	Mo–C5–S4	71.6 (2)
S2–Mo–S4	89.67 (6)	Mo–C5–S3	71.4 (2)
S2–Mo–S3	139.8 (1)	S4–C5–O2	115.1 (4)
S1–Mo–O3	108.1 (1)	S3–C5–O2	125.3 (4)
S1–Mo–C5	134.4 (1)	S4–C5–O2	115.1 (4)
S1–Mo–S4	138.71 (9)	Mo–C5–O2	124.3 (4)
S1–Mo–S3	91.47 (6)	C5–O2–C6	121.0 (4)
S1–Mo–S2	73.56 (6)	O2–C6–C8	109.0 (5)
Mo–S1–C1	90.77 (1)	O2–C6–C7	105.9 (5)
Mo–S2–C1	90.6 (1)	C7–C6–C8	112.4 (6)
Mo–S3–C5	65.1 (2)	C1–P1–C11	110.9 (2)
Mo–S4–C5	65.3 (2)	C1–P1–C10	107.9 (2)
S1–C1–S2	103.3 (2)	C1–P1–C9	110.0 (3)
S2–C1–P1	108.1 (2)	C10–P1–C11	110.2 (3)
S2–C1–O1	116.8 (3)	C9–P1–C11	108.4 (3)
		C9–P1–C10	109.5 (3)

Table III. Crystal Data of MoO[$S_2C(PMe_3)O$-*i*-Pr](S_2CO-*i*-Pr)

empirical formula	$C_{11}H_{23}PS_4O_3Mo$
color	orange
mol wt	458.5
space group	*Pbca*
cell constants, Å	
a	13.168 (7)
b	13.622 (9)
c	21.732 (6)
cell vol, Å^3	3898.2
molecules/unit cell	8
calcd density, g cm^{-3}	1.57
linear abs coeff, cm^{-1}	11.5
radiation	Mo Kα (0.71073 Å)
reflecns measd	3432
reflecns used ($I \geqslant 3\sigma(I)$)	2446
R	0.034
R_w	0.039

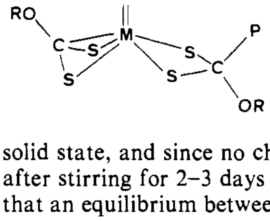
Table IV. Final Fractional Coordinates for MoO[$S_2C(PMe_3)O$-*i*-Pr](S_2CO-*i*-Pr)

atom	*x*/*a*	*y*/*b*	*z*/*c*
Mo	0.02657 (3)	0.19081 (2)	0.12412 (2)
S1	−0.07401 (9)	0.31788 (8)	0.07905 (5)
S2	0.00088 (8)	0.31106 (8)	0.20249 (5)
S3	0.11915 (11)	0.16930 (10)	0.03131 (6)
S4	0.19532 (9)	0.16695 (10)	0.15966 (7)
C1	−0.09081 (30)	0.37552 (28)	0.15383 (18)
O1	−0.08786 (21)	0.47790 (19)	0.15492 (14)
C2	0.00974 (36)	0.52391 (33)	0.14085 (24)
C3	−0.00597 (60)	0.58658 (52)	0.08434 (31)
C4	0.03903 (45)	0.58137 (53)	0.19629 (33)
C5	0.16597 (39)	0.10512 (36)	0.09362 (25)
O2	0.17468 (31)	0.00716 (26)	0.09697 (17)
C6	0.15141 (46)	−0.05453 (38)	0.04451 (24)
C7	0.11576 (56)	−0.15021 (51)	0.07054 (35)
C8	0.24468 (76)	−0.06560 (60)	0.00593 (36)
P1	−0.21860 (8)	0.35241 (9)	0.18467 (5)
C9	−0.31061 (41)	0.41080 (50)	0.13824 (32)
C10	−0.22370 (39)	0.40180 (44)	0.26059 (25)
C11	−0.24549 (40)	0.22386 (40)	0.18634 (27)
O3	−0.04930 (27)	0.09582 (23)	0.13920 (17)
H41	−0.012	0.635	0.206
H113	−0.316	0.210	0.204
H2	0.063	0.473	0.133
H31	−0.029	0.546	0.048
H32	−0.059	0.639	0.091
H33	0.060	0.619	0.074
H42	0.047	0.540	0.234
H43	0.107	0.615	0.188
H6	0.114	−0.016	0.017
H71	0.169	−0.181	0.097
H72	0.053	−0.140	0.098
H73	0.098	−0.192	0.035
H81	0.269	−0.001	−0.009
H82	0.299	−0.099	0.030
H83	0.228	−0.108	−0.032
H91	−0.297	0.483	0.138
H92	−0.306	0.385	0.095
H93	−0.380	0.398	0.155
H101	−0.172	0.369	0.287
H102	−0.211	0.474	0.260
H103	−0.294	0.389	0.277
H111	−0.242	0.196	0.144
H112	−0.195	0.190	0.214

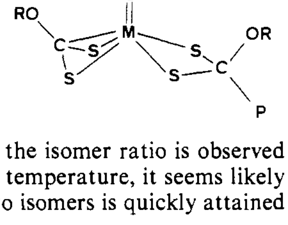
complex Ni($C_2S_4PMe_3$)(PMe_3),[8] which contains an SC(S)SC(PMe_3)S group resulting formally from the condensation of two molecules of CS_2 with one molecule of PMe_3. As shown in Table I, the ^{13}C resonance of the carbon atom adjacent to oxygen, i.e. $S_2C(PMe_3)O\mathit{C}{<}$, is also split by coupling to ^{31}P, with $^3J_{PC} \simeq 10$ Hz. Finally, the ^{13}C resonance of the CS_2 carbon of the second xanthate group appears, as indicated above, in the range 122–140 ppm. Although ^{13}C NMR data for xanthate complexes are very scarce, and therefore no conclusions as to the bonding mode of the $ROCS_2$ moiety to the metal can be drawn, this marked high-field shift of the CS_2 carbon upon complexation ($KS_2\mathit{C}OMe$ and $KS_2\mathit{C}OEt$ resonate[10] at ca. 234 ppm), together with the similarity of the solution and solid-state IR spectra, suggests that the η^3-CS_2 coordination mode found for this xanthate group by X-ray crystallography (see below) is maintained in solution. It is worth mentioning at this point that for transition-metal dithiocarbamate complexes considerably smaller shifts of the CS_2 resonance are observed upon coordination.[11]

The NMR spectra of the complexes also indicate the existence of two isomers in solution, since in addition to the main resonances already discussed, smaller signals arising from a minor species are observed. This minor component contains also different xanthate ligands, and the PMe_3 group originates a doublet of separation ~13 Hz in the ^1H NMR spectrum, suggesting again the presence of the zwitterionic ligand $^-S_2C^-(P^+Me_3)OR$. On this basis, the two isomers are proposed to differ in the orientation of the PMe_3 and OR groups with respect to the M=O group, as shown in A and B. Since only one isomer seems to exist in the solid state, and since no change in the isomer ratio is observed after stirring for 2–3 days at room temperature, it seems likely that an equilibrium between the two isomers is quickly attained

A



B



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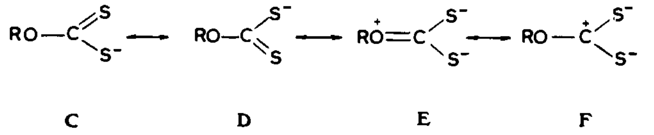
and that this equilibrium does not change with time. For the molybdenum ethyl complex $MoO[S_2C(PMe_3)OEt](S_2COEt)$, a value of 3.5 for the equilibrium constant has been deduced from $^{31}P\{^1H\}$ NMR data.

Crystal Structure of $MoO[S_2C(PMe_3)O\text{-}i\text{-}Pr](S_2CO\text{-}i\text{-}Pr)$. Table II contains relevant intramolecular bond distances and angles for this complex; atomic positional parameters with standard deviations are included in Table IV. A perspective view of the molecular geometry giving the atom-labeling scheme is presented in Figure 1. The structure consists of monomeric molecules of $Mo[S_2C(PMe_3)O\text{-}i\text{-}Pr](S_2CO\text{-}i\text{-}Pr)$, with the metal in a distorted-square-pyramidal environment of approximate C_{2v} site symmetry, lying 0.83 Å above the basal plane formed by the sulfur atoms. The coordination sphere around the metal consists of an oxo group, with a M–O separation of 1.668 (3) Å, and of two distinct types of xanthate ligands: a zwitterionic $^{-}S_2C^{-}(P^{+}Me_3)O\text{-}i\text{-}Pr$, with normal bidentate binding through the two sulfur aotms, and a very unusual η^3-xanthate ligand, which is bonded to the metal atom through the two sulfur atoms and the carbon atom of the CS_2 unit, in a way resembling a π-allyl–transition-metal interaction. A similar coordination mode has been found previously by Zubieta for one of the thioxanthate ligands in the related complex $MoO(S_2CS\text{-}i\text{-}Pr)_2$.[4a] Other complexes containing μ-η^3-xanthate ligands have been reported.[4b] In our complex the main distortion from C_{4v} symmetry is found when the S1–Mo–S2 and S3–Mo–S4 angles (73.56 (6) and 77.26 (6)°, respectively) are compared with the S1–Mo–S3 and S2–Mo–S4 angles (90.6°, average). On the other hand, the S1–Mo–S2 angle of 73.56 (6)° is very close to the value found for related bidentate ligands in four-membered rings,[4] while the S3–Mo–S4 angle of 77.26 (6)° compares well with the value of 77.9 (2)° found for the η^3-thioxanthate ligand in $MoO(S_2CS\text{-}i\text{-}Pr)_2$.[4] Small differences are found in the Mo–S distances, those corresponding to the $S_2C(PMe_3)O\text{-}i\text{-}Pr$ ligand being slightly longer than those belonging to the η^3-xanthate group (2.389 (2) vs. 2.375 (2) Å). The Mo–C(xanthate) bond distance is 2.274 (5) Å (2.25 (1) in the thioxanthate[4]). As expected, important differences are found in the angles around the carbon atoms of the CS_2 units in the two types of xanthate ligands. The angles around C1 are approximately tetrahedral, and the C1–P1 linkage (1.839 (4) Å) is considerably longer than the P1–CH_3 bonds (1.78 Å, average). In contrast, the angles around C5 are very close to the ideal value of 120° expected for the sp^2 hybridization, in agreement with the above observations regarding the coordination mode of the η^3-xanthate ligand. Finally, the existence of the phosphonium betainic xanthate ligand, formed by attack of trimethylphosphine on the electrophilic CS_2 carbon of one of the xanthate groups, suggests that resonance structure F contributes significantly to the total structure of the xanthate group in this type of complex.



C D E F

Experimental Section

Microanalyses were carried out by Pascher Microanalytical Laboratory, Bonn, West Germany. Infrared spectra were recorded as Nujol mulls or in solution with use of matched cells 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 are referenced to external 85% H_3PO_4.

All preparations and operations were carried out under oxygen-free nitrogen or argon, following the conventional Schlenk techniques. Solvents were dried by standard techniques and degassed before use. The petroleum ether had a boiling point of 40–60 °C. The compounds $MOCl_2(PMe_3)_3$ were prepared according to the literature procedures.[3] The potassium xanthates were obtained by slow addition of CS_2 to solutions of KOH in the corresponding alcohols (MeOH, EtOH, *i*-PrOH) and used without further purification.

Since all the compounds can be obtained and crystallized by essentially identical procedures, only one general preparation is given below.

Preparation of the Compounds. A solution of $MOCl_2(PMe_3)_3$ (M = Mo, W; ca. 1 mmol) in THF (45 mL) was reacted with KS_2COR (R = Me, Et, *i*-Pr; ca. 2 mmol) at room temperature over a period of 12–16 h. The color of the solution changed from the initial green or blue (M = Mo) or violet (M = W) to yellow-orange. The resulting suspension was centrifuged. Concentration of the solution in vacuo and cooling at −20 °C afford yellow crystals of the desired product in ca. 60–70% yield.

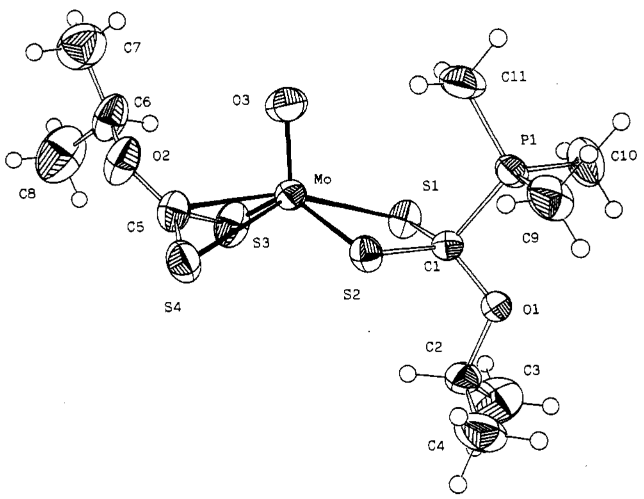


Figure 1. Molecular structure and atom-labeling scheme for $MoO[S_2C(PMe_3)O\text{-}i\text{-}Pr](S_2CO\text{-}i\text{-}Pr)$.

Crystals of the compound $MoO[S_2C(PMe_3)\text{-}i\text{-}OPr](S_2CO\text{-}i\text{-}Pr)$ suitable for X-ray analysis were obtained by slow crystallization of acetone solutions at 0 °C.

X-ray Data Collection, Structure Determination, and Refinement. A block-shaped orange single crystal of $MoO[S_2C(PMe_3)O\text{-}i\text{-}Pr](S_2CO\text{-}i\text{-}Pr)$ was sealed under N_2 in a thin-walled glass capillary. The final lattice parameters as determined from a least-squares refinement of the angular settings of 25 accurately centered reflections are given in Table III. A total of 3432 independent reflections were measured in an octant up to $2\theta = 40°$ on an Enraf-Nonius CAD4 diffractometer using the ω–2θ scan technique. The space group was uniquely determined as *Pbca* from systematic absences. The data were corrected for Lorentz and polarization effects, and a set of 2446 reflections was considered observed ($I \geq 3\sigma(I)$) and used in subsequent calculations, with use of the X-RAY system.[12] The independent Mo atom was located by means of a Patterson synthesis, and successive F_o and difference Fourier maps showed all the non-H atoms.[13]

Refinement was carried out with use of full-matrix least-squares procedures, and an empirical absorption correction[14] based on the isotropically refined model was made. The last refinement cycles were performed with use of anisotropic thermal parameters for all the atoms. Empirical weights were used in order to make flat dependence of $\langle \Delta F \rangle$ vs. $\langle F_o \rangle$ and vs. $\langle (\sin\theta)/\lambda \rangle$.[15] The final discrepancy indices were $R_1 = 0.034$ and $R_2 = 0.039$.

Acknowledgment. We are indebted to the Comisión Asesora de Investigación Científica y Técnica (E.C. and E.G.-P.) and Ministerio de Educación y Ciencia (A.G.) for supporting this work and to Professor David Cole-Hamilton for the recording of some NMR spectra.

Registry No. $MoO[S_2C(PMe_3)OMe](S_2COMe)$, 103885-31-0; $MoO[S_2C(PMe_3)OEt](S_2COEt)$, 103885-32-1; $MoO[S_2C(PMe_3)O\text{-}i\text{-}Pr](S_2CO\text{-}i\text{-}Pr)$, 103885-33-2; $WO[S_2C(PMe_3)OMe](S_2COMe)$, 103885-34-3; $WO[S_2C(PMe_3)OEt](S_2COEt)$, 103885-35-4; $WO[S_2C(PMe_3)O\text{-}i\text{-}Pr](S_2CO\text{-}i\text{-}Pr)$, 103885-36-5; $MoOCl_2(PMe_3)_3$, 90397-97-0; $WOCl_2(PMe_3)_3$, 87737-49-3; KS_2COMe, 2667-20-1; KS_2COEt, 140-89-6; $KS_2CO\text{-}i\text{-}Pr$, 140-92-1.

Supplementary Material Available: A table of final anisotropic thermal parameters (1 page); a table of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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