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Molybdenum and Tungsten Complexes of S_2CPMe_3 and Related Ligands. Crystal and Molecular Structures of $W(\eta^3\text{-}S_2CPMe_3)(CO)_2(PMe_3)_2$, $[Mo(\eta^2\text{-}S_2C(H)PMe_3)(CO)_2(PMe_3)_2]BF_4$, and $[Mo(\eta^3\text{-}SC(SMe)PMe_3)(CO)_2(PMe_3)_2]I$

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The known compound $Mo(S_2CPMe_3)(CO)_2(PMe_3)_2$ (**1a**) and the newly prepared tungsten analog $W(S_2CPMe_3)(CO)_2(PMe_3)_2$ (**1b**), obtained by HCl elimination from $WH(Cl)(CO)_2(PMe_3)_3$ upon treatment with CS_2 and PMe_3, contain a trihapto-bonded *S,S′,C*-trimethylphosphonium dithiocarboxylate ligand as demonstrated by X-ray studies carried out with **1b**. Interaction of compounds **1** with protic acids affords the dithioformate species $[M(\eta^2\text{-}S_2C(H)PMe_3)(CO)_2(PMe_3)_2]^+$ (M = Mo (**2a**), W (**2b**)) while alkyl-derived electrophiles X^+ (X = Me, Et) furnish the cationic complexes $[M(\eta^3\text{-}SC(SR)PMe_3)(CO)_2(PMe_3)_2]^+$ (isolated in the form of iodide salts; M = Mo, R = Me (**3a**), R = Et (**4**); M = W, R = Me (**3b**)). These contain unprecedented *S*-alkyl phosphonio dithioester ligands as a result of alkylation at one of the sulfur atoms. The protonation reactions are proposed to occur by initial attack of H^+ at the strongly basic metal center followed by hydride migration to the electrophilic carbon atom. In accord with this, the reaction of the hydrides $MH(Cl)(CO)_2(PMe_3)_3$ (M = Mo, W) with CS_2 gives, under appropriate conditions, the cationic species **2a** and **2b**. Compounds **1b**, **2a**$[BF_4]$, and **3a** have been characterized by X-ray crystallography. Crystals of **1b** are orthorhombic, $P2_12_12_1$, with a = 11.957(4) Å, b = 12.724(3) Å, c = 13.758(2) Å, and Z = 4. **2a**$[BF_4]$ possesses a triclinic space group $P\bar{1}$ and has unit cell constants a = 6.935(3) Å, b = 13.372(3) Å, c = 13.722(2) Å, α = 103.49(2)°, β = 94.04(2)°, γ = 104.69(2)°, and Z = 2. **3a** is also triclinic, $P\bar{1}$, with a = 11.193(2) Å, b = 12.988(7) Å, c = 8.791(4) Å, α = 99.81(4)°, β = 94.54(5)°, γ = 78.11(4)°, and Z = 2.

Introduction

Transition metal compounds of S-containing ligands are the subject of much current research activity. Compounds of this type are important in biochemical processes and seem to be the active centers in many life redox reactions.[2] Sulfur donors have, in fact, been found to surround the metal centers of various metalloenzymes such as nitrogenases, ferredoxins, hydrogenases, and nitrate reductases.[3]

A large number of studies on metal–sulfur compounds has been concerned with group 6 metal complexes of dithioacid ligands. This is due not only to their conceivable biological relevance but also to the ability of dithioacid ligands to produce complexes with high coordination numbers in different oxidation states and to afford unusual structural types of carbon- and sulfur-containing ligands through various transformations.[4] Closely related to the above are complexes of the betaine, trialkylphosphonium carboxylate ligands, S_2CPR_3, for which a rich diversity of coordination modes has been authenticated by X-ray crystallography.[5] The reactivity of the coordinated S_2CPR_3 unit has also been the subject of recent chemical studies, and at present, there is sufficient evidence indicating the electrophilic character of the central carbon atom.[6]

As a continuation of our own work on Mo and W complexes of the S_2CPMe_3 group,[7] we report herein the results of our research on $M(S_2CPMe_3)(CO)_2(PMe_3)_2$ compounds[8] (M = Mo (**1a**), W (**1b**)). This includes an analysis of the structural characteristics of the $M\text{–}S_2CPMe_3$ linkage, ascertained with the aid of an X-ray determination effected with the W derivative **1b**. The behavior of compounds **1** toward electrophiles X^+ (X = H, Me, Et) has also been examined. While reactions with H^+ yield complexes

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(1) (a) University of Sevilla. (b) University of Madrid (X-ray crystal structures).

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of the trimethylphosphonium dithioformate ligand, $^{-}S_2C(H)PMe_3$, carbon-based electrophiles furnish somewhat unusual compounds containing S,C,S′-coordinated *S*-alkyl phosphoniodithio ester ligands, $^{-}SC(SR)PMe_3$. One such compound, the Mo derivative $[Mo(\eta^3\text{-}SC(SMe)PMe_3)(CO)_2(PMe_3)_2]I$ (**3a**), has been characterized by X-ray crystallography.

Results

$M(S_2CPMe_3)(CO)_2(PMe_3)_2$ Compounds (M = Mo (1a), W (1b)). Crystal and Molecular Structure of 1b. The molybdenum complex $M(S_2CPMe_3)(CO)_2(PMe_3)_2$ (**1a**) has been reported to form[7a] in the unusual reaction of the head-to-tail C_2S_4 dimer $Mo(C_2S_4)(C_2H_4)(PMe_3)_3$ with CO. Heating a solution of the latter compound at 50 °C for 3–4 h, under 2 atm of CO, provides red crystals of **1a** (eq 1). Since extension of this synthetic methodology to the tungsten system analog is not straightforward, an alternative route to compounds **1** is clearly desirable and this has been achieved using the recently prepared chlorohydride derivatives $MH(Cl)(CO)_2(PMe_3)_3$,[9a] although only in the case of the W compound, **1b**, are reasonable yields obtained. The interaction of these species with CS_2 yields (see below) the trimethylphosphonium dithioformate derivatives $[Mo(S_2C(H)PMe_3)(CO)_2(PMe_3)_2]Cl$ (M = Mo, **2a**[Cl]; W, **2b**[Cl]). If the reaction is effected in the presence of added PMe_3, HCl elimination is facilitated and the desired compounds, **1a** and **1b**, are formed (eq 2). Yields of **1b** are on the order of 80%, but for the Mo compound **1a**, further reaction to other unidentified products decreases the yield of isolated product to *ca.* 5–10%.

$$Mo(C_2S_4)(C_2H_4)(PMe_3)_3 + CO \rightarrow \underset{\mathbf{1a}}{Mo(S_2CPMe_3)(CO)_2(PMe_3)_2} + \text{other products} \quad (1)$$

$$\underset{Mo,\ W}{MH(Cl)(CO)_2(PMe_3)_3} + CS_2 + PMe_3 \xrightarrow[-HCl\cdot PMe_3]{} M(S_2CPMe_3)(CO)_2(PMe_3)_2 \quad (2)$$
$$M = Mo\ (\mathbf{1a}),\ W\ (\mathbf{1b})$$

Complex **1b** is a red crystalline solid that exhibits good solubility properties in CH_2Cl_2, THF, acetone, and other polar organic solvents. The presence of the CO ligands is inferred by the observation of two strong carbonyl stretchings at the very low frequencies of 1865 and 1730 cm^{-1}. Similar low-energy terminal CO absorptions have been found in other electron rich Mo and W complexes.[9b] Like the Mo analog, compound **1b** is a fluxional molecule that exhibits temperature-dependent NMR spectra. For example the $^{31}P\{^1H\}$ NMR spectrum recorded at 20 °C consists of a triplet at δ 31.7 ($^3J_{PP}$ = 4.5 Hz) and a very broad hump at about δ -30, the latter signal converting into a somewhat broad singlet upon heating the sample to 80 °C. The δ 31.7 triplet can be assigned to the S_2CPMe_3 group while the broad resonance at −30 ppm is due to the coordinated PMe_3 ligands. This broad signal separates into two resonances at temperatures below −20 °C, and at −70 °C a doublet (δ −16.2, $^2J_{PP}$ = 24 Hz) and a doublet of doublets (δ −38.6, $^2J_{PP}$ = 24 Hz, $^3J_{PP}$ = 6 Hz) are clearly discerned. Curiously enough the room temperature triplet at δ 31.7 appears at this temperature as a broad doublet, only one resolvable coupling of ca. 6 Hz being observed. Although the nature of this fluxional process has not been investigated in detail, its intramolecular nature is unambigously demonstrated by the observation of ^{31}P–^{31}P coupling in the fast exchange regime.

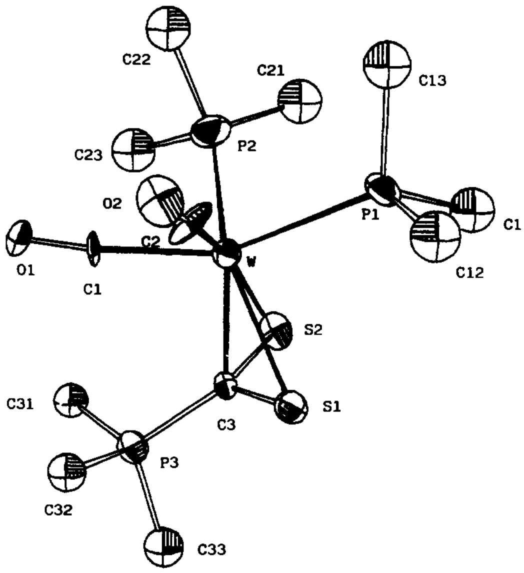

Figure 1. ORTEP diagram and atomic numbering scheme for **1b**.

Table I. Selected Bond Distances (Å) and Angles (deg) in **1b**

W–S1	2.505(8)	W–C3	2.12(2)
W–S2	2.541(7)	S1–C3	1.73(2)
W–P1	2.552(8)	S2–C3	1.77(2)
W–P2	2.437(9)	P3–C3	1.74(2)
W–C1	1.96(1)	C1–O1	1.12(2)
W–C2	1.88(3)	C2–O2	1.21(4)
C2–W–C3	121(1)	S2–W–P1	98.3(3)
C1–W–C3	90.9(9)	S1–W–C2	91.1(9)
C1–W–C2	75(1)	S1–W–C1	113.7(6)
P2–W–C3	122.9(6)	S1–W–P2	155.7(3)
P2–W–C2	112(1)	S1–W–P1	85.0(3)
P2–W–C1	82.1(6)	S1–W–S2	72.6(3)
P1–W–C3	116.7(5)	W–S1–C3	56.7(7)
P1–W–C2	83(1)	W–S2–C3	55.6(7)
P1–W–C1	151.2(7)	W–C1–O1	173(2)
P1–W–P2	88.7(3)	W–C2–O2	177(3)
S2–W–C2	163(1)	P3–C3–S2	121(1)
S2–W–C1	108.0(6)	S1–C3–S2	117(1)
S2–W–P2	85.1(3)	S1–C3–P3	120(1)

The S_2CPMe_3 group in **1b** gives characteristic ^1H (δ 1.2, d, $^2J_{PH}$ = 14 Hz), $^{13}C\{^1H\}$ (δ 10.8, d, $^2J_{PC}$ = 60 Hz), and $^{31}P\{^1H\}$ (δ 31.7, t, $^2J_{PP}$ = 4 Hz) resonances, attributable to a quaternary phosphorus atom bearing a formal positive charge.[10] In addition, a ^{13}C doublet centered at ca. 67.8 ppm ($^1J_{CP}$ = 92; $^1J_{CW}$ = 28 Hz) can be assigned to the CS_2 carbon of the S_2CPMe_3 ligand. Although this is at a somewhat higher field than in **1a**, the chemical shift of this signal can be taken as indicative of trihapto S,S′,C, coordination of the trimethylphosphonium dithiocarboxylate ligand. For chelate S,S′ coordination, the corresponding ^{13}C resonance has been found at very low field, ca. 230–220 ppm.[5i]

Unequivocal confirmation for the bonding mode of the S_2CPMe_3 ligand in compounds **1** comes from an X-ray structural determination carried out with the tungsten derivative **1b**. Figure 1 gives a perspective view of the molecules of this complex, selected bond distances and angles are collected in Table I. Crystal data for **1b** and for other derivatives structurally characterized in this work (**2a**[BF_4] and **3a**) are shown in Table IV. A useful structural representation of **1b** derives from a distorted square pyramid, with the S_2CPMe_3 ligand residing in the apical position and two cisoid carbonyls (C1–W–C2 = 75(1)°) and phosphine (P1–W–P2 = 88.7(3)°) ligands in the basal plane. The P3–C3–S1–S2 fragment is planar, and the angles around the central carbon are very close to the ideal 120° value expected for sp^2 hybridization (S1–C3–S2 = 117(1)°; P3–C3–S1 = 120(1)°; P3–C3–S2 = 121(1)°). The W–S distances are somewhat different (W–S1 = 2.505(8) Å; W–S2 = 2.541(7) Å), the longer one being associated with the sulfur atom transoid with respect to one of the CO ligands (C2–W–S2 = 163(1)°). This may therefore reflect the high

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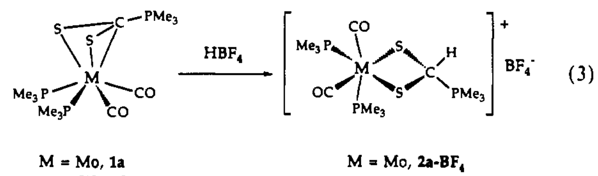
trans influence characteristic of this coordinated group. These W–S separations are, however, normal and compare well with those found in other related complexes, e.g. ca. 2.5 Å in $MoCl(S_2CPMe_3)(NO)(PMe_3)_2$[7b] and $[Mo(\mu\text{-}S_2CPEt_3)(CO)_2(PEt_3)]_2$.[5a] As in these two compounds, the CS_2 carbon of the phosphonium dithiocarboxylate unit is well within bonding distance to tungsten (2.12(2) Å). This very closely matches the 2.14-Å value found for the corresponding Mo–C distance in the above complexes. These structural parameters indicate that the zwitterionic S_2CPMe_3 ligand, which acts formally as a 4-electron donor, is coordinated to the metal through the C and the two S atoms of the CS_2 moiety in a pseudoallylic manner. This coordination mode has been observed previously, both in mononuclear[7b] and in binuclear compounds,[5a, h–j] and it is highly reminiscent of the pseudoallylic η^3 S,S′,C coordination described for some oxo complexes of Mo and W with xanthate and thioxanthate ligands.[11]

Reaction of Compounds 1 with HBF_4. X-ray Structure of $[Mo(\eta^2\text{-}S_2C(H)PMe_3)(CO)_2(PMe_3)_2]BF_4$ (2a[BF_4]). Addition of HBF_4 to solutions of compounds **1** affords the cationic M(II) complexes depicted in eq 3 in the form of red, crystalline solids.



M = Mo, **1a**
W, **1b**

M = Mo, **2a-BF₄**
W, **2b-BF₄**

In accord with the ionic formulation proposed for these species, they behave as 1:1 electrolytes in acetone and show poor solubility in nonpolar solvents. The identification of the $S_2C(H)PMe_3$ ligand is straightforward on the basis of the available spectroscopic data. Once again distinctive signals are found for the methyl groups in the ^1H and $^{13}C\{^1H\}$ NMR spectra (see Experimental Section), and a characteristically low-field singlet, which converts into a doublet (δ 33.1, $^2J_{PH} = 4$ Hz, data for **2a**) upon selective decoupling of the CH_3 protons, is observed in the $^{31}P\{^1H\}$ NMR spectrum. Supporting data come from the C-bound hydrogen atom, which originates a ^1H NMR doublet at δ 6.34 ($^2J_{PH} = 4.5$ Hz) while the central carbon provides a ^{13}C resonance centered at δ 64.9 ($^1J_{CH} = 156$ Hz; $^1J_{PC} = 46$ Hz; $^3J_{PC} = 4$ Hz). The observation of a triplet at δ 242.3 ($^2J_{PC} = 29$ Hz) for the CO ligands and of a virtual pseudoquintet for the methyl carbons of the cordinated PMe_3 molecules (AXX′ spin system, δ_A 18.5; $^2J_{XX'} = 24$; $^1J_{AX} = 35$ Hz) is also consistent with the suggested structure.

Closely related derivatives, **2**[Cl], containing the same cationic species **2a,b**, but with Cl^- as the counteranion, can be made by treatment of the hydrides $MH(Cl)(CO)_2(PMe_3)_3$[9a] (M = Mo, W) with CS_2 (eq 4). These chloride salts display physical and

$$MH(Cl)(CO)_2(PMe_3)_3 + CS_2 \rightarrow [M(S_2C(H)PMe_3)_2(CO)_2(PMe_3)_2]Cl \quad (4)$$

$$M = Mo\ (\mathbf{2a}[Cl]),\ W\ (\mathbf{2b}[Cl])$$

spectroscopic properties very similar to those of **2**[BF_4] and, accordingly, need no further description.

In order to confirm the structural characteristics of compounds **2** an X-ray investigation of **2a**[BF_4] has been performed. Figure 2 displays an ORTEP perspective view of this complex, Table II shows some selected bond distances and angles. The Mo atom is six-coordinated in a severely distorted octahedral enviroment consisting of the two sulfurs of the trimethylphosphonium dithioformate group (Mo–S1 = 2.409(2) Å, Mo–S2 = 2.418(2) Å), two carbonyls (Mo–C1 = 1.962(7) Å, Mo–C2 = 1.935(9) Å) and two phosphine ligands (Mo–P1 = 2.462(2) Å, Mo–P2 = 2.457(2) Å). The distortion from the idealized geometry is manifested by the P1–Mo–P2 and C1–Mo–C2 angles of 131.3(1) and 107.0(3)°, respectively, and may be due in part to the small bite angle of the $Me_3P(H)CS_2$ ligand (S1–Mo–S2 = 73.5(1)°). These distortions are commonly encountered in other complexes containing phosphonium dithioformate groups.[12] A comparison of the bond distances and angles within this entity with those corresponding to the S_2CPMe_3 complex **1b** clearly

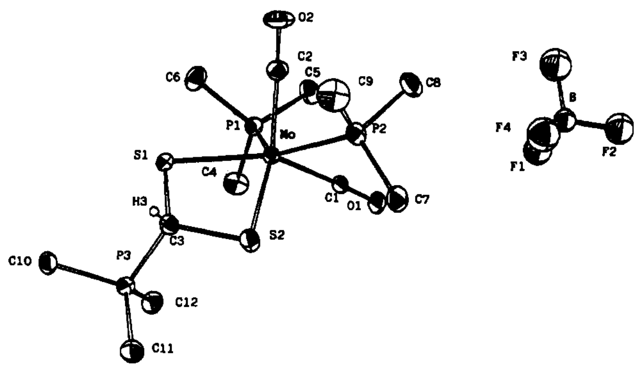


Figure 2. Molecular structure of complex **2a**[BF_4] showing the atomic numbering scheme.

Table II. Bond Distances (Å) and Angles (deg) in **2a**[BF_4]

Mo–P1	2.462(2)	P3–C10	1.779(8)
Mo–P2	2.457(2)	P3–C11	1.77(1)
Mo–S1	2.409(2)	P3–C12	1.776(8)
Mo–S2	2.418(2)	S1–C3	1.816(8)
Mo–C1	1.962(7)	S2–C3	1.809(8)
Mo–C2	1.935(9)	O1–C1	1.150(9)
P1–C4	1.804(9)	O2–C2	1.16(1)
P1–C5	1.80(1)	C3–H3	1.020(6)
P1–C6	1.809(9)	B–F1	1.35(1)
P2–C7	1.81(2)	B–F2	1.33(1)
P2–C8	1.80(1)	B–F3	1.33(2)
P2–C9	1.81(1)	B–F4	1.33(2)
P3–C3	1.795(8)		
C1–Mo–C2	107.0(3)	C8–P2–C9	103.5(5)
S2–Mo–C2	143.0(3)	C7–P2–C9	103.3(5)
S2–Mo–C1	99.0(3)	C7–P2–C8	103.4(4)
S1–Mo–C2	97.0(3)	C11–P3–C12	108.9(5)
S1–Mo–C1	146.0(2)	C10–P3–C12	110.3(4)
S1–Mo–S2	73.5(1)	C10–P3–C11	110.7(4)
P2–Mo–C2	76.2(3)	C3–P3–C12	109.7(4)
P2–Mo–C1	74.7(2)	C3–P3–C11	109.8(4)
P2–Mo–S2	86.0(1)	C3–P3–C10	107.4(4)
P2–Mo–S1	135.7(1)	Mo–S1–C3	90.4(2)
P1–Mo–C2	74.0(3)	Mo–S2–C3	90.3(3)
P1–Mo–C1	78.3(2)	Mo–C1–O1	177.5(7)
P1–Mo–S2	138.3(1)	Mo–C2–O2	177.3(8)
P1–Mo–S1	85.9(1)	S1–C3–S2	105.6(4)
P1–Mo–P2	131.3(1)	P3–C3–S2	113.5(4)
Mo–P1–C5	115.3(3)	P3–C3–S1	110.6(4)
Mo–P1–C5	117.8(3)	H3–C3–S2	107.5(6)
Mo–P1–C4	112.9(3)	H3–C3–S1	107.8(6)
C5–P1–C6	102.2(5)	H3–C3–P3	111.5(6)
C4–P1–C6	102.6(4)	F3–B–F4	107.8(9)
C4–P1–C5	104.1(5)	F2–B–F4	110.6(9)
Mo–P2–C9	111.7(4)	F2–B–F3	108.2(9)
Mo–P2–C8	117.2(3)	F1–B–F4	107.8(9)
Mo–P2–C7	116.0(4)	F1–B–F3	108.7(9)
F1–B–F2	113.5(9)		

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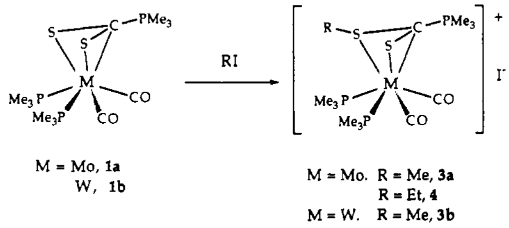
[12] See, for example: (a) Einstein, F. W.; Enwall, E.; Flitcroft, N.; Leach, J. M. *J. Inorg. Nucl. Chem.* **1972**, *34*, 885. (b) Ashworth, T. V.; Singleton, E. Laing, M. *J. Chem. Soc., Chem. Commun.* **1976**, 875. (c) Bianchini, C.; Meli, A.; Nuzzi, F.; Dapporto, P. *J. Organomet. Chem.* **1982**, *236*, 245. (d) Faridoon; Spalding, T. R.; Ferguson, G.; Kennedy, J. D.; Fontaine, X. L. R. *J. Chem. Soc., Chem. Commun.* **1989**, 906. (e) Miguel, D.; Miguel, J. A.; Riera, V.; Solans, X. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1014.

demonstrates the attachment of the H atom to the CS_2 carbon. In particular, the bond angles P3–C3–S1 = 110.6(4), P3–C3–S2 = 113.5(4) and S1–C3–S2 = 105.6(4)° (corresponding angles in **1b** are 120(1), 121(1), and 117(1)°, respectively) indicate that the central carbon atom, C3, is sp^3 hybridized. In agreement with this, the C–S distances are also somewhat longer than those in **1b** and approach the values expected for single bonds (C3–S1 = 1.816(8) Å, C3–S2 = 1.809(8) Å).

Reactions of Compounds 1 with RI (R = Me, Et). Crystal Structure of [Mo(η^3-SC(SMe)PMe$_3$)(CO)$_2$(PMe$_3$)$_2$]I 3a. The analogous reaction of the molybdenum derivative **1a** with MeI and EtI produces orange or red crystalline materials, **3a** and **4** respectively, that incorporate the alkyl group into the original S_2CPMe_3 ligand. Complex **1b** reacts similarly with MeI and provides the corresponding derivative **3b**. The new iodide complexes, **3** and **4**, have solubility and spectroscopic properties resembling those of compounds **2**. Thus, they behave as 1:1 electrolytes and contain two terminal carbonyl groups, and two nonequivalent molecules of PMe_3 coordinated to the metal center and a third incorporated into a phosphonium dithiocarboxylate-derived ligand. In accord with the latter observation, their $^{31}P\{^1H\}$ NMR spectra display typical AMX spin systems. Representative parameters, corresponding to the Mo complex **3a**, are δ_A 44.1, δ_M 3.3, and δ_X −10.1 ppm; $^3J_{AM}$ = 6, $^3J_{AX}$ = 2, and $^2J_{MX}$ = 50 Hz.

On this basis, a formulation for compounds **3** and **4** similar to that proposed for **2**, namely as derivatives of a trimethylphosphonium dithiocarboxylate ligand, $Me_3PC(R)S_2$, could be advanced.[13] Nonetheless, there are some spectroscopic features in compounds **3** and **4** which seem difficult to reconcile with such a structural proposal. For example, the $^{13}C\{^1H\}$ NMR spectra of **3a** and **3b** exhibit singlets at δ 11.9 and 9.7, respectively, due to the methyl group supposedly bound to the CS_2 carbon within the phosphonium dithiocarboxylate unit. No coupling with the ^{31}P nucleus of this entity is observed, in marked contrast with the value of ca. 15 Hz found for the analogous coupling in the complex $CpW(S_2C(Me)PMe_3)(CO)_2$.[13b] Moreover the above $^{13}C\{^1H\}$ signal at δ 11.9 corresponding to the Me group in **3a** appears unchanged in the spectrum of a sample of this complex ca. 33% enriched in $^{13}CS_2$. These observations unambigously show that the R group in compounds **3** and **4** is not bonded to the CS_2 carbon. Alkylation can then be proposed to occur at one of the sulfur atoms according to eq 5, and this has been confirmed by



(5)

an X-ray study carried out with complex **3a**. Figure 3 shows an ORTEP perspective of this species, while Table III contains some important bond distances and angles. As can be seen, the original S_2CPMe_3 ligand has undergone methylation at one of the sulfur atoms giving an unprecedented trimethylphosphonium dithioester ligand, SC(SMe)PMe$_3$, which is trihapto bonded to the metal center through the carbon and the sulfur atoms. S,S′,C coordination of the CS_2 group of other related ligands is known,[14,15] but to our knowledge only two somewhat similar complexes have been reported to date: the nickel compound Ni(SC(SMe)PPh$_2$CH$_2$CH$_2$N(CH$_2$CH$_2$PPh$_2$)$_2$, having an *S*,*C*-SC(SMe)PR$_3$ group[16] and the recently described binuclear species Mn$_2$(CO)$_6$(μ-SC(SR′)PR$_3$), which contains a bridging (*S*,*S*′;*S*′,*C*)-dithioester ligand.[6a]

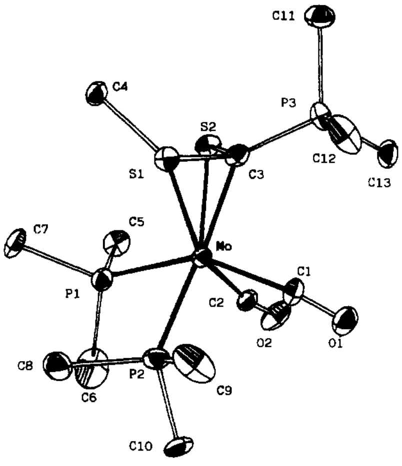


Figure 3. Molecular structure of the cation of complex **3a**.

Table III. Principal Bond Lengths (Å) and Angles (deg) in **3a**

Mo–S1	2.567(2)	Mo–C3	2.125(5)
Mo–S2	2.506(2)	S1–C3	1.793(5)
Mo–P1	2.565(2)	S1–C4	1.791(5)
Mo–P2	2.495(2)	S2–C3	1.727(5)
Mo–C1	1.942(5)	O1–C1	1.167(7)
Mo–C2	1.954(6)	O2–C2	1.149(7)
C2–Mo–C3	115.8(3)	S2–Mo–P2	159.4(1)
C1–Mo–C3	87.6(2)	S2–Mo–P1	85.7(1)
C1–Mo–C2	78.2(3)	S1–Mo–C3	43.7(1)
P2–Mo–C3	129.4(1)	S1–Mo–C2	159.4(2)
P2–Mo–C2	108.1(2)	S1–Mo–C1	99.0(2)
P2–Mo–C1	77.6(2)	S1–Mo–P2	90.9(1)
P1–Mo–C3	121.7(2)	S1–Mo–P1	107.7(1)
P1–Mo–C2	81.5(2)	S1–Mo–S2	72.7(1)
P1–Mo–C1	149.6(2)	Mo–S1–C4	116.9(2)
P1–Mo–P2	87.6(1)	Mo–S1–C3	54.9(2)
S2–Mo–C3	42.8(2)	Mo–S2–C3	56.7(2)
S2–Mo–C2	90.2(2)	C3–S1–C4	106.1(3)
S2–Mo–C1	116.5(2)		

An approximate representation of the molecules of **3** is as a severely distorted square pyramid, with the sulfur-containing ligand in the apical position. The dihedral angle between the S1, S2, and C3 plane and the best mean-square plane containing atoms P1, P2, C1, and C2 is 165°. Once more, the most interesting aspect of the structure is the coordination mode of the sulfur-containing ligand. The Mo–C3 separation at 2.125(5) Å is almost identical to the analogous distance in the parent compound **1b** (W–C3 = 2.12(2) Å). As a result of the incorporation of the methyl group into the CS_2 moiety, the two C3–S bonds become different: C3–S1 is essentially a single bond and identical within experimental error, to the C4–S1 separation (1.791(5) vs 1.793(5) Å) while C3–S2 keeps some double bond character (1.727(5) Å). The Mo–S distance of the methyl-bound sulfur, i.e. Mo–S2, is appreciably shorter than the other (2.506(2) vs 2.567(2) Å) but similar differences are also found in **1b** (W–S separations of 2.505(8) and 2.541(7) Å). Bond angles around the CS_2 carbon C3 are comparable to the corresponding ones in **1b** (S1–C3–S2

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(13) Compounds of this type are already known: (a) Reference 6b. (b) Kreissl, F. R.; Ullrich, N.; Wirsing, A.; Thewalt, U. *Organometallics* **1991**, *10*, 3275.

(14) (a) Tatsumisago, M.; Matsubayashi, G.; Tanaka, T.; Nishigaki, S.; Nakatsu, K. *J. Chem. Soc., Dalton Trans.* **1982**, 121. (b) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, G. A. *J. Organomet. Chem.* **1984**, *273*, 361. (c) Wright, L. L.; Haltiwanger, R. C.; Noordik, J.; DuBois Rakowski, M. *J. Am. Chem. Soc.* **1987**, *109*, 282. (d) Wright, L. L.; Haltiwanger, R. C.; Noordik, J.; DuBois Rakowski, M. *J. Am. Chem. Soc.* **1987**, *109*, 283.

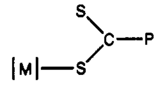
(15) (a) Schenk, W. A.; Rüb, D.; Burschka, C. *J. Organomet. Chem.* **1987**, *328*, 287. (b) Schenk, W. A.; Rüb, D.; Burschka, C. *J. Organomet. Chem.* **1987**, *328*, 305.

(16) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Orlandini, A. *J. Organomet. Chem.* **1984**, *270*, 251.

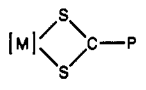
= 117.3(3)°; P3–C3–S1 = 117.5(3)°; P3–C3–S2 = 119.3(3)°) and approach closely the ideal values expected for sp^2 hybridization.

Discussion

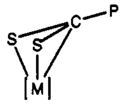
The structural characteristics of the zwitterionic S_2CPR_3 ligands[5–7] arouse considerable interest. In mononuclear systems, two bonding modes can be readily envisaged for this group, namely the monohapto interaction **A**, in which the S_2CPR_3 group donates formally two electrons to the metal by coordination through one of the sulfurs, and the chelating mode **B** in which both sulfur atoms are engaged in the bonding with the metal center furnishing formally four electrons. In recent years a third coordination type **C** has been authenticated by X-ray crystallography in complexes of this[7b] and other dithiolate ligands (e.g. xanthates and thioxanthates[11] and even dithiocarboxylates[17]). Structures of type **C** have also been shown to exist in polinuclear systems.[5a,h–j] Since in this alternative structure the S_2CPR_3 group acts also as a four-electron donor, the distintive M–C interaction of coordination mode **C** may be a reflection of the well-known electrophilicity of the CS_2 carbon atom.



A



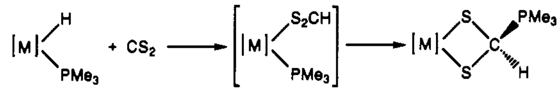
B



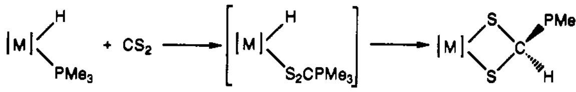
C

Unequivocal identification of the bonding modes **A**–**C** on the basis of the NMR parameters of the S_2CPR_3 ligand is not yet possible due to the paucity of ^{13}C NMR data for complexes of these types. Nonetheless, some relatively safe predictions can already be made. The CS_2 carbon of $Mo(S_2CPMe_3)(CO)_2(PMe_3)_2$ (**1a**) resonates at δ 80.1 (dd, $^1J_{PC}$ = 85 Hz, $^2J_{PC}$ = 4 Hz). At the time this compound was prepared no distinction could be made between the chelate S,S′ and the pseudo-allylic S,S′,C-bonding modes. Subsequent work by our group[7b] and by Miguel, Riera and coworkers[5h–j] has led to the preparation of a number of complexes containing S,S′,C-coordinated S_2CPR_3 groups (some of them have been structurally characterized by X-ray crystallography). In all the cases studied the ^{13}C resonance of the dithiocarboxylate carbon appears in the proximity of 80 ppm. Since this signal is detected at much lower field in complexes exhibiting the chelating S,S′ structure **B** (230–220 ppm[5i]) the observation of the above ^{13}C resonance near δ 80 can be taken as indicative of trihapto coordination of the S_2CPMe_3 ligand. In excellent accord with this, the tungsten complex **1b** gives the corresponding resonance at δ 67.8.

The reactivity of the S_2CPR_3 group toward nucleophiles has been studied in recent years, and it has been demonstrated that the central carbon atom is very prone to undergo attack by nucleophilic reagents. Various transformations, including displacement of the PR_3 by the nucleophile, addition reactions, and others, have been observed.[6b] The analogous reactions toward electrophiles, X^+, have however received less attention. Treatment of compounds **1** with H^+ affords the cationic species $[M(S_2C(H)PMe_3)(CO)_2(PMe_3)_2]^+$ (**2**), which contain a phosphonium dithioformate ligand. Direct attack of H^+ at the CS_2 carbon of the S_2CPMe_3 entity does not seem likely in view of the electrophilicity of this atom. Hence it can be proposed that protonation occurs at the electron-rich metal center (recall the very low CO stretching frequencies found for **1a** and **1b**, ca. 1850 and 1725 cm^{-1}, clearly indicative of a very high electron density at the metal) with formation of a hydride intermediate which would then transform into the finally observed product. In good agreement with this assumption, the reaction of the metal hydrides $MH(Cl)(CO)_2(PMe_3)_3$ with CS_2 affords the same cationic species **2** (see eq 3). Two different routes can be conceived for this transformation. One involves insertion of CS_2 into the M–H bond with formation of a dithioformate complex that would then undergo nucleophilic attack by PMe_3 at the dithiocarboxylate carbon, as depicted schematically in eq 6. The second implies initial formation of a trimethylphosphonium dithiocarboxylate group, followed by hydride transfer from the metal to the electrophilic carbon atom (eq 7). At present we have no data in favor of either of these mechanistic possibilities. The analogous reaction with carbon-based electrophiles (X = Me, Et) provides the cationic phosphonium dithioester compounds $[Mo(SC(SX)PMe_3)(CO)_2(PMe_3)_2]^+$ (**3** and **4**). As before, the formation of these species could be rationalized either by direct alkylation at one of the sulfur atoms or alternatively by formation of a metal–alkyl intermediate followed by migration to sulfur, but once again there is no experimental evidence supporting either of these reaction routes.



(6)



(7)

Experimental Section

Microanalyses were by Pascher Microanalytical Laboratory, Remagen, Germany, and by the Microanalytical Service of the University of Sevilla. Infrared spectra were recorded on a Perkin-Elmer Model 684 or Model 883 spectrophotometer. ^1H, ^{13}C and ^{31}P NMR spectra were run on a Varian XL-200 spectrometer. ^{31}P shifts were measured with respect to external 85% H_3PO_4. ^{13}C NMR spectra were referenced using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had bp 40–60 °C. The compounds $[MClH(CO)_2(PMe_3)_3]$[9a] (M = Mo, W) were prepared according to the literature procedures.

Preparation of $[M(S_2CPMe_3)(CO)_2(PMe_3)_2]$ (M = Mo (1a), W (1b)). The synthesis of the molybdenum complex **1a** has been reported in the literature.[7a] An alternative procedure is described below for the tungsten analog **1b**. CS_2 (0.6 mmol) was added to a stirred mixture of $[WClH(CO)_2(PMe_3)_3]$ (0.2 g, *ca.* 0.4 mmol) and PMe_3 (0.1 mL, *ca.* 1 mmol) in THF (60 mL) to produce a red solution. After the mixture was stirred for 8 h at room temperature, the solvent was removed and the residue washed with petroleum ether (2 × 20 mL). Crystallization from 1:1 petroleum ether–CH_2Cl_2 mixtures produced red crystals of **1b** in 80% yield. IR (Nujol, cm^{-1}): ν_{CO} 1866, 1731. ^1H NMR (toluene-d_8): δ 1.19 (d, 9 H, J_{HP} = 14 Hz, $S_2CP(CH_3)_3$), 1.33 (d, 18 H, J_{HP} = 7 Hz, 2 $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR(toluene-d_8, room temperature): δ −29.4 (br s, 2 PMe_3), 31.7 (t, J_{PP} = 4 Hz, S_2CPMe_3). $^{31}P\{^1H\}$ NMR (toluene-d_8, −70 °C): δ −38.6 (dd, J_{PP} = 24, J_{PP} = 5, J_{PW} = 195 Hz, PMe_3), −16.1 (d, J_{PP} = 24, J_{PW} = 319 Hz, PMe_3), 33.3 (d, J_{PP} = 5 Hz, S_2CPMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 10.8 (d, J_{CP} = 60 Hz, $P(CH_3)_3$), 20.1 (d, J_{CP} = 28 Hz, $P(CH_3)_3$), 67.8 (d, $^1J_{CP}$ = 92 Hz, S_2CPMe_3), 239.44 (m, CO). Anal. Calcd for $C_{12}H_{27}O_2P_3S_2W$: C, 26.5; H, 5.0. Found: C, 26.3; H, 4.9. The complex **1b*** was prepared similarly using $^{13}CS_2$ (33% enriched). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 67.8 (d, $^1J_{CP}$ = 92 Hz; $^1J_{CW}$ = 28 Hz, S_2CPMe_3). For **1a***, prepared by the procedure reported in ref 7a ($^{13}CS_2$, 33% enriched), $^{13}C\{^1H\}$ NMR (C_6D_6): δ 80.1 (dd, $^1J_{CP}$ = 85, $^2J_{CP}$ = 4 Hz).

Synthesis of the Cationic Trimethylphosphonium Dithioformate Species $[M(S_2C(H)PMe_3)(CO)_2(PMe_3)_2]^+$ (M = Mo (2a), W (2b)). (a) Reactions of Compounds 1 with HBF_4. An excess of HBF_4 (0.9 mmol) was added to a stirred solution of **1a** (0.29 g, *ca.* 0.65 mmol) in Et_2O (100 mL) to produce a red solid. After the mixture was stirred for 30 min at room temperature, the solid was filtered off, washed with Et_2O (2 × 20 mL), and recrystallized from acetone. Red crystals of **2a**$[BF_4]$ (0.17 g)

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[17] (a) Scott, F.; Krugger, G. J.; Cronje, S.; Lombard, A.; Raubenheimer, H. G.; Benn, R.; Rufinska, A. *Organometallics* **1990**, *9*, 1071. (b) Raubenheimer, H. G.; Scott, F.; Cronje,S.; van Rooyen, P. H. *J. Chem. Soc., Dalton Trans.* **1992**, 1859.

Table IV. Crystallographic Data for **1b**, **2a**[BF$_4$] and **3a**

	1b	**2a**[BF$_4$]	**3a**
chem formula	$\mathrm{C_{12}H_{27}O_2P_3S_2W}$	$\mathrm{C_{12}H_{28}O_2P_3S_2MoBF_4}$	$\mathrm{C_{13}H_{30}O_2P_3S_2MoI}$
fw	544.2	544.1	598.3
space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
a, Å	11.957(4)	6.935(3)	11.193(2)
b, Å	12.724(3)	13.372(3)	12.988(7)
c, Å	13.758(2)	13.722(2)	8.791(4)
α, deg		103.49(2)	99.81(4)
β, deg		94.04(2)	94.54(5)
γ, deg		104.69(2)	78.11(4)
V, Å^3	2093.2(9)	1185.0(9)	1231.0(9)
Z	4	2	2
T, K	295	295	295
λ, Å	0.710 69	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.73	1.52	1.61
μ, cm^{-1}	60.6	9.43	21.2
R^a	0.049	0.048	0.034
$R_w{}^b$	0.057	0.055	0.038

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ (unit weights).

Table V. Atomic Coordinates for **1b**

atom	x/a	y/b	z/c
W	0.722 11(9)	0.265 20(6)	0.263 58(6)
S1	0.552 90(69)	0.355 08(54)	0.331 64(54)
P3	0.461 56(57)	0.236 58(58)	0.160 23(43)
S2	0.588 34(71)	0.122 85(49)	0.320 82(57)
P1	0.811 78(63)	0.307 99(68)	0.427 23(56)
P2	0.856 06(71)	0.122 30(70)	0.244 85(80)
C1	0.725 86(200)	0.261 88(191)	0.120 80(99)
O1	0.739 03(153)	0.264 15(186)	0.040 52(93)
C2	0.784 41(287)	0.394 94(215)	0.227 21(235)
O2	0.824 81(225)	0.477 09(202)	0.199 51(204)
C3	0.546 34(151)	0.241 09(157)	0.263 12(128)
C11	0.772 77(320)	0.225 69(289)	0.532 14(226)
C12	0.779 46(367)	0.435 89(283)	0.469 62(264)
C13	0.963 01(309)	0.308 66(279)	0.428 89(269)
C21	0.887 39(371)	0.038 90(318)	0.348 27(295)
C22	0.992 99(303)	0.154 50(276)	0.197 96(251)
C23	0.815 65(364)	0.024 50(318)	0.152 96(313)
C31	0.491 72(262)	0.131 64(224)	0.083 56(228)
C32	0.467 51(269)	0.354 33(232)	0.096 72(230)
C33	0.319 22(252)	0.216 39(248)	0.193 50(216)

Table VI. Atomic Coordinates for **2a**[BF$_4$]

atom	x/a	y/b	z/c
B	0.526 29(168)	0.336 32(90)	0.861 83(84)
F1	0.325 48(105)	0.303 76(55)	0.832 89(52)
F2	0.578 73(108)	0.379 12)58)	0.961 23(56)
F3	0.599 02(118)	0.252 65(64)	0.835 48(59)
F4	0.606 55(120)	0.406 35(65)	0.810 56(61)
Mo	0.211 20(9)	0.184 82(5)	0.323 51(4)
P1	0.088 96(28)	−0.001 97(15)	0.220 64(14)
P2	0.385 83(32)	0.261 86(16)	0.497 40(15)
P3	−0.032 05(28)	0.366 22(15)	0.137 26(14)
S1	0.238 25(28)	0.231 83(17)	0.164 91(14)
S2	0.117 34(33)	0.349 94(15)	0.343 05(14)
O1	−0.080 50(82)	0.081 72(48)	0.457 73(42)
O2	0.581 93(89)	0.096 01(58)	0.322 68(51)
C1	0.030 24(105)	0.118 37(56)	0.408 53(52)
C2	0.440 57(111)	0.127 34(66)	0.324 12(57)
C3	0.173 38(102)	0.354 93(55)	0.217 35(54)
C4	−0.169 63(128)	−0.037 15(67)	0.163 35(69)
C5	0.097 55(145)	−0.106 41(65)	0.282 19(66)
C6	0.218 40(147)	−0.035 35(73)	0.112 92(65)
C7	0.257 65(159)	0.336 83(77)	0.585 12(62)
C8	0.450 47(148)	0.170 84(76)	0.564 05(64)
C9	0.625 06(156)	0.358 17(82)	0.502 00(88)
C10	0.048 74(117)	0.369 80(63)	0.017 57(57)
C11	−0.097 92(155)	0.484 82(74)	0.191 99(68)
C12	−0.243 79(113)	0.254 23(72)	0.124 03(65)

Table VII. Atomic Coordinates for **3a**

atom	x/a	y/b	z/c
I	0.828 23(4)	0.313 27(4)	0.489 09(5)
Mo	0.293 66(4)	0.218 14(3)	0.893 32(4)
S1	0.224 56(12)	0.314 00(10)	0.659 72(13)
S2	0.306 64(12)	0.410 03(10)	0.976 50(14)
P1	0.113 52(12)	0.257 55(11)	1.071 26(15)
P2	0.213 84(13)	0.058 53(10)	0.761 33(16)
P3	0.486 35(12)	0.348 47(11)	0.722 40(15)
C1	0.440 36(53)	0.123 43(42)	0.812 33(68)
O1	0.532 46(42)	0.065 99(34)	0.778 91(63)
C2	0.384 41(51)	0.182 21(42)	1.082 53(67)
O2	0.440 43(46)	0.166 65(39)	1.194 38(53)
C3	0.346 45(42)	0.340 20(35)	0.796 36(51)
C4	0.105 59(51)	0.430 13(44)	0.688 57(69)
C5	−0.037 57(54)	0.316 82(54)	1.002 72(75)
C6	0.088 28(72)	0.145 91(59)	1.156 92(84)
C7	0.137 71(58)	0.351 21(51)	1.245 12(62)
C8	0.050 39(59)	0.070 49(49)	0.718 12(78)
C9	0.251 72(61)	−0.060 54(44)	0.852 22(84)
C10	0.271 56(84)	0.009 15(62)	0.569 55(83)
C11	0.485 24(59)	0.481 83(49)	0.698 08(66)
C12	0.611 83(52)	0.311 54(49)	0.854 09(71)
C13	0.506 15(59)	0.266 12(58)	0.539 44(70)

were collected in 48% yield. IR (Nujol, cm^{-1}): ν_{CO} 1950, 1840. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.72 (d, 18 H, J_{HP} = 8 Hz, 2 $\mathrm{P(C}H_3\mathrm{)_3}$), 1.79 (d, 9 H, J_{HP} = 11 Hz, $\mathrm{S_2CP(C}H_3\mathrm{)_3}$), 6.34 (d, 1 H, J_{HP} = 4.5 Hz, $\mathrm{S_2C(}H\mathrm{)PMe_3}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 28.9 (s, 2 $P\mathrm{Me_3}$), 33.1 (s, $\mathrm{S_2C}P\mathrm{Me_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 4.7 (d, J_{CP} = 57 Hz, $\mathrm{S_2CP(}C\mathrm{H_3)_3}$), 18.6 (virtual pseudoquintet, $^1J_{\mathrm{CP}}$ = 35 Hz, $^2J_{\mathrm{PP'}}$ = 24 Hz, $\mathrm{P(}C\mathrm{H_3)_3}$), 64.9 (dt, $^1J_{\mathrm{CP}}$ = 46 Hz, $^3J_{\mathrm{CP}}$ = 4 Hz, $\mathrm{S_2}C\mathrm{(H)PMe_3}$), 242.3 (t, $^2J_{\mathrm{CP}}$ = 30 Hz, $C\mathrm{O}$). Anal. Calcd for $\mathrm{C_{12}H_{28}O_2S_2P_3MoBF_4}$: C, 26.5; H, 5.15. Found: C, 26.7; H, 5.0.

A similar procedure (starting with complex **1b**) afforded the tungsten derivative $\mathrm{[W(S_2C(H)PMe_3)(CO)_2(PMe_3)_2]BF_4}$(**2b**[BF$_4$]). Yield: 54%. IR (Nujol, cm^{-1}): ν_{CO} 1930, 1824. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.81 (d, 9 H, J_{HP} = 14 Hz, $\mathrm{S_2CP(C}H_3\mathrm{)_3}$), 1.83 (d, 18 H, J_{HP} = 10 Hz, 2 $\mathrm{P(C}H_3\mathrm{)_3}$), 6.61 (d, 1 H, $^2J_{\mathrm{HP}}$ = 4.5 Hz, $\mathrm{S_2C(}H\mathrm{)PMe_3}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ −0.3 (s, $^1J_{\mathrm{PW}}$ = 143 Hz, 2 $P\mathrm{Me_3}$), 36.5 (s, $\mathrm{S_2C}P\mathrm{Me_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 4.6 (d, J_{CP} = 56 Hz, $\mathrm{S_2CP(}C\mathrm{H_3)_3}$), 18.9 (m, $\mathrm{P(}C\mathrm{H_3)_3}$), 67.2 (dt, $^1J_{\mathrm{CP}}$ = 45, $^3J_{\mathrm{CP}}$ = 4 Hz, $\mathrm{S_2}C\mathrm{(H)PMe_3}$), 237.2 (t, $^2J_{\mathrm{CP}}$ = 22 Hz, $C\mathrm{O}$). Anal. Calcd for $\mathrm{C_{12}H_{28}O_2S_2P_3WBF_4}$: C, 22.8; H, 4.4. Found: C, 22.9; H, 4.3.

(b) Reaction of the Hydrides $\mathrm{MClH(CO)_2(PMe_3)_3}$ (M = Mo, W) with $\mathrm{CS_2}$. $\mathrm{CS_2}$ (0.6 mmol) was added to a solution of $\mathrm{[MoClH(CO)_2(PMe_3)_3]}$ (0.2 g, *ca.* 0.5 mmol) in THF (50 mL), and the resulting mixture was stirred overnight at room temperature. The solvent was then removed under vacuum and the residue washed with petroleum ether (2 × 20 mL). Crystallization from acetone produced red crystals of $\mathrm{[Mo(S_2C(H)PMe_3)(CO)_2(PMe_3)_2]Cl}$ (**2a**[Cl]) in *ca.* 70% yield. Only small differences were found in the spectroscopic data of this complex with those of **2a**[BF$_4$]. IR ($\mathrm{CH_2Cl_2}$, cm^{-1}): ν_{CO} 1937, 1853. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.72 (d, 18 H, J_{HP} = 10 Hz, 2 $\mathrm{P(C}H_3\mathrm{)_3}$), 2.03 (d, 9 H, J_{HP} = 14 Hz, $\mathrm{S_2CP(C}H_3\mathrm{)_3}$), 6.65 (d, 1 H, J_{HP} = 5 Hz, $\mathrm{S_2C(}H\mathrm{)PMe_3}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 28.7 (br s, 2 $P\mathrm{Me_3}$), 34.3 (br s, $\mathrm{S_2C}P\mathrm{Me_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 5.3 (d, J_{CP} = 56 Hz, $\mathrm{S_2CP(}C\mathrm{H_3)_3}$), 18.5 (m, $\mathrm{P(}C\mathrm{H_3)_3}$), 65.4 (br d, $^1J_{\mathrm{CP}}$ = 44 Hz, $\mathrm{S_2}C\mathrm{(H)PMe_3}$), 243.3 (t, $^2J_{\mathrm{CP}}$ = 34 Hz, $C\mathrm{O}$). Anal. Calcd for $\mathrm{C_{12}H_{28}O_2S_2P_3MoBF_4}$: C, 29.2; H, 5.7. Found: C, 29.6; H, 5.8.

The tungsten complex was prepared following an analogous procedure: red crystals of $\mathrm{[W(S_2C(H)PMe_3)(CO)_2(PMe_3)_2]Cl}$ (**2b**[Cl] were obtained in *ca.* 60% yield. Again, only small differences were found in the spectroscopic data of this complex with those of **2b**[BF$_4$]. IR ($\mathrm{CH_2Cl_2}$, cm^{-1}): ν_{CO} 1932, 1845. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.81 (d, 9 H, J_{HP} = 10 Hz, $\mathrm{S_2CP(C}H_3\mathrm{)_3}$), 2.05 (d, 18 H, J_{HP} = 14 Hz, 2 $\mathrm{P(C}H_3\mathrm{)_3}$), 6.90 (d, 1 H, $^2J_{\mathrm{HP}}$ = 4.5 Hz, $\mathrm{S_2C(}H\mathrm{)PMe_3}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ −0.3 (s, $^1J_{\mathrm{PW}}$ = 143 Hz, 2 $P\mathrm{Me_3}$), 37.6 (s, $\mathrm{S_2C}P\mathrm{Me_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 5.2 (d, J_{CP} = 56 Hz, $\mathrm{S_2CP(}C\mathrm{H_3)_3}$), 18.8 (m, $\mathrm{P(}C\mathrm{H_3)_3}$), 67.6 (br d, $^1J_{\mathrm{CP}}$ = 44 Hz, $\mathrm{S_2}C\mathrm{(H)PMe_3}$).

Reactions of $\mathrm{M(S_2CPMe_3)(CO)_2(PMe_3)_2}$ Complexes with RI (R = Me, Et). Synthesis of Compounds 3 and 4. A solution of **1a** (0.4 g, 0.9 mmol)in $\mathrm{Et_2O}$ (30 mL) was reacted with MeI (1.8 mL of a *ca.* 1 mol L^{-1} solution in toluene). A yellow-orange solid slowly precipitated and was collected after 4 h of stirring, washed with $\mathrm{Et_2O}$, and recrystallized from acetone–$\mathrm{Et_2O}$ mixtures to yield 0.24 g of **3a** (45 %). IR (Nujol, cm^{-1}): ν_{CO} 1925, 1850. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.59 (d, 9 H, J_{HP} = 7 Hz, $\mathrm{P(C}H_3\mathrm{)_3}$), 1.63 (d, 9 H, J_{HP} = 8 Hz, $\mathrm{P(C}H_3\mathrm{)_3}$), 2.06 (d broad, 3 H, J_{HP} = 1.3 Hz, $\mathrm{SC}H_3$), 2.11 (d, 9 H, J_{HP} = 13 Hz, $\mathrm{SC(SMe)P(C}H_3\mathrm{)_3}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ −10.1 (dd, $^2J_{\mathrm{PP}}$ = 50 Hz, $^3J_{\mathrm{PP}}$ = 2 Hz, $P\mathrm{Me_3}$), 3.3 (dd, $^2J_{\mathrm{PP}}$ = 50 Hz, $^3J_{\mathrm{PP}}$ = 6 Hz, $P\mathrm{Me_3}$), 44.1 (dd, $^3J_{\mathrm{PP}}$ = 6 Hz, $^3J_{\mathrm{PP}}$ = 2 Hz, SC-

(SMe)$\mathit{P}\mathrm{Me}_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 11.5 (d, J_{CP} = 57 Hz, SC(SMe)$\mathrm{P}(\mathit{C}\mathrm{H}_3)_3$), 11.9 (s, $\mathit{C}\mathrm{H}_3$) 19.1 (d, J_{CP} = 23 Hz, $\mathrm{P}(\mathit{C}\mathrm{H}_3)_3$), 21.0 (dd, J_{CP} = 27 Hz, J_{CP} = 4 Hz, $\mathrm{P}(\mathit{C}\mathrm{H}_3)_3$), 66.6 (d, $^1J_{\mathrm{CP}}$ = 87 Hz, SC(SMe)), 232.8 (dd, J_{CP} = 15 Hz, J_{CP} = 5 Hz, CO), 246.7 (dt, J_{CP} = 28 Hz, J_{CP} = 10 Hz, CO). Anal. Calcd for $\mathrm{C_{13}H_{30}O_2P_3S_2MoI}$: C, 26.1; H, 5.0. Found: C, 26.4; H, 4.9. A sample of **3a***, *ca.* 33% enriched in $^{13}\mathrm{CS_2}$, was prepared similarly starting from **1a***.

Complex **3b** was obtained using the same experimental procedure but employing **1b** as the starting material. Yield: 50%. IR (Nujol, cm^{-1}): ν_{CO} 1913, 1836. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.70 (d, 9 H, J_{HP} = 8 Hz, $\mathrm{P}(\mathrm{C}\mathit{H}_3)_3$), 1.76 (d, 9 H, J_{HP} = 9 Hz, $\mathrm{P}(\mathrm{C}\mathit{H}_3)_3$), 2.10 (d, 9 H, J_{HP} = 13 Hz, SC(SMe)$\mathrm{P}(\mathrm{C}\mathit{H}_3)_3$), 2.18 (d broad, 3 H, J_{HP} = 1 Hz, $\mathrm{SC}\mathit{H}_3$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ −27.6 (dd, $^2J_{\mathrm{PP}}$ = 36 Hz, $^3J_{\mathrm{PP}}$ = 4.5 Hz, $^1J_{\mathrm{PW}}$ = 196 Hz, $\mathit{P}\mathrm{Me}_3$), −18.0 (d, $^2J_{\mathrm{PP}}$ = 36 Hz, $^1J_{\mathrm{PW}}$ = 267 Hz, $\mathit{P}\mathrm{Me}_3$), 43.5 (d, $^3J_{\mathrm{PP}}$ = 4.5 Hz, S(SMe)C$\mathit{P}\mathrm{Me}_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 9.75 (s, $\mathit{C}\mathrm{H}_3$), 11.42 (d, J_{CP} = 58 Hz, S(SMe)CP$(\mathit{C}\mathrm{H}_3)_3$), 19.66 (d, J_{CP} = 28 Hz, $\mathrm{P}(\mathit{C}\mathrm{H}_3)_3$), 21.85 (dd, J_{CP} = 30 Hz, J_{CP} = 4 Hz, $\mathrm{P}(\mathit{C}\mathrm{H}_3)_3$), 58.25 (d, $^1J_{\mathrm{CP}}$ = 83 Hz, S(SMe)$\mathit{C}\mathrm{PMe}_3$), 226.6 (m, CO), 240.8 (m, CO). Anal. Calcd for $\mathrm{C_{13}H_{30}O_2P_3S_2WI}$: C, 22.8; H, 4.4. Found: C, 22.8; H, 4.5.

Complex **4** was prepared similarly using EtI. Heating the reaction mixture at 40 °C for 7 h was however required. Yield: 55%. IR (Nujol, cm^{-1}): ν_{CO} 1950, 1840. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.25 (t, 3 H, J_{HP} = 7 Hz, $\mathrm{C}\mathit{H}_3$), 1.51 (d, 9 H, J_{HP} = 5 Hz, $\mathrm{P}(\mathrm{C}\mathit{H}_3)_3$), 1.57 (d, 9 H, J_{HP} = 8 Hz, $\mathrm{P}(\mathrm{C}\mathit{H}_3)_3$), 1.75 (d, 9 H, J_{HP} = 13 Hz, SC(SEt)$\mathrm{P}(\mathrm{C}\mathit{H}_3)_3$), 2.3 (m, 1 H, $\mathrm{C}\mathit{H}_2$), 2.5 (m, 1 H, $\mathrm{C}\mathit{H}_2$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 9.6 (d, J_{PP} = 16 Hz, $\mathit{P}\mathrm{Me}_3$), 14.5 (d, J_{PP} = 16 Hz, $\mathit{P}\mathrm{Me}_3$), 38.3 (s, SC(SEt)$\mathit{P}\mathrm{Me}_3$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 10.6 (d, J_{CP} = 58 Hz, SC(SEt)$\mathrm{P}(\mathit{C}\mathrm{H}_3)_3$), 17.5 (s, $\mathit{C}\mathrm{H}_3$), 20.5 (pseudo t, J_{CPapp} = 26 Hz, 2 $\mathrm{P}(\mathit{C}\mathrm{H}_3)_3$), 28.2 (s, $\mathit{C}\mathrm{H}_2$), 62.6 (d broad, J_{CP} = 19Hz, SC(SEt)). Anal. Calcd for $\mathrm{C_{14}H_{32}O_2S_2P_3MoI}$: C, 27.5; H, 5.4. Found: C, 27.1; H, 5.4.

X-ray Diffraction Studies of 1b, 2a[BF$_4$], and 3a. Crystal data for complexes **1b**, **2a**[BF$_4$], and **3a** are collected in Table IV. Tables V–VII show the final fractional atomic coordinates for these three complexes, respectively. Single crystals of **1b**, **2a**[BF$_4$], and **3a** were introduced into Lindeman capillaries, which were sealed under a $\mathrm{N_2}$ atmosphere and mounted on a Enraf-Nonius CAD4 automatic difractometer. The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. There were no appreciable changes in the periodically standard reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo, W, S, P, and I were taken from reference 18.[18] The structure was solved by Patterson and Fourier methods. Empirical absorption corrections[19] were applied at the end of the isotropic refinement. Anisotropic full-matrix least-squares refinements were made for non-hydrogen atoms. As can be observed in the thermal parameters of complex **1b**, there exists some nonresolvable disorder from the thermal motions of the C atoms of the methyl groups, and consequently these atoms were only refined isotropically. No trends in ΔF vs. F_o or $(\sin\theta)/\lambda$ were observed. Final mixed refinements with unit weights and fixed isotropic factors and coordinates for H atoms were undertaken, except for the H3 atom in compound **2a**[BF$_4$]. The H3 atom was located in a ΔF map as the highest peak of the map, and its coordinates were refined. Final difference synthesis showed no significantly electron density. Final R values are collected in Table IV. Most of the calculations were carried out with the XRAY80 system.[20]

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Supplementary Material Available: Tables of complete crystallographic data, complete bond distances and angles, atomic fractional coordinates for hydrogen atoms, and anisotropic thermal parameters for **1b**, **2a**[BF$_4$], and **3a** (14 pages). Ordering information is given on any current masthead page.

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