tridentate fashion to each metal center. These complexes, however, posses considerable rotational flexibility about the central eHTP methylene bridge giving rise to a number of low energy rotational conformations. The various conformations of these systems have been probed by X-ray crystallography, NMR spectroscopy, and VDW energy calculations. Although the VDW energy calculations are quite crude, they provide an excellent qualitative road map to the conformations accessible to these systems and provide considerable insight into understanding the structural differences between the Ni and Pd/Pt complexes.

The rotational flexibility of these systems could be extremely important in allowing the metals to access one another for cooperative bimetallic behavior. One reaction that is potentially well suited to binuclear systems is hydroformylation and there have been several reports on the effects of homo- and heterobimetallic homogeneous catalysts on the rate and selectivity of hydroformylation reactions.[16,17] We are, therefore, particularly interested in studying the hydroformylation activity of bimetallic complexes based on our considerably less sterically hindered binucleating *tetra*phosphine ligand system $(Et_2PCH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PEt_2)$, eLTTP.[18-20] This ligand has essentially the same bridging/chelating coordinating properties as eHTP, yet will readily allow two square-planar metal centers to come into close proximity. Indeed, it is in large part these conformational studies on eHTP complexes of the group 10 metals that lead to the design and synthesis of the eLTTP ligand system.

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Supplementary Material Available: A stereopair figure of the SYBYL least-squares overlapped structures of $Ni_2Cl_2(HTP)^{2+}$ and $Pd_2Cl_2(HTP)^{2+}$, the ^1H NMR spectra of **2a** in CD_3OH, CD_3CN, and CD_2Cl_2, and Tables S-I–S-IV of crystal and data collection parameters and anisotropic thermal parameters (10 pages); Tables S-V and S-VI of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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Reactions of Sulfur-Containing Heterocumulenes with Low-Valent Molybdenum and Tungsten Complexes. Oxidative Cleavage of a Head-to-Tail Carbon Disulfide Dimer in a Molybdenum Complex

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Head-to-tail carbon disulfide dimers of composition $M(C_2S_4)(C_2H_4)(PMe_3)_3$ (M = Mo (**3**), W (**4**)) have been prepared by action of CS_2 on the ethylene complexes *trans*-$M(C_2H_4)_2(PMe_3)_4$ (M = Mo (**1**), W (**2**)). An X-ray analysis, carried out on complex **3**, shows the C_2S_4 unit is acting formally as a four-electron donor ligand, η^3-bonded to the metal through one of the carbon and two of the sulfur atoms. The complex is monoclinic, $C2/c$, with $a = 26.633$ (7) Å, $b = 8.615$ (4) Å, $c = 19.903$ (6) Å, $\beta = 103.51$ (2)°, and $D(\text{calcd}) = 1.60$ g cm^{-3} for $Z = 8$ and $R(F_o) = 0.048$. The analogous reactions of **1** and **2** with SCNPh provide related head-to-tail dimers, $Mo(S_2C_2(NPh)_2)(C_2H_4)_x(PMe_3)_{4-x}$, ($x = 1$ (**7**); $x = 2$ (**8**)) and $W(S_2C_2(NPh)_2)(C_2H_4)_x(PMe_3)_{4-x}$, ($x = 1$ (**9**); $x = 2$ (**10**)). Treatment of **3** with MeX (X = I, OSO_2CF_3), followed by anion exchange with NH_4PF_6, gives $[Mo(C_2S_4Me)(C_2H_4)(PMe_3)_3]PF_6$ (**11**), which has a structure similar to that found for **3** (as determined by X-ray studies) but with a methyl group bonded to the exocyclic sulfur atom of the C_2S_4 unit. **11** is monoclinic, $P2_1/c$, with $a = 13.726$ (2) Å, $b = 14.272$ (3) Å, $c = 14.686$ (4) Å, $\beta = 106.28$ (2)°, and $D(\text{calcd}) = 1.509$ g cm^{-3} for $Z = 4$ and $R(F_o) = 0.058$. Complex **3** reacts with $CNBu^t$ to afford a complex mixture of compounds from which the substitution product $Mo(C_2S_4)(CNBu^t)(PMe_3)_3$ (**12**) can be isolated. With carbon monoxide, however, a molybdenum(0) complex, $Mo(S_2CPMe_3)(CO)_2(PMe_3)_2$ (**13**), is formed in an unprecedented reaction that corresponds to an oxidative symmetric cleavage of the MC_2S_4 linkage.

Introduction

The interaction of heterocumulene molecules with transition-metal compounds has been extensively studied in the past decade, and a wealth of information is now available on their coordination modes and their metal-induced transformations.[2,3] Sulfur-containing heterocumulenes such as carbon disulfide, carbonyl sulfide, and organic isothiocyanates have received considerable attention and have been shown to form complexes with a number of transition metals and to undergo a variety of chemical transformations including insertion, dimerization, and disproportionation reactions.[3]

Electron-rich transition-metal compounds are able to promote the so-called reductive dimerization of carbon disulfide,[4] either

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Table I. Bond Distances (Å) and Angles (deg) in $Mo(C_2H_4)(PMe_3)_3(C_2S_4)$

Mo–S1	2.486 (2)	S4–C2	1.666 (8)
Mo–S3	2.493 (2)	P1–C11	1.805 (12)
Mo–P1	2.573 (2)	P1–C12	1.783 (10)
Mo–P2	2.526 (2)	P1–C13	1.811 (12)
Mo–P3	2.534 (2)	P2–C21	1.816 (9)
Mo–C1	1.991 (6)	P2–C22	1.833 (8)
Mo–C3	2.267 (8)	P2–C23	1.818 (11)
Mo–C4	2.270 (8)	P2–C31	1.805 (11)
S1–C1	1.647 (7)	P3–C32	1.834 (11)
S2–C1	1.684 (7)	P3–C33	1.812 (11)
S2–C2	1.760 (8)	C3–C4	1.395 (13)
S3–C2	1.682 (7)		
C3–Mo–C4	35.8 (3)	S1–Mo–S3	115.93 (7)
C1–Mo–C4	145.4 (3)	Mo–S1–C1	53.0 (2)
C1–Mo–C3	145.9 (3)	C1–S2–C2	98.9 (3)
P3–Mo–C4	76.9 (2)	Mo–S3–C2	111.9 (3)
P3–Mo–C3	112.7 (2)	Mo–P1–C13	117.5 (4)
P3–Mo–C1	83.3 (2)	Mo–P1–C12	119.2 (5)
P2–Mo–C4	113.9 (3)	Mo–P1–C11	117.3 (4)
P2–Mo–C3	77.9 (2)	C12–P1–C13	98.4 (6)
P2–Mo–C1	85.0 (2)	C11–P1–C13	99.5 (6)
P2–Mo–P3	168.22 (8)	C11–P1–C12	101.4 (5)
P1–Mo–C4	88.7 (2)	Mo–P2–C23	120.7 (3)
P1–Mo–C3	88.7 (2)	Mo–P2–C22	118.4 (3)
P1–Mo–C1	121.1 (2)	Mo–P2–C21	113.4 (3)
P1–Mo–P3	94.32 (8)	C22–P2–C23	100.8 (5)
P1–Mo–P2	91.00 (8)	C21–P2–C23	99.6 (5)
S3–Mo–C4	76.8 (2)	C21–P2–C22	100.5 (4)
S3–Mo–C3	76.0 (2)	Mo–P3–C33	122.2 (4)
S3–Mo–C1	74.6 (2)	Mo–P3–C32	117.8 (4)
S3–Mo–P3	88.39 (8)	Mo–P3–C31	114.3 (3)
S3–Mo–P2	89.32 (7)	C32–P3–C33	100.5 (6)
S3–Mo–P1	164.29 (8)	C31–P3–C33	98.8 (5)
S1–Mo–C4	158.1 (2)	C31–P3–C32	99.4 (5)
S1–Mo–C3	159.5 (2)	S1–C1–S2	135.2 (4)
S1–Mo–C1	41.4 (2)	Mo–C1–S2	139.2 (4)
S1–Mo–P3	85.30 (8)	Mo–C1–S1	85.7 (3)
S1–Mo–P2	85.32 (7)	S3–C2–S4	127.6 (5)
S1–Mo–P1	79.75 (7)	S2–C2–S4	117.0 (9)
		S2–C2–S3	115.4 (4)

Table II. Bond Distances (Å) and Angles (deg) in $[Mo(C_2S_4Me)(C_2H_4)(PMe_3)_3]PF_6$

Mo–S1	2.512 (2)	S4–C2	1.743 (9)
Mo–S3	2.447 (2)	S4–C5	1.778 (11)
Mo–P1	2.601 (3)	P1–C11	1.830 (11)
Mo–P2	2.535 (2)	P1–C12	1.815 (10)
Mo–P3	2.567 (3)	P1–C13	1.811 (12)
Mo–C1	1.995 (7)	P2–C21	1.806 (10)
Mo–C3	2.299 (9)	P2–C22	1.824 (11)
Mo–C4	2.295 (9)	P2–C23	1.813 (14)
S1–C1	1.665 (10)	P3–C31	1.822 (14)
S2–C1	1.674 (9)	P3–C32	1.813 (11)
S2–C2	1.732 (9)	P3–C33	1.814 (12)
S3–C2	1.648 (7)	C3–C4	1.417 (14)
P4–F1	1.567 (9)	P4–F2	1.569 (10)
P4–F3	1.571 (12)	P4–F4	1.523 (12)
P4–F5	1.520 (11)	P4–F6	1.493 (14)
C3–Mo–C4	35.9 (3)	S1–Mo–S3	115.4 (1)
C1–Mo–C4	145.9 (3)	Mo–S1–C1	52.4 (3)
C1–Mo–C3	145.2 (4)	C1–S2–C2	95.6 (4)
P3–Mo–C4	77.3 (3)	Mo–S3–C2	111.1 (3)
P3–Mo–C3	113.1 (2)	C2–S4–C5	101.0 (5)
P3–Mo–C1	84.7 (2)	S1–C1–S2	133.4 (5)
P2–Mo–C4	113.4 (4)	Mo–C1–S2	140.3 (5)
P2–Mo–C3	77.5 (5)	Mo–C1–S1	86.2 (4)
P2–Mo–C1	84.7 (2)	S3–C2–S4	127.2 (5)
P2–Mo–P3	169.0 (1)	S2–C2–S4	113.9 (5)
P1–Mo–C4	88.1 (3)	S2–C2–S3	118.8 (5)
P1–Mo–C3	88.0 (3)	S1–Mo–C4	158.3 (3)
P1–Mo–C1	122.0 (2)	S1–Mo–C3	159.3 (3)
P1–Mo–P3	93.2 (1)	S1–Mo–C1	41.4 (2)
P1–Mo–P2	89.9 (1)	S1–Mo–P3	84.9 (1)
S3–Mo–C4	77.4 (2)	S1–Mo–P2	85.2 (8)
S3–Mo–C3	76.0 (2)	S1–Mo–P1	80.6 (1)
S3–Mo–C1	74.1 (3)		
S3–Mo–P3	90.6 (1)		
S3–Mo–P2	89.3 (1)		
S3–Mo–P1	163.8 (1)		

Table III. Crystallographic Data for Complexes **3** and **11**

	3	**11**
chem formula	$MoC_{13}H_{31}S_4P_3$	$MoC_{14}H_{34}S_4P_4F_6$
fw	504.5	664.5
space group	$P2_1/c$	$C2/c$
a, Å	13.726 (2)	26.633 (7)
b, Å	14.272 (3)	8.615 (4)
c, Å	14.686 (4)	19.903 (6)
β, deg	106.28 (2)	103.51 (2)
V, Å^3	2761 (1)	4440 (3)
Z	4	8
T, °C	22	22
λ, Å	0.71069	0.71069
ρ_{calcd}, g cm^{-3}	1.60	1.509
μ, cm^{-1}	10.25	11.46
$R(F_o)$, %	5.8	4.2
$R_w(F_o)$, %	6.6	4.8

in the head-to-head way, yielding tetrathiooxalate, $C_2S_4^{2-}$, or in the alternative head-to-tail fashion to provide asymmetric heterometallacycles, MC_2S_4. The former way of activation has been demonstrated recently by several research groups,[5-7] and at least three examples of MC_2S_4 asymmetric heterometallacyclic units have been authenticated by X-ray methods.[8-10] The condensation of two molecules of isothiocyanates, to provide related head-to-tail dimers, is also known, but commonly only the degradation products of isothiocyanate reactions are observed.[3c,11] Carbonyl sulfide, in turn, experiences carbonylation reactions, sulfur abstraction, or reductive disproportionation to metal dithiocarbonates.[3b,12,13]

Although much of the interest in transition-metal carbon disulfide has arisen in an attempt to develop a C_1 chemistry for the less reactive CO_2, it is now evident that both molecules display very distinct chemical behavior. We have recently found that the interaction of CO_2 with the ethylene complexes *trans*-$M(C_2H_4)_2(PMe_3)_4$ (M = Mo (**1**), W (**2**)) takes place with formation of the acrylate[14] derivatives $[M(H)(OOCCH{=}CH_2)(C_2H_4)(PMe_3)_2]_2$.

The electronic properties of CO_2, and in particular the marked electrophilicity of its carbon atom, must doubtless play an important role in this transformation. As a natural extension of this chemistry, we have investigated the reactivity of the above ethylene complexes toward other heterocumulenes such as CS_2, COS, and SCNPh.

The results of this study are reported herein together with an X-ray structural determination of the heterometallacycle $\overline{\text{Mo-(SC(S)SC}}{=}S)(C_2H_4)(PMe_3)_3$ and an investigation of some of

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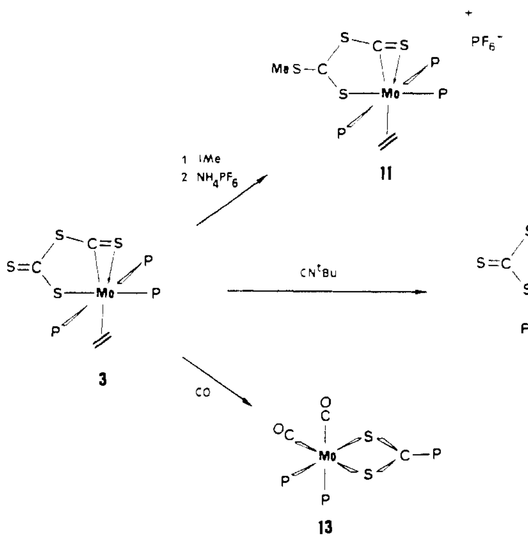
Scheme I



its characteristic chemical properties.

Results

Diethyl ether solutions of *trans*-$M(C_2H_4)_2(PMe_3)_4$ (M = Mo (**1**), W (**2**)) react instantly with a solution of CS_2 in the same solvent (1:2 molar ratio M:CS_2) to afford black, finely divided materials of composition $M(CS_2)_2(C_2H_4)(PMe_3)_3$ (eq 1). Both

$$\textit{trans}\text{-}M(C_2H_4)_2(PMe_3)_4 + 2CS_2 \rightarrow \underset{\substack{M = Mo\ (\mathbf{3})\\ M = W\ (\mathbf{4})}}{M(C_2S_4)(C_2H_4)(PMe_3)_3} + C_2H_4 + PMe_3 \quad (1)$$

$$M = Mo\ (\mathbf{1}) \qquad M = W\ (\mathbf{2})$$

compounds show rather low solubility in common organic solvents, but crystallization from relatively large volumes of acetone, tetrahydrofuran (THF), or dichloromethane provides very dark red, almost black, crystals of **3** and **4**. These are moderately insensitive to air in the crystalline state, but decompose readily in solution.

Spectroscopic data for these compounds are presented in the Experimental Section and suggest the existence in the molecules of **3** and **4** of heterometallacyclic MC_2S_4 linkages resulting from the metal-induced reductive dimerization of CS_2 in a head-to-tail fashion. This has been confirmed by an X-ray study, carried out with complex **3**, whose results are summarized in Tables I, III, and IV. In addition and as shown in Scheme I, some chemical studies have been undertaken with complex **3**. The results of these structural and chemical investigations will be discussed at appropriate places in the sections that follow.

When COS is bubbled through a diethyl ether solution of **1** or **2** an almost instantaneous reaction occurs that induces precipitation of the dithiocarbonate complexes $M(S_2CO)(CO)_2(PMe_3)_3$ (M = Mo (**5**), W (**6**)) (eq 2). Identification of **5** and

$$\textit{trans}\text{-}M(C_2H_4)_2(PMe_3)_4 + COS \rightarrow \underset{\substack{M = Mo\ (\mathbf{5})\\ M = W\ (\mathbf{6})}}{M(S_2CO)(CO)_2(PMe_3)_3} + PMe_3 + C_2H_4 + \ldots \quad (2)$$

$$M = Mo\ (\mathbf{1}) \qquad M = W\ (\mathbf{2})$$

Table IV. Atomic Coordinates for Non-Hydrogen Atoms of **3**

atom	*x/a*	*y/b*	*z/c*
Mo	0.130 74 (2)	0.146 84 (7)	0.112 62 (3)
S1	0.060 01 (7)	−0.037 55 (21)	0.062 62 (9)
S2	0.068 52 (8)	0.172 36 (24)	−0.059 51 (9)
S3	0.151 17 (7)	0.344 65 (22)	0.031 47 (9)
S4	0.115 91 (11)	0.428 16 (30)	−0.118 70 (12)
P1	0.128 20 (8)	−0.015 37 (26)	0.220 28 (10)
P2	0.059 60 (7)	0.320 79 (23)	0.133 67 (10)
P3	0.188 69 (8)	−0.041 86 (25)	0.068 71 (11)
C1	0.082 47 (25)	0.103 27 (77)	0.021 89 (35)
C2	0.114 20 (28)	0.323 36 (85)	−0.048 95 (36)
C3	0.175 68 (31)	0.331 07 (98)	0.183 09 (39)
C4	0.211 23 (30)	0.227 39 (107)	0.166 54 (43)
C11	0.065 58 (42)	−0.055 03 (151)	0.236 68 (56)
C12	0.163 07 (53)	0.050 19 (162)	0.303 03 (49)
C13	0.153 37 (46)	−0.211 26 (133)	0.224 33 (59)
C21	0.053 40 (35)	0.501 06 (102)	0.085 25 (50)
C22	−0.007 11 (31)	0.250 00 (112)	0.109 27 (49)
C23	0.061 86 (39)	0.397 74 (126)	0.219 40 (50)
C31	0.220 16 (35)	0.039 27 (111)	0.005 67 (51)
C32	0.158 40 (41)	−0.212 41 (118)	0.020 09 (66)
C33	0.244 33 (41)	−0.131 38 (156)	0.125 50 (61)

6 can be readily achieved by comparison of their spectroscopic properties with those of authentic samples. Both **5** and **6** have been previously prepared in our laboratory by different routes, namely by reaction of *cis*-$Mo(N_2)_2(PMe_3)_4$ (or *trans*-$Mo(CO_2)_2(PMe_3)_4$) with COS in the case of **5**[13] and for **6** by treatment of $WCl_2(CO)_2(PMe_3)_3$ with KS_2COMe.[15] Although the presence of a dithiocarbonate ligand in the molecules of **5** and **6** suggests that COS undergoes a metal-promoted reductive disproportionation reaction (eq 3), the overall process must be

$$2COS + 2e^- = S_2CO^{2-} + CO \qquad (3)$$

more complex as indicated by the incorporation of a second CO ligand to the molecules of **5** and **6**. A reasonable explanation for the formation of the second CO group could be S-abstraction by PMe_3, but we have been unable to confirm this assumption.

SCNPh displays a behavior similar to that described above for CS_2 and undergoes, even under very mild conditions, a metal-induced reductive dimerization with formation of a head-to-tail dimer, $S_2C_2(NPh)_2$. This reaction is, however, somewhat more complex and yields normally a mixture of two compounds, as depicted in eq 4 for the molybdenum system. Some interesting

$$\mathbf{1} \xrightarrow{2SCNPh} \underset{\mathbf{7}}{Mo(S_2C_2(NPh)_2)(C_2H_4)(PMe_3)_3} + \underset{\mathbf{8}}{Mo(S_2C_2(NPh)_2)(C_2H_4)_2(PMe_3)_2} \quad (4)$$

features of this reaction, in particular the differences observed in the behavior of the Mo and W complexes, **1** and **2**, toward SCNPh, will be discussed in the following section.

Discussion

As already indicated, spectroscopic data for compounds **3** and **4** suggest their formulation as heterometallacyclic species containing a head-to-tail MC_2S_4 linkage. Thus, their IR spectra display a strong absorption at 1020 cm^{-1} associated with a noncoordinated C=S bond, which is shifted to 990 cm^{-1} in the spectrum of **3*** (ca. 50% $^{13}CS_2$ enriched sample). ^1H, ^{13}C, and ^{31}P NMR data indicate a meridional distribution of the phosphine ligands and suggest in addition that the C_2H_4 molecule is composed of two equivalent methylenic units with the two protons within these units being chemically inequivalent. As for the MC_2S_4 linkage, the $^{13}C\{^1H\}$ NMR spectrum of **3*** displays a singlet at 226.9 and a quartet at 292.3 ppm ($^2J_{CP}$ = 16 Hz). This demonstrates the existence of two different CS_2 units and further indicates that one of them is C-bonded to the metal atom. These data rule out the formation of a head-to-head dimer, i.e., tetrathioxalate, $C_2S_4^{2-}$, and are consistent with a head-to-tail reductive dimerization of CS_2 and formation of a heterometallacyclic unit $\overline{M[SC(S)SC}{=}S]$.

This assumption has been confirmed by an X-ray study carried out on complex **3**, whose results are shown schematically as structure A and as an ORTEP view in Figure 1. Bond distances and angles are given in Table I.

As can be seen, one of the CS_2 molecules is bonded to Mo through the carbon and one of the sulfur atoms (C1 and S1) while the second sulfur (S2) is engaged in a direct interaction with

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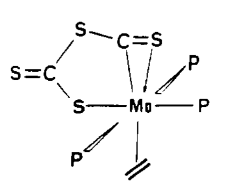
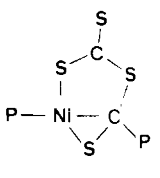
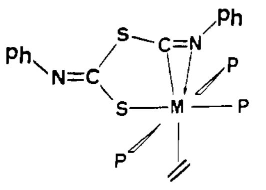
[15] Carmona, E.; Contreras, L.; Sanchez, L.; Gutiérrez-Puebla, E.; Monge, A. *J. Chem. Soc., Dalton Trans.* **1989**, 2003.



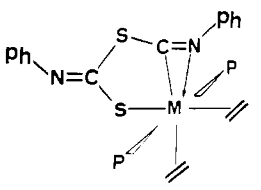
A



B



C



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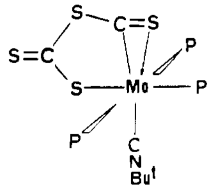
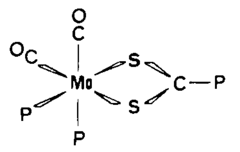


E



F

carbon atom C2 of the second molecule of CS_2. The latter has one exocyclic sulfur (S4) that is not involved in the bonding while the other sulfur, S3, forms a bond to molybdenum thus completing the five-membered metallacyclic unit. This is a new binding mode for the C_2S_4 ligand, which in compound **3** (and by analogy in **4**) is acting as a trihapto, four-electron donor. Two closely related compounds have been reported previously: the binuclear complex, $Rh_2(C_2S_4)Cl_2(CO)(Ph_2PCH_2PPh_2)_2$,[10] and in particular the nickel species $Ni(C_2S_4PMe_3)(PMe_3)$, prepared by Ibers and co-workers,[8] which has an η^3-C_2S_4 ligand with bonding properties similar to those found for the C_2S_4 unit in compound **3**, but with a molecule of PMe_3 incorporated at the metal-bound carbon atom, as shown schematically in structure B.

If the coordinated C–S bond (C1–S1) is considered to formally occupy a single coordination site, the geometry of the molecules of **3** can be described as a distorted octahedron, with the C_2S_4 ligand occupying two mutually cis coordination positions. The distribution of the remaining ligands is such that there is a mirror plane which contains the C_2S_4 group as well as the molybdenum and the P1 atoms. This plane relates by symmetry the two trans phosphine ligands and bisects the C=C bond of the ethylene ligand, in excellent agreement with the geometrical distribution deduced for these groups from the solution NMR data. Interestingly, the coordinated C=C and C=S bonds occupy mutually trans positions and are staggered with respect to one another and eclipsing the corresponding *trans*-L–M–L vectors located in the plane that contains the remaining donor atoms (P1, P2, P3, and S3). This has been found to be the preferred orientation of the olefin ligands in a number of bis(olefin) complexes of molybdenum and tungsten.[16,17]

Other salient features of the structure of **3** are the following: (i) The Mo–C1 distance at 1.991 (6) Å is unusually short, and approaches a normal metal–carbonyl distance. This may be indicative of a multiple interaction between these atoms. On the other hand, the two Mo–S separations (2.486 (2) Å, Mo–S1, and 2.494 (2) Å, Mo–S2) have similar values and compare well with those reported in the literature for other complexes of Mo containing sulfur donor ligands.[18] The Mo–C and Mo–S bond lengths in **3** are however shorter than those found in the CS_2 complex $Cp_2Mo_2(CO)_5(\mu_2,\eta^3\text{-}CS_2)$, which contains a bridging CS_2 ligand, bonded to one Mo center through the C and one of the S atoms and to the other through the second sulfur atom.[19] (ii) As already mentioned, bond distances and angles within the Mo–S1–C1–S2 unit very closely resemble those found for M–(η^2-CS_2) complexes, with the obvious exception of the C1–S2 distance. Particularly noteworthy are the values of 1.647 (7) Å and 135.2 (4)° found respectively for the C1–S1 bond length and the S1–C1–S2 angle, which are well in the range found for M–(η^2-CS_2) complexes[3a] (1.63–1.72 Å, 134–143°).

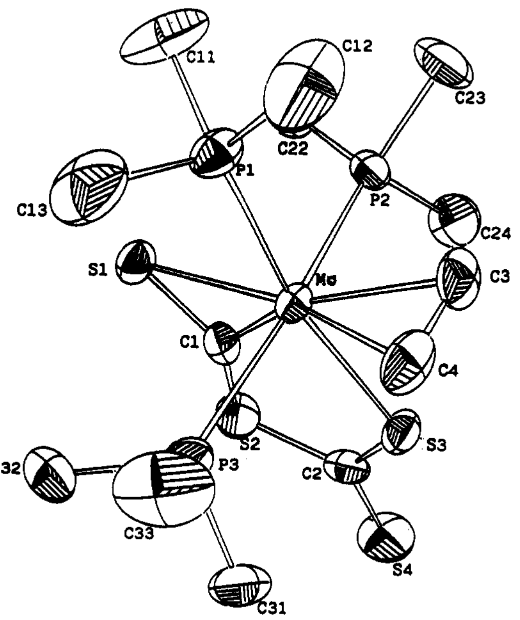


Figure 1. Molecular structure of complex **3**.

The interaction of the Mo complex **1** with SCNPh, in a 1:2 molar ratio, in petroleum ether, causes precipitation of a red-violet microcrystalline complex identified as **7** (ca. 80% yield of isolated product) whereas from the mother liquors small amounts of red-orange crystals of **8** can be collected after cooling at −30 °C overnight (see eq 4). The tungsten complex **2** provides similar results, but interestingly, the bis(ethylene) derivative, $W(S_2C_2(NPh)_2)(C_2H_4)_2(PMe_3)_2$ (**10**), is now the major species, with only spectroscopic detectable amounts of $W(S_2C_2(NPh)_2)(C_2H_4)(PMe_3)_3$ (**9**) being formed. The latter complex can be isolated, albeit in very low yields, if the reaction is carried out in the presence of PMe_3 (see Experimental Section). These mono- and bis(ethylene) complexes of Mo and W seem to form via independent routes. Thus, when **1** and SCNPh are reacted at −70 °C, in THF, the formation of **7** and **8** is observed (NMR) along with that of small amounts of a third, unidentified species, which slowly transforms into **7** at higher temperatures. Treatment of **7** with 3 atm of C_2H_4, at room temperature for 3 days, does not yield **8**, and when this mixture is heated at 50 °C for 2 days, a mixture of other different compounds, which we have not investigated any further, is produced. Similarly, a mixture of **7** and **8** remains unaltered when heated at 40 °C, for ca. 8 h, in the

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[16] (a) Byrne, J. N.; Blaser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871. (b) Grevels, F. W.; Jacke, J.; Ozkar, S. *J. Am. Chem. Soc.* **1987**, *109*, 7536. (c) Carmona, E.; Galindo, A.; Marín, J. M.; Gutiérrez, E.; Monge, A.; Ruiz, C. *Polyhedron* **1988**, *7*, 1831.

[17] (a) Carmona, E.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014. (b) Carmona, E.; Galindo, A.; Poveda, M. L.; Rogers, R. D. *Inorg. Chem.* **1987**, *24*, 4033.

[18] (a) Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Pérez, P. J.; Sánchez, L. *Inorg. Chem.* **1989**, *28*, 2120. (b) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1. (c) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233. (d) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301. (e) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

[19] Deutsch, W.; Gieren, A.; Ruiz-Pérez, C.; Schwarhans, K. E. *J. Organomet. Chem.* **1988**, *355*, 197.

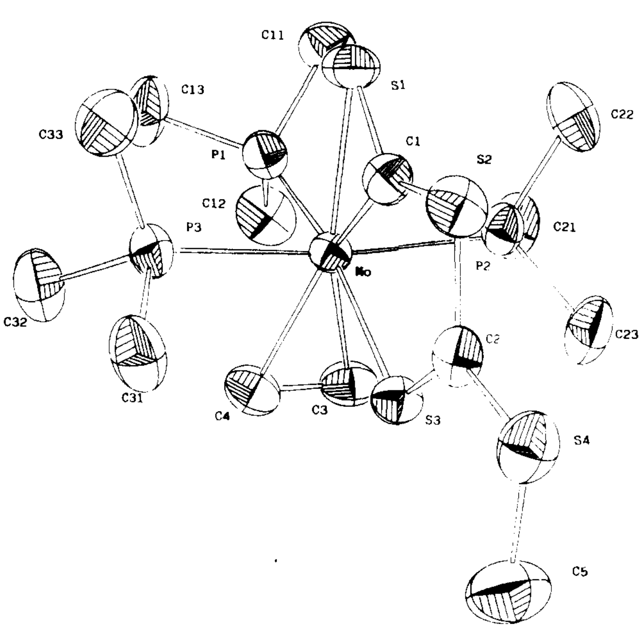

Figure 2. Ortep drawing and atom-labeling scheme for the cation of complex **11**.

presence of PMe_3. It is therefore clear that **7** and **8** (and by analogy **9** and **10**) are not in equilibrium but rather form in independent, competitive reactions. We have found no means to determine if the above compounds have a common intermediate, although this seems a reasonable hypothesis in view of the characteristic chemistry displayed by **1** and **2**.[14,16c,17] The factors underlying the preferential formation of either the mono- or the bis(ethylene) derivatives for the Mo and W systems, respectively, are presently not well understood but may be electronic in origin and could be related to differences in metal basicity (W > Mo).[20]

The spectroscopic data collected in the Experimental Section allow the structural characterization of compounds **7**–**10**. On the basis of these data, structures C and D can be proposed for the mono- and bis(ethylene) derivatives respectively.

Some chemical properties of complex **3** have been investigated (Scheme I). Treatment of **3** with MeI causes the precipitation of a purple solid, which can be shown to be a cocrystallized mixture of $PMe_4{}^+I^-$ and a cationic molybdenum complex. While separation of these products by fractional crystallization did not prove to be possible, the molybdenum-containing product can be isolated in a pure state by anion exchange using NH_4PF_6, followed by repeat washing of the resulting precipitate with water. A pure crystalline species, formulated as $[Mo(C_2S_4Me)(C_2H_4)(PMe_3)_3]PF_6$ (**11**) is obtained in this way. The same compound results from the reaction of **3** with $MeOSO_2CF_3$ followed by anion exchange with NH_4PF_6, as above, and an analogous BF_4^- salt, $[Mo(C_2S_4Me)(C_2H_4)(PMe_3)_3]BF_4$, can be obtained by methylation of **3** with $Me_3O^+BF_4^-$.

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **11** are very similar to those reported for **3** with respect to resonances due to the C_2H_4 and PMe_3 groups. ^1H and $^{13}C\{^1H\}$ singlets at 3.1 and 22.2 ppm, respectively, show the presence of a methyl group in this species, but the absence of coupling to the ^{31}P nuclei clearly indicates this group is not directly bonded to the metal atom. This observation, along with the disappearance of the characteristic band at ca. 1020 cm^{-1} attributed to the exocyclic C=S bond, suggests that methylation has in fact occurred at the exocyclic sulfur atom. An X-ray structural determination of compound **11** has confirmed this assumption. An ORTEP drawing of the cation is shown in Figure 2, intermolecular distances and angles are collected in Table II. The structural parameters of the MoC_2S_4 linkage show the expected changes upon methylation of the exocyclic sulfur atom. In the MoC_2S_4 unit of **3**, the carbon–sulfur distances range from 1.682 (7) to 1.760 (8) Å and compare favorably with those reported for analogous heterometallacycles.[8–10] These parameters are indicative of delocalization over the carbon–sulfur framework. In **11**, the corresponding carbon–sulfur distances are shorter and range from 1.648 (7) to 1.732 (9) Å. In particular, the C–S bond lengths at C2 (C2-S2 = 1.732 (9) Å; C2–S3 = 1.648 (7) Å) are appreciably shorter than the corresponding distances in **3** (1.760 (8) and 1.682 (7) Å, respectively). This suggests increased delocalized bonding within this fragment of the ligand. Not surprisingly, the exocyclic C–S bond lengthens from 1.666 (8) in **3** to 1.743 (9) Å in **11**, while the newly formed C5–S4 bond is somewhat longer at 1.78 (1) Å.

Compound **3** reacts with $CNBu^t$ at 50–60 °C to give a complex mixture of several species from which orange crystals of the substitution product $Mo(C_2S_4)(CNBu^t)(PMe_3)_3$ (**12**) can be obtained in low yields. Attempts to isolate other reaction products from the above mixture have proved unsuccessful. The IR spectrum of **12** shows a strong absorption at 2110 cm^{-1} due to the ν(C≡N) of the isocyanide ligand and another strong band at ca. 1000 cm^{-1}, which is associated with the C=S bond of the metallacycle. From these and other data (see Experimental Section) compound **12** can be proposed to have a structure of the type found for **3**, with the $CNBu^t$ group replacing the ethylene ligand, as shown in structure E.

In an attempt to induce the cleavage of the MC_2S_4 unit with formation of $CS_3{}^{2-}$ and CS, i.e. the products of the reductive disproportionation of CS_2, compound **3** was heated at about 120 °C for 3–4 h. Some decomposition was observed under these conditions, but evidence for the formation of the above products could not be found. In fact, most of the starting $Mo(C_2S_4)(C_2H_4)(PMe_3)_3$ was recovered unaltered. A rather unexpected transformation takes place however when **3** is reacted with carbon monoxide. Stirring a solution of **3** at ca. 50 °C for 3–4 h under 2 atm of carbon monoxide produces, after evaporation of the solvent, a dark red residue from which red crystals of compound **13** can be collected after workup. Its IR spectrum shows two absorptions at 1850 and 1725 cm^{-1} that are assigned to ν(CO) of two carbonyl ligands, but no absorption in the region 1300–1000 cm^{-1} attributable to ν(C=S) can be found. In addition, there are two bands at 990 and 940 cm^{-1} that are due to PMe_3 groups. The lower energy band appears invariably in compounds that contain coordinated PMe_3, but the somewhat higher energy of the other absorption suggests the existence of a phosphonium group. From this, and from pertinent NMR data to be discussed below, a $Mo(S_2CPMe_3)(CO)_2(PMe_3)_2$ formulation can be proposed for this compound.

Complex **13** is a very air-sensitive solid that decomposes rapidly in the presence of air, both in solution and in the solid state. It also displays relatively low stability and decomposes slowly in solution even under an inert atmosphere. NMR studies show the complex is fluxional and provide unequivocal evidence for the above formulation. The ^1H NMR spectrum exhibits two broad singlets at 1.19 and 1.22 ppm due to the metal-bound PMe_3 ligands along with a doublet at 1.20 ppm. The large ^1H–^{31}P coupling of 12 Hz associated with this latter signal is characteristic of phosphonium derivatives. The trimethylphosphonium group affords also a characteristic $^{13}C\{^1H\}$ NMR signal, which appears as a relatively high-field doublet (10.9 ppm) with a large, one-bond phosphorus-to-carbon coupling constant of 60 Hz. Finally, the room temperature $^{31}P\{^1H\}$ NMR spectrum displays a low-field triplet at 31.2 ppm, with a long-range ^{31}P–^{31}P coupling of 3 Hz. Again the chemical shift of this signal is well in the region corresponding to quaternary phosphorus atoms bearing a positive charge.[18a,21] In addition, there are two very broad humps at ca. 12 and −16 ppm, which practically broaden into the base line. When the solution is heated at 65 °C the low-field signal remains essentially unchanged while the others give rise to a broad resonance centered at ca. −8 ppm. The rigid structure of **13** can be frozen out at −80 °C, the $^{31}P\{^1H\}$ NMR spectrum consisting at this temperature of two doublets at 13.9 ($^2J_{PP}$ = 35 Hz, Mo–PMe_3) and 39.5 ppm ($^4J_{PP}$ = 5 Hz, S_2CPMe_3) and of a doublet

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(20) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231.

(21) See ref 8 and references therein.

of doublets at −14.9 ppm ($^2J_{PP}$ = 35 Hz, $^4J_{PP}$ = 5 Hz, Mo–*P*Me$_3$).

From the spectroscopic data discussed above, structure F can be proposed for this compound. A similar structure with the Me_3PCS_2 group acting as trihapto ligand, bonded to molybdenum through the carbon and the two sulfur atoms would also be consistent with the available data. This coordination mode of Me_3PCS_2 groups seems to be more common than previously thought, and for example, it has been demonstrated recently by X-ray methods in the binuclear complex $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$[22] as well as in the mononuclear species $MoCl(NO)(S_2CPMe_3)(PMe_3)_2$[18a] prepared in our laboratory.

^{13}C NMR studies of the reaction mixture resulting from the interaction of **3*** (50% $^{13}CS_2$-enriched sample) with CO show the presence of a signal at 192.7 ppm that corresponds to free $^{13}CS_2$. The yield of carbon disulfide produced in this transformation, as determined by its precipitation from the volatile fraction as Me_3PCS_2 (ca. 23–28% yield), is consistently similar, albeit slightly lower, to that of complex **13** (28–32 %). This indicates that the observed CS_2 is formed in a stoichiometric, although low-yield, reaction in which the MoC_2S_4 linkage breaks up in a symmetric manner. As shown in eq 5, this transformation yields two molecules of carbon disulfide.

$$\underset{\mathbf{3}}{Mo(C_2S_4)(C_2H_4)(PMe_3)_3} + CO \rightarrow \underset{\mathbf{13}}{Mo(S_2CPMe_3)(CO)_2(PMe_3)_2} + CS_2 + \text{other products} \quad (5)$$

One of these molecules remains in the coordination sphere of molybdenum in the form of a trimethylphosphonium dithiocarboxylate ligand, S_2CPMe_3, while the other is produced as free CS_2. This is an unprecedented transformation that corresponds to an oxidative, symmetric cleavage of the head-to-tail MC_2S_4 unit, with concomitant reduction of the Mo complex, and can therefore be viewed as the reverse of the metal-induced reductive dimerization of CS_2 (eq 6).

$$Mo(0) + 2CS_2 = Mo^{2+} + C_2S_4{}^{2-} \quad (6)$$

Although the chemical transformation despicted in eq 5 does not require the presence of PMe_3, the addition of ca. 0.5 equiv of free PMe_3 makes workup of the reaction mixture easier, and furthermore, it improves the yield of the reaction to a total of ca. 40–45%. An attractive, although somewhat speculative, hypothesis concerning this observation is to consider Ibers' complex B as a model for the transition state or intermediate of this reaction, i.e., to suppose that the symmetric rupture of the C_2S_4 unit is induced by a nucleophilic attack of a phosphine ligand at the electrophilic C1 carbon atom of **3**.

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 883 spectrophotometer. ^{1}H, ^{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 by 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 by following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had bp = 40–60 °C. The compounds *trans*-$M(C_2H_4)_2(PMe_3)_4$[17] (M = Mo, W) and the ligands PMe_3[23] and $CNBu^t$[24] were prepared according to the literature procedures.

Synthesis of $M(C_2S_4)(C_2H_4)(PMe_3)_3$ (M = Mo (3), W (4)). A solution of *trans*-$M(C_2H_4)_2(PMe_3)_4$ (M = Mo, 0.46 g, ca. 1 mmol; M = W, 0.54 g, ca. 1 mmol) in 40 mL of Et_2O was reacted with CS_2 (2.0 mL of a 1.0 M Et_2O solution). The solution darkened instantaneously, and the formation of a black solid was immediately observed. The mixture was stirred for 30 min at room temperature and then filtered. The resulting black solid was washed with 2 × 10 mL of Et_2O and dried under vacuum. Yield: 90%. The crude product obtained is usually pure enough to be used for synthetic purposes without further purification. Crystallization from acetone or dichloromethane solutions afforded the title compounds as very dark red crystalline materials.

$Mo(C_2S_4)(C_2H_4)(PMe_3)_3$ (**3**): IR (Nujol) 1020 cm^{-1} (ν(C=S)) (990 cm^{-1} for **3***, ca. 50% $^{13}CS_2$-enriched); ^{1}H NMR (CD_2Cl_2) δ 1.0 (pt, 18 H, 2 $P(CH_3)_3$ trans, $J_{HP_{app}}$ = 3.5 Hz), 1.4 (d, 9 H, 1 $P(CH_3)_3$ cis, $^2J_{HP}$ = 7 Hz), 1.6 (m, 2 H, *H*HC=C*H*H), 2.2 (m, 2 H, H*H*C=CH*H*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2), AX_2 system, δ −9.9 (t, 1 P_A, $^2J_{P_AP_X}$ = 27 Hz), −3.2 (d, 2 P_X); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, data for **3***) δ 15.7 (pt, 2 $P(CH_3)_3$ trans, $J_{CP_{app}}$ = 12 Hz), 19.9 (d, 1 $P(CH_3)_3$, $^1J_{CP}$ = 22 Hz), 43.9 (s, C_2H_4), 226.0 (s, MoS*C*(S)CS) 292.3 (q, MoSC(S)*C*S), $^2J_{CP}$ = 16 Hz). Anal. Calcd for $MoC_{13}H_{31}S_4P_3$: C, 30.9; H, 6.2. Found: C, 31.1; H, 6.2.

$W(C_2S_4)(C_2H_4)(PMe_3)_3$ (**4**): IR (Nujol) 1020 cm^{-1} (ν(C=S)); ^{1}H NMR (CD_2Cl_2) δ 1.1 (pt, 18 H, 2 $P(CH_3)_3$ trans, $J_{HP_{app}}$ = 3.5 Hz), 1.5 (d, 9 H, 1 $P(CH_3)_3$ cis, $^2J_{HP}$ = 7 Hz), 1.6 (m, 2 H, *H*HC=C*H*H), 2.2 (m, 2 H, H*H*C=CH*H*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2), AB_2 system, δ −28.4 (1 P_A, $^2J_{P_BP_A}$ = 22 Hz), −27.3 (2 P_B); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 15.4 (pt, 2 $P(CH_3)_3$ trans, $J_{CP_{app}}$ = 13 Hz), 20.7 (d, 1 $P(CH_3)_3$, $^1J_{CP}$ = 25 Hz), 36.4 (t, C_2H_4, $^2J_{CP}$ = 5 Hz). Anal. Calcd for $WC_{13}H_{31}S_4P_3$: C, 26.4; H, 5.2. Found: C, 27.0; H, 5.2.

Synthesis of the $M(S_2C_2(NPh)_2)(C_2H_4)_x(PMe_3)_{4-x}$ Complexes (x = 1, M = Mo (7), W (9); x = 2, M = Mo (8), W (10)). To a solution of **1** (0.5 g, ca. 1 mmol) in 40 mL of petroleum ether was added SCNPh (2 mL of a ca. 1 M solution in toluene). A red-violet microcrystalline solid precipitated immediately, and it was separated by filtration. This crude product was crystallized from a Et_2O–CH_2Cl_2 mixture to give **7** as red-violet crystals after cooling at −30 °C overnight. Yield: 80%. From the resulting mother liquors, small quantities of complex **8** can be isolated as orange-red crystals. Complex **7** is obtained as the only organometallic product if the reaction is carried out in the presence of PMe_3. The experimental procedure for the tungsten system is analogous, although in this case the major product is **10**. To a solution of **2** (0.54 g, ca. 1 mmol) in 40 mL of petroleum ether was added SCNPh (2 mL of a ca. 1 M solution in toluene). After 10 min of stirring at room temperature, the reaction mixture was evaporated in vacuo and the residue extracted with Et_2O. Complex **10** was obtained as orange crystals in ca. 75% yield. Complex **9** was collected in the first crop of crystals, in very small yield, as a red-violet crystalline solid. The yield of this complex increases if the reaction is carried out in the presence of PMe_3.

$Mo(S_2C_2(NPh)_2)(C_2H_4)(PMe_3)_3$ (**7**): ^{1}H NMR (C_6D_6) δ 0.77 (d, 9 H, 1 $P(CH_3)_3$, $^2J_{HP}$ = 6 Hz), 0.93 (pt, 18 H, 2 $P(CH_3)_3$, $J_{HP_{app}}$ = 3 Hz), 1.43 (m, 2 H, *H*HC=C*H*H), 1.76 (m, 2 H, H*H*C=CH*H*), 7.0, 7.3, and 7.75 (m, 10 H, C_6H_5); $^{31}P\{^1H\}$ NMR (C_6D_6), AX_2 system, δ −7.69 (t, 1 P_A, $^2J_{P_AP_X}$ = 21 Hz), −3.06 (d, 2 P_X); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 16.8 (pt, 2 $P(CH_3)_3$ trans, $J_{CP_{app}}$ = 10.5 Hz), 20.9 (d, 1 $P(CH_3)_3$, $^1J_{CP}$ = 21 Hz), 44.2 (t, C_2H_4, $^2J_{CP}$ = 5 Hz), 121.6, 122.3, 127.0, 127.5, 128.7, and 128.9 (s, aromatics *C*–H), 145.7 and 152.6 (s, aromatics C_q). Anal. Calcd for $MoC_{25}H_{41}S_2P_3N_2$: C, 48.2; H, 6.6; N, 4.5. Found: C, 47.4; H, 6.5; N, 4.3.

$Mo(S_2C_2(NPh)_2)(C_2H_4)_2(PMe_3)_2$ (**8**): ^{1}H NMR ($CDCl_3$) δ 1.28 (pt, 18 H, 2 $P(CH_3)_3$ trans, $J_{HP_{app}}$ = 3 Hz), 0.86 (m, 2 H, *H*HC=C*H*H), 2.35 (m, 2 H, H*H*C=CH*H*), 6.95, 7.22, and 7.38 (m, 10 H, C_6H_5), (the remaining =CH_2 olefinic resonances are obscured by the PMe_3 absorptions); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 7.54 s; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.8 (pt, 2 $P(CH_3)_3$ trans, $J_{CP_{app}}$ = 12 Hz), 46.7 (br s, C_2H_4), 51.3 (br s, C_2H_4), 121.1, 122.2, 125.7, 127.7, 128.1, and 128.5 (s, aromatics *C*–H), 143.8 and 150.3 (s, aromatics C_q).

$W(S_2C_2(NPh)_2)(C_2H_4)(PMe_3)_3$ (**9**): ^{1}H NMR (CD_2Cl_2) δ 0.93 (m, 2 H, *H*HC=C*H*H), 1.40 (m, 2 H, H*H*C=CH*H*), 1.22 (pt, 18 H, 2 $P(CH_3)_3$, $J_{HP_{app}}$ = 3 Hz), 1.48 (d, 9 H, 1 $P(CH_3)_3$, $^2J_{HP}$ = 7 Hz), 7.0 and 7.4 (m, 10 H, C_6H_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2), AX_2 system, δ −24.8 (t, 1 P_A, $^2J_{P_AP_X}$ = 15 Hz, $^1J_{PW}$ = 261 Hz), −28.9 (d, 2 P_X, $^1J_{PW}$ = 227 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 16.9 (pt, 2 $P(CH_3)_3$ trans, $J_{CP_{app}}$ = 13 Hz), 22.2 (d, 1 $P(CH_3)_3$, $^1J_{CP}$ = 25 Hz), 37.5 (t, C_2H_4, $^2J_{CP}$ = 6 Hz), 121.5, 122.4, 127.0, 127.4, 128.7, and 128.9 (s, aromatics *C*–H), 146.1 (s, aromatics C_q).

$W(S_2C_2(NPh)_2)(C_2H_4)_2(PMe_3)_2$ (**10**): ^{1}H NMR (C_6D_6) δ 0.37 (m, 2 H, *H*HC=C*H*H), 0.72 (m, 2 H, H*H*C=CH*H*), 1.07 (t, 18 H, 2 $P(CH_3)_3$, $J_{HP_{app}}$ = 4 Hz), 1.55 (m, 2 H, *H*HC=C*H*H), 2.24 (m, 2 H, H*H*C=CH*H*), 7.0, 7.3, and 7.42 (m, 10 H, C_6H_5); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −27.7 (s, $^1J_{PW}$ = 186 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 13.2 (pt, 2 $P(CH_3)_3$ trans, $J_{CP_{app}}$ = 14 Hz), 39.8 (t, C_2H_4, $^2J_{CP}$ = 5 Hz), 44.4 (t, C_2H_4, $^2J_{CP}$ = 5 Hz), 121.5, 122.5, 126.7, 128.5, 128.8, and 129.2 (s, aromatics *C*–H), 145.0 (s, aromatics C_q). Anal. Calcd for $WC_{24}H_{36}S_2P_2N_2$: C, 43.5; H, 5.4; N, 4.2. Found: C, 44.1; H, 5.5; N, 4.1.

Reaction of *trans*-$M(C_2H_4)_2(PMe_3)_4$ with COS. Carbonyl sulfide was bubbled through a solution of complex **1** (0.46 g, 1 mmol) in 40 mL of Et_2O for ca. 2 min. The color of the solution darkened, and a dark green solid precipitated. The mixture was stirred for an additional 10-min

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Table V. Atomic Coordinates for Non-Hydrogen Atoms of **11**

atom	*x/a*	*y/b*	*z/c*
MO	0.260 21 (5)	0.335 95 (5)	0.220 04 (5)
P1	0.092 06 (17)	0.349 62 (17)	0.267 80 (17)
P2	0.291 91 (18)	0.509 51 (16)	0.251 11 (18)
P3	0.255 37 (19)	0.156 07 (16)	0.218 20 (18)
P4	0.828 39 (18)	0.311 98 (20)	0.474 50 (18)
S1	0.329 58 (18)	0.318 29 (17)	0.396 59 (15)
S2	0.518 15 (16)	0.316 13 (17)	0.323 79 (16)
S3	0.386 68 (15)	0.335 31 (16)	0.131 19 (14)
S4	0.616 00 (17)	0.325 08 (19)	0.171 73 (19)
C1	0.394 27 (61)	0.319 82 (56)	0.316 23 (57)
C2	0.502 55 (57)	0.327 29 (58)	0.203 12 (61)
C3	0.176 59 (72)	0.401 49 (72)	0.076 44 (64)
C4	0.164 25 (70)	0.302 97 (71)	0.068 36 (66)
C5	0.570 51 (88)	0.337 01 (108)	0.046 36 (81)
C11	0.100 58 (77)	0.415 38 (76)	0.376 69 (75)
C12	−0.015 61 (74)	0.404 58 (86)	0.184 00 (85)
C13	0.035 41 (83)	0.241 53 (79)	0.292 66 (97)
C21	0.187 77 (81)	0.591 69 (63)	0.228 64 (90)
C22	0.364 00 (89)	0.543 84 (71)	0.370 56 (86)
C23	0.368 82 (86)	0.560 82 (71)	0.181 81 (89)
C31	0.344 80 (88)	0.106 13 (72)	0.160 38 (90)
C32	0.143 52 (85)	0.089 56 (75)	0.157 57 (92)
C33	0.292 82 (117)	0.095 88 (76)	0.331 54 (86)
F1	0.907 72 (60)	0.232 64 (61)	0.476 23 (60)
F2	0.753 52 (70)	0.396 29 (66)	0.468 30 (68)
F3	0.833 99 (81)	0.334 46 (81)	0.371 42 (78)
F4	0.912 88 (88)	0.383 59 (82)	0.509 39 (86)
F5	0.743 11 (79)	0.247 23 (84)	0.422 38 (80)
F6	0.824 62 (88)	0.293 06 (83)	0.573 36 (87)

period, the excess COS was eliminated by partial evaporation of the solvent under vacuum, and the resulting solid was filtered off and washed with Et_2O. Spectroscopic studies allowed its identification as $Mo(S_2CO)(CO)_2(PMe_3)_2$ by comparison of its IR and NMR spectra with those of an authentic sample.[13]

The tungsten complex analogue, $W(S_2CO)(CO)_2(PMe_3)_2$,[15] was obtained from **2** and COS by following a similar procedure.

Reaction of 3 with CNBu^t: $Mo(C_2S_4)(CNBu^t)(PMe_3)_3$ (12). To a solution of **3** (0.5 g, ca. 1 mmol) in 100 mL of THF was added $CNBu^t$ (2.0 mL of a ca. 1.0 M THF solution). The mixture was stirred for 2–3 days at 40 °C, when a change in the color of the solution from dark green to red was observed. The solvent was then removed under vacuum and the residue washed with 2 × 20 mL of Et_2O. The resulting dark red solid was extracted with acetone (30 mL) and centrifuged. Partial removal of the solvent and cooling at −20 °C afforded complex **12** as an orange microcrystalline solid in 20–30% yield: IR (Nujol) 2110 (ν(C≡N)), 1000 (ν(C=S)) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.4 (d, 9 H, 1 $P(CH_3)_3$ cis, $^2J_{HP}$ = 8 Hz), 1.6 (s, $CNC(CH_3)_3$), 1.6 (filled-in d, 18 H, 2 $P(CH_3)_3$ trans, $J_{HP_{app}}$ = 4 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2), AX_2 system, δ 5.2 (t, 1 P_A, $^2J_{P_AP_X}$ = 21 Hz), 20.5 (d, 2 P_X); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 12.6 (d, 1 $P(CH_3)_3$, $^1J_{CP}$ = 25 Hz), 15.1 (pt, 2 $P(CH_3)_3$ trans, $J_{CP_{app}}$ = 16 Hz), 30.3 (s, $CNC(CH_3)_3$) 152.0 (s, $CNCMe_3$). Anal. Calcd for $MoC_{16}H_{36}NS_4P_3$: C, 34.3; H, 6.4; N, 2.5; S, 22.9. Found: C, 34.4; H, 6.2; N, 2.4; S, 22.6.

Reaction of 3 with MeX (X = I, SO_3CF_3) and Me_3OBF_4. MeI (0.2 mL, ca. 3 mmol) was added to a solution of **3** (0.5 g, ca. 1 mmol) in 50 mL of THF. After 90 min of stirring at room temperature, the formation of a purple solid was observed. The solvent was partially evaporated to ca. 8–10 mL, and the precipitation of insoluble materials was completed by addition of Et_2O (20 mL). The resulting solid was filtered off, dried under vacuum, and crystallized from acetone to afford a purple material that contained $PMe_4^+I^-$ as an impurity. Pure complex **11** was obtained by anion exchange with NH_4PF_6, as described below for the reaction with $MeOSO_2CF_3$.

To a solution of **3** (0.5 g, ca. 1 mmol) in CH_2Cl_2 (40 mL) was added $MeOSO_2CF_3$ (1.0 mL of a 1.0 M CH_2Cl_2 solution), and the reaction mixture was stirred for 40 min at room temperature. Removal of the solvent and washing of the residue with Et_2O (15 mL) afforded a purple solid. The crude product was extracted with acetone (20 mL) and the resulting solution added onto a stirred solution of NH_4PF_6 (0.16 g, ca. 1 mmol) in 10 mL of water. A very dark purple solid precipitated instantaneously, and it was filtered off, washed with water (10 mL) and Et_2O (2 × 5 mL), and dried under vacuum. Yield: 85–90%. Crystallization from a water–acetone (1:1) mixture provided very dark red crystals of **11**: ^{1}H NMR (CD_3COCD_3) δ 0.9 (pt, 18 H, 2 $P(CH_3)_3$ trans, $J_{HP_{app}}$ = 3.5 Hz), 1.6 (d, 9 H, 1 $P(CH_3)_3$ cis, $^2J_{HP}$ = 8 Hz), 2.4 (m, 2 H, HHC=CHH), 3.1 (s, $C_2S_4CH_3$), 3.2 (m, 2 H, HHC=CHH); $^{31}P\{^1H\}$ NMR (CD_3COCD_3), AX_2 system, δ −10.6 (t, 1 P_A, $^2J_{P_AP_X}$ = 31 Hz), −5.3 (d, 2 P_X); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 15.0 (pt, 2 $P(CH_3)_3$ trans, $J_{CP_{app}}$ = 12 Hz), 18.7 (d, 1 $P(CH_3)_3$, $^1J_{CP}$ = 25 Hz), 22.1 (s, SCH_3), 45.5 (s, C_2H_4). Anal. Calcd for $MoC_{14}H_{34}S_4P_4F_6$: C, 25.3; H, 5.1; S, 19.3. Found: C, 25.5; H, 5.5; S, 19.1.

A solution of Me_3OBF_4 (0.15 g, ca. 1 mmol) in 15 mL of CH_2Cl_2 was transferred onto a CH_2Cl_2 solution (30 mL) of **3** (0.5 g, ca. 1 mmol). After 15 min of stirring at room temperature, the color of the solution changed from the initial dark red to purple. The stirring was continued for another 45 min, and the solution was evaporated to dryness. The black residue was extracted with 30 mL of a toluene–dichloromethane (1:1) mixture and centrifuged, and the supernatant clear solution was then concentrated in vacuo and cooled to −20 °C. The complex $[Mo(C_2S_4Me)(C_2H_4)(PMe_3)_3]BF_4$ was obtained as a black microcrystalline solid. Alternatively, crystallization from a water–acetone mixture afforded very dark red crystals of this compound.

Reaction of 3 with CO. Synthesis of $Mo(S_2CPMe_3)(CO)_2(PMe_3)_2$ (13). A solution of complex **3** (1.0 g, ca. 2 mmol) in 100 mL of THF was treated with PMe_3 (ca. 1 mmol), pressurized with 2 atm of CO and stirred at 50 °C for 3 h. At the end of this period, the reaction mixture was evaporated to dryness and the resulting dark red residue was extracted with 30 mL of Et_2O and centrifuged. Partial removal of the solvent and cooling at −30 °C overnight afforded red crystals of the title compound in ca. 40% yield (0.36 g of **13** from this and subsequent crystallizations of the mother liquors). The yield of compound **13**, in the absence of added PMe_3, is lower (around 30%). The amount of free CS_2 produced in this reaction was determined by its precipitation as S_2CPMe_3. Typical yields are on the order of 23–28 %. IR (Nujol): 1850 and 1725 cm^{-1} (ν(CO)); ^{1}H NMR (C_6D_6): δ 1.19 (br s, 9 H, 1 $P(CH_3)_3$), 1.20 (d, 9 H, $S_2CP(CH_3)_3$, $^2J_{HP}$ = 12 Hz) 1.22 (br s, 9 H, 1 $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (THF, −80 °C): AMX system, δ −14.9 (dd, P_X, $^2J_{P_XP_M}$ = 35 Hz, $^4J_{P_XP_A}$ = 5 Hz), 13.9 (d, P_M), 39.5 (d, P_A, S_2CPMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 10.9 (d, $S_2CP(CH_3)_3$, $^1J_{CP}$ = 60 Hz), 19 (br s, $P(CH_3)_3$). Anal. Calcd for $MoC_{12}H_{27}O_2S_2P_3$: C, 31.6; H, 5.9; S, 14.0. Found: C, 31.5; H, 5.9; S, 14.0.

Single-Crystal X-ray Diffraction Studies of 3 and 11. Crystal data and the parameters used during the collection and refinement of the diffraction data for **3** and **11** are summarized in Table III. Final fractional coordinates of non-hydrogen atoms for complexes **3** and **11** are collected in Tables IV and V, respectively. Red single crystals of **3** and **11** were introduced into Lindeman capillaries, which were sealed under a N_2 atmosphere and mounted on a Enraf-Nonius CAD4-F automatic diffractometer.

The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. There were no appreciable changes in the periodically monitored standard reflexions. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo, S, and P were taken from ref 25. Both structures were solved by Patterson and Fourier synthesis, and an empirical absorption correction[26] was applied at the end of the isotropic refinement. Anisotropic full-matrix least-squares refinement with unit weights minimizing $\sum_w[F_o - F_c]^2$ led to R = 0.048 for complex **3**. No trend in ΔF vs. F_o or $(\sin \theta)/\lambda$ was observed. Final refinement with fixed isotropic temperature factors and coordinates for H atoms gave R = 0.042 (complex **3**) and R = 0.058 (complex **11**). Most of the calculations were carried out with XRAY80.[27]

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Supplementary Material Available: Tables of atomic fractional coordinates for hydrogen atoms, anisotropic thermal parameters, and crystal and refinement data for **3** and **11** (5 pages); listings of structure factors for **3** and **11** (69 pages). Ordering information is given on any current masthead page.

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