Sulfur Insertion into the Molybdenum Acyl Bond of $Mo(C(O)R)(S_2COR)(CO)(P)_2$ Complexes. Desulfurization of the Xanthate Ligand

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Partial desulfurization of the xanthate ligand of complexes $Mo(C(O)Me)(S_2COR)(CO)(PMe_3)_2$ (R = Me, **1a**; Et, **1b**; *i*-Pr, **1c**) occurs at room temperature with concomitant insertion of the sulfur atom into the Mo−acetyl bond to produce compounds $Mo(\kappa^2C,S\text{-}C(S)OR)(\kappa^2O,S\text{-}OSCMe)(CO)(PMe_3)_2$ (**2a**−**c**), which contain coordinated, bidentate alkoxythiocarbonyl, ROC(S), and monothioacetate, $MeCOS^-$, ligands. The analogous rearrangement of the dmpe derivative **1d** (dmpe = $Me_2PCH_2CH_2PMe_2$) yields a similar species, $Mo(\kappa^2C,S\text{-}C(S)O\text{-}i\text{-}Pr)(\kappa^2O,S\text{-}SOCMe)(CO)(dmpe)$ (**3**), but heating at 100 °C is needed in this case. The monothiocarboxylate group of compounds **2** can be replaced by a bidentate xanthate salt, giving $Mo(\kappa^2C,S\text{-}C(S)OR)(\kappa^2S,S'\text{-}S_2COR')(CO)(PMe_3)_2$ (**4**), which when R = R′ may also be obtained, albeit in lower yields, in a one-pot reaction starting from the chloroacetyl $Mo(C(O)Me)Cl(CO)(PMe_3)_3$ and 2 molar equiv of KS_2COR. The facility with which a sulfur atom of the xanthate ligand of compounds **1** inserts into the Mo−η^2-acetyl bond is demonstrated by the formation of $Mo(\kappa^2C,S\text{-}C(S)OR)(\kappa^1S\text{-}SC(O)Me)(CO)_2(PMe_3)_2$ (R = Me, **5a**; *i*-Pr, **5c**) when **1a** and **1c** are treated with CO (20 °C, 1 atm). The Mo−κ^2-C(S)OR linkage of these complexes has been authenticated by X-ray studies carried out with **4d** and **5c**, and it is characterized by a short Mo−C distance of ca. 2.0 Å. Spectroscopically this entity features an IR absorption in the proximity of 1270 cm^{-1} and a low-field ^{13}C resonance near 295 ppm.

Introduction

The study of reactions that involve the rupture or the formation of C−S bonds is presently an area of intense activity. Important industrial transformations that require the activation of C−S bonds include the hydrodesulfurization process[1] or the production of synthesis gas from sulfur-rich coal.[2] In turn, the large-scale generation of carbonyl sulfide, C(O)S, by sulfurization of CO entails the formation of a C−S bond over heterogeneous transition metal-based catalysts.[3]

Examples are known of reactions in which new C−S bonds are formed by coupling of sulfur (or other chalcogens) with metal−carbon multiple-bond or metal-unsaturated hydrocarbon functionalities.[4] However, contrary to prior expectations the generation of thiolates, −SR, by the reaction of sulfur with metal−alkyl groups, M−R, is still an unusual reaction.[5] Evidence has been produced recently showing that metal-bound thiolate and acyl groups can undergo reductive elimination to give thioesters.[5c,6] Notwithstanding the above and the biological implications of the latter rearrangement, to our knowledge, the somewhat related coupling of sulfur and acyl groups to engender thiocarboxylate funtionalities has not been observed. In view of the rich chemistry exhibited by metal−acyl units,[7,8] this can be considered as somewhat surprising.

During the course of studies devoted to the investigation of the structural characteristics of acyl derivatives

(1) (a) Sánchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287. (b) Angelici, R. A. *Polyhedron* **1997**, *16*, 3073.
(2) See: Fu, P.-F.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1993**, *12*, 3790, and references therein.
(3) *Kirk-Othmer Concise Enciclopedia of Chemical Technology*; Wiley: New York, 1985; p 1135. For a model system see ref 2.
(4) (a) Mayr, A.; McDermott, G. A.; Dorries, A. M.; Holder, A. K.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 310. (b) Morrow, J. R.; Templeton, J. L.; Bandy, J. A.; Bannister, C.; Prout, C. K. *Inorg. Chem.* **1986**, *25*, 1923. (c) Carthy, A. J.; Hartstock, F.; Taylor, N. J.; Le Bozec, H.; Robert, P.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1980**, 361. (d) Seyferth, D.; Huke, J. B.; Dewan, J. C. *Organometallics* **1987**, *6*, 895. (e) Bedford, R. B.; Hill, A. F.; White, A. J. P.; Willians, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 95. (f) Cook, D. J.; Hill, A. F. *Chem. Commun.* **1997**, 955.
(5) (a) Legzdins, P.; Sánchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525. (b) Tainturier, G.; Fahim, M.; Trouve-Bellan, G.; Gautheron, B. *J. Organomet. Chem.* **1989**, *376*, 321. (c) Han, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1998**, *120*, 7657.
(6) (a) Matsunnaga, P. T.; Hillhouse, G. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1748. (b) Tucci, G. C.; Holm, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 6489.
(7) (a) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (b) Van Asselt, R.; Gielens, E. E. C. G.; Rulke, R. E.; Vrieze, K.; Elsevier: C. J. *J. Am. Chem. Soc.* **1994**, *116*, 976. (c) Brumbaugh, J. S.; Whittle, R. R.; Parvez, M.; Sen, A. *Organometallics* **1990**, *9*, 1735. (d) Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Marín, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1989**, *8*, 967. (e) Curtis, M. D.; Real, J.; Hirpo, W.; Butler, W. M. *Organometallics* **1990**, *9*, 66.

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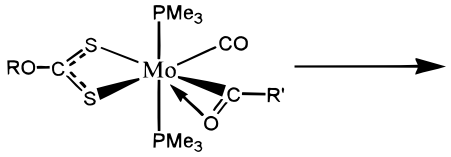
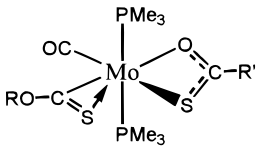
of molybdenum we have found that Mo−C(O)CH_2R complexes that contain coordinated anionic dithio acid ligands (e.g., dithiocarbamate, $R_2NCS_2^-$, and xanthate, $ROCS_2^-$, groups) may exist as the dihaptoacyl or β-agostic acyl isomers, Mo(C(O)CH_2R or Mo(C(O)CH_2R), respectively.[9] These compounds exhibit only moderate thermal stability; the xanthate derivatives start decomposing at temperatures close to 0 °C. We have now investigated this decomposition reaction in detail and have found that it proceeds with formal insertion of a sulfur atom originated from the coordinated xanthate ($R'OCS_2^-$) into the Mo−C(O)R bond to give metal-bound monothiocarboxylate, $RCOS^-$, and alkoxythiocarbonyl, $R'OC(S)^-$, ligands. Details of this transformation for different xanthate compounds are herein included along with complementary single-crystal X-ray studies on two representative compounds that contain the somewhat unusual κ^2-alkoxythiocarbonyl group, κ^2C,S-C(S)OR′. Part of this work has appeared in preliminary form.[10]

Results and Discussion

Acetyl complexes of molybdenum that contain coordinated dithiocarbamate or xanthate ligands may be prepared by treatment of Mo(η^2-C(O)Me)Cl(CO)$(PMe_3)_3$ with the corresponding dithio acid sodium or potassium salt.[9] The xanthate derivatives Mo(η^2-C(O)Me)(S_2COR)-(CO)$(PMe_3)_2$ (**1a−c)** have moderate thermal stability and decompose at room temperature in solution over a period of 1−2 days. As shown in eq 1, new compounds



1a-d



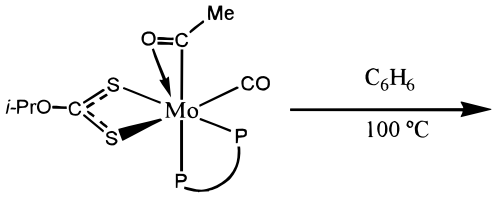
(1)

2a-d

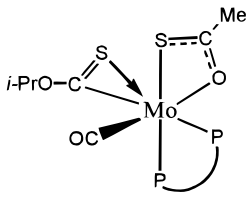
(R' = Me; R = Me, **2a**; Et, **2b**; *i*-Pr, **2c**)
(R' = CH_2SiMe_3; R = *t*-Bu, **2d**)

that contain monothioacetate, SOCMe, and alkoxythiocarbonyl, C(S)OR, ligands result from this reaction. The latter derives from the partial desulfurization of the xanthate, whereas the generation of the thiocarboxylate unit requires formal insertion of the sulfur atom into the metal−acyl bond. Sulfur−carbon bond cleavage within a coordinated dithio acid ligand is a relatively common process,[4a,11,12] and even though we are not aware of a reaction that involves formally sulfur insertion into a metal−acyl bond, the oxidation of a Mo−η^2-acyl linkage has been reported.[13] A compound related to the above, of composition Mo(κ^2C,S-C(S)O-*t*-Bu)-(κ^2S,O-SC(O)CH_2SiMe_3)(CO)$(PMe_3)_2$ (**2d**), has been prepared similarly starting from the acyl Mo(η^2-C(O)CH_2-$SiMe_3$)$(S_2CO$-*t*-Bu)(CO)$(PMe_3)_2$.

The analogous xanthate derivative of the chelating diphosphine dmpe (dmpe = $Me_2PCH_2CH_2PMe_2$), **1d**, undergoes a similar transformation, although as shown in eq 2, somewhat more forcing conditions are required for its full conversion into species **3**.



1d



(2)

3

Compounds **2** are very soluble in common organic solvents. This property, along with the generation of minor impurities during the course of the rearrangements of eq 1, has precluded their isolation (see Experimental Section) in pure, crystalline form. Differently, the dmpe analogue **3** is less soluble and crystallizes as a red solid.

The formulation proposed for **2** and **3** follows from spectroscopic data and from the results of their subsequent reaction with 1 equiv of a xanthate salt. As discussed below, this occurs with incorporation of the xanthate $ROCS_2^-$ and liberation of KS(O)CMe. Most notable among the spectroscopic data, leaving aside

(8) (a) Sheridan, J. B.; Johnson, J. R.; Handwerker, B. M.; Geoffroy, G. L. *Organometallics* **1988**, *7*, 2404. (b) Adams, H.; Bailey, N. A.; Tattershall, C. E.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1991**, 912. (c) Han, S.-H.; Song, J.-S.; Macklin, P. D.; Nguyen, S. T., Geoffroy, G. L.; Rheingold, G. L. *Organometallics* **1989**, *8*, 2127. (d) Yang, G.-M.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Chem. Soc., Chem. Commun.* **1991**, 478. (e) Hart, I. H.; Jeffery, J. C.; Lowry, R. M.; Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1703.

(9) (a) Contreras, L.; Monge, A.; Pizzano, A.; Ruiz, C.; Sánchez, L.; Carmona, E. *Organometallics* **1992**, *11*, 3971. (b) Ujaque, G.; Maseras, F.; Lledós, A.; Contreras, L. Pizzano, A.; Rodewald, D.; Sánchez, L.; Carmona, E.; Monge, A.; Ruiz, C *Organometallics* **1999**, *18*, 3294.

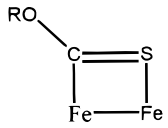
(10) Contreras, L.; Pizzano, A.; Sánchez, L.; Carmona, E.; Monge, A.; Ruiz, C. *Organometallics* **1995**, *14*, 589.

(11) (a) Kreisel, F. R.; Ullrich, N.; Wirsing, A.; Thewalt, U. *Organometallics* **1991**, *10*, 3275. (b) Coffey, T. A.; Forster, G. D.; Hogarth, G. *J. Chem. Soc., Dalton Trans.* **1996**, 183. (c) Brower, D. C.; Tonker, T. L.; Morrow, J. R.; Rivers, D. S.; Templeton, J. L. *Organometallics* **1986**, *5*, 1093. (d) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745. (e) Gilletti, P. F.; Femec, D. A.; Keen, F. I.; Brown, T. M. *Inorg. Chem.* **1992**, *31*, 4008.

(12) Although the cleavage of one or both of the C−S bonds of a coordinated dithiocarbamate is a known process, the analogous transformation of a coordinated xanthate is a much rarer reaction. (a) Herrick, R. S.; Nieter-Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 2599. (b) Hitchcock, P. B.; Lappert, M. F.; McGeary, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 5658. (c) Hitchcock, P. B.; Lappert, M. F.; McGeary, M. J. *Organometallics* **1990**, *9*, 2645. (d) Coffey, T. A.; Forster, G. D.; Hogarth, G. *J. Chem. Soc., Chem. Commun.* **1993**, 1524. (e) Ricard, L. Estienne, J.; Weiss, R. *Inorg. Chem.* **1973**, *12*, 2182.

(13) Bonnensen, P. V.; Yau, P. K. L.; Mersh, W. H. *Organometallics* **1987**, *6*, 1587.

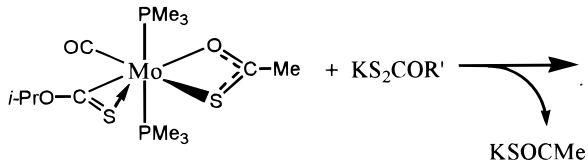
those attributable to the phosphine and carbonyl ligands, are the following. (i) There is a strong IR absorption in the proximity of 1270 cm^{-1} and a low-field ^{13}C resonance at about 295 ppm, both associated with the −C═S part of a bidentate, C- and S-bonded alkoxythiocarbonyl ligand, −C(S)OR. The above data compare favorably with those reported for related complexes of these or similar ligands. For example, compounds that contain an Fe−κ^2*C,S*-C(S)OR linkage[14] exhibit a strong IR band near 1290 cm^{-1}, which can also be found in the spectra of Ru−κ^2-thioacyls, e.g., Ru(κ^2*C,S*-C(S)Ph)Cl(CO)-$(PPh_3)_2$.[4e,f] The latter compound and other analogous κ^2-thioacyls give rise to ^{13}C signals in the range 280−310 ppm, while in binuclear complexes that have a bridging moiety of type **A** the metal-bound carbon resonates at ca. 300 ppm.[15] (ii) There is a low-field ^{13}C signal in the



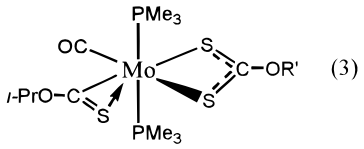
A

region 215−220 ppm that may be assigned to the carboxylate carbon of a coordinated monothioacetate, Mo−SOCMe. In the salt KSOCMe, this resonance appears at δ 221.6. Other related groups (e.g., $^-$SOCPh), either free or coordinated, give the corresponding signal in the vicinity of 210 ppm.[16] In the ^1H NMR spectrum the methyl protons Mo−SOC*Me* resonate at ca. 2.0 ppm. Even though these chemical shift values cannot be taken as diagnostic for the $^-$SOCMe coordination mode, comparison with complexes **5** and **6** that contain κ^1*S*-S(O)CMe authenticated by X-ray crystallography (see below) and with data reported in the literature for complexes of κ^1*S*-S(O)CMe and κ^2*S,O*-SOCMe donor ligands[17] suggests κ^2*S,O*-SOCMe binding in **2** and **3**. In fact the IR absorptions attributable to ν(CO) and ν(CS) of this group in these compounds can be taken as supportive of this kind of coordination.[18] Interestingly, both the thiocarboxylate ^{13}C nucleus and the methyl protons of this ligand exhibit resolved, albeit small (ca. 5−7 and 3 Hz, respectively) long-range coupling to the ^{31}P nuclei.

As briefly noted, chemical evidence is also in agreement with the rearrangement of the S_2COR and C(O)-Me groups of **1** to the C(S)OR and SOCMe of **2** and **3**. Treatment of derivatives **2** with 1 equiv of a xanthate salt (KS_2COR'; R′ = Et, *i*-Pr, see eq 3) induces substitution of SOCMe by S_2COR' and formation of the new compounds **4**. The displaced potassium thioacetate has been isolated from the reaction mixture and authenticated by comparative IR and NMR analysis with a true sample.



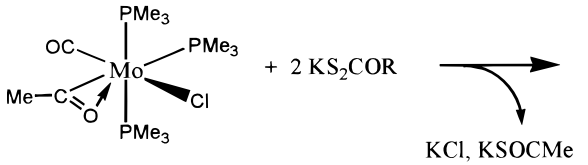
2c

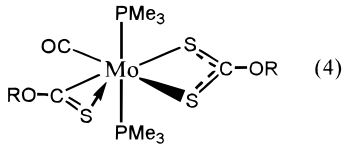


(3)

4b,4c

The reactivity summarized in eqs 1−3 suggests that compounds of type **4** may be obtained in a one-pot reaction, by interaction of the acyls **1** with 2 equiv of KS_2COR (eq 4). Moderate yields of **4c** and **4d** can be produced in this way, but the reaction is more complex than depicted in eq 4 and other complexes are formed (e.g., $Mo(S_2COR)_2(CO)(PMe_3)_2$), besides the desired derivatives **4**.





(4)

R = *i*-Pr, **4c**; *t*-Bu, **4d**

Complexes **4b−d** are red crystalline solids whose IR spectra contain bands in the proximity of 1800 (Mo−CO) and 1270 cm^{-1} (ν(CS) of Mo−C(S)OR). Similarly to **2** and **3**, the ^{13}C nucleus of the C(S)OR functionality resonates at ca. 295 ppm (t, $^2J_{CP}$ = 20 Hz). These and other spectroscopic data collected in the Experimental Section are in accord with the structure proposed for these complexes. X-ray studies (vide infra) carried out with the *t*-Bu derivative **4d** provides unequivocal confirmation of this proposal.

In an attempt to induce the formation of a cationic thiocarbonyl ligand, the protonation of compound **4c**, chosen as a representative example, has been attempted. Upon addition of HBF_4 at −80 °C, a fast reaction is observed, but this gives rise to a complex mixture of products from which only the species [Mo-$(S_2CO$-*i*-Pr$)(CO)_2(PMe_3)_3]BPh_4$ could be isolated, following anion exchange by addition of $NaBPh_4$. No attempts have been made to optimize the synthesis of this complex nor to rationalize its formation.

(14) (a) Samb, A.; Demerseman, B.; Dixneuf, P. H.; Mealli, C. *Organometallics* **1988**, *7*, 26. (b) Robert, P.; Le Bozec, H.; Dixneuf, P. H.; Hartstock, F.; Taylor, N. J.; Carty, A. J. *Organometallics* **1982**, *1*, 1148.

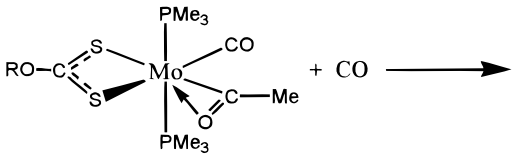
(15) Lhadi, E. K.; Patin, H.; Benoit, A.; Le Marouille, J.-Y.; Darchen, A. *J. Organomet. Chem.* **1983**, *259*, 321.

(16) Vittal, J. J.; Dean, P. A. W. *Inorg. Chem.* **1996**, *35*, 3089.

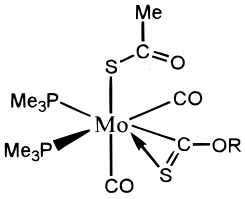
(17) Shifts to lower fields of about 0.5−0.8 ppm have been observed in the chemical shifts of monothioacetate protons upon change of coordination from κ^2 to κ^1. See for instance: (a) Esteruelas, M. A.; Oro, L. A.; Ruiz, N. *Inorg. Chem.* **1993**, *32*, 3793. (b) Critchlow, P. B.; Robinson, S. D. *Inorg. Chem.* **1978**, *17*, 1902.

(18) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley-Interscience: New York, 1997.

Additional evidence for the facility with which a sulfur atom of the xanthate ligand of complexes **1** inserts into the M−acyl bond is provided by the reaction of some of these compounds with CO (eq 5). Bubbling carbon



1a, 1c

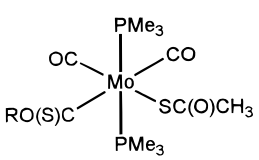


(5)

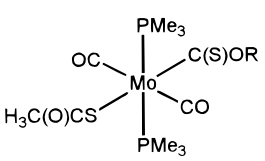
R = Me, **5a-*cis***; *i*-Pr, **5c-*cis***

monoxide through solutions of **1a** or **1c** turns the color rapidly (ca. 10 min) from the initial red to yellow, and after workup of the resulting solutions yellow crystals of **5a-*cis*** or **5c-*cis*** can be collected. IR spectroscopy reveals the presence of two carbonyl ligands, responsible for bands in the ranges 1990−1970 and 1915−1875 cm^{-1}. Two additional, also distinctive, absorptions appear at ca. 1620 and 1270 cm^{-1}. The latter is due to ν(CS) of the bidentate C(S)OR ligand, while the former can be attributed to ν(CO) of a κ^1S- bonded S(O)CMe group. NMR spectroscopic measurements using solutions of **5c** prepared at −20 °C reveal the existence of only one isomer with the stereochemistry proposed in eq 5. Interestingly, the methyl protons of the κ^1S-S(O)-CMe group resonate at lower field than for **2** and **3** (ca. 2.6 ppm),[17] and similarly, the carboxylate carbon also appears at lower field (around 201 ppm). No long-range coupling to the ^{31}P nucleus can be measured for these signals.

The X-ray studies of complex **5c-*cis*** that are discussed below confirm this stereochemical assignment. However, when solutions of **5c-*cis*** are allowed to stand at room temperature, two new isomers which possess equivalent, *trans* PMe_3 groups (isomer ratio 1(*cis*):0.75:0.20) are observed. Assuming, as it is customarily done with ligands of this type,[19] that the C(S)OR moiety occupies a single coordination site, structures **B** and **C** can be advanced for these species.

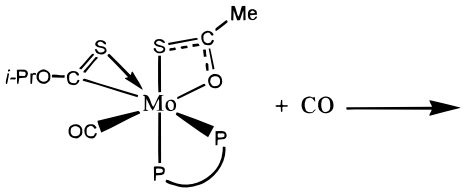


B

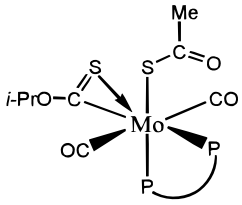


C

The dmpe derivative **3** reacts likewise with CO, generating compound **6** as the only isolable product of the reaction (eq 6). The formulation of **6** follows unambiguously from spectroscopic data. Thus $^{13}C\{^1H\}$ signals



3



(6)

6

at 295.6 (dd, $^2J_{CP}$ = 33; 4 Hz) and 201.8 (s) can be respectively assigned to the Mo−*C*(S)O-*i*-Pr and Mo−κ^1S-S(O)*C*Me nuclei, whereas the two equivalent carbonyls are responsible for the triplet ($^2J_{CP}$ = 8 Hz) detected at 210.6 ppm. Two types of dmpe−methyl groups are found in the ^1H and $^{13}C\{^1H\}$ NMR spectra, and moreover the two ^{31}P nuclei are seen inequivalent by $^{31}P\{^1H\}$ NMR spectroscopy. It is worth noting that at room temperature and in the absence of CO the bis(carbonyl) derivative **6** slowly loses CO in solution to produce the starting monocarbonyl **3**. As a matter of fact, an alternative and more convenient synthetic procedure for the latter compound takes advantage of this reactivity.

Structural Characterization by X-ray Techniques of the Molybdenum Alkoxycarbonyl Unit Mo−C(S)OR. The Crystal and Molecular Structures of Complexes 4d and 5c-*cis*. Even though the κ^2-C(S)OR functionality was first characterized in 1982 by Dixneuf and co-workers,[14b] the number of mononuclear complexes that contain this kind of ligand is still limited. We therefore considered appropriate to determine the structures of some of the Mo−C(S)OR compounds reported, of which **4d** and **5c-*cis*** were chosen as representative examples. The first contains a xanthate ligand bound in a bidentate, κ^2S,S'-S_2CO-*t*-Bu, fashion, while compound **5c-*cis*** contains a thioacetate ligand, but the incorporation of a second CO group determines the adoption of a κ^1S-S(O)CMe coordination mode.

Crystal data for these compounds are summarized in Table 1, and selected bond distances and angles are collected in Tables 2 and 3. Figures 1 and 2 show the structure of the complexes in the form of ORTEP perspective views. The two compounds have a distorted octahedral geometry if the κ^2-C(S)OR ligand is considered to occupy a single coordination site. This is a

(19) This assumption is based on the small magnitude (ca. 37.2°) of the C−M−S angle in the metal−η^2-alcoxythiocarbonyl fragment. An analogous supposition has been applied to η^2-acyls: (a) Pizzano, A.; Sánchez, L.; Altmann, M.; Monge, A.; Ruiz, C.; Carmona, E. *J. Am. Chem. Soc.* **1995**, *117*, 1759. (b) Carmona, E.; Sánchez, L. J.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Riester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214.

Table 1. Crystal Data for Compounds 4d and 5c-*cis*

formula	$C_{17}H_{36}O_3P_2S_3Mo$	$C_{14}H_{28}O_4P_2Mo$
mol wt	542.5	482.4
cryst syst	triclinic	monoclinic
space group	*P*1	$P2_1/m$
a, Å	9.619(3)	9.574(1)
b, Å	10.794.2	33.815(4)
c, Å	14.736(2)	7.809(7)
α, deg	75.64(1)	90
β, deg	83.45(1)	111.54(1)
γ, deg	111.10(2)	90
V, Å^3	1347(3)	2352(2)
Z	2	4
D_{calcd}, g cm^{-3}	1.34	1.36
F(000)	564	992
temp, °C	22	22
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	graphite-monochromated Mo Kα (*λ* = 0.71069) Å	graphite-monochromated Mo Kα (*λ* = 0.71069) Å
μ, cm^{-1}	8.281	8.6
crystal dimens, mm	0.4 × 0.2 × 0.2	0.2 × 0.3 × 0.15
scan technique	*ω*/2*θ*	*ω*/2*θ*
data collected	(−13,−15,0) to (13,15,20)	(−11,0,0) to (11,40,9)
no. of unique data	7856	4142
no. of observed reflns, $I > 2\sigma(I)$	5941	2823
R_{int}, %	1.6	7.5
standard reflns	3/233	3/52
$R = \sum\|\Delta^2F\|/\sum\|F_o\|$	3.2	7.7
$R_w = \sum w\Delta^2F/\sum w\|F_o\|^2)^{1/2}$	3.4	8.6
shift/error	0.13 (average)	0.07 (maximum)

Table 2. Selected Bond Distances and Angles for 4d

MO−S1	2.5388(9)	S2−C2	1.6771(28)
MO−S2	2.5952(11)	S3−C4	1.6705(36)
MO−S3	2.5338(10)	O1−C1	1.1602(42)
MO−P1	2.4591(11)	O2−C2	1.3311(26)
MO−P2	2.5103(12)	O2−C3	1.4939(39)
MO−C1	1.9145(31)	O3−C4	1.3072(44)
MO−C4	2.0176(29)	O3−C5	1.4975(41)
S1−C2	1.6987(31)		
C1−MO−C4	98.40(14)	S1−MO−S2	67.64(04)
P2−MO−C4	126.42(9)	MO−S1−C2	89.02(10)
P1−MO−C4	81.87(10)	MO−S2−C2	87.60(11)
P1−MO−C1	82.22(11)	MO−S3−C4	52.61(10)
P1−MO−P2	150.13(04)	C2−O2−C3	125.35(24)
S3−MO−C4	41.14(08)	C4−O3−C5	125.44(26)
S3−MO−C1	96.88(11)	MO−C1−O1	179.32(32)
S3−MO−P2	85.30(05)	S2−C2−O2	129.11(23)
S3−MO−P1	122.54(04)	S1−C2−O2	115.20(21)
S2−MO−C4	87.22(10)	S1−C2−S2	115.69(18)
S2−MO−S3	88.14(04)	S3−C4−O3	131.89(21)
S1−MO−C4	146.33(11)	MO−C4−O3	141.31(21)
S1−MO−S3	149.96(05)	MO−C4−S3	86.25(13)

common assumption when discussing the structural characteristics of the η^2-acyl and other related fragments,[20] and it is justified by the small value of the C−Mo−S angle (ca. 41° in **4d**; 37° in **5c-*cis***). The structure of **4d** is highly reminiscent of that found for the tungsten η^2-acyls W(η^2-C(O)R)(S_2COR′)(CO)(PMe_3)$_2$.[20] As in these derivatives, the two PMe_3 groups of **4d** occupy mutually *trans* positions. Considering these as axial, the equatorial plane would then be defined by the three sulfur atoms, S1−S3, and the carbonyl ligand. The metal-bound carbon atom of the alkoxycarbonyl is slightly raised above that plane, so that in the rigid

(20) (a) Carmona, E.; Contreras, L.; Poveda, M. L.; Sánchez, L. J.; Atwood, J. L.; Rogers, R. D. *Organometallics* **1991**, *10*, 61. (b) Carmona, E.; Contreras, L.; Gutiérrez-Puebla, E.; Monge, A.; Sánchez, L. J. *Organometallics* **1991**, *10*, 71.

Table 3. Selected Bond Distances and Angles for 5c-*cis*

Mo−P1	2.492(4)	O1−C1	1.16(2)
Mo−P2	2.540(5)	O2−C2	1.16(2)
Mo−S1	2.511(4)	O3−C3	1.19(2)
Mo−S2	2.663(4)	O4−C5	1.35(2)
Mo−C1	1.93(1)	O4−C6	1.56(3)
Mo−C2	1.97(1)]	C3−C4	1.48(2)
Mo−C5	1.96(1)	C6−C7	1.44(4)
S1−C3	1.72(2)	C6−C8	1.47(4)
S2−C5	1.62(1)		
C2−Mo−C5	76.2(5)	Mo−S1−C3	113.6(6)
C1−Mo−C5	74.6(5)	Mo−S2−C5	47.2(5)
C1−Mo−C2	98.3(5)	C5−O4−C6	120(1)
S2−Mo−C5	37.2(4)	Mo−C1−O1	176(1)
S2−Mo−C2	95.2(3)	Mo−C2−O2	176(1)
S2−Mo−C1	103.1(4)	S1−C3−O3	125(1)
S1−Mo−C5	121.6(4)	O3−C3−C4	120(2)
S1−Mo−C2	95.1(4)	S1−C3−C4	116(1)
S1−Mo−C1	161.3(4)	S2−C5−O4	129(1)
S1−Mo−S2	88.6(2)	Mo−C5−O4	135(1)
P2−Mo−C5	102.3(5)	Mo−C5−S2	95.6(7)
P2−Mo−C2	176.8(3)	P1−Mo−C2	81.3(4)
P2−Mo−C1	84.0(4)	P1−Mo−C1	78.7(4)
P2−Mo−S2	82.0(2)	P1−Mo−S2	176.4(2)
P2−Mo−S1	83.2(2)	P1−Mo−S1	90.5(2)
P1−Mo−C5	141.8(4)	P1−Mo−P2	101.4(2)

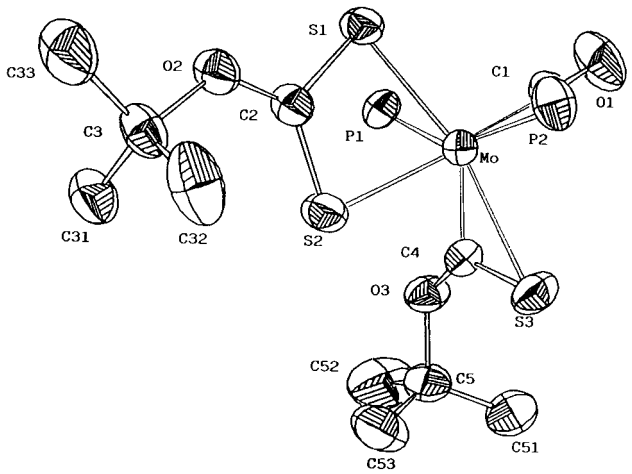


Figure 1. ORTEP perspective view of **4d**.

structure of **4d** the two *trans* phosphines would become inequivalent. As in the related η^2-acyls,[20,21] their equivalency under ambient conditions may be explained by a librational motion of the C═S group around the equatorial plane.

At variance with **4d**, the ligand rearrangement in **5c-*cis*** is such that the two PMe_3 groups are disposed in mutually *cisoid* positions (P1−Mo−P2 angle of 101.4(2)°). One of the phosphorus atoms, P1, is *trans* with respect to the C(S)OR group (P1−Mo−S2 = 176.4(2)°)), whereas the other, P2, forms an angle of 176.8(3)° with one of the carbonyls (C2O2). The two remaining coordination positions contain the other carbonyl (C1O1) and the sulfur atom of the monodentate thioacetate (C1MoS1 angle of 161.3(4)°).

Doubtless, the most interesting feature in the structures of these compounds is the Mo−κ^2*C,S*-C(S)OR linkage. Some relevant geometrical parameters for the Mo−C(S)OR entity of **4d** and **5c-*cis*** are presented in

(21) Curtis, M. D.; Shiu, K. B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550.

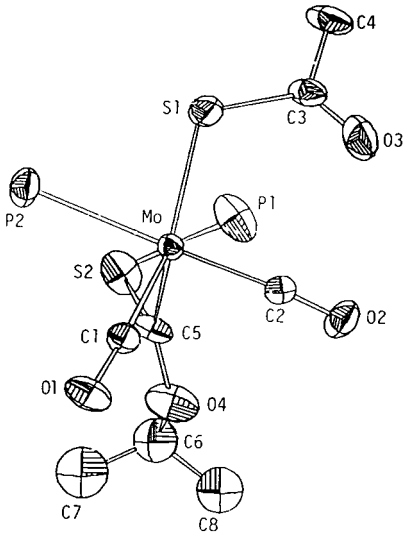
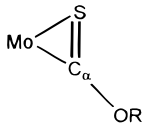


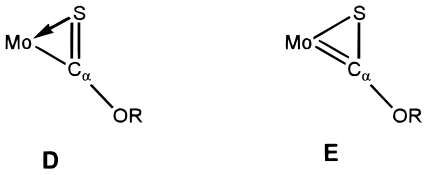
Figure 2. ORTEP perspective view of **5c-*cis***.



	4d	**5c-*cis***
Mo-Cα (Å)	2.018(3)	1.96(1)
Cα-S (Å)	1.670(4)	1.62(1)

Figure 3. Some relevant geometrical parameters for the Mo−C(S)OR entity of **4d** and **5c-*cis***.

Figure 3. Bonding to molybdenum is clearly evinced by



the small value of the Mo−C−S angle within this unit, which approaches 90° (for example, 86.2(1)° for **4d**) and additionally by the significant bonding interaction between the metal center and the sulfur atom. Actually, this Mo−S distance is comparable to the Mo−S separations that involve the xanthate or the thioacetate groups. For instance, in complex **4d** Mo−S3 = 2.534(1) Å, while Mo−S1 and Mo−S2 amount to 2.538(1) and 2.595(1) Å, respectively. In **5c-*cis***, the high *trans* influence of the PMe_3 ligands causes the Mo−S2 bond length to increase to 2.663(4) Å.

The Mo−C(S)OR group is also characterized by a short Mo−C_α bond. In **4d**, this length (2.017(3) Å) is slightly longer than the Mo−CO separation of 1.914(3) Å, but in **5c-*cis*** it becomes identical to the two Mo−CO bond lengths within the limits of the experimental error. These Mo−C(S)OR bonds are significantly shorter than typical Mo(II)−alkyl bonds.[22] The C_α−S bond distances of 1.670(4) and 1.62(1) Å found respectively for **4d** and **5c-*cis*** are midway between the values reported in the literature for related C=S and C−S bonds (ca. 1.55 and 1.80 Å).[23] All these data along with the very low-field chemical shift characteristic of this carbon atom (vide supra) seem to indicate that the carbene resonance form **E** has some contribution to the electronic structure of the Mo−C(S)OR moiety.

Finally, as shown in Figure 3 the monothioacetate ligand of **5c-*cis*** is bonded to the molybdenum atom through the sulfur, i.e., in a monodentate form. The Mo−S1 separation of 2.511(4) Å is typical of a single bond, whereas the C3−O3 distance of 1.19(2) Å corresponds to a double bond between these atoms. Presumably, the Mo−S1−C3 angle of 113.6° is somewhat larger than the tetrahedral to minimize steric repulsions with the PMe_3 ligands. Other bonding parameters are comparable to those already reported for κ^1S-S(O)CR ligands.[24]

Experimental Section

Microanalyses were carried out either by the Analytical Service of the University of Sevilla or by Pascher Microanalytical Laboratory, Remagen (Germany). IR spectra were recorded both as Nujol mulls and in an appropriate solvent on a Perkin-Elmer 684 instrument. ^{1}H, ^{13}C, and ^{31}P NMR spectra were adquired on a Varian XL-200 or a Bruker AMX 300 or 500 spectrometer. $^{31}P\{^1H\}$ NMR shifts were referenced to external 85% H_3PO_4, while $^{13}C\{^1H\}$ and ^{1}H shifts were referenced to the residual protio signals of deuterated solvents. All data are reported in ppm downfield from $SiMe_4$. All manipulations were performed under oxygen-free nitrogen or argon following conventional Schlenk techniques or by using a Vacuum Atmospheres drybox. Solvents were dried under an appropriate desiccant, deoxygenated and freshly distilled prior to use. $Mo(C(O)CH_3)Cl(CO)(PMe_3)_3$ and $Mo(C(O)CH_3)(S_2COR)(CO)(PMe_3)_2$ were prepared as described previously.[9a] Dithiocarbamate and xanthate salts as well as PMe_3 were synthesized according to literature procedures. All other reagents were purchased from commercial suppliers.

Mo(κ^2C,S-C(S)OR)(κ^2S,O-SC(O)R)(CO)(PMe_3)$_2$ (2a−d). All these compounds were prepared in a similar manner. Reactions were monitored by $^{31}P\{^1H\}$ NMR spectroscopy until conversions around 80% were observed. The very high solubility of derivatives **2** in typical organic solvents precluded their purification from minor impurities produced along the reaction. Below is exemplified the procedure for the generation of **2c**. A red solution of $Mo(C(O)CH_3)(S_2CO$-*i*-Pr$)(CO)(PMe_3)_2$ (0.45 g, 1.0 mmol) in THF (40 mL) was stirred at room temperature for 3 days, when the reaction mixture showed a conversion of 80%. Volatiles were then removed under reduced pressure, and the residue was extracted with petroleum ether (10 mL). Centrifugation of the mixture and subsequent evaporation of the solvent yielded the desired compound as a red oil slightly impure.

Mo(κ^2C,S-C(S)OMe)(κ^2S,O-SC(O)Me)(CO)(PMe_3)$_2$ (2a). IR (Nujol mull cm^{-1}): 1802 (s) (ν_{CO}). ^{1}H NMR (20 °C, C_6D_6):

(22) (a) Carmona, E.; Wilkinson, G.; Rogers, R. D.; Hunter, W. E.; Zaworotko, M. J.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1980**, 229. (b) Girolami, G. S.; Mainz, V. V.; Andersen, R. A.; Vollmer, S. H.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 3953.

(23) Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *Organometallics* **1992**, *11*, 3931.

(24) (a) El-Hinnawi, M. A.; Al-Ajlouni, A. M.; AbuNasser, J. S.; Powell, A. K.; Vahrenkamp, H. *J. Organomet. Chem.* **1989**, *359*, 79. (b) El-Hinnawi, M. A.; Sumadi, M. L.; Esmadi, F. T.; Jibril, I.; Imhof, W.; Huttner, G. *Organomet. Chem.* **1989**, *377*, 373.

δ 1.42 (t, J_{HP} = 3.7 Hz, 2 PMe_3), 1.98 (t, J_{HP} = 3.0 Hz, CMe), 3.75 (s, OMe). $^{31}P\{^1H\}$ NMR (20 °C, C_6D_6): δ 7.9 (s). $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6): δ 16.2 (t, J_{CP} = 12 Hz, 2 PMe_3), 34.8 (s, C*Me*), 68.7 (s, OMe), other resonances not observed.

Mo(κ^2*C,S*-C(S)OEt)(κ^2*S,O*-SC(O)Me)(CO)(PMe_3)$_2$ (2b). IR (Nujol mull cm^{-1}): 1812 (s) (ν_{CO}). ^1H NMR (20 °C, C_6D_6): δ 0.92 (t, J_{HH} = 7.1 Hz, CH_2*Me*), 1.45 (t, J_{HP} = 3.8 Hz, 2 PMe_3), 1.99 (t, J_{HP} = 2.8 Hz, CMe), 4.22 (t, J_{HH} = 7.1 Hz, *CH_2*Me). $^{31}P\{^1H\}$ NMR (20 °C, C_6D_6): δ 6.3 (s). $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6): δ 16.4 (t, J_{CP} = 12 Hz, 2 PMe_3), 14.5 (s, OCH_2*Me*), 35.0 (s, SC(O)*Me*), 79.9 (s, OCH_2), 217.5 (t, J_{CP} = 5 Hz, S*C*(O)Me), 247.5 (t, J_{CP} = 14 Hz, CO), 297.1 (t, J_{CP} = 19 Hz, *C*(S)OEt).

Mo(κ^2*C,S*-C(S)O-*i*-Pr)(κ^2*S,O*-SC(O)Me)(CO)(PMe_3)$_2$ (2c). IR (Nujol mull cm^{-1}): 1815 (s) (ν_{CO}). ^1H NMR (20 °C, C_6D_6): δ 1.05 (d, J_{HH} = 6.2 Hz, CH*Me_2*) 1.46 (t, J_{HP} = 3.8 Hz, 2 PMe_3), 2.00 (t, J_{HP} = 2.8 Hz, CMe), 4.84 (h, J_{HH} = 6.2 Hz, C*H*Me_2). $^{31}P\{^1H\}$ NMR (20 °C, C_6D_6): δ 6.3 (s). $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6): δ 16.1 (t, J_{CP} = 12 Hz, 2 PMe_3), 21.6 (s, CH*Me_2*), 34.8 (s, SC(O)*Me*), 89.6 (s, *C*HMe_2), 217.2 (t, J_{CP} = 5 Hz, S*C*(O)Me), 247.4 (t, J_{CP} = 14 Hz, CO), 295.0 (t, J_{CP} = 20 Hz, *C*(S)O-*i*-Pr).

Mo(κ^2*C,S*-C(S)O-*t*-Bu)(κ^2*S,O*-SC(O)CH_2SiMe_3)(CO)(PMe_3)$_2$ (2d). IR (diethyl ether cm^{-1}): 1825 (s) (ν_{CO}). $^{31}P\{^1H\}$ NMR (20 °C, C_6D_6): δ 6.2 (s). $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6): δ −1.3 (s, $SiMe_3$), 16.6 (t, J_{CP} = 12 Hz, 2 PMe_3), 27.3 (s, C*Me_3*), 43.1 (s, SC(O)*C*H_2), 91.5 (s, *C*Me_3), 218.2 (t, J_{CP} = 7 Hz, S*C*(O)CH_2), 248.8 (t, J_{CP} = 15 Hz, CO), 290.9 (t, J_{CP} = 20 Hz, *C*(S)O-*t*-Bu).

Mo(κ^2*C,S*-C(S)O-*i*-Pr)(κ^2*S,O*-SC(O)Me)(CO)(dmpe) (3). This compound can be made from Mo(η^2-C(O)Me)(S_2CO-*i*-Pr)(CO)(dmpe), following a procedure analogous to that described above for complexes **2**. An alternative and synthetically more convenient procedure involves the decarbonylation of **6**. A solution of **6** (0.24 g, 0.5 mmol) in THF (20 mL) was stirred under reduced pressure for several hours, then the volatiles were removed under vacuum, and the resulting residue was crystallized from petroleum ether. The desired complex **3** was isolated as red crystals in 90% yield. Anal. Calcd for $C_{13}H_{26}O_3P_2S_2Mo$: C, 34.5; H, 5.8. Found: C, 34.5; H, 6.0. IR (Nujol mull cm^{-1}): 1795 (s), 1594 (w) (ν_{CO}), 1266 (s), 1155 (s), 1090 (s) (ν_{CS}). ^1H NMR (20 °C, C_6D_6): δ 0.95 (d, J_{HP} = 8.1 Hz, PMe), 1.10 (d, J_{HH} = 6.2 Hz, CH*Me_2*), 1.16 (d, J_{HH} = 6.2 Hz, CH*Me_2*), 1.34 (d, J_{HP} = 9.2 Hz, PMe), 1.40 (brs, PCH_2CH_2), 1.50 (d, J_{HP} = 8.9 Hz, PMe), 1.53 (d, J_{HP} = 9.4 Hz, PMe), 2.11 (d, J_{HP} = 2.0 Hz, SC(O)Me), 5.17 (h, J_{HH} = 6.2 Hz, C*H*Me_2). $^{31}P\{^1H\}$ NMR (20 °C, C_6D_6): δ 44.6, 61.7 (d, J_{PP} = 42 Hz). $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6): δ 11.3 (d, J_{CP} = 15 Hz, PMe), 14.9 (d, J_{CP} = 30 Hz, PMe), 15.5 (d, J_{CP} = 23 Hz, PMe), 17.0 (d, J_{CP} = 30 Hz, PMe), 27.7 (dd, J_{CP} = 29, 16 Hz, PCH_2), 30.9 (dd, J_{CP} = 27, 22 Hz, PCH_2), 21.7 (s, CH*Me_2*), 21.8 (s, CH*Me_2*), 35.8 (s, SC(O)*Me*), 223.9 (d, J_{CP} = 3 Hz, S*C*(O)Me), 237.0 (dd, J_{CP} = 10, 9 Hz, CO), 289.9 (d, J_{CP} = 36 Hz, *C*(S)O-*i*-Pr).

Mo(κ^2*C,S*-C(S)O-*i*-Pr)(κ^2*S,S*′-S_2COEt)(CO)(PMe_3)$_2$ (4b). To a solution of compound **2c** (0.75 mmol estimated by $^{31}P\{^1H\}$ from evolution of acyl xanthate Mo(C(O)CH_3)(S_2CO-*i*-Pr)(CO)(PMe_3)$_2$) in THF (40 mL) was added KS_2COEt (0.12 g, 0.75 mmol). The resulting mixture was stirred over a period of 2 h at room temperature, then the volatiles were removed under vacuum, and the residue was extracted with petroleum ether (30 mL). Centrifugation, followed by concentration and cooling of the resulting liquor, afforded **4b** as a red crystalline material (90% yield). Anal. Calcd for $C_{14}H_{30}O_3P_2S_3Mo$: C, 33.6; H, 6.0. Found: C, 33.1; H, 6.0. IR (Nujol mull cm^{-1}): 1792 (s) (ν_{CO}), 1267 (s), 1202 (s), 1152 (s), 1089 (s), 1049 (s) (υ_{CS}). ^1H NMR (20 °C, C_6D_6): δ 0.97 (t, J_{HH} = 6.2 Hz, CH_2*Me*), 1.08 (d, J_{HH} = 6.2 Hz, CH*Me_2*), 1.50 (t, J_{HP} = 3.8 Hz, 2 PMe_3), 4.21 (q, J_{HP} = 6.2 Hz, C*H_2*Me), 4.90 (t, J_{HH} = 6.2 Hz, C*H*Me_2). $^{31}P\{^1H\}$ NMR (20 °C, C_6D_6): δ 3.6 (s). $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6): δ 13.6 (s, OCH_2*Me*), 16.4 (t, J_{CP} = 12 Hz, 2 PMe_3), 21.6 (s, CH*Me_2*), 66.4 (s, OCH_2), 89.1 (s, O*C*HMe_2), 220.9 (t, J_{CP} = 6 Hz, S_2C), 241.1 (t, J_{CP} = 15 Hz, CO), 296.9 (t, J_{CP} = 20 Hz, *C*(S)O-*i*-Pr).

Mo(κ^2*C,S*-C(S)O-*i*-Pr)(κ^2*S,S*′−*S_2CO*-*i*-Pr)(CO)(PMe_3)$_2$ (4c). This compound was obtained as red crystals (90% yield) using the procedure described for **4b**, but employing KS_2CO-*i*-Pr. Alternatively it could be prepared by addition of an excess of KS_2CO-*i*-Pr (0.5 g, 3 mmol) to a stirred solution of Mo(η^2-C(O)CH_3)Cl(CO)(PMe_3)$_3$ (0.43 g, 1.0 mmol) in Et_2O (45 mL). After 24 h the solvent was removed under vacuum, and the residue extracted with petroleum ether. Centrifugation and concentration of the resulting liquor produced **4c** in 30% yield. Anal. Calcd for $C_{15}H_{32}O_3P_2S_3Mo$: C, 35.0; H, 6.2. Found: C, 35.4; H, 6.2. IR (Nujol mull cm^{-1}): 1801 (s) (ν_{CO}), 1270 (s), 1221 (s), 1093 (s), 1043 (ν_{CS}). ^1H NMR (20 °C, C_6D_6): δ 1.07 (d, J_{HH} = 6.2 Hz, CH*Me_2*), δ 1.08 (d, J_{HH} = 6.2 Hz, CH*Me_2*), 1.51 (t, J_{HP} = 3.8 Hz, 2 PMe_3), 4.90 (t, J_{HH} = 6.2 Hz, C*H*Me_2), 5.37 (t, J_{HH} = 6.2 Hz, C*H*Me_2). $^{31}P\{^1H\}$ NMR (20 °C, C_6D_6): δ 5.3 (s). $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6): δ 16.5 (t, J_{CP} = 12 Hz, 2 PMe_3), 21.4 (s, CH*Me_2*), 21.6 (s, CH*Me_2*), 74.2 (s, O*C*HMe_2), 89.2 (s, O*C*HMe_2), 220.5 (t, J_{CP} = 7 Hz, S_2C), 241.3 (t, J_{CP} = 15 Hz, CO), 297.0 (t, J_{CP} = 20 Hz, *C*(S)O-*i*-Pr).

Mo(κ^2*C,S*-C(S)O-*t*-Bu)(κ^2*S,S*′−*S_2CO*-*t*-Bu)(CO)(PMe_3)$_2$ (4d). This complex was obtained by treating Mo(η^2-C(O)CH_3)Cl(CO)(PMe_3)$_3$ with an excess of KS_2CO-*t*-Bu as described for **4c** (yield 40%). Anal. Calcd for $C_{17}H_{36}O_3P_2S_3Mo$: C, 37.6; H, 6.6. Found: C, 37.2; H, 6.6. IR (Nujol mull cm^{-1}): 1790 (s) (ν_{CO}), 1278 (s), 1237 (s), 1131 (s), 1048 (ν_{CS}). ^1H NMR (20 °C, C_6D_6): δ 1.44 (s, CMe_3), 1.47 (s, CMe_3), 1.51 (t, J_{HP} = 3.8 Hz, 2 PMe_3). $^{31}P\{^1H\}$ NMR (20 °C, C_6D_6): δ 6.2 (s). $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6): δ 16.6 (t, J_{CP} = 12 Hz, 2 PMe_3), 27.3 (s, C*Me_3*), 28.1 (s, C*Me_3*), 86.9 (s, *C*Me_3), 91.4 (s, *C*Me_3), 220.2 (t, J_{CP} = 7 Hz, S_2C), 242.3 (t, J_{CP} = 15 Hz, CO), 293.4 (t, J_{CP} = 19 Hz, *C*(S)O-*t*-Bu).

Mo(κ^2*C,S*-C(S)O-*i*-Pr)(κ^1*S*-SC(O)Me)$(CO)_2$(PMe_3)$_2$ (5c-*cis*). Through a cooled solution (−20 °C) of Mo(C(O)CH_3)(S_2CO-*i*-Pr)(CO)(PMe_3)$_2$ (0.45 g, 1.0 mmol) in Et_2O (40 mL) carbon monoxide was slowly bubbled for ca. 10 min. The color of the solution changed from red to pale yellow. Temperatures below −20 °C were kept over all the workup procedure. The solvent was stripped under vacuum, and the residue extracted with petroleum ether (35 mL). After filtration, the solution volume was concentrated and cooled at −35 °C to produce **5c-*cis*** as yellow crystals (70%). Anal. Calcd for $C_{14}H_{28}O_4P_2S_2Mo$: C, 34.9; H, 5.8. Found: C, 34.9; H, 5.7. IR (Nujol mull cm^{-1}): 1996 (s), 1887 (s), 1618 (m) (ν_{CO}), 1286 (s), 1142 (s), 1088 (ν_{CS}). ^1H NMR (−30 °C, $C_6D_5CD_3$): δ 1.04 (d, J_{HP} = 9.5 Hz, PMe_3), 1.08 (d, J_{HH} = 6.2 Hz, CH*Me_2*), 1.17 (d, J_{HP} = 9.5 Hz, PMe_3), 2.63 (s, SC(O)Me), 5.05 (h, J_{HH} = 6.2 Hz, C*H*Me_2). $^{31}P\{^1H\}$ NMR (−30 °C, $C_6D_5CD_3$): δ −0.9, −16.3 (d, J_{PP} = 42 Hz). $^{13}C\{^1H\}$ NMR (20 °C, $C_6D_5CD_3$): δ 14.4 (d, J_{CP} = 21 Hz, PMe_3), 18.7 (d, J_{CP} = 27 Hz, PMe_3), 21.7 (s, CH*Me_2*), 35.5 (s, SC(O)*Me*), 90.8 (s, *C*HMe_2), 201.6 (s, S*C*(O)Me), other resonances not observed.

Upon standing at room temperature, solutions of **5c-*cis*** convert into a mixture of this compound and two *trans* isomers in a ratio of 1:0.75:0.20, respectively. NMR data for the major *trans* isomer are as follows. IR (petroleum ether, cm^{-1}): 1966 (s), 1900 (s), 1640 (m) (ν_{CO}). ^1H NMR (20 °C, $C_6D_5CD_3$): δ 1.07 (d, J_{HH} = 6.2 Hz, CH*Me_2*), 1.39 (t, J_{HP} = 3.9 Hz, 2 PMe_3), 2.53 (t, J_{HH} = 1.0 Hz, SC(O)Me), 4.76 (h, J_{HH} = 6.2 Hz, C*H*Me_2). $^{31}P\{^1H\}$ NMR (20 °C, $C_6D_5CD_3$): δ −7.6 (s). $^{13}C\{^1H\}$ NMR (20 °C, $C_6D_5CD_3$): δ 18.7 (t, J_{CP} = 14 Hz, 2 PMe_3), 21.6 (s, CH*Me_2*), 34.4 (s, SC(O)*Me*), 88.9 (s, *C*HMe_2), 201.6 (s, S*C*(O)Me), other resonances not observed.

Mo(κ^2*C,S*-C(S)OMe)(κ^1*S*-SC(O)Me)$(CO)_2$(PMe_3)$_2$ (5a-*cis*). It was prepared as described for **5c-*cis*** (see above). Yield: 50%. IR (Nujol mull cm^{-1}): 1970 (s), 1915 (s), 1620 (m) (ν_{CO}), 1280 (s), 1130 (s), 1100 (ν_{CS}). ^1H NMR (−20 °C, $C_6D_5CD_3$): δ 1.02 (d, J_{HP} = 9.5 Hz, PMe_3), 1.19 (d, J_{HP} = 9.4 Hz, PMe_3), 2.64 (s, SC(O)Me), 3.71 (s, OMe). $^{31}P\{^1H\}$ NMR (−20 °C, $C_6D_5CD_3$): δ −2.1, −17.8 (d, J_{PP} = 15 Hz). $^{13}C\{^1H\}$ NMR (20 °C, $C_6D_5CD_3$): δ 14.4 (d, J_{CP} = 22 Hz, PMe_3), 18.6 (d, J_{CP}

= 28 Hz, PMe_3), 36.0 (s, SC(O)*Me*), 68.1 (s, OMe), 202.0 (s, S*C*(O)Me), 205.4 (d, J_{CP} = 9 Hz CO), other resonances not observed.

Mo(κ^2*C,S*-C(S)OMe)(κ^1*S*-SC(O)Me)(CO)$_2$(PMe$_3$)$_2$ (5a-*trans*). IR (diethyl ether cm^{-1}): 1970 (s), 1896 (s) (ν_{CO}). ^{1}H NMR (20 °C, $C_6D_5CD_3$): δ 1.37 (t, J_{HP} = 3.9 Hz, 2 PMe_3), 2.51 (t, J_{HP} = 1.0 Hz, SC(O)Me), 3.70 (s, OMe). ^{31}P{^{1}H} NMR (−20 °C, $C_6D_5CD_3$): δ −9.0 (s). ^{13}C{^{1}H} NMR (20 °C, $C_6D_5CD_3$): δ 19.1 (t, J_{CP} = 13 Hz, 2 PMe_3), 34.6 (s, SC(O)*Me*), 68.5 (s, OMe), 201.7 (s, S*C*(O)Me), 213.4 (brm, CO), 293.4 (t, J_{CP} = 22 Hz, *C*(S)OMe).

Mo(κ^2*C,S*-C(S)O-*i*-Pr)(κ^1*S*-SC(O)Me)(CO)$_2$(dmpe) (6). Obtained as described for **5c-*cis*** (see above). Yield: 60%. Anal. Calcd for $C_{14}H_{26}O_4P_2S_2Mo$: C, 35.0; H, 5.5. Found: C, 35.0; H, 5.7. IR (Nujol mull cm^{-1}): 1990 (s), 1875 (s), 1625 (m) (ν_{CO}), 1275 (s), 1140 (s), 1095 (ν_{CS}). ^{1}H NMR (20 °C, C_6D_6): δ 1.00 (d, J_{HH} = 6.2 Hz, CH*Me*$_2$), 1.0 (brd, PCH_2CH_2), 1.29 (d, J_{HP} = 8.8 Hz, 2 PMe), 1.35 (d, J_{HP} = 9.0 Hz, 2 PMe), 2.81 (s, SC(O)-Me), 4.85 (h, J_{HH} = 6.2 Hz, C*H*Me$_2$). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 37.1, 51.3 (d, J_{PP} = 28 Hz). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 16.5 (d, J_{CP} = 28 Hz, 2 PMe), 16.6 (d, J_{CP} = 26 Hz, 2 PMe), 21.3 (s, CH*Me*$_2$), 27.7 (dd, J_{CP} = 26, 16 Hz, PCH_2), 30.2 (dd, J_{CP} = 29, 18 Hz, PCH_2), 35.1 (s, SC(O)*Me*), 89.0 (s, *C*HMe$_2$), 201.8 (s, S*C*(O)Me),), 210.6 (t, J_{CP} = 8 Hz, 2 CO), 295.6 (dd, J_{CP} = 33, 4 Hz, *C*(S)O-*i*-Pr).

X-ray Structure Determinations of 4d and 5c-*cis*. Studies were performed with a Kappa difractometer. The cell dimensions were refined by least-squares fitting the θ values of 25 reflections with a 2θ range of 13−35°. 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.[25] The Structures were solved by Patterson and Fourier methods. An empirical absorption correction was applied at the end of the isotropic refinement. Most calculations were carried out with the X-ray 80 system.[26]

Complex 4d. A dark red crystal was coated with an epoxy resin. It was found to crystallize in space group *P*1. Final refinement with a fixed isotropic factor for H atoms led to final values of R = 0.032 and R_w = 0.034.

Compound 5c-*cis*. A pale yellow crystal was sealed in a glass capillary. It crystallizes in the space group $P2_1/m$. Because of decomposition of the crystal and nonresolvable disorder from thermal motion of the SCO-*i*-Pr and PMe_3 groups, some carbon atoms have been refined isotropically, leading to R values higher than usual. No trend in ΔF versus F_o or sinθ/λ was observed. A final refinement was undertaken with isotropic and anisotropic thermal parameters, and the hydrogen atoms were included with fixed isotropic contributions at their calculated positions. Final difference synthesis showed no significant electron density.

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Supporting Information Available: Tables of atomic parameters, bond lengths and angles, and thermal parameters for **4d** and **5c-*cis***. This material is available free of charge via the Internet at http://pubs.acs.org.

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