Agostic Acetyl Complexes of Molybdenum. Solution Behavior and Solid-State Structure

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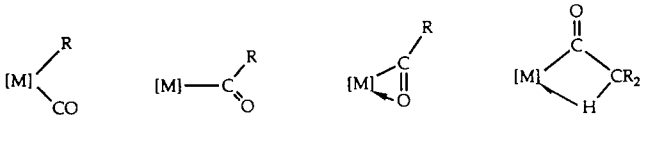
Molybdenum acetyl complexes of composition $Mo(C(O)CH_3)(L\text{-}L)CO(PMe_3)_2$ containing different bidentate anionic S- and O-donor ligands have been prepared and characterized. The dithiocarbamate derivatives (L-L = S_2CNR_2; R = Me (**1a**), *i*-Pr (**1b**), C_5H_{10} (**1c**)) have been found to display the agostic acetyl structure $Mo(C(O)CH_3)$ both in solution and in the solid state, as confirmed by X-ray studies carried out on complex **1c**. This compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters a = 9.408 (3) Å, b = 10.972 (8) Å, c = 11.720 Å, β = 76.60 (2)°, and D_c = 1.44 g cm^{-3} for Z = 2. Least-squares refinement using 6459 independent observed reflections led to a final R value of 0.051. The related xanthate ligands form two types of complexes: the normal xanthates $Mo(C(O)CH_3)(S_2COR)CO(PMe_3)_2$ (R = Me (**2a**), Et (**2b**), *i*-Pr (**2c**)) and phosphonium xanthates $Mo(C(O)CH_3)(S_2C(PMe_3)OR)CO(PMe_3)_2$ (R = Me (**3a**), CF_3CH_2 (**3b**), *i*-Pr (**3c**)). Compounds **2** are agostic in the solid state but exist in solution as equilibrium mixtures of the agostic acetyl $Mo(C(O)CH_3)(S_2COR)CO(PMe_3)_2$, the bidentate acyl $Mo(\eta^2\text{-}C(O)CH_3)(S_2COR)CO(PMe_3)_2$, and the methyl dicarbonyl $Mo(CH_3)(S_2COR)(CO)_2(PMe_3)_2$. For **3**, the Me and *i*-Pr derivatives readily lose PMe_3 to convert into the normal xanthates **2a** and **2c**, respectively, but **3b** is stable toward loss of PMe_3 and has an agostic structure both in solution and in the solid state. Crystals of **3b** are monoclinic, space group $C2/c$, with cell parameters a = 29.698 (3) Å, b = 9.368 (3) Å, c = 20.992 (3) Å, β = 117.10 (1)°, and D_c = 1.46 g cm^{-3} for Z = 8. Least-squares refinement based on 4773 observed reflections led to a final R value of 0.027. Other related complexes containing the O-donor ligands acac and *t*-Bu-acac (acac = $CH_3C(O)CHC(O)CH_3$ (**4a**); *t*-Bu-acac = $Me_3CC(O)CHC(O)CMe_3$ (**4b**)) have also been prepared and characterized.

Introduction

Acyl complexes of the transition metals constitute an important class of organometallic compounds.[1] Their preparation is frequently based on the migration of an alkyl group to a coordinated carbon monoxide ligand (structure A). Most of the acyl complexes initially described exhibit unidentate coordination[2] (B), although in recent years a growing number of η^2-acyl complexes (C) have been prepared and characterized.[3-6] In 1983, we reported the formation of a unique acetyl complex,[6b,c] $Mo(C(O)CH_3)(S_2CNMe_2)CO(PMe_3)_2$ (**1a**), in which the Mo atom attains an 18-electron configuration by virtue of an agostic[7] interaction with a β-C–H bond[8] of the acyl ligand (D). This was found to be thermodynamically competitive, both in solution and in the solid state, with the η^2-acyl coordination.



A B C D

Although 9 years has elapsed since our original report, no other agostic acyls have, to our knowledge, been described in the literature, despite the large number of agostic interactions discovered during this period of time.[7] Our attempts to reproduce these results in the tungsten system analog have led instead to alkyl carbonyl complexes[6e] or to equilibrium mixtures of compounds exhibiting the isomeric structures A and C.[6f] In order to better understand the factors that govern the adoption of coor-

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dination mode D, we have set out to prepare a number of complexes related to **1a**, containing different bidentate anionic S- and O-donor ligands. Herein we report the results of this study, which include observation of fast solution equilibria involving the isomeric structures A, C, and D, as well as the structural characterization by X-ray methods of two other agostic complexes, $\overline{Mo(C(O)CH_3)}(S_2CNC_5H_{10})CO(PMe_3)_2$ (**1c**) and $\overline{Mo(C(O)CH_3)}(S_2C(PMe_3)OCH_2CF_3)CO(PMe_3)_2$ (**3b**). Part of this work has been communicated in preliminary form.[6i]

Results and Discussion

Preparation and Properties of the Acetyls $Mo(C(O)CH_3)(L\text{-}L)CO(PMe_3)_2$. X-ray Structure of Complexes 1c (L-L = $S_2CNC_5H_{10}$) and 3b (L-L = $S_2C(PMe_3)OCH_2CF_3$). The agostic acyl **1a** was originally prepared by the room-temperature reaction of the η^2-acyl $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$ with NaS_2CNMe_2,[6c] over a period of 2–3 h (eq 1). Although the analogous dithiocarbamate complexes $\overline{Mo(C(O)CH_3)}(S_2CNR_2)CO(PMe_3)_2$ (R_2 = i-Pr_2 (**1b**), C_5H_{10} (piperidine derived, **1c**)) can be obtained similarly, the synthesis of the xanthate derivatives $Mo(C(O)CH_3)(S_2COR)CO(PMe_3)_2$ (R = Me (**2a**), Et (**2b**), i-Pr (**2c**)) requires shorter reaction times (between 15 and 30 min) and temperatures in the range from 0 to −10 °C. At variance with the above results, the reaction of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$ with the potassium salt of the weaker donor pyrrole-derived dithiocarbamate ligand provides instead the bidentate acyl **1d** as depicted in eq 2.

$$Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3 \xrightarrow[-NaCl,\ -PMe_3]{NaS_2CNMe_2} \underset{\mathbf{1a}}{\overline{Mo(C(O)CH_3)}(S_2CNMe_2)CO(PMe_3)_2} \quad (1)$$

$$Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3 \xrightarrow[-KCl,\ -PMe_3]{KS_2CNC_4H_4} \underset{\mathbf{1d}}{Mo(\eta^2\text{-}C(O)CH_3)(S_2CNC_4H_4)CO(PMe_3)_2} \quad (2)$$

The Mo–xanthate system is somewhat more complex than the dithiocarbamate analog, and two types of product can be isolated, depending upon the nature of the R group. Thus, the electron-withdrawing CF_3CH_2 group yields the phosphonium xanthate[9] species **3b** (eq 3), while the xanthate ligands derived from the stronger donor methyl, ethyl, and isopropyl groups afford in addition the normal xanthates $\overline{Mo(C(O)CH_3)}(S_2COR)CO(PMe_3)_2$ (**2**). For R = Me and i-Pr, both types of derivatives, **2a,c** and **3a,c**, have been isolated and shown to interconvert by PMe_3 association or dissociation (eq 4). For these ligands, however, the equilibrium is shifted well to the left and isolation of the phosphonium xanthates **3** is made possible by their low solubility in common organic solvents. At room temperature complexes **3a,c** lose PMe_3 in solution to produce the corresponding xanthates **2a,c**.

$$Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3 \xrightarrow[-NaCl]{NaS_2COCH_2CF_3} \underset{\mathbf{3b}}{\overline{Mo(C(O)CH_3)}(S_2C(PMe_3)OCH_2CF_3)CO(PMe_3)_2} \quad (3)$$

$$\underset{\mathbf{2a,c}}{\overline{Mo(C(O)CH_3)}(S_2COR)CO(PMe_3)_2} \underset{-PMe_3}{\overset{PMe_3}{\rightleftharpoons}} \underset{\mathbf{3a,c}}{\overline{MoC(O)CH_3)}(S_2C(PMe_3)OR)CO(PMe_3)_2} \quad (4)$$

Oxygen-containing bidentate anionic ligands provide similar results, and for example the complexes $\overline{Mo(C(O)CH_3)}(L\text{-}L)CO(PMe_3)_2$ (**4**: L-L = $CH_3C(O)CHC(O)CH_3$ (acac, **4a**), $Me_3CC(O)CHC(O)CMe_3$ (t-Bu-acac, **4b**)) can be prepared similarly to the xanthates **2**. The acac derivative **4a** is somewhat more unstable in solution and disproportionates slowly, at room temperature, into a mixture of the η^2-acyl $Mo(\eta^2\text{-}C(O)CH_3)(acac)(CO)_2(PMe_3)$ and the alkyl $Mo(CH_3)(acac)CO(PMe_3)_3$. Details for this disproportionation are provided in the Experimental Section.

All the agostic acyl complexes mentioned above are red crystalline solids that can be handled in air for short periods of time without noticeable decomposition. When stored under N_2 at −10 °C, they appear to be indefinitely

Table I. Crystal and Refinement Data for 1c and 3b

formula	$C_{15}H_{31}MoNO_2P_2S_2$	$C_{15}H_{32}F_3MoO_3P_3S_2$
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a, Å	9.408 (3)	29.698 (3)
b, Å	10.972 (8)	9.368 (3)
c, Å	11.720 (2)	20.992 (3)
α, deg	80.93 (2)	
β, deg	76.60 (2)	117.10 (1)
γ, deg	70.57 (5)	
V, Å^3	1105.5 (9)	5199 (1)
Z	2	8
$F(000)$	496	2336
d_{calcd}, g cm^{-3}	1.44	1.46
temp, °C	22	21
μ(Mo Kα), cm^{-1}	9.1	8.61
cryst dimens, mm	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.2
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	graphite-monochromated Mo Kα (λ = 0.71069 Å)	graphite-monochromated Mo Kα (λ = 0.71069 Å)
scan technique	$\Omega/2\theta$	$\Omega/2\theta$
data collected	(−13,−15,0) to (13,15,16)	(−35,0,0) to (35,11,25)
no. of unique data	6459	4773
no. of unique data $I \geq 2\sigma(I)$	5219	3524
R(int), %	0.9	1.0
std rflns	3/278 rflns	3/201 rflns
R_F, %	3.5	2.6
R_{wF}, %	5.1	2.7
av shift/error	0.09	0.47

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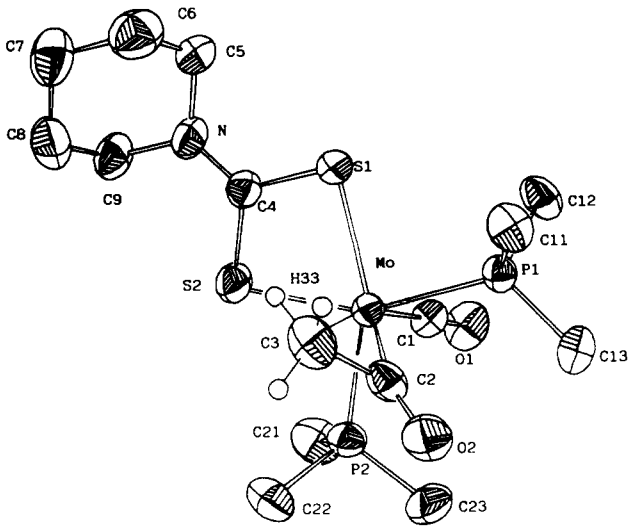

Figure 1. ORTEP diagram of $\overline{Mo(C(O)CH_3)}(S_2CNC_5H_{10})CO(PMe_3)_2$ (**1c**).

Table II. Atomic Parameters for 1c

atom	*x/a*	*y/b*	*z/c*
Mo	0.12821 (3)	0.22925 (3)	0.21849 (2)
P1	0.19281 (10)	0.25369 (8)	0.39965 (7)
P2	−0.17299 (11)	0.22370 (10)	0.22321 (9)
S1	0.40722 (10)	0.20317 (11)	0.13072 (8)
S2	0.18729 (12)	0.18157 (11)	0.00531 (8)
O1	0.10887 (41)	−0.01842 (28)	0.37523 (30)
O2	−0.11795 (36)	0.46844 (28)	0.33884 (29)
N	0.47531 (39)	0.17202 (33)	−0.09912 (27)
C1	0.11919 (40)	0.07517 (31)	0.31235 (30)
C2	−0.01319 (41)	0.40651 (33)	0.26800 (33)
C3	0.05521 (56)	0.48313 (38)	0.15723 (42)
C4	0.37134 (41)	0.18427 (34)	−0.00165 (30)
C5	0.62738 (46)	0.18432 (48)	−0.10786 (36)
C6	0.63915 (66)	0.30595 (59)	−0.18282 (53)
C7	0.60322 (72)	0.30834 (54)	−0.30305 (47)
C8	0.45051 (64)	0.28656 (49)	−0.29204 (43)
C9	0.44431 (57)	0.16435 (48)	−0.21430 (35)
C11	0.26310 (51)	0.39007 (37)	0.39611 (38)
C12	0.35225 (50)	0.11872 (40)	0.44379 (39)
C13	0.04694 (54)	0.26701 (45)	0.53233 (35)
C21	−0.13467 (63)	0.07735 (52)	0.17219 (52)
C22	−0.24282 (54)	0.34810 (50)	0.12957 (47)
C23	−0.25631 (53)	0.23474 (59)	0.36570 (45)

stable. With the exception of the less soluble phosphonium xanthates **3**, they are freely soluble in common organic solvents (benzene, toluene, Et_2O, THF, and acetone). In solution they are sensitive to air, and in addition most of these complexes decompose at temperatures above 0 °C, even when kept under N_2.

The Mo–agostic acyl linkage in complexes **1–4** displays an IR C=O absorption in the region 1615–1580 cm^{-1}, while for related η^2-acyl complexes of Mo and W this band appears in the range[5,6] 1550–1425 cm^{-1}. Therefore, in compounds of this type a distinction between coordination modes C and D can be made on the basis of the energy of the C=O stretching vibration of the acyl ligand. This distinction is further substantiated by detailed NMR studies, to be described in the following section, and also by crystal structure determinations, carried out on two representative complexes.

The molecular structures and atom-labeling schemes for compounds **1c** and **3b** are presented in Figures 1 and 2, respectively. Tables I–V collect crystal data and selected bond lengths and angles for these compounds. If the agostic acyl is considered to formally occupy a single coordination site, the geometry of these complexes can be thought of as derived from a distorted octahedron, with

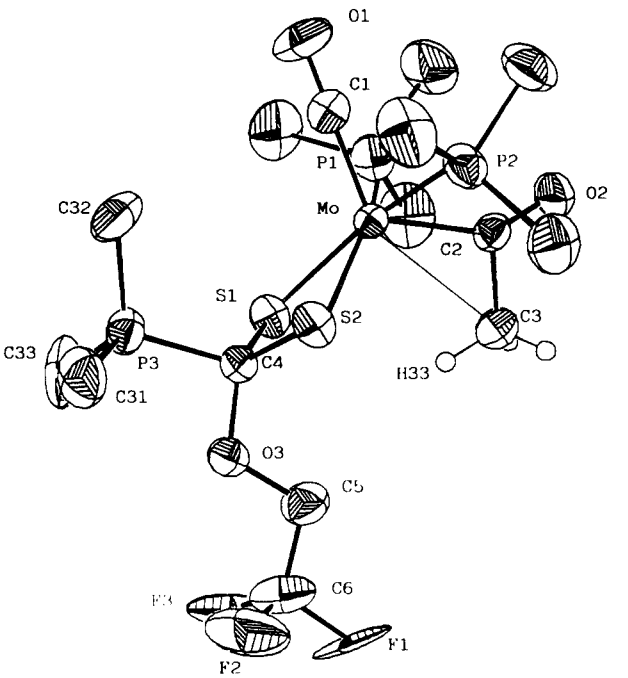

Figure 2. ORTEP diagram of $\overline{Mo(C(O)CH_3)}(S_2C(PMe_3)OCH_2CF_3)CO(PMe_3)_2$ (**3b**).

Table III. Atomic Parameters for 3b

atom	*x/a*	*y/b*	*z/c*
Mo	0.64107 (2)	0.46141 (5)	0.26997 (2)
S1	0.56967 (5)	0.46298 (17)	0.14559 (7)
S2	0.63119 (6)	0.70998 (16)	0.22260 (8)
P1	0.62752 (7)	0.20611 (18)	0.26275 (10)
P2	0.70517 (6)	0.56714 (19)	0.37795 (8)
P3	0.61072 (6)	0.65150 (19)	0.07220 (8)
O1	0.74128 (19)	0.33703 (68)	0.28612 (30)
O2	0.63257 (16)	0.35001 (52)	0.40501 (22)
O3	0.54185 (14)	0.73924 (46)	0.10015 (21)
C1	0.70233 (24)	0.38579 (72)	0.27893 (33)
C2	0.62020 (21)	0.41397 (64)	0.34848 (31)
C3	0.57022 (23)	0.50231 (78)	0.31922 (35)
C4	0.58470 (20)	0.64658 (60)	0.13613 (28)
C5	0.51273 (23)	0.76266 (75)	0.13635 (37)
C6	0.47095 (36)	0.85472 (106)	0.09250 (56)
C11	0.67089 (36)	0.09815 (85)	0.33711 (46)
C12	0.56649 (34)	0.14335 (90)	0.25192 (50)
C13	0.62994 (39)	0.12220 (80)	0.18673 (47)
C21	0.74452 (26)	0.44867 (92)	0.45061 (35)
C22	0.75222 (28)	0.67327 (99)	0.36623 (41)
C23	0.68248 (29)	0.69449 (86)	0.42269 (38)
C31	0.62763 (29)	0.82811 (82)	0.06153 (40)
C32	0.66569 (28)	0.54466 (94)	0.10170 (43)
C33	0.56337 (30)	0.59039 (104)	−0.01185 (35)
F1	0.44222 (23)	0.88616 (68)	0.12415 (32)
F2	0.48538 (22)	0.98057 (71)	0.07920 (32)
F3	0.43992 (24)	0.80260 (72)	0.02999 (36)

the two sulfur and the two phosphorus atoms in the equatorial plane and the acetyl and carbonyl ligands in the axial positions. The most interesting feature of these structures is doubtless the Mo–acetyl interaction, which displaces C(3) and H(33) toward the metal and O(2) away from the metal. This is manifested by the values of the bond distances and angles involving these atoms. Thus, while the Mo–C(2) bond length of 2.060 Å is similar to the corresponding distance in Mo–η^2-acyls (e.g. 2.024 Å in $Mo(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$[6c]), the Mo–C(2)–O(2) angle opens up considerably to a value of ca. 145–149°. For comparison, in the complex $(C_5H_5)Mo(\eta^1\text{-}C(O)CH_3)(CO)_2(PPh_3)$,[10] which contains a monodentate acyl

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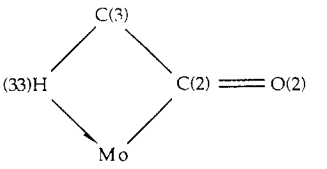
Table IV. Selected Bond Lengths (Å) and Angles (deg) for 1c

Mo-P1	2.417 (2)	S1-C4	1.715 (7)
Mo-P2	2.419 (2)	S2-C4	1.724 (7)
Mo-S1	2.522 (2)	O1-C1	1.174 (8)
Mo-S2	2.532 (2)	O2-C2	1.200 (7)
Mo-C1	1.883 (6)	N-C4	1.317 (7)
Mo-C2	2.060 (6)	N-C5	1.462 (10)
P1-C11	1.810 (9)	N-C9	1.459 (10)
P1-C12	1.835 (7)	C2-C3	1.573 (10)
P1-C13	1.794 (7)	C5-C6	1.524 (12)
P2-C21	1.816 (11)	C6-C7	1.520 (14)
P2-C22	1.821 (8)	C7-C8	1.510 (15)
P2-C23	1.809 (8)	C8-C9	1.504 (11)
Mo-H33	2.33 (8)	Mo-C3	2.659 (4)
C1-Mo-C2	121.6 (3)	Mo-S1-C4	88.1 (3)
S2-Mo-C2	120.2 (2)	Mo-S2-C4	87.6 (2)
S2-Mo-C1	107.6 (2)	C5-N-C9	112.2 (6)
S1-Mo-C2	118.9 (2)	C4-N-C9	123.9 (7)
S1-Mo-C1	107.4 (2)	C4-N-C5	123.3 (6)
S1-Mo-S2	69.72 (7)	S2-C4-N	122.7 (5)
P2-Mo-C2	75.3 (2)	S1-C4-N	123.0 (5)
P2-Mo-C1	76.4 (2)	S1-C4-S2	114.3 (3)
P2-Mo-S2	86.33 (8)	Mo-C1-O1	176.7 (5)
P2-Mo-S1	155.87 (7)	Mo-C2-O2	147.5 (5)
P1-Mo-C2	74.3 (2)	O2-C2-C3	118.6 (6)
P1-Mo-C1	76.2 (2)	Mo-C2-C3	93.9 (4)
P1-Mo-S2	154.7 (1)	N-C5-C6	109.2 (7)
P1-Mo-S1	85.16 (8)	C5-C6-C7	110.2 (8)
P1-Mo-P2	118.52 (7)	C6-C7-C8	111.3 (7)
Mo-H33-C3	93 (4)	C7-C8-C9	110.9 (8)
		N-C9-C8	110.0 (6)

Table V. Selected Bond Lengths (Å) and Angles (deg) for 3b

Mo-S1	2.504 (1)	O1-C1	1.189 (9)
Mo-S2	2.497 (2)	O2-C2	1.226 (6)
Mo-P1	2.419 (2)	O3-C4	1.437 (6)
Mo-P2	2.411 (1)	O3-C5	1.408 (10)
Mo-C1	1.879 (7)	C2-C3	1.561 (9)
Mo-C2	2.057 (7)	C5-C6	1.446 (11)
S1-C4	1.810 (6)	C6-F1	1.332 (16)
S2-C4	1.809 (5)	C6-F2	1.328 (13)
P3-C4	1.828 (7)	C6-F3	1.306 (11)
Mo-H33	2.56 (6)	Mo-C3	2.762 (4)
Cl-Mo-C2	118.0 (3)	Mo-C1-O1	178.5 (6)
P2-Mo-C2	74.5 (2)	Mo-C2-O2	144.4 (5)
P2-Mo-C1	75.4 (2)	O2-C2-C3	116.9 (6)
P1-Mo-C2	74.6 (2)	Mo-C2-C3	98.6 (4)
P1-Mo-C1	76.1 (2)	P3-C4-O3	99.6 (3)
P1-Mo-P2	120.2 (1)	S2-C4-O3	114.7 (4)
S2-Mo-C2	119.8 (2)	S2-C4-P3	110.1 (3)
S2-Mo-C1	108.9 (2)	S1-C4-O3	115.4 (4)
S2-Mo-P2	83.7 (1)	S1-C4-P3	108.2 (3)
S2-Mo-P1	155.7 (1)	S1-C4-S2	108.4 (3)
S1-Mo-C2	114.6 (2)	O3-C5-C6	108.0 (6)
S1-Mo-C1	115.3 (2)	C5-C6-F3	115.2 (8)
S1-Mo-P2	155.4 (1)	C5-C6-F2	113.4 (9)
S1-Mo-P1	84.4 (1)	C5-C6-F1	111.9 (8)
S1-Mo-S2	71.9 (1)	F2-C6-F3	105.6 (8)
Mo-S1-C4	89.2 (2)	F1-C6-F3	105.4 (9)
Mo-S2-C4	89.5 (2)	F1-C6-F2	104.5 (9)
C4-O3-C5	115.2 (5)	Mo-H33-C3	91 (3)

ligand, the corresponding angle is 120.9°, and in the η^2-acyl complexes this angle becomes considerably smaller and has a value of ca. 82°.[3-6] As a result of the displacement of the C(3)–H(33) bond toward molybdenum, the Mo–C(2)–C(3) angle becomes smaller (93.9 (4)°, **1c**; 98.6 (4)°, **3b**). Note for comparison that the corresponding values in η^1- and η^2-acyls are respectively ca. 121°[10] and 154°.[3-6] The Mo–C(3) (2.659 (4) Å, **1c**; 2.762 (4) Å, **3b**) and Mo–H(33) distances (2.33 (8) Å, **1c**; 2.56 (6) Å, **3b**), while longer than in **1a** (2.60 (1) and 2.06 (9) Å, respectively[6c]), are sufficiently short to indicate substantial Mo–C(3) and Mo–H(33) bonding interactions.



	S_2CNMe_2	$S_2CNC_5H_{10}$	$S_2C(PMe_3)OCH_2CF_3$
Mo-C(3)	2.60	2.659	2.762
Mo-H(33)	2.06	2.33	2.56
Mo-C(2)-O(2)	149.2	147.5	144.5
Mo-C(2)-C(3)	90.9	93.9	98.6

Figure 3. Relevant bond distances (Å) and angles (deg) for the $\overline{Mo(C(O)CH_3)}$ moiety in compounds **1a,c** and **3b**.

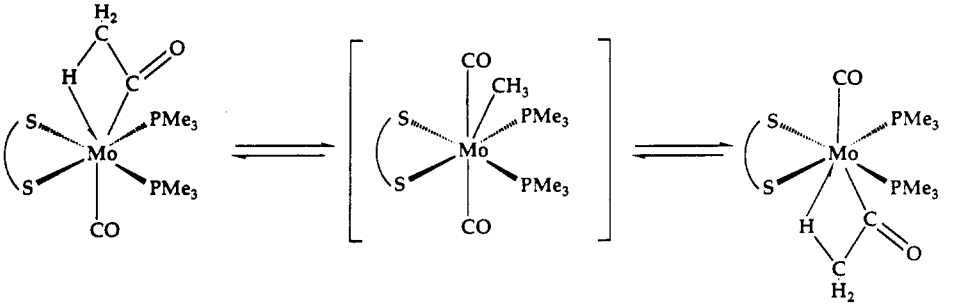
Figure 3 shows a schematic representation of the Mo–agostic acyl linkage and provides in addition some relevant bond distances and angles for this moiety in compounds **1a,c** and **3b**. This allows a comparison of the strength of the agostic interaction in the above complexes to be made. As can be seen from the data in Figure 3, this bonding interaction decreases in the order **1a > 1c > 3b**. This is shown by the values of the Mo–C(3) and Mo–H(33) bond lengths and Mo–C(2)–O(2) and Mo–C(2)–C(3) bond angles. The decrease of the former angle in the order **1a > 1c > 3b** is paralleled by an opposite variation of the latter, which changes from 90.9 (8)° in **1a** to 93.9 (4)° in **1c** and 98.6 (4)° in **3b**. Bond lengths and angles involving the dithio acid and phosphine ligands have normal values and merit no further discussion.

Variable-Temperature NMR Studies of the Agostic Acetyls. Solution Equilibria and Dynamics. As already indicated, IR spectroscopy constitutes an efficient method of characterizing the agostic interaction in these molybdenum acyl complexes. In addition, the agostic methyl group gives rise to a relatively high-field ^1H resonance, in the range δ 1.5–2.1, which appears as a triplet due to coupling to the two magnetically equivalent ^{31}P nuclei (J_{HP} = ca. 2 Hz). For comparison, in related η^2-acyls[6c] this signal appears at lower fields (ca. δ 2.4–2.8) and exhibits no coupling to the ^{31}P nuclei. A similar shift to high field is found for the $^{13}C\{^1H\}$ resonance of the agostic methyl, which appears in the region δ 0–15 and also displays coupling to the ^{31}P nuclei (J_{HP} = ca. 3–4 Hz). For instance, in the normal xanthates **2** this signal appears at low temperatures (see below) in the proximity of δ 0.5 ($^2J_{CP} \simeq 4$ Hz).

All these compounds exhibit fluxional behavior. The agostic structure shown in Figure 3 cannot be completely frozen; in solution fast exchange of the H atoms of the acetyl group occurs even at temperatures of about −90 °C. This behavior is, however, common in compounds of this type,[7,8] although in some cases $\overline{M-C-H}$ rigid structures can be detected.[11] In addition, other dynamic processes take place in solution. For example, the room-temperature $^{13}C\{^1H\}$ NMR spectra of the dithiocarbamate derivatives **1** show only one triplet in the carbonyl region. When the temperature is lowered, this signal broadens, eventually disappears into the base line, and finally converts into two

(11) See for example refs 8a,e,f.

Scheme I



E F G

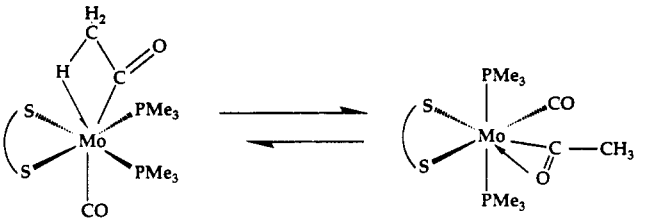
triplets at temperatures below −75 °C (δ 243.8, $^2J_{CP}$ = 30 Hz, M–CO; δ 259.2, $^2J_{CP}$ = 30 Hz, M–$COCH_3$; data for **1a** at −90 °C). From the coalescence temperature (−55 °C, 50 MHz; data for **1a**) a value of 9.4 kcal mol^{-1} can be estimated for the free energy of activation for this process. These observations can be accounted for in terms of the existence at room temperature of a fast equilibrium between the two ground-state degenerate structures E and G shown in Scheme I, through the intermediacy of the alkyl carbonyl F. It seems likely that the first step in this exchange is the formation of an η^1-acyl, which could then undergo rotation around the Mo–C(acyl) bond, followed by deinsertion to yield the proposed alkyl intermediate F. Hence, the agostic formulation D, in addition to a plausible intermediate in the migratory insertion reaction, could be considered as an alternative structural possibility which under appropriate circumstances can compete favorably with the η^2-acyl interaction and the isomeric alkyl carbonyl formulation. No coupling between the methyl and carbonyl carbons can be observed in a sample of **1a** enriched in ^{13}CO, even at −120 °C. We note, however, that very small $^1J_{CC}$ couplings are sometimes found in transition-metal acyl complexes.[12]

The $^{31}P\{^1H\}$ NMR spectrum of **1a**, recorded in toluene or dichloromethane, is a sharp singlet in the temperature range studied (−90 to +40 °C) but becomes broad at temperatures above −40 °C when recorded in acetone. Similarly, compounds **1b,c** also afford sharp $^{31}P\{^1H\}$ singlets at −90 °C in different solvents, but the corresponding signal broadens upon raising the temperature. These data are consistent with the achievement of an equilibrium between the agostic acyls **1** and small amounts of a second species whose concentration is solvent- and temperature-dependent. This is proposed to be the alkyl carbonyl isomer (structure A), but since the xanthate complexes **2** exhibit a similar behavior, more amenable to dynamic NMR studies, the discussion of these features will be postponed until these compounds are considered.

Finally, concerning the dithiocarbamate complexes **1**, magnetic equivalence is observed for the Me_2NCS_2 protons in **1a** in the temperature range studied (−90 to +40 °C), but the *i*-Pr derivative **1b** gives characteristic NMR features that can be ascribed to restricted rotation about the isopropyl–nitrogen bond at low temperatures.[13]

The phosphonium xanthate complexes **3**, of which the Me and CF_3CH_2 derivatives (**3a,b**, respectively) have been studied in detail, and the 2,4-pentanedionate (acac) and 2,2,6,6-tetramethyl-3,5-heptanedionate (*t*-Bu-acac) derivatives (**4a,b**, respectively) display spectroscopic features similar to those discussed above for the dithiocarbamates **1**. Both types of compounds (**3** and **4**) are agostic in the solid state. The phosphonium xanthates **3** seem to exist in solution exclusively as the agostic acyls, no detectable amounts of the proposed alkyl carbonyl isomers being observed. In the case of the dionates **4**, IR and NMR data suggest the achievement in solution of an equilibrium between the agostic structure and small amounts of the corresponding alkyl carbonyl. Thus, the $^{31}P\{^1H\}$ NMR spectrum of solutions of **4a** in $C_6D_5CD_3$, at −90 °C, is a sharp singlet which broadens at temperatures above −40 °C. Observation of the fast-exchange regime in the ^{31}P NMR spectra of this complex is prevented by its limited thermal stability. Room-temperature IR spectra of solutions of **4a** display absorptions at 1787 and 1613 cm^{-1} due to the agostic structure, along with less intense bands at 1897 and 1820 cm^{-1} attributed to the alkyl carbonyl isomer and additional bands at 1935, 1839, and 1742 cm^{-1} corresponding to the products resulting from its disproportionation (see Experimental Section).

Scheme II



IR and NMR data for the xanthate complexes **2** are in accord with an agostic structure for these compounds in the solid state. When crystals of **2a–c** are dissolved at −60 °C and the resulting solution cooled quickly to −100 °C, IR studies reveal the presence of only the agostic structure D (strong bands at 1803 and 1618 cm^{-1}, due to respectively to the terminal carbonyl and acyl ligands; data for **2c** in THF). At −50 °C, an equilibrium is established with a second species (Scheme II) identified as the isomeric η^2-acyl $Mo(\eta^2\text{-}C(O)CH_3)(S_2CO\text{-}i\text{-}Pr)CO(PMe_3)_2$ (IR band at 1784 cm^{-1} due to ν(CO), also in THF). Interconversion between these two species is slow on the NMR time scale, and a sharp $^{31}P\{^1H\}$ singlet (δ ca. 10) is observed for the η^2-acyl isomer in the temperature range from −50 to +55 °C (Figure 4). In addition, a third species whose concentration is temperature dependent starts forming at −50 °C and exchanging with the agostic acyl structure D, whose $^{31}P\{^1H\}$ resonance broadens and shifts dramatically to high field, becoming a relatively sharp singlet at 55 °C (Δδ = 16 ppm from −90 to +50 °C). Further heating of the sample is prevented by its thermal instability. The third species is proposed to be the isomeric methyl carbonyl complex $Mo(CH_3)(S_2CO\text{-}i\text{-}Pr)(CO)_2(PMe_3)_2$, since the ^1H

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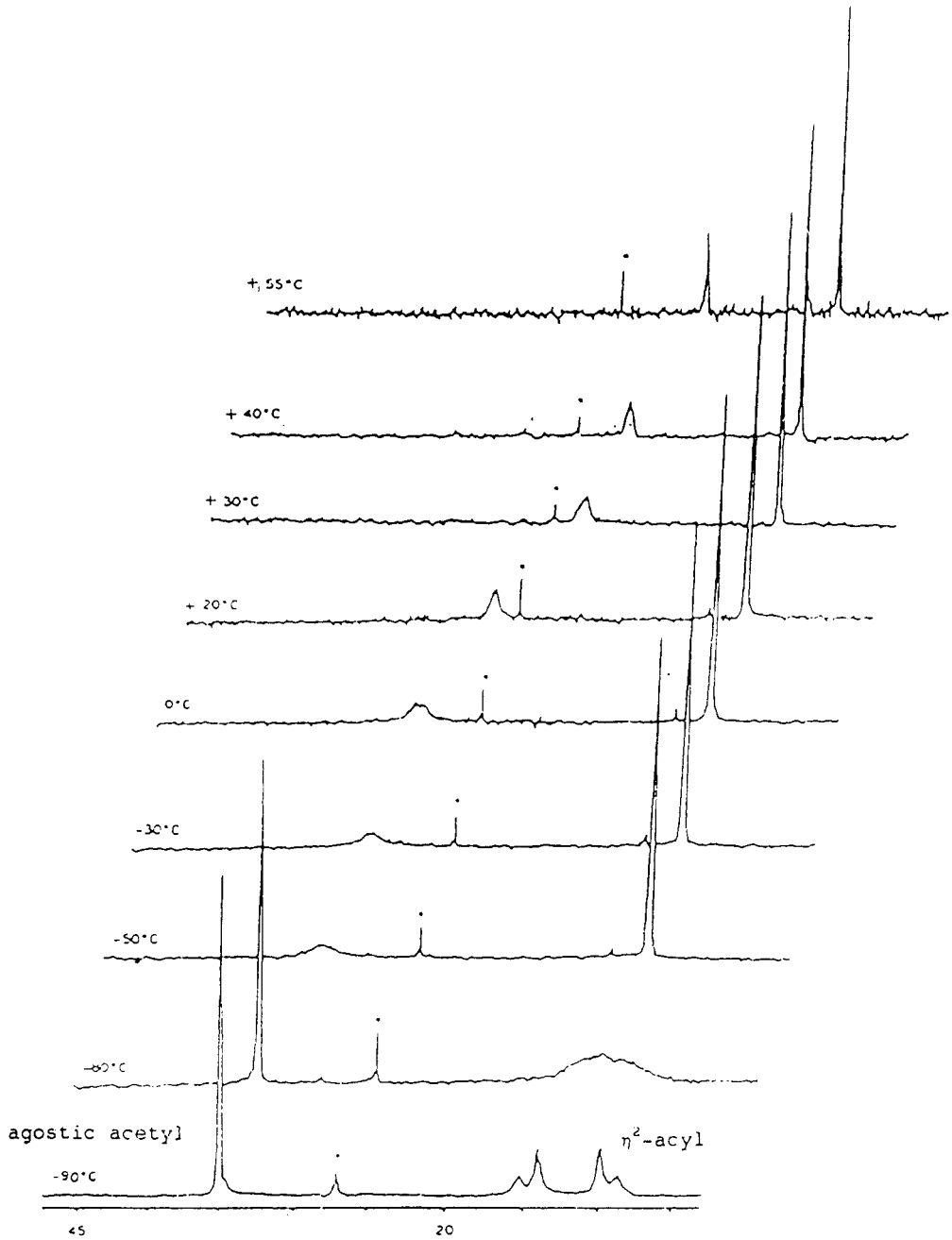


Figure 4. Variable-temperature $^{31}P\{^1H\}$ NMR spectra (CD_3COCD_3) of the thermodynamic mixture of the three isomers of **2c**. The dot denotes a minor impurity. At −90 °C, the rocking motion[5d] of the η^2-acyl ligand is slow and makes the two PMe_3 groups diastereotopic.

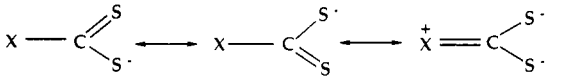
resonance of the acyl group shifts from δ 1.8 at −50 °C to δ 1.5 at 20 °C (**2c**, $C_6D_5CD_3$ solution), that is, to the region expected for a Mo-bound methyl group, and the coupling of the acyl protons to the ^{31}P nuclei is augmented from 1.8 Hz at −20 °C (at lower temperatures this signal is somewhat broad) to 3.0 Hz at 20 °C.[14] This proposal is further supported by the observation of two carbonyl absorptions at ca. 1910 and 1835 cm^{-1} in the room-temperature solution IR spectra of compounds **2**, which can be tentatively assigned to the methyl dicarbonyl species $Mo(CH_3)(S_2COR)(CO)_2(PMe_3)_2$. These bands are barely discernible in the IR spectra of solutions of **2** cooled to −100 °C and appear as small shoulders in the spectra recorded at −20 °C and above this temperature. The low intensity of these bands, as compared to those corresponding to the agostic acyl and η^2-acyl isomers, and the complexity of the IR spectrum in this region preclude us from making a definitive assignment.

(14) In the structurally characterized $W(CH_3)(L\text{-}L)(CO)_2(PMe_3)_2$ complexes (L-L = acac, S_2CNR_2, S_2COR) this coupling ranges from 3.5 to 8 Hz.[6f]

Concluding Remarks

The results described in the previous section clearly demonstrate that, in the system under investigation, there are small energy differences among the isomeric structures A, C, and D, so that the two types of acyl coordination (C and D) become kinetically and thermodynamically accessible from their isomeric alkyl carbonyl structure (A). The fact that a large number of the acyl complexes of molybdenum known to date have a η^2 structure while the only known agostic acyls are those described in this contribution suggests that stabilization of the agostic interaction (with respect to the η^2-acyl and alkyl carbonyl structures) requires the presence of strongly electron-releasing ligands.

The dithiocarbamates are stronger donors than the xanthates, this being in part a reflection of the larger contribution[15] of the structure III to the former as compared to that to the latter. Hence, all the dithio-



I II III

carbamates studied give agostic acyls, both in solution and in the solid state. There is only one exception, namely the pyrrole-derived dithiocarbamate complex $Mo(\eta^2\text{-}C(O)CH_3)(S_2CNC_4H_4)CO(PMe_3)_2$, which exists exclusively as a bidentate acyl. The $C_4H_4NCS_2^-$ ligand is, however, a weaker donor than the other dithiocarbamates studied. Note that for this ligand resonance structure III cannot play a major role in the overall structure, since it implies a loss of aromaticity of the pyrrole group.[16] In excellent accord with this line of argumentation, the dithiocarbamate and acac complexes of composition $Mo(\eta^2\text{-}C(O)CH_3)(L\text{-}L)(CO)_2(PMe_3)$, derived from compounds 1 and 4 by substitution of PMe_3 by CO, and therefore containing less basic metal centers, also have Mo–η^2-acyl linkages.[6c,17] This bidentate acyl structure is again the most favorable in acyl complexes of molybdenum of composition $Mo(\eta^2\text{-}C(O)R)X(CO)_n(PMe_3)_{4-n}$ (n = 0–2) that have halide or pseudohalide anionic ligands.[6c,g]

Finally it is worth recalling that the xanthate complexes 2 are agostic in the solid state but exist in solution as equilibrium mixtures of the agostic and bidentate acyls, the former being in addition equilibrated with the alkyl carbonyl isomers. Compounds 3, having the stronger donor phosphonium xanthate ligands, exist exclusively as the agostic acyls, no evidence for the formation of η^2-acyl structures having been found.

The above observations clearly suggest that a high electron density at the metal center is required to stabilize the agostic acetyl interaction. However, fine tuning of the metal basicity so as to achieve stabilization of the agostic structure D and observation of equilibria among the isomeric structures A, B, and D cannot be accomplished in a wholly predictable manner. In this respect we note that the tungsten system analogs, displaying a higher metal basicity, provide exclusively the alkyl carbonyl isomers. An additional factor that should not be underestimated is the influence in this stabilization of the different ligand stereochemistry exhibited by related complexes having the isomeric structures A, C, and D. Notwithstanding, it is our expectation that careful manipulation of both the electron density at the metal center and the steric requirements of the ligands may allow observation of the agostic structure in other transition-metal–acyl compounds.

Experimental Section

Microanalyses were carried out by Pascher Microanalytical Laboratories, Remagen, Germany, and the Analytical Service of the University of Seville. Infrared spectra were recorded as Nujol mulls or in an appropriate solvent on Perkin-Elmer Models 577 and 684 spectrometers. Spectra in the temperature range 173–283 K were obtained with a Specac NaCl variable-temperature cell. The ^1H, ^{13}C, and ^{31}P NMR spectra were run on a Varian XL-200 instrument. $^{31}P\{^1H\}$ NMR shifts were referenced to external 85% H_3PO_4, while ^1H and ^{13}C NMR shifts were referenced to the residual signals of the deuterated solvent employed and all data are reported in ppm downfield from Me_4Si.

All preparations and manipulations were carried out under oxygen-free nitrogen or argon, following conventional Schlenk techniques. Solvents were dried and degassed before use. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was checked by elemental analysis, NMR techniques, and/or other suitable methods.

The acetyl complex $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$ was used as the starting material and was synthesized by a slight, albeit critical, modification of our original procedure.[6c] Reproducible, acceptable yields (60%) of this complex could only be obtained by alkylation of $MoCl_2(CO)_2(PMe_3)_3$[18] in the presence of $ZnCl_2(PMe_3)_2$[19] (ca. 25–30% w/w). The role of the added $ZnCl_2(PMe_3)_2$ is presently unknown. We also note that the presence of other Zn or Al reagents ($ZnCl_2$, ZnR_2, or $AlCl_3$) in the reaction medium does not produce a similar effect.

Preparation of $Mo(C(O)CH_3)(L\text{-}L)CO(PMe_3)_2$ Complexes. (A) L-L = $S_2CN\text{-}i\text{-}Pr_2$ (1b), $S_2CNC_5H_{10}$ (1c), $S_2CNC_4H_4$ (1d), S_2COMe (2a), S_2COEt (2b), $S_2CO\text{-}i\text{-}Pr$ (2c), $CH_3C(O)CHC(O)CH_3$ (4a), $Me_3CC(O)CHC(O)CMe_3$ (4b). Although complexes 1b,c may be prepared in a manner similar to that used for the synthesis of the previously published dimethyldithiocarbamate derivative 1a, the preparation of all the complexes of this type is best accomplished by using the following procedure, which is described by taking the Mo–S_2CO-*i*-Pr complex as a representative example.

$Mo(C(O)CH_3)(S_2CO\text{-}i\text{-}Pr)CO(PMe_3)_2$ (2c). Solid samples of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$ (0.43 g, ca. 1 mmol) and anhydrous KS_2CO-*i*-Pr (0.2 g, ca. 1.2 mmol) were weighed into a nitrogen-flushed Schlenk flask and cooled to 0 °C for 15 min. Freshly distilled THF (40 mL) was syringed into the flask, and the resulting mixture was stirred for 30 min at 0 °C. This temperature was kept during the workup procedure. The solvent was stripped in vacuo and the residue placed under reduced pressure for several hours, to remove the PMe_3 released during the course of the reaction. It was then extracted with 1:1 petroleum ether–Et_2O mixtures (ca. 40 mL) to give a white solid that was discarded by filtration. The volume of this petroleum ether–Et_2O solution was reduced in vacuo to obtain a saturated solution, which was cooled (−20 °C) overnight to induce the deposition of red crystals of the title product. The supernatant solution was again concentrated in vacuo, and one additional crop of crystals was collected (75%, overall yield).

From the appropriate bidentate ligand, NaS_2CNR_2, $KS_2CNC_4H_4$, KS_2COR, or $Tl(RC(O)CHC(O)R)$, the following compounds were obtained by the above procedure: $Mo(C(O)CH_3)(S_2CN\text{-}i\text{-}Pr_2)CO(PMe_3)_2$ (**1b**), 75%; $Mo(C(O)CH_3)(S_2CNC_5H_{10})CO(PMe_3)_2$ (**1c**), 65%; $Mo(\eta^2\text{-}C(O)CH_3)(S_2CNC_4H_4)CO(PMe_3)_2$ (**1d**), 40%; $Mo(C(O)CH_3)(S_2COMe)CO(PMe_3)_2$ (**2a**), 68%; $Mo(C(O)CH_3)(S_2COEt)CO(PMe_3)_2$ (**2b**), 75%; $Mo(C(O)CH_3)(CH_3C(O)CHC(O)CH_3)CO(PMe_3)_2$ **4a**), 60%; $Mo(C(O)CH_3)(Me_3CC(O)CHC(O)CMe_3)CO(PMe_3)_2$ (**4b**), 70%. Longer reaction times (ca. 6 h) are required, however, for the last complex. They were all isolated as red crystalline solids by cooling their concentrated petroleum ether–Et_2O solutions to temperatures of about −20 °C. The more soluble $Mo(Me_3CC(O)CHC(O)CMe_3)$ complex (**4b**) was crystallized from petroleum solutions.

Complex 1c may also be obtained by the reaction of $Mo(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$[6c] with $NaS_2CNC_5H_{10}$ in Et_2O at room temperature; yield ca. 50%. We have been unable to isolate the complex "$Mo(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CNC_5H_{10})CO(PMe_3)_2$", expected precursor of 1c in the latter preparation.

Selected Analytical and Spectroscopic Data. Although some spectroscopic data for the complex $Mo(C(O)$-

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(19) Prepared from anhydrous $ZnCl_2$ and 2 mol equiv of PMe_3 in THF.

CH_3)(S_2CNMe_2)CO(PMe_3)$_2$ (**1a**) have already been reported,[6c] for the sake of completeness, it is pertinent to recall at this point the most relevant spectroscopic data. IR (THF solution, 20 °C, cm^{-1}): 1800 (vs), 1614 (s) (ν(CO) of the main species), 1908 (vw), 1847 (vw) (ν(CO)), 1515 (m) (ν(CN)). ^1H NMR ($C_6D_5CD_3$, −90 °C): δ 1.40 (br s, 2 PMe_3), 2.09 (br s, $COCH_3$), 2.59 (s, S_2CNMe_2). ^1H NMR ($C_6D_5CD_3$, 20 °C): δ 1.38 (d, $^2J_{HP}$ = 8.9 Hz, 2 PMe_3), 1.87 (t, J_{HP} = 1.3 Hz, $COCH_3$), 2.68 (s, S_2CNMe_2). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): δ 31.2 (s, −90 °C); 29.3 (s, 20 °C). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 35.1 (s, −90 °C); 32.6 (vbr s, 20 °C). $^{13}C\{^1H\}$ NMR (CH_2Cl_2–CD_3COCD_3, −90 °C): δ 6.6 (br s, $COCH_3$), 15.3 (br d, $^1J_{CP}$ = 31 Hz, PMe_3), 41.9 (s, S_2CNMe_2), 204.8 (t, $^3J_{CP}$ = 11 Hz, S_2CNMe_2), 242.3 (t, $^2J_{CP}$ = 30 Hz, CO), 257.7 (t, $^2J_{CP}$ = 32 Hz, $COCH_3$, this assignment is based on gated decoupling experiments). $^{13}C\{^1H\}$ NMR (CH_2Cl_2–CD_3COCD_3, 20 °C): δ 7.5 (br s, $COCH_3$), 14.9 (d, $^1J_{CP}$ = 30 Hz, PMe_3), 38.5 (s, S_2CNMe_2), 207.5 (t, $^3J_{CP}$ = 10 Hz, S_2CNMe_2), 251.3 (t, $^2J_{CP}$ = 30 Hz, CO and $COCH_3$).

Preparation of Mo($^{13}COCH_3$)(S_2CNMe_2)(^{13}CO)(PMe_3)$_2$. A solution of $MoCl_2(PMe_3)_4$ (0.47 g, 1 mmol) in THF (50 mL) was prepared in a 250-mL pressure vessel at ambient temperature. The reaction vessel was partially evacuated and then filled with 1 mmol of ^{13}CO. After being stirred at 60 °C for approximately 12 h, the solution was evaporated to dryness to obtain a yellow microcrystalline residue of $MoCl_2(^{13}CO)_2(PMe_3)_3$, which was washed with petroleum ether and dried in vacuo; yield ca. 55%.

The complexes Mo(η^2-$^{13}C(O)CH_3$)Cl(^{13}CO)(PMe_3)$_3$ and Mo($^{13}C(O)CH_3$)(S_2CNMe_2)(^{13}CO)(PMe_3)$_2$ were prepared in a manner similar to that reported for the analogous complexes with CO of normal isotopic composition. IR (Nujol mull, cm^{-1}): 1737 (s), 1571 (s) (ν(CO)), 1535 (m) (ν(CN)). ^1H NMR (CD_2Cl_2, 20 °C): δ 1.43 (d, $^2J_{HP}$ = 9.2 Hz, 2 PMe_3), 1.73 (t, J_{HP} = 1.6 Hz, $COCH_3$), 3.17 (s, S_2CNMe_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 31.4 (t, $^2J_{PC}$ = 30 Hz, −90 °C), 29.7 (t, $^2J_{PC}$ = 30 Hz, 20 °C). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −90 °C): δ 6.2 (br s, $COCH_3$), 15.3 (d, $^1J_{CP}$ = 31 Hz, PMe_3), 41.0 (s, S_2CNMe_2), 206.0 (t, $^3J_{CP}$ = 11 Hz, S_2CNMe_2), 243.8 (t, $^2J_{CP}$ = 29 Hz, CO), 259.2 (t, $^2J_{CP}$ = 31 Hz, $COCH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 7.8 (br t, $^2J_{CP}$ = 4 Hz, $COCH_3$), 15.3 (d, $^1J_{CP}$ = 31 Hz, PMe_3), 40.5 (s, S_2CNMe_2), 208.5 (t, $^3J_{CP}$ = 10 Hz, S_2CNMe_2), 251.3 (t, $^2J_{CP}$ = 30 Hz, CO and $COCH_3$).

Mo(C(O)CH_3)(S_2CN-*i*-Pr_2)CO(PMe_3)$_2$ (1b). Anal. Calcd for $C_{16}H_{35}NO_2P_2S_2Mo$: C, 38.8; H, 6.5; N, 2.8. Found: C, 38.4; H, 7.1; N, 2.7. IR (Nujol mull, cm^{-1}): 1775 (vs), 1607 (s) (ν(CO)), 1480 (m) (ν(CN)). IR (THF solution, −100 °C, cm^{-1}): 1790 (vs), 1606 (s) (ν(CO)). IR (THF solution, 20 °C, cm^{-1}): 1799 (vs), 1611 (s) (ν(CO) of the main species), 1904 (vw), 1847 (vw) (ν(CO)). ^1H NMR ($C_6D_5CD_3$, −60 °C): δ 0.70, 0.79 (d, $^3J_{HH}$ = 6.1 Hz, diastereotopic CHMe_2 groups), 1.51 (br d, $^2J_{HP}$ = 7.5 Hz, 2 PMe_3), 1.57, 1.67 (d, $^3J_{HH}$ = 5.5 Hz, diastereotopic CHMe_2 groups), 2.20 (br s, $COCH_3$), 3.13 (h, $^3J_{HH}$ = 6.1 Hz, C*H*Me_2), 5.81 (h, $^3J_{HH}$ = 5.5 Hz, C*H*Me_2). ^1H NMR ($C_6D_5CD_3$, 20 °C): δ 1.2 (vbr s, 2 CHMe_2), 1.50 (d, $^2J_{HP}$ = 8.8 Hz, 2 PMe_3), 2.02 (t, J_{HP} = 1.6 Hz, $COCH_3$), 4.1 (vbr s, 2 C*H*Me_2). $^{31}P\{^1H\}$ NMR (THF–CD_3COCD_3): δ 30.0, 29.1 (AB spin system, $^2J_{PP}$ = 13 Hz, −90 °C), 29.0 (vbr s, −60 °C), 27.5 (s, −50 °C), 26.6 (vbr s, 20 °C). $^{13}C\{^1H\}$ NMR (THF–C_6D_6, 20 °C): δ 8.2 (br s, $COCH_3$), 14.7 (d, $^1J_{CP}$ = 29 Hz, PMe_3), 19.4 (s, CHMe_2), 26.3 (s, C*H*Me_2), 208.6 (t, $^3J_{CP}$ = 9 Hz, S_2CNR_2), 251.7 (t, $^2J_{CP}$ = 30 Hz, CO and $COCH_3$).

Mo(C(O)CH_3)($S_2CNC_5H_5$)CO(PMe_3)$_2$ (1c). Anal. Calcd for $C_{15}H_{31}NO_2P_2S_2Mo$: C, 37.6; H, 6.5; N, 2.9. Found: C, 38.6; H, 6.6; N, 2.6. IR (Nujol mull, cm^{-1}): 1789 (vs), 1608 (s) (ν(CO)), 1503 (m) (ν(CN)). IR (THF solution, −100 °C, cm^{-1}): 1792 (vs), 1608 (m) (ν(CO)). IR (THF solution, 20 °C, cm^{-1}): 1798 (vs), 1613 (m) (ν(CO) of the main species), 1903 (vw), 1844 (vw) (ν(CO)). ^1H NMR ($C_6D_5CD_3$, −60 °C): δ 0.98 (br s, −$(CH_2)_3$−), 1.47 (br d, $^2J_{HP}$ = 6.7 Hz, 2 PMe_3), 2.12 (br s, $COCH_3$), 3.16, 3.91 (br s, 2 NCH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 27.4 (br s). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 20 °C): δ 13.2 (br s, $COCH_3$), 20.0 (d, $^1J_{CP}$ = 31 Hz, PMe_3), 28.8, 30.2, 52.6 (s, 1:2:2 ratio, CH_2), 206.3 (t, $^3J_{CP}$ = 10 Hz, S_2CNR_2), 250.7 (t, $^2J_{CP}$ = 30 Hz, CO and $COCH_3$).

Mo(η^2-C(O)CH_3)($S_2CNC_4H_4$)CO(PMe_3)$_2$ (1d). Anal. Calcd for $C_{14}H_{25}NO_2S_2P_2Mo$: C, 36.4; H, 5.4; N, 3.0. Found: C, 36.5; H, 5.4; N, 3.0. IR (Nujol mull, cm^{-1}): 1781 (s), 1465 (w) (ν(CO)). IR (THF solution, 20 °C, cm^{-1}): 1790 (s) (ν(CO)). ^1H NMR (CD_3COCD_3, −50 °C): δ 1.55 (t, $J_{HP(app)}$ = 3.8 Hz, 2 PMe_3), 2.97 (s, $COCH_3$), 6.31 (t, $^3J_{HH}$ = 2.3 Hz, 2 CH), 7.62 (t, 2 CH). ^1H NMR (C_6D_6, 20 °C): δ 1.35 (t, $J_{HP(app)}$ = 3.7 Hz, 2 PMe_3), 2.33 (s, $COCH_3$), 6.11 (t, $^3J_{HH}$ = 2.3 Hz, 2 CH), 7.82 (t, 2 CH). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 10.5, 15.3 (AB spin system, $^2J_{PP}$ = 72 Hz, −94 °C), 11.9 (s, −50 °C), 11.2 (s, 20 °C). $^{13}C\{^1H\}$ NMR (THF–CD_3COCD_3, 20 °C): δ 15.4 (t, $J_{CP(app)}$ = 12 Hz, PMe_3), 112.4, 117.3 (s, 1:1 ratio, CH), 237.0 (t, $^2J_{CP}$ = 13.5 Hz, CO), 281.0 (t, $^2J_{CP}$ = 18 Hz, $COCH_3$). The η^2-$COCH_3$ methyl carbon and the dithiocarboxylate carbon of the $S_2CNC_4H_4$ ligand are probably obscured by solvent resonances.

Mo(C(O)CH_3)(S_2COMe)CO(PMe_3)$_2$ (2a). Anal. Calcd for $C_{11}H_{24}O_3S_2P_2Mo$: C, 31.0; H, 5.6. Found: C, 31.1; H, 6.4. IR (Nujol mull, cm^{-1}): 1789 (s), 1614 (s) (ν(CO)). IR (THF solution, 20 °C, cm^{-1}): 1814 (m), 1627 (m) (ν(CO) of the agostic acetyl isomer), 1915 (w), 1845 (w) (ν(CO) of the proposed alkyl carbonyl isomer), 1790 (s) (ν(CO) η^2-acyl isomer). ^1H NMR (C_6D_6, 20 °C): agostic acetyl, δ 1.22 (d, $^2J_{HP}$ = 8.5 Hz, 2 PMe_3), 1.33 (t, J_{HP} = 3.1 Hz, $COCH_3$), 3.53 (s, OCH_3); η^2-acyl isomer, δ 1.39 (t, $J_{HP(app)}$ = 3.7 Hz, 2 PMe_3), 2.38 (s, $COCH_3$), 3.59 (s, OCH_3). $^{31}P\{^1H\}$ NMR (THF–CD_3COCD_3): agostic acetyl, δ 34.7 (s, −94 °C), 34.1 (s, −60 °C); η^2-acyl isomer, δ 13.9, 8.2 (AB spin system, $^2J_{PP}$ = 97 Hz, −94 °C), 10.6 (s, −60 °C). The equilibrium constant, measured by integration of the corresponding $^{31}P\{^1H\}$ resonances at −60 °C under conditions of complete spin relaxation, has been found to be K = [η^2-acyl]/agostic] ≃ 1.5. $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): agostic acetyl, δ 19.9 br s; η^2-acyl isomer, δ 4.5 s. $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): agostic acetyl, δ 0.1 (t, $^2J_{CP}$ = 5 Hz, $COCH_3$), 14.7 (d, $^1J_{CP}$ = 28 Hz, PMe_3), 57.3 (s, OCH_3), 225.1 (t, $^3J_{CP}$ = 8 Hz, S_2COR), 247.1 (t, $^2J_{CP}$ = 26 Hz, CO and $COCH_3$); η^2-acyl isomer, δ 15.7 (t, $J_{CP(app)}$ = 12 Hz, PMe_3), 29.1 (s, $COCH_3$), 57.3 (s, OCH_3), 223.3 (t, $^3J_{CP}$ = 7 Hz, S_2COR), 237.6 (t, $^2J_{CP}$ = 15 Hz, CO), 279.9 (t, $^2J_{CP}$ = 16 Hz, $COCH_3$).

Mo(C(O)CH_3)(S_2COEt)CO(PMe_3)$_2$ (2b). Anal. Calcd for $C_{12}H_{26}O_3S_2P_2Mo$: C, 32.7; H, 5.9. Found: C, 32.9; H, 6.0. IR (Nujol mull, cm^{-1}): 1800 (s), 1608 (s) (ν(CO)). IR (THF solution, 20 °C, cm^{-1}): 1810 (m), 1623 (m) (ν(CO) of the agostic acetyl), 1910 (w), 1835 (w) (ν(CO) of the proposed alkyl carbonyl isomer), 1789 (s) (ν(CO) η^2-acyl isomer). ^1H NMR (CD_3COCD_3, 20 °C): agostic acetyl, δ 1.11 (t, J_{HP} = 3.1 Hz, $COCH_3$), 1.42 (d, $^2J_{HP}$ = 8.6 Hz, 2 PMe_3), 1.44 (t, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3), 4.64 (q, OCH_2); η^2-acyl isomer, δ 1.32 (t, $^3J_{HH}$ = 7.1, CH_2CH_3), 1.55 (t, $J_{HP(app)}$ = 3.7 Hz, 2 PMe_3), 2.87 (s, $COCH_3$), 4.44 (q, OCH_2). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): agostic acetyl, δ 35.2 (s, −93 °C), 33.9 (vbr s, −50 °C), 24.1 (s, 20 °C); η^2-acyl isomer, δ 8.9, 14.5 (AB spin system, $^2J_{PP}$ = 95 Hz, −93 °C), 10.9 (s, −50 °C), 10.1 (s, 20 °C). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 0 °C): agostic acetyl, δ 0.7 (t, $^2J_{CP}$ = 5 Hz, $COCH_3$), 14.5 (s, CH_2CH_3), 15.4 (t, $J_{CP(app)}$ = 14 Hz, PMe_3), 69.0 (s, OCH_2), 225.4 (t, $^3J_{CP}$ = 9 Hz, S_2COR), 248.7 (t, $^2J_{CP}$ = 25 Hz, CO and $COCH_3$); η^2-acyl isomer, δ 14.6 (s, CH_2CH_3), 16.4 (t, $J_{CP(app)}$ = 12 Hz, PMe_3), 68.2 (s, OCH_2), 223.9 (t, $^3J_{CP}$ = 6 Hz, S_2COR), 238.6 (t, $^2J_{CP}$ = 14 Hz, CO), 281.3 (t, $^2J_{CP}$ = 16 Hz, $COCH_3$). The resonance of the methyl carbon of the η^2-$COCH_3$ ligand is probably obscured by the deuterated solvent.

Mo(C(O)CH_3)(S_2CO-*i*-Pr)CO(PMe_3)$_2$ (2c). Anal. Calcd for $C_{13}H_{28}O_3S_2P_2Mo$: C, 34.4; H, 6.2. Found: C, 34.9; H, 6.2. IR (Nujol mull, cm^{-1}): 1802 (s), 1614 (s) (ν(CO)). IR (THF solution, 20 °C, cm^{-1}): 1807 (m), 1624 (m) (ν(CO) of the agostic acetyl), 1912 (w), 1836 (w) (ν(CO) of the proposed alkyl carbonyl isomer), 1789 (s) (ν(CO) η^2-acyl isomer). ^1H NMR ($C_6D_5CD_3$, −40 °C): agostic acetyl, δ 1.06 (d, $^3J_{HH}$ = 6.2 Hz, $CH(CH_3)_2$, 1.40 (d, $^2J_{HP}$ = 8.8 Hz, 2 PMe_3), 1.76 (br s, $COCH_3$), 5.50 (h, $CH(CH_3)_2$); η^2-acyl isomer, δ 1.18 (d, $^3J_{HH}$ = 6.0 Hz, $CH(CH_3)_2$), 1.53 (t, $J_{HP(app)}$ = 3.6 Hz, 2 PMe_3), 2.40 (s, $COCH_3$), 5.45 (h, $CH(CH_3)_2$). ^1H NMR ($C_6D_5CD_3$, 20 °C): agostic acetyl, δ 1.16 (d, $^3J_{HH}$ = 6.5 Hz, $CH(CH_3)_2$), 1.37 (d, $^2J_{HP}$ = 8.5 Hz, 2 PMe_3), 1.46 (t, J_{HP} = 3.0 Hz, $COCH_3$), 5.50 (h, $CH(CH_3)_2$); η^2-acyl isomer, δ 1.20 (d, $^3J_{HH}$ = 6.5 Hz, $CH(CH_3)_2$), 1.55 (t, $J_{HP(app)}$ = 3.6 Hz, 2 PMe_3), 2.50 (s, $COCH_3$), 5.45 (h, $CH(CH_3)_2$. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): agostic acetyl, δ 35.0 (s, −90 °C), 32.2 (vbr s, −50 °C), 19.2 (s, 55 °C); η^2-acyl isomer, δ 9.15, 14.7 (AB spin system, $^2J_{PP}$ = 110 Hz, −90 °C), 11.1 (br s, −80 °C), 10.7 (s, −50 °C), 9.5 (s, 20 °C). $^{13}C\{^1H\}$ NMR (THF–CD_3COCD_3, −90 °C): agostic acetyl, δ 0.7 (t, $^2J_{CP}$ = 4 Hz,

$COCH_3$), 15.7 (d, $^1J_{CP}$ = 29 Hz, PMe_3), 22.7 (s, $CH(CH_3)_2$), 78.7 (s, $CH(CH_3)_2$), 226.4 (t, $^3J_{CP}$ = 11 Hz, S_2COR), 246.3 (vbr s, CO and $COCH_3$); η^2-acyl isomer, δ 17.2 (t, $J_{CP(app)}$ = 12 Hz, PMe_3), 22.7 (s, $CH(CH_3)_2$), 23.2 (br s, $COCH_3$), 76.2 (s, $CH(CH_3)_2$), 223.0 (t, $^3J_{CP}$ = 6 Hz, S_2COR), 238.5 (t, $^2J_{CP}$ = 13 Hz, CO), 281.8 (t, $^2J_{CP}$ = 16.0 Hz, $COCH_3$). $^{13}C\{^1H\}$ NMR (THF–CD_3COCD_3, 20 °C): agostic acetyl, δ 0.6 (t, $^2J_{CP}$ = 6 Hz, $COCH_3$), 15.2 (t, $J_{CP(app)}$ = 14 Hz, PMe_3), 21.9 (s, $CH(CH_3)_2$) 76.8 (s, $CH(CH_3)_2$), 224.5 (t, $^3J_{CP}$ = 8 Hz, S_2COR), 248.2 (t, $^2J_{CP}$ = 25 Hz, CO and $COCH_3$); η^2-acyl isomer, δ 16.2 (t, $J_{CP(app)}$ = 12 Hz, PMe_3), 21.9 (s, $CH(CH_3)_2$), 22.4 (br s, $COCH_3$), 75.3 (s, $CH(CH_3)_2$), 223.0 (t, $^3J_{CP}$ = 6 Hz, S_2COR), 237.6 (t, $^2J_{CP}$ = 14 Hz, CO), 280.3 (t, $^2J_{CP}$ = 16 Hz, $COCH_3$). The following variable-temperature spectroscopic data (IR and $^{31}P\{^1H\}$ NMR) were obtained by dissolving crystalline samples of this complex at –60 °C in THF, the resulting solutions being maintained at this temperature for 3 h and then cooled to –100 °C. IR (cm^{-1}): –100 °C, 1803 (s), 1618 (m) (ν(CO)); –40 °C, 1805 (m), 1784 (s), 1620 (m) (ν(CO)); 20 °C, 1912 (w), 1836 (w), 1807 (m), 1789 (s), 1624 (m) (ν(CO)). $^{31}P\{^1H\}$ NMR (δ): –100 °C, δ 35.8 (s), –40 °C, 33.4 (br s), 11.0 (s of very small intensity; the intensity of the resonance grows gradually with temperature but remains constant once the sample reaches room temperature); 20 °C, 24.7 (br s), 10.5 (s); 55 °C, 18.7 (s), 9.9 (s). Cooling the sample again does not change the intensity ratio of these signals.

$\overline{Mo(C(O)CH_3)}(CH_3C(O)CHC(O)CH_3)CO(PMe_3)_2$ (4a). Anal. Calcd for $C_{14}H_{28}O_4P_2Mo$: C, 40.2; H, 6.7. Found: C, 40.1; H, 6.6. IR (Nujol mull, cm^{-1}; two types of crystals are usually obtained which have identical solution spectroscopic properties): orange crystals, 1773 (s), 1610 (m) (ν(CO)), 1572 (m), 1554 (w), 1517 (m) (ν(CO) acac); red crystals, 1781 (s), 1605 (m) (ν(CO)), 1563 (m), 1523 (m) (ν(CO) acac). IR (THF solution, 20 °C, cm^{-1}): 1787 (s), 1613 (m) (ν(CO) of the agostic acetyl), 1897 (w), 1820 (w) (ν(CO) of the proposed alkyl carbonyl isomer), 1571 (m) (ν(CO) acac). ^1H NMR ($C_6D_5CD_3$, –20 °C): δ 1.34 (d, $^2J_{HP}$ = 9.2 Hz, 2 PMe_3), 1.41 (t, J_{HP} = 1.5 Hz, $COCH_3$), 1.74 (s, 2 CH_3), 5.22 (s, CH). ^1H NMR ($C_6D_5CD_3$, 20 °C): δ 1.28 (d, $^2J_{HP}$ = 8.9 Hz, 2 PMe_3), 1.38 (t, J_{HP} = 1.9 Hz, $COCH_3$), 1.78 (s, 2 CH_3), 5.23 (s, CH). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): δ 37.2 (s, –90 °C), 35.1 (br s, –40 °C), 34.7 (vbr s, –15 °C), 29.0 (vbr s, 20 °C). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, –90 °C); δ 11.8 (s, $COCH_3$), 13.6 (br t, $J_{CP(app)}$ = 14 Hz, PMe_3), 28.7 (s, CH_3), 102.0 (s, CH), 189.3 (s, CO acac), 253.0 (t, $^2J_{CP}$ = 33 Hz, CO), 259.9 (t, $^2J_{CP}$ = 37 Hz, $COCH_3$). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, –50 °C): δ 12.3 (br s, $COCH_3$), 13.9 (filled-in d, $^2J_{CP}$ = 29 Hz, PMe_3), 28.5 (s, CH_3), 101.3 (s, CH), 189.2 (s, CO acac). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 20 °C): δ 11.7 (br s, $COCH_3$), 14.3 (d, $^1J_{CP}$ = 27 Hz, PMe_3), 28.3 (s, CH_3), 101.2 (s, CH), 189.1 (s, CO acac), 252.7 (t, $^2J_{CP}$ = 33 Hz, CO and $COCH_3$). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 20 °C): δ 11.6 (br s, $COCH_3$), 13.9 (d, $^1J_{CP}$ = 27 Hz, PMe_3), 27.6 (s, CH_3), 100.3 (s, CH), 187.7 (s, CO acac), 251.9 (t, $^2J_{CP}$ = 31 Hz, CO and $COCH_3$).

$\overline{Mo(C(O)CH_3)}(Me_3CC(O)CHC(O)CMe_3)CO(PMe_3)_2$ (4b). Anal. Calcd for $C_{20}H_{40}O_4P_2Mo$: C, 47.8; H, 8.0. Found: C, 47.5; H, 8.1. IR (Nujol mull, cm^{-1}): 1777 (s), 1605 (s) (ν(CO)), 1535 (s), 1503 (m) (ν(CO) acac). IR (THF solution, 20 °C, cm^{-1}): 1790 (s), 1614 (m) (ν(CO) of the agostic acetyl), 1898 (w), 1840 (w) (ν(CO) of the proposed alkyl carbonyl isomer), 1540 (m) (ν(CO) acac). ^1H NMR ($C_6D_5CD_3$, –20 °C): δ 1.12 (t, J_{HP} = 3.1 Hz, $COCH_3$), 1.23 (s, 2 CMe_3), 1.50 (d, $^2J_{HP}$ = 9.1 Hz, 2 PMe_3), 6.06 (s, CH). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): δ 37.0 (s, –90 °C), 32.6 (vbr s, 20 °C). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, –90 °C): δ 11.6 (s, $COCH_3$), 13.1 (br s, PMe_3), 28.7 (s, CMe_3), 41.2 (s, CMe_3), 91.0 (s, CH), 197.0 (s, CO acac), 251.3 (t, $^2J_{CP}$ = 33 Hz, CO), 258.1 (t, $^2J_{CP}$ = 37 Hz, $COCH_3$). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 20 °C): δ 12.2 (br s, $COCH_3$), 14.1 (d, $^1J_{CP}$ = 28 Hz, PMe_3), 28.4 (s, CMe_3), 41.2 (s, CMe_3), 90.7 (s, CH), 197.6 (s, CO acac), 253.7 (t, $^2J_{CP}$ = 36 Hz, CO and $COCH_3$).

(B) L-L = $S_2C(PMe_3)OMe$ (3a), $S_2C(PMe_3)OCH_2CF_3$ (3b), $S_2C(PMe_3)O$-*i*-Pr (3c). These complexes were prepared by performing the reaction of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$ with the corresponding xanthate salts under the conditions indicated in the above procedure. The reaction mixture was stirred for 0.5 h in the case of the methyl xanthate and for 3.5 h in the case of the $CF_3CH_2OCS_2$ derivative. The final THF reaction mixture was filtered at 0 °C and then cooled to –20 °C to give large red crystals of the desired complexes. These were washed with petroleum ether or Et_2O and dried under a stream of nitrogen.

$\overline{Mo(C(O)CH_3)}(S_2C(PMe_3)OMe)CO(PMe_3)_2$ (3a) was obtained in 60% yield, and it is very prone to loss of PMe_3 to give complex **2a**. **$\overline{Mo(C(O)CH_3)}(S_2C(PMe_3)OCH_2CF_3)CO(PMe_3)_2$** is stable toward loss of PMe_3 and was isolated in 70% yield.

$\overline{Mo(C(O)CH_3)}(S_2C(PMe_3)OMe)CO(PMe_3)_2$ (3a). Anal. Calcd for $C_{14}H_{33}O_3S_2P_3Mo$: C, 33.5; H, 6.6. Found: C, 32.6; H, 6.5. IR (Nujol mull, cm^{-1}): 1773 (s), 1584 (m), 1534 (m) (ν(CO), the splitting of the acetyl CO band is probably due to solid-state effects). IR (THF solution, 20 °C, cm^{-1}): 1770 (s), 1596 (m) (ν(CO)). ^1H NMR (CD_3COCD_3, 20 °C): δ 1.38 (d, $^2J_{HP}$ = 8.5 Hz, 2 PMe_3), 1.81 (d, $^2J_{HP}$ = 13.5 Hz, S_2CPMe_3), 2.10 (br s, $COCH_3$), 3.60 (d, $^4J_{HP}$ = 1.6 Hz, OCH_3). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, –90 °C): δ 34.4 (d, $^4J_{PP}$ = 7 Hz, 2 PMe_3), 37.3 (t, S_2CPMe_3). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 20 °C): δ 33.2 (d, $^4J_{PP}$ = 5 Hz, 2 PMe_3), 36.2 (t, S_2CPMe_3). $^{13}C\{^1H\}$ NMR (CH_2Cl_2–CD_3COCD_3, –20 °C): δ 6.9 (d, $^1J_{CP}$ = 59 Hz, S_2CPMe_3), 14.4 (s, $COCH_3$), 15.4 (d, $^1J_{CP}$ = 27 Hz, PMe_3), 48.7 (d, $^3J_{CP}$ = 12 Hz, OCH_3), 204.1 (d, $^1J_{CP}$ = 85 Hz, S_2C), 271.4 (t, $^2J_{CP}$ = 32 Hz, $COCH_3$). The carbon nucleus of the carbonyl ligand could not be observed under these conditions due to the low solubility of the complex at this temperature and to its unfavorable relaxation properties. $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 20 °C): δ 7.4 (d, $^1J_{CP}$ = 57 Hz, S_2CPMe_3), 14.3 (s, $COCH_3$), 16.2 (d, $^1J_{CP}$ = 28 Hz, PMe_3), 49.2 (d, $^3J_{CP}$ = 13 Hz, OCH_3).

$\overline{Mo(C(O)CH_3)}(S_2C(PMe_3)OCH_2CF_3)CO(PMe_3)_2$ (3b). Anal. Calcd for $C_{15}H_{32}O_3S_2P_3F_3Mo$: C, 31.6; H, 5.6. Found: C, 31.6; H, 5.7. IR (Nujol mull, cm^{-1}): 1777 (s), 1584 (m), 1534 (m) (ν(CO)). IR (THF solution, 20 °C, cm^{-1}): 1773 (s), 1599 (m) (ν(CO)). ^1H NMR (CD_3COCD_3, 20 °C): δ 1.38 (d, $^2J_{HP}$ = 9.1 Hz, 2 PMe_3), 1.88 (d, $^2J_{HP}$ = 13.7 Hz, S_2CPMe_3), 2.08 (br s, $COCH_3$), 4.44 (qd, $^3J_{HF}$ = 9.2 Hz, $^4J_{HP}$ = 1.4 Hz, CH_2CF_3). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 20 °C): δ 33.3 (d, $^4J_{PP}$ = 5 Hz, 2 PMe_3), 39.3 (t, S_2CPMe_3). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, –30 °C): δ 6.5 (d, $^1J_{CP}$ = 56 Hz, S_2CPMe_3), 14.0 (s, $COCH_3$), 15.4 (d, $^1J_{CP}$ = 27 Hz, PMe_3), 58.7 (qd, $^2J_{CF}$ = 33 Hz, $^3J_{CP}$ = 12 Hz, OCH_2CF_3), 125.8 (q, $^1J_{CF}$ = 284 Hz, CF_3), 205.2 (d, $^1J_{CP}$ = 72 Hz, S_2C), 252.9 (t, $^2J_{CP}$ = 32 Hz, CO), 268.2 (t, $^2J_{CP}$ = 29 Hz, $COCH_3$). The NMR spectra of pure crystals of **3b** dissolved in CD_3COCD_3 show, in addition to bands due to the main species, a set of resonances of very low intensity (less than 5%) which may be attributed to a normal $S_2COCH_2CF_3$ derivative of composition $Mo(\eta^2\text{-}C(O)CH_3)(S_2COCH_2CF_3)CO(PMe_3)_2$. ^1H NMR (CD_3COCD_3): δ 1.56 (filled-in d, $^2J_{HP}$ = 7.5 Hz, 2 PMe_3), 2.92 (s, $COCH_3$), 5.04 (q, $^3J_{HF}$ = 8.6 Hz, CH_2CF_3). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 9.9 s. Attempts to obtain this product by reaction of **3b** with acids (HCl, HBF_4, etc.) have proved unsuccessful.

$\overline{Mo(C(O)CH_3)}(S_2C(PMe_3)O$-*i*-Pr$)CO(PMe_3)_2$ (3c). This complex was prepared by the reaction of **2c** with an excess of PMe_3 in Et_2O. After 6–7 h a yellow powder resulted, which was washed with cold petroleum ether and dried under a stream of nitrogen. IR (Nujol mull, cm^{-1}): 1775 (s), 1600 (w), 1534 (m) (ν(CO)). At room temperature complex **3c** immediately loses PMe_3 in solution to produce the corresponding xanthate **2c**.

Disproportionation of Complex 4a into $Mo(\eta^2\text{-}C(O)CH_3)(acac)(CO)_2(PMe_3)$ and $Mo(CH_3)(acac)CO(PMe_3)_3$. A solution of the acac complex $Mo(C(O)CH_3)(acac)CO(PMe_3)_2$ in toluene was stirred overnight at room temperature. During this time a yellow solution and a syrupy solid resulted. This suspension was evaporated to dryness and the residue extracted with a 1:1 petroleum ether–Et_2O mixture. Centrifuging and cooling to –20 °C afforded $Mo(\eta^2\text{-}C(O)CH_3)(acac)(CO)_2(PMe_3)$ (**5**) as yellow crystals in 40% yield. Attempts to isolated the second product of this transformation, namely the alkyl $Mo(CH_3)(acac)CO(PMe_3)_3$, have proved unsuccessful, although it can be satisfactorily characterized by spectroscopic methods. Spectroscopic data for these complexes are as follows.

$Mo(\eta^2\text{-}C(O)CH_3)(CH_3C(O)CHC(O)CH_3)(CO)_2(PMe_3)$. Anal. Calcd for $C_{12}H_{19}O_5PMo$: C, 38.9; H, 5.1. Found: C, 38.8; H, 4.8. IR (Nujol mull, cm^{-1}): 1941 (vs), 1843 (vs), 1593 (s) (ν(CO)), 1577 (m), 1556 (m), 1523 (s) (ν(CO) acac). IR (THF solution, 20 °C): 1935 (m), 1839 (s), 1595 (w) (ν(CO)), 1575 (w), 1525 (w) (ν(CO) acac). ^1H NMR ($C_6D_5CD_3$, 20 °C): δ 1.18 (d, $^2J_{HP}$ = 9.5 Hz, PMe_3), 1.81 (s, 2 CH_3 acac), 2.84 (s, $COCH_3$), 5.45 (s, CH acac). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 20 °C): δ 12.4 s. $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 20 °C): δ 15.2 (d, $^1J_{CP}$ = 28 Hz, PMe_3), 27.3 (s, CH_3 acac), 30.7 (s,

$COCH_3$), 101.2 (s, CH acac), 188.9 (s, CO acac), 231.8 (d, $^2J_{CP}$ = 18 Hz, CO), 257.7 (d, $^2J_{CP}$ = 9 Hz, $COCH_3$).

This complex may also be obtained by bubbling carbon monoxide through a solution of $Mo(\eta^2\text{-}C(O)CH_3)(acac)CO(PMe_3)_2$ in THF for ca. 20 min. The solution changed from red to yellow, and from the resulting reaction mixture the dicarbonyl complex was isolated in ca. 80% yield.

$Mo(CH_3)(CH_3C(O)CHC(O)CH_3)CO(PMe_3)_3$. IR (THF solution, 20 °C, cm^{-1}): 1742 (s) (ν(CO)). ^1H NMR ($C_6D_5CD_3$, 20 °C): δ -3.48 (td, $^3J_{HP}$ = 9.9, 1.3 Hz, Mo–CH_3), 1.00 (d, $^2J_{HP}$ = 7.6 Hz, PMe_3), 1.20 (d, $^2J_{HP}$ = 8.9 Hz, 2 PMe_3), 2.08 (s, 2 CH_3 acac), 5.23 (s, CH). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 20 °C): δ 42.5 (d, $^2J_{PP}$ = 20 Hz, 2 PMe_3), 8.0 (t, PMe_3). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 20 °C): δ 15.7 (d, $^1J_{CP}$ = 24 Hz, 2 PMe_3), 15.9 (d, $^1J_{CP}$ = 17.6 Hz, PMe_3), 28.0 (s, CH_3 acac), 98.9 (s, CH acac), 185.3 (s, CO acac), 219.5 (m, CO). The ^{13}C resonance due to the Mo-bound methyl group could not be located under these conditions.

X-ray Structure Determinations of 1c and 3b. A summary of the fundamental crystal data is given in Table I. A crystal of **1c** was sealed in a glass capillary, while for **3b** the chosen single crystal was coated with an epoxy resin. Both were mounted in a Kappa diffractometer. The cell dimensions were refined by least-squares fitting of the values of 25 reflections. 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 20. The structures were solved by Patterson and Fourier methods. An empirical absorption correction[21] was applied at the end of the isotropic refinement.

Compound **1c** crystallizes in the space group $P\bar{1}$. After several cycles of mixed refinement, H(31), H(32), and H(33) were located in a difference synthesis calculated with reflections having (sin θ)/λ < 0.5 $Å^{-1}$ as the highest peaks of the map. In order to prevent bias on ΔF vs F_o or (sin θ)/λ, the last steps of the refinement were carried out with $w = 1/(a + b|F_o|^2)$, where a = 2.06, b = –0.16 if $|F_o| < 12$ and a = 0.29, b = 0.01 if $|F_o| > 12$, calculated by PESOS.[22] Final refinement with fixed isotropic factors and coordinates for H atoms, except for H(31), H(32), and H(33), for which the corresponding coordinates were refined, led to final values of R = 0.035 and R_w = 0.051.

Similar refinement for complex **3b**, whose space group is $C2/c$, led to final values of R = 0.026 and R_w = 0.027.

The final values of the positional parameters are given in Table II for complex **1c** and Table III for complex **3b**.

Most of the calculations were carried out with the X-Ray 80 system.[23]

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Supplementary Material Available: Tables of H atom coordinates and thermal parameters for **1c** and **3b** (4 pages). Ordering information is given on any current masthead page.

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Electrophilic Cleavage of Rhenium–Oxygen Bonds by Brønsted and Lewis Acids

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The rhenium–oxygen bond in complexes of the type $(CO)_3(L)_2ReOR$ (**1** (R = CH_3) or **2** (R = CH_2CH_3)) may be cleaved by a number of Brønsted and Lewis acids. When an acid X–H is added to **1** or **2**, one observes the formation of the exchanged rhenium product $(CO)_3(L)_2ReX$ and the free alcohol (L = 1,2-bis(dimethylarsino)benzene (diars, a), 1,2-bis(diethylphosphino)ethane (depe, b), PMe_3 (c), (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (bdpp, d), or 1,2-bis(diphenylphosphino)ethane (dppe, e)). For the reactions with Brønsted acids, the reaction is reversible when aniline and certain other amines are added to **1** or **2**, but the reaction may be driven to the right by the removal of the alcohol from the reaction mixture. Using this technique, the arylamido complex $(CO)_3(depe)ReNHC_6H_5$ (**13b**) has been synthesized and its structure determined by a single-crystal X-ray diffraction study. Irreversible exchange occurs upon reaction with other acids such as R_2PH, RPH_2, H_2S, and $CpW(CO)_3H$. The terminal phosphido complexes are fluxional in solution, undergoing phosphorus inversion at temperatures much lower than the free phosphines. The alkoxides do not react cleanly with carbon acids, but the alkoxide ligands may be removed using alkyl- and alkenylboranes, leading to alkenylrhenium complexes.

Introduction

The coordination chemistry of alkoxides is dominated by examples from the left side of the periodic table in which the metal is in a high oxidation state. These complexes are believed to have strong M–O bonds because of π-donation of the heteroatom's lone pairs to vacant orbitals on the metal center.[1] There are far fewer examples of similar complexes for metals in low oxidation states. It is believed that this is due to an unfavorable interaction between the "hard" alkoxide ligand with the "soft" metal center, resulting in inherently weak bonds. The pioneering

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