All evidence points to an iodine oxidation process which is largely ligand centered (indeed, Mössbauer spectral parameters are virtually insensitive to doping) and which does not produce the type of π electron band structure found in the partially oxidized group 4 $\{[M(Pc)O]I_y\}_n$ polymers. These results suggest very interesting and substantial differences in structure and charge-transport mechanism vis-à-vis other low-dimensional, partially oxidized metallomacrocycles. Further efforts to characterize these differences are in progress.

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Registry No. Fe(Pc)(pyz)$_2$, 74558-67-1; $[Fe(Pc)(\mu\text{-pyz})]_n$, 74591-77-8; iodine, 7553-56-2.

η^2-Acyl Coordination and β-C–H Interaction in Acyl Complexes of Molybdenum. Crystal and Molecular Structures of $Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)(PMe_3)_3$ and $\overline{\mathrm{Mo(COCH}}\mathrm{_3)(S_2CNMe_2)(CO)(PMe_3)_2}$

Ernesto Carmona,*[†] Luis Sánchez,[†] José M. Marín,[†] Manuel L. Poveda,[†] Jerry L. Atwood,*[‡] Ralph D. Priester,[‡] and Robin D. Rogers*[§]

Contribution from the Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla, Sevilla, Spain, the Department of Chemistry, University of Alabama, University, Alabama 35486, and the Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115. *Received October 31, 1983*

Abstract: A number of acyl complexes of composition $Mo(\eta^2\text{-}COR)X(CO)(PMe_3)_3$ (X = Cl, Br, I or NCO; R = CH_3, CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph) have been prepared by reaction of $MoCl_2(CO)_2(PMe_3)_3$ with the corresponding Grignard or lithium reagents. IR and NMR studies suggest dihapto coordination of the acyl group to the molybdenum center, and this has been confirmed by X-ray crystallography for $MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3$ (**1**). Complex **1** crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell parameters a = 10.747 (3) Å, b = 12.511 (3) Å, c = 18.897 (4) Å and D_c = 1.31 g cm^{-3} for Z = 4. Least-squares refinement using 2141 independent observed reflections led to a final R value of 0.025. The metal atom is essentially octahedral, and the acyl ligand is coordinated in an η^2 fashion with Mo–C(acyl) = 2.024 (6) Å and Mo–O(acyl) = 2.324 (4) Å. The η^2-acyl linkage in the above complexes remains unchanged upon carbonylation to afford the corresponding $Mo(\eta^2\text{-}COR)X(CO)_2(PMe_3)_2$ derivatives. Similarly, interaction of the $Mo(\eta^2\text{-}COR)X(CO)_n(PMe_3)_{4-n}$ (n = 1,2) complexes with NaS_2CNMe_2 causes loss of one of the trimethylphosphine ligands and formation of new η^2-acyl derivatives $Mo(\eta^2\text{-}COR)(S_2CNMe_2)(CO)_n(PMe_3)_{3-n}$ (n = 1,2). The reaction of **1** with $NaS_2CNMe_2{\cdot}2H_2O$ yields an unprecendented acetyl complex $Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2$ (**2**), in which the molybdenum atom attains an 18-electron configuration by virtue of a strong interaction with a β-C-H bond of the acetyl group. Complex **2** can also be prepared by reaction of $Mo(\eta^2\text{-}COCH_2SiMe_3)(S_2CNMe_2)(CO)(PMe_3)_2$ with H_2O or by interaction of $Mo(\eta^2\text{-}COCH_3)X(CO)(PMe_3)_3$ (X = Cl,I) with NaS_2CNMe_2 and has been characterized by a complete X-ray structure determination. **2** crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters a = 11.633 (5) Å, b = 9.962 (4) Å, c = 17.266 (6) Å, β = 95.80 (3)°, and D_c = 1.42 g cm^{-3} for Z = 4. Least-squares refinement based on 1720 independent observed reflections led to a final R value of 0.029. The acyl carbon is bonded to the Mo atom at a Mo–C separation of 2.05 (1) Å, and the acyl methyl group is displaced toward the Mo atom with Mo–C and Mo–H separations of 2.60 (1) and 2.06 (9) Å, respectively.

The carbon monoxide migratory insertion reaction is a key step in many catalytic transformations and as such, and because of its fundamental importance, it has been the subject of a large number of synthetic, mechanistic, and theoretical studies.[1] The generally accepted mechanism for this reaction invokes the intermediacy of a coordinatively unsaturated acyl, whose nature remains unclear. A number of stable transition-metal acyl complexes have been prepared and structurally characterized in recent years, and the acyl group has been found to coordinate to the metal atom in either a monohapto, M–C(O)R, or dihapto, $\overline{\mathrm{M{-}C(O}}\mathrm{)R}$, fashion.[2] In addition, bridging acyl units, η^2 bonded to two or three metal atoms via the acyl C and O atoms, have been also verified.[3] While for some CO insertion reactions the proposed intermediates are formulated as coordinatively unsaturated σ-acyls, i.e., monohapto M–C(O)R species, the existence of an increasing number of compounds in which the acyl group functions formally as a three-electron donor ligand through its C and O atoms seems to support the η^2-acyl formulation proposed for the intermediates in some carbonyl insertion and decarbonylation reactions. Nevertheless, although for the well-known $Mn(CO)(CH_3)$–$Mn(COCH_3)$ system both MO[1f] and mechanistic studies[1c] are neither against nor in favor of an η^2-acetyl structure for the Mn(COC-

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[†] Universidad de Sevilla.

[‡] University of Alabama.

[§] Northern Illinois University.

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$H_3)(CO)_4$ intermediate, recent matrix isolation studies reach the conclusion that the acetyl ligand in such a species is in fact σ-bonded to the metal.[4]

We have been interested for some time in the chemistry of transition-metal acyl complexes, one of our objectives being the synthesis of this type of complex and the study of their chemical reactivity, particularly decarbonylation reactions,[5] insertion of unsaturated molecules into the metal–acyl bond,[6] and other related processes. During studies on alkyl complexes of molybdenum and tungsten, in oxidation state +4, it was found[7] that the trialkyl derivatives $M(CH_2SiMe_3)_3Cl(PMe_3)$ (M = Mo, W) undergo carbonylation at room temperature and pressure to afford dimeric η^2-acyl complexes of composition $[MCl(\eta^2\text{-}COCH_2SiMe_3)(CO)_2(PMe_3)]_2$. However, the low yields of the overall reactions and the thermal instability of the tungsten derivative precluded a detailed investigation of their chemical properties. We set out to prepare and characterize monomeric acyl complexes of Mo(II) and W(II) containing carbonyl and tertiary phosphine ligands and to study their reaction chemistry, particularly the substitution of the additional coligands. In this paper we wish to report the results found for the molybdenum system which include the synthesis of a series of complexes of composition $Mo(COR)X(CO)(PMe_3)_3$ for various combinations of R = CH_3, CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph and X = Cl, Br, I, NCO. IR and NMR studies (vide infra) suggest the acyl group coordinates to the metal in a dihapto fashion, and this has been confirmed by X-ray studies for the complex $Mo(COCH_2SiMe_3)Cl(CO)(PMe_3)_3$. We have also carried out the reactions of the above complexes with carbon monoxide which afford the dicarbonyl derivatives $Mo(COR)X(CO)_2(PMe_3)_2$, also containing a η^2-acyl ligand. We have finally attempted substitution of the X group both in the monocarbonyl and the dicarbonyl complexes by the powerful chelating, formally three-electron donor ligand, dimethyldithiocarbamate. Again the reactions produced no apparent changes in the metal–η^2-acyl linkage and led instead to the corresponding $Mo(COR)(S_2CNMe_2)(CO)_n(PMe_3)_{3-n}$ (n = 1,2) derivatives. Unexpectedly, the trimethylsilylmethyl derivative $Mo(COCH_2SiMe_3)(S_2CNMe_2)(CO)(PMe_3)_2$ undergoes a facile C–Si heterolysis, under remarkably mild conditions, to yield an unprecendented complex, $Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2$, in which the molybdenum atom attains an 18-electron configuration by virtue of a strong interaction with a β-C–H bond of the acetyl group, as shown by NMR and X-ray studies. Part of this work has been briefly communicated.[8] While our work was in progress, other molybdenum η^2-acyl complexes containing poly(1-pyrazolylborato) ligands have been briefly reported.[9]

Results and Discussion

Synthesis of $Mo(\eta^2\text{-}COR)X(CO)(PMe_3)_3$ and $Mo(\eta^2\text{-}COR)X(CO)_2(PMe_3)_2$ Complexes. X-ray Structure of $MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3$ (1). The acyl complex **1** can be conveniently prepared, in 60–70% yield, by the two-step sequence of eq 1.

$$\mathrm{MoCl_2(PMe_3)_4} \xrightarrow[\text{THF}]{\text{CO, 60 °C}} \mathrm{MoCl_2(CO)_2(PMe_3)_3} \xrightarrow[\mathrm{Et_2O}]{\mathrm{Mg(CH_2SiMe_3)Cl}} \mathrm{MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3} \qquad (1)$$

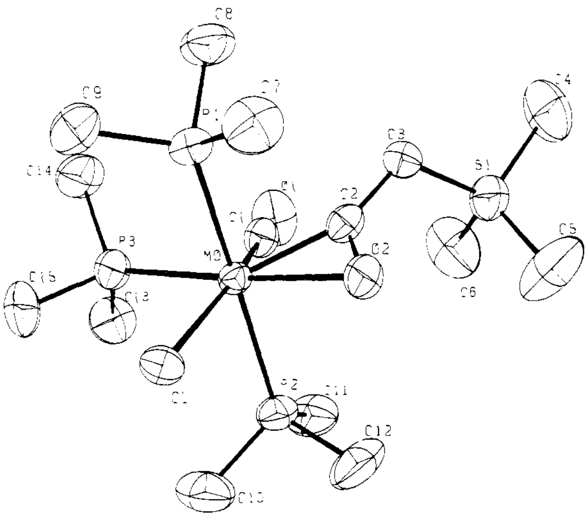
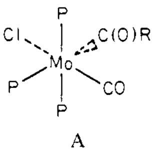
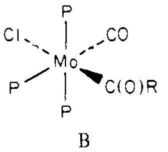


Figure 1. Molecular structure of $Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)(PMe_3)_3$ with the atoms represented by their 50% probability ellipsoids for thermal motion.

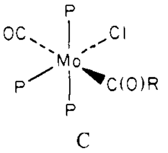
The pure acyl is a dark red crystalline solid with IR bands at 1810 and 1500 cm^{-1}. The latter is due to ν(C–O) of the acyl ligand, and its low energy indicates dihapto coordination. The ^1H NMR of **1** establishes the presence of two equivalent *trans*-PMe_3 ligands (δ 1.2, virtually coupled triplet, $J_{PH} + J_{PH'} = 8$ Hz) and of a third PMe_3 molecule which occupies a cis position with respect to the others (δ 1.3, doublet, $J_{PH} = 3$ Hz). If the η^2-acyl ligand is considered to formally occupy a single coordination site, a distorted octahedral geometry, with meridional distribution of the phosphine ligands, can be proposed for **1**. This is in agreement with ^{31}P NMR studies, since the $^{31}P\{^1H\}$ NMR consists of an AX_2 pattern, with δ_{P_A} 12.3, δ_{P_X} −1.4, and $^2J_{P_AP_X} = 21.1$ Hz. The meridional distribution of the PMe_3 groups leaves three possibilities, A, B, and C, for accommodating the other ligands in the molecule of **1**.



A



B



C

A distinction among these alternatives could not be easily made with the available data and was achieved with the aid of an X-ray study. Figure 1 shows the molecular structure and atom numbering scheme for $MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3$, which is isostructural with the tungsten analogue.[8a] As can be seen, **1** is essentially octahedral, with the Mo–C(1), Mo–P(3), Mo–Cl, and Mo–O(2) bonds lying approximately in the same plane and the Mo–C(2) bond scarcely raised above that plane. The most interesting aspect in this structure is doubtless the η^2-coordination of the acyl ligand, which is characterized by a short metal–carbon bond of 2.024 (6) Å approaching a normal metal–carbonyl distance and a metal–oxygen separation (2.324 (4) Å) indicative of a single bond. The Mo–C(acyl) bond length is shorter than that of the Mo–O(acyl) by 0.30 Å, and a dihedral angle of 26.95° is observed between the plane formed by atoms Mo, Cl, P(3), and C(1) and that of Mo, C(2), and O(2). In the related compounds $[MCl(\eta^2\text{-}COCH_2SiMe_3)(CO)_2(PMe_3)]_2$ (M = Mo, W)[7] similar values have been found, viz., $\Delta_{(Mo-O)-(Mo-C)} = 0.27$ Å (0.26 Å, M = W) and dihedral angles of 32.39° (M = Mo) and 32.13° (M = W). It is unlikely, however, that the value of Δ and the size of the dihedral angle are related in this type of compound. Thus we have recently determined the structure of $MoBr(\eta^2\text{-}COCH_2CMe_3)(PMe_3)_4$,[11] which shows $\Delta_{(Mo-O)-(Mo-C)} = 0.24$ Å and a dihedral angle of only 0.57°. The recently reported $Mo(\eta^2\text{-}COR)(CO)_2HB(3,5\text{-}Me_2C_3HN_2)_3$ (R = C_6H_4-*p*, C_6H_{11})

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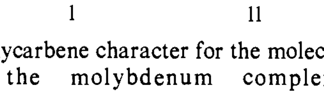
exhibit similar structural features for the Mo–(η^2-acyl) linkage.[9] In other η^2-acyl complexes which have been structurally determined, Ru(η^2-COCH$_3$)I(CO)(PPh$_3$)$_2$,[12] V(η^2-COC$_3$Ph$_3$H$_2$)(CO)$_3$(Ph$_2$AsCH$_2$CH$_2$PPh$_2$),[13] Cp$_2$TiCl(η^2-COCH$_3$),[14] and Cp$_2$Zr(η^2-COCH$_3$)(CH$_3$),[15] corresponding differences in the metal–oxygen acyl bond length and the metal–carbon acyl separation of 0.44, 0.23, 0.12, and 0.09 Å have been found. As can be seen, the Ru complex shows the weakest η^2 interaction, a fact that has been associated[12] with the facility with which the reverse migration reaction, to form the alkyl dicarbonyl Ru(CH$_3$)I(CO)$_2$(PPh$_3$)$_2$, occurs in solution. On the other hand, in the recently described (C$_5$Me$_5$)$_2$ThCl(η^2-COCH$_2$CMe$_3$)[16] the Th–O(acyl) bond is shorter than the Th–C(acyl) length by 0.07 Å, indicating a large contribution of resonance structure II and hence


I II

an important oxycarbene character for the molecule which is not obvious in the molybdenum complex, MoCl(η^2-COCH$_2$SiMe$_3$)(CO)(PMe$_3$)$_3$.

It is interesting to point out that both in complex **1** and in the related chloride-bridged [Mo(μ-Cl)(η^2-COCH$_2$SiMe$_3$)(CO)$_2$(PMe$_3$)]$_2$ the chloride ligands are trans to CO and the Mo–Cl bond lengths are very similar (2.550 (1) Å in **1**, 2.560 Å (average) in the dimer).[7a] As expected, these distances are appreciably longer than the value of 2.420 (6) Å found for the average Mo–Cl bond lengths in *trans*-MoCl$_2$(PMe$_3$)$_4$.[17] This leads to the obvious conclusion that CO is higher than chloride in the trans-influence series for Mo(II) complexes. By extension of the above comparison to the Mo–Cl distances in quadruply bonded dinuclear Mo(II) complexes[18] it can be written that CO > PR$_3$ > O, Cl. On the other hand, comparison of the lengths of the Mo–P bonds in **1** leads to PMe$_3$ > η^2-C(O)R. If the order of the above ligands in the trans-influence series parallels that of the trans-effect series, easy substitution of chloride by other anionic ligands and of one of the *trans*-PMe$_3$ molecules by neutral ligands is to be expected. This is in excellent agreement with the results, to be discussed below, on the reactivity of **1**, but contrasts with previous studies on group 8 transition-metal η^1-acetyl derivatives,[1e,19] where a greater trans-directing and -labilizing effect has been found for η^1-acetyl relative to CO and group 5 donors.

The reactions of MoCl$_2$(CO)$_2$(PMe$_3$)$_3$ with other Grignard reagents, Mg(R)Cl (R = CH$_2$CMe$_3$, CH$_2$CMe$_2$Ph), are in general slow and require the use of an excess of the Grignard reagents (usually 2 equiv) and reaction periods of several hours. In an attempt to prepare the chloroacetyl complex MoCl(η^2-COCH$_3$)(CO)(PMe$_3$)$_3$ by reaction of MoCl$_2$(CO)$_2$(PMe$_3$)$_3$ with Mg(CH$_3$)I, we obtained instead the iodo derivative Mo(η^2-COCH$_3$)I(CO)(PMe$_3$)$_3$. Similar halogen exchanges have been observed previously[20] and have been associated with the "hard" nature of the Mg^{2+} ion. The chloroacetyl complex MoCl(η^2-COCH$_3$)(CO)(PMe$_3$)$_3$ can be obtained by alkylation of MoCl$_2$(CO)$_2$(PMe$_3$)$_3$ with MeLi (vide infra).

While acyl formation reactions can occur either by the well-known[1a] alkyl migration path or by direct attack on a coordinated CO molecule,[9] the first route seems more reasonable for the present compounds. In order to directly observe the primary product in the alkylation of MoCl$_2$(CO)$_2$(PMe$_3$)$_3$, different alkyl groups were used (see above), although the reactions invariably yielded η^2-acyl products. To take advantage of the decrease in reaction rates expected for third-row transition metals relative to second- and first-row elements,[1f] we investigated the reaction of WCl$_2$(CO)$_2$(PMe$_3$)$_3$ and Mg(CH$_2$SiMe$_3$)Cl but obtained again a η^2-acyl derivative, WCl(η^2-COCH$_2$SiMe$_3$)(CO)(PMe$_3$)$_3$, isostructural to the molybdenum analogue.[8a] Since a decrease in the chain length and in the donor ability of the alkyl group decreases the ease of migration, we finally carried out the reaction of WCl$_2$(CO)$_2$(PMe$_3$)$_3$ with MeLi, which yielded the 7-coordinate complex W(CH$_3$)Cl(CO)$_2$(PMe$_3$)$_3$. Thus, it seems likely that alkylation occurs at the metal center and that it is followed by a migratory insertion reaction which, for M = Mo, is very rapid for all the alkyl groups investigated. The synthesis of other η^2-acyl-tungsten complexes and the reactions of MoCl$_2$(CO)$_2$(PMe$_3$)$_3$ with Grignard reagents Mg(R)X bearing more electronegative R groups are presently under investigation and will be addressed in a later paper.

As indicated above, the chloride ligand in the MoCl(η^2-COR)(CO)(PMe$_3$)$_3$ complexes is labile and can be easily exchanged by other halide or pseudohalide groups. Thus, metathesis reactions with KX (X = Br, NCO) in dry acetone or tetrahydrofuran yield the remaining MoX(η^2-COR)(CO)(PMe$_3$)$_3$ complexes (X = Br, NCO; R = CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph; X = NCO; R = CH$_2$CMe$_3$) studied in this work. IR and ^{1}H NMR data are in accord with a structure of the type found for **1**. Thus the IR spectrum shows a medium-intensity band in the range 1530–1480 cm^{-1}, due to ν(C–O) of the acyl unit. This is in the region characteristic for η^2-acyl groups[4] (approximately 1620–1450 cm^{-1}). Recent reports[21] concerning the complex Fe(η^5-C$_5$H$_5$)(COC$_2$H$_5$)(PMe$_3$)$_2$, which in spite of displaying $\nu_{\mathrm{CO(acyl)}}$ at 1520 cm^{-1} has been shown by X-ray crystallography to contain a normal σ-propionyl ligand, question the validity of IR data as a diagnosis for the mode of bonding of the acyl groups. However the close similarity found in the properties of the Mo(COR)X(CO)(PMe$_3$)$_3$ complexes with those of **1** strongly supports the proposed dihapto formulation. NMR data for the Mo(η^2-COR)X(CO)(PMe$_3$)$_3$ compounds are collected in Table 1 of the supplementary material.

In an attempt to expand the coordination sphere around the molybdenum atom by coordination of an additional ligand, with concomitant change in the bonding mode of the acyl unit, we have carried out the reaction of the Mo(η^2-COR)X(CO)(PMe$_3$)$_3$ complexes with carbon monoxide. However, instead of the desired Mo(η^1-COR)X(CO)$_2$(PMe$_3$)$_3$ derivatives we have observed substitution of one of the PMe$_3$ ligand by a second CO molecule and formation of new η^2-acyls of composition Mo(η^2-COR)X(CO)$_2$(PMe$_3$)$_2$ according to eq 2. The reactions take place under

$$\mathrm{Mo}(\eta^2\text{-COR})\mathrm{X(CO)(PMe_3)_3} + \mathrm{CO} \rightarrow \mathrm{Mo}(\eta^2\text{-COR})\mathrm{X(CO)_2(PMe_3)_2} + \mathrm{PMe_3} \quad (2)$$

very mild conditions, and in order to avoid further substitution and formation of intractable mixtures, they must be carried out at room temperature or below, avoiding overexposure to CO. Under the conditions specified in the Experimental Section high yields of the dicarbonyl complexes Mo(η^2-COR)X(CO)$_2$(PMe$_3$)$_2$ (X = Cl, R = CH$_3$, CH$_2$CMe$_3$, CH$_2$CMe$_2$Ph; X = I, R = CH$_3$) can be obtained. These compounds are yellow crystalline solids, appreciably less soluble than the parent monocarbonyls. Interestingly MoCl(η^2-COCH$_2$SiMe$_3$)(CO)(PMe$_3$)$_3$ does not yield the corresponding acyl dicarbonyl but rather the acetyl MoCl(COCH$_3$)(CO)$_2$(PMe$_3$)$_2$, obviously formed by C–Si heterolysis by adventitious water during the carbonylation process.

IR studies for the dicarbonyl complexes show the presence of two strong bands between 1935 and 1825 cm^{-1} due to the C–O stretching vibrations of the two coordinated CO groups, clearly indicating a cis distribution of the carbonyl ligands. In addition,

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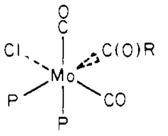
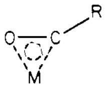
the complexes exhibit a well-defined, medium intensity absorption in the proximity of 1580 cm^{-1} due to the C-O stretching of the acyl groups. Although, as noted above, the energy of this band cannot infallibly be taken as evidence for the presence of a η^2-acyl linkage, the pronounced tendency of the molybdenum atom to achieve an 18-electron configuration in carbonyl complexes of this type strongly favors the proposed dihapto formulation. The dicarbonyl complexes show similar NMR spectra. The ^{1}H NMR of the acetyl complex $Mo(COCH_3)I(CO)_2(PMe_3)_2$ displays two doublets at δ 1.30 (J = 8.4 Hz) and 1.1 (J = 7.8 Hz), indicating that the PMe_3 ligands are in different environments. The acetyl protons give rise to a singlet at ca. 2.6 ppm. Of the possible structures consistent with the above IR and NMR data we favor D by similarity with the distribution of the ligands found in **1** and



D

in $[Mo(\mu\text{-}Cl)(\eta^2\text{-}COCH_2SiMe_3)(CO)_2(PMe_3)]_2$.[7] Note that the overall reaction of formation of the dicarbonyl, $Mo(\eta^2\text{-}COR)X(CO)_2(PMe_3)_2$, from the parent monocarbonyl would simply imply substitution of one of the *trans*-PMe_3 molecules by the π-acid CO ligand, a process which seems in principle feasible considering the high trans influence (and high trans effect) of the PMe_3 ligands, manifested in the long *trans*-Mo-P bonds found in complex **1**. The process apparently requires no change in the metal–η^2-acyl linkage, although the variation in the electron density at the metal that accompanies the substitution of the basic PMe_3 by a CO ligand must cause a modification in the strength of the metal–acyl bond. This is clearly evidenced by the large (ca. 80–90 cm^{-1}) shift to high frequency observed for $\nu_{CO(acyl)}$ (from 1505 (n = 1) to 1590 (n = 2) cm^{-1} in the $Mo(\eta^2\text{-}COCH_3)I(CO)_n(PMe_3)_{4-n}$ complexes). If the Mo-acyl bond could be viewed as a side-on interaction similar to that found in olefin, CO_2 and related complexes, E, the



E

observed shift would be consistent with a decrease in the π-back-donation from the filled Mo-dπ orbitals to the empty π^* orbitals of the C=O unit, which is to be expected upon substitution of PMe_3 by CO.

$Mo(COR)(S_2CNMe_2)(CO)(PMe_3)_2$ Complexes. Synthesis and Reaction with CO. X-ray Structure of $Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2$ (2). In investigating the reactivity of the $Mo(\eta^2\text{-}COR)X(CO)(PMe_3)_3$ complexes attempts were made to induce a change in the coordination mode of the acyl group by substituting the X group by the powerful chelating three-electron donor ligand dimethyldithiocarbamate. The reaction of **1** with $NaS_2CNMe_2\cdot 2H_2O$ in tetrahydrofuran afforded, after workup, high yields of yellow-orange crystals of a new dithiocarbamate complex. In addition to a relatively weak and broad absorption at 1510 cm^{-1} due to ν(C–N) of the dithiocarbamate group, the Nujol mull IR spectrum of this complex shows two strong bands at 1775 and 1595 cm^{-1}, due respectively to ν(C–O) of the terminal CO group and of the acyl ligand. These bands shift to slightly higher frequencies (1790 and 1610 cm^{-1}) in the solution (benzene) spectrum. The position of the latter is in the upper end of the region characteristic for η^2-COR ligands and suggests the presence of a σ-acyl group. Most surprising the IR spectrum does not show the characteristic doublet of bands at ca. 1250–1240 cm^{-1} due to vibrations associated with the Me_3SiCH_2 group. The absence of this ligand was further confirmed by NMR studies. The ^{1}H NMR shows reasonances at δ 2.68 (s, 6 H, S_2CNMe_2) and 1.38 (d, 18 H, PMe_3, observed J_{PH} = 9.9 Hz), indicating the presence of a S_2CNMe_2 group and two *cis*-PMe_3 ligands, but no other resonances were observed with the exception of a triplet at δ 1.87 (J_{PH} = 1.3 Hz) with relative intensity corresponding to three H atoms. It is thus clear that a hydrolytic cleavage of the $Me_3Si\text{-}CH_2$ bond has occurred, with formation of an acetyl complex. Since the reaction of complex **1** with H_2O gives no isolable products, it seems that the desilylation reaction takes place after formation of the dithiocarbamate derivative $Mo(COCH_2SiMe_3)(S_2CNMe_2)(CO)(PMe_3)_2$. This has been confirmed by the isolation of this complex and subsequent transformation (see below) into the acetyl (eq 3). Although

$$MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3 \xrightarrow[-NaCl,\ -PMe_3]{NaS_2CNMe_2} Mo(COCH_2SiMe_3)(S_2CNMe_2)(CO)(PMe_3)_2 \xrightarrow{H_2O} Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2 \quad (3)$$

similar desilylation reactions have been observed by other workers,[22] those reported in this paper, leading to $Mo(\eta^2\text{-}COCH_3)Cl(CO)_2(PMe_3)_2$ (vide supra) and $Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2$ (**2**), take place under remarkably mild conditions.

Although analytical data for **2** and the IR and NMR studies described above seem in accord with the proposed formulation, with the acetyl group possibly σ-bonded to the metal, there are two aspects of importance in connection with the structure of **2** that should be mentioned here. First, if as indicated the $COCH_3$ behaves as an η^1-acyl, the application of electron-counting rules would yield an open-shell, 16-electron configuration at the molybdenum center, which as noted above is highly unlikely in complexes of this type. The second important point arises when a comparison of the chemical shift of the hydrogen atoms bonded to the β-carbon atom of the acyl group in complexes of the types $Mo(\eta^2\text{-}COCH_2R')Cl(CO)(PMe_3)_3$ and $Mo(COCH_2R')(S_2CNMe_2)(CO)(PMe_3)_2$ is made. For R′ = CMe_3, the methylene protons in the above complexes give resonances at δ 3.39 and 3.30, respectively, with a difference of less than 0.1 ppm. This is also the case when R′ = CMe_2Ph (3.84 and 3.80), but when R′ = H the corresponding values are 2.82 and 1.87, with a difference of almost 1 ppm. Thus there is an abnormal high-field shift for the acetyl protons in $Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2$ which cannot be easily explained. In addition, and rather unexpectedly, the corresponding resonance is clearly split into a triplet due to coupling to the phosphorus nuclei (J_{PH} = 1.3 Hz). It therefore seems that the acetyl group in **2** is engaged in a direct interaction with the molybdenum atom that would render the otherwise electron-deficient metal center electronically saturated. This has been confirmed by ^{13}C NMR studies. The $^{13}C\{^1H\}$ NMR spectrum (22.50 MHz) displays bands at δ 38.6 (s) and 7.9 (br t, J_{CP} = 3.4 Hz) that become quartets in the gated decoupled spectrum. The first (J_{CH} = 137 Hz) can be assigned to the $S_2CN\mathit{Me}_2$ groups while the second is due to the acetyl methyl carbon. The value of $^2J_{CH}$ for the acetyl methyl group of ca. 130 Hz is somewhat lower than that found for the S_2CNMe_2 groups, but it is in the range typical for saturated (sp^3) C–H bonds and cannot therefore be taken as evidence for the existence of a Mo–C–H interaction. However, as in other similar cases this could be due to an increase of J(C–H nonbridging) upon formation of the M–H–C bridge, which has been attributed to an increase in s character in the nonbridging C–H bonds.[23] Unequivocal evidence for the existence of a strong Mo–C–H interaction in complex **2** comes from a consideration of the resonance due to the acetyl methyl carbon atom which appears at markedly higher field than is found in other acetyl complexes. Typical values are ca. 50 ppm in $[Fe(CO)_2(COCH_3)L(diars)]^+$ complexes (L = P donor ligand),[1e] 43–48 ppm in $RuX(CO)_2(COCH_3)(PMe_2Ph)_2$ (X = Cl, I),[19] and 48.3 ppm in $[Cp_2Zr(COCH_3)Mo(CO)_2Cp]$ (the latter complex containing a μ-η^2-acetyl group).[3c] This and the observed coupling to the phosphorus nuclei of ca. 3.4 Hz clearly indicate a strong interaction between the molybdenum atom and the methyl

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(22) Allen, S. R.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 826–828.

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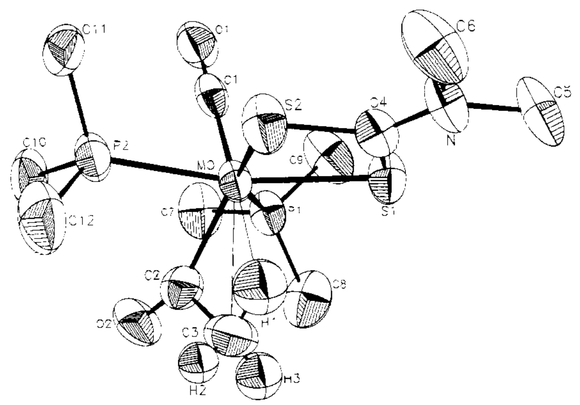


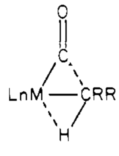
Figure 2. Molecular structure and atom labeling scheme for Mo($COCH_3$)(S_2CNMe_2)(CO)(PMe_3)$_2$. All hydrogens except those on C(3) have been omitted. The atoms are represented by their 50% probability ellipsoids for thermal motion.

acetyl group. To further confirm this observation an X-ray structure determination of complex **2** was undertaken.

The molecular structure and atom labeling scheme for Mo($COCH_3$)(S_2CNMe_2)(CO)(PMe_3)$_2$ are presented in Figure 2. The most interesting aspect of the structure is the Mo–acyl interaction in which C(3) and H(1) are displaced toward the metal. The displacement can readily be observed in the Mo–C(2)–O(2) and Mo–C(2)–C(3) angles of 149.2 (8)° and 90.9 (8)° (Table V), respectively. In (η^5-C_5H_5)Mo(COMe)(CO)$_2$(PPh_3)[24] where no appreciable Mo–O(acyl) or Mo–Me(acyl) interaction was noted, these angles were approximately equal at 120.9° and 121.2°. When the acyl oxygen atom is bonded to the metal center the M–C–O and M–C–C angles show the opposite displacement as in the 87.5° and 149.0° values found for complex **1**. The Mo–C(2)(acyl) bond distance, 2.05 Å, is similar to that found for **1** (2.024 Å) and [MoCl(η^2-$COCH_2SiMe_3$)(CO)$_2$(PMe_3)$_2$]$_2$ (2.023 Å).[7a] The Mo–C(3) distance of 2.60 (1) Å is only ca. 0.3 Å longer than the average Mo–Me bond length in (η^6-C_6H_5R)Mo(CH_3)$_2$(PMe_2Ph)$_2$ (R = H, Me),[25] and the Mo–H(1) separation of 2.06 (9) Å is only 0.24 Å longer than in $Mo_2H_4(PMe_3)_6$.[26] Both distances indicate substantial Mo–C(3) and Mo–H(1) bonding interactions, and consideration of this system as having a nonclassical two-electron, three-center interaction would allow the Mo atom to formally obtain an 18-electron configuration. It should be pointed out that the C–H···Mo interaction appears to be structurally and thermodynamically competitive with η^2-acyl coordination. An analogous competition has been observed between C–H···Mo interaction and olefin–metal bonding in a molybdenum–pyrazolylborato complex.[27] The rest of the bonding in Mo($COCH_3$)(S_2CNMe_2)(CO)(PMe_3)$_2$ appears normal and similar to the situation found in complexes containing related ligands.[28]

The geometry found for compound **2** provides the first example of a severely distorted transition-metal-β-C–H interaction in an acyl complex and furnishes striking additional evidence for the so-called β-effect in transition-metal–hydrocarbyl systems. On the other hand, the isolation of **2** offers an attractive alternative to the proposed intermediates for the CO migratory insertion reaction, namely that the migration of the alkyl group can be anchimerically assisted by an *agostic* interaction[23] with the metal center, as shown in F.

The geometry of **2** can therefore be viewed as a model for the transition state (or intermediate) of the CO insertion reaction into M–C bonds.



F

As noted above (eq 3), the formation of complex **2** in the reaction of **1** with $NaS_2CNMe_2 \cdot 2H_2O$ takes place by C–Si heterolysis in the dithiocarbamate complex Mo($COCH_2SiMe_3$)(S_2CNMe_2)(CO)(PMe_3)$_2$ (**3**). Accordingly, the reaction of **1** with anhydrous NaS_2CNMe_2, under strictly anhydrous conditions, yields **3**, which converts into **2** by addition of small amounts of water. Using D_2O, Mo($COCH_2D$)(S_2CNMe_2)(CO)(PMe_3)$_2$ can be obtained. No ν(C–D) can be observed in the IR spectrum of this complex, and its ^1H NMR is identical with that of **3** with the exception of the acetyl region where the CH_2D protons give an almost unresolved triplet. As expected, **2** can also be prepared in high yields by reaction of Mo($COCH_3$)X(CO)(PMe_3)$_3$ (X = Cl, I) with NaS_2CNMe_2. Crystallization of crude **3** from Et_2O–hexane mixtures usually yields yellow-orange prisms of **3b**. In some instances dark red crystals of another isomer **3a** have also been obtained and separated manually from those of **3b**. Attempted recrystallization of **3a** afforded however **3b**, and in spite of our efforts we have been unable to ascertain the conditions under which complex **3a** is generated. The red **3a** exhibits IR bands at 1750 and 1490 cm^{-1}, due respectively to ν(CO) for the Mo–CO and Mo–COR groups, while the yellow-orange **3b** gives rise to absorptions at 1760 and 1615 cm^{-1}. Comparison with IR data for **1** and **2** suggests **3a** is a η^2-acyl complex, similar to **1**, while **3b** could be an agostic acyl, analogous to **2**. Unfortunately we have been unable to conclusively confirm these assumptions. Both forms have identical ^1H NMR spectra, consistent with the existence in solution of an equilibrium mixture of two isomers. The main component in this mixture exhibits a pseudotriplet at δ 1.75 for the PMe_3 ligands and a singlet at 3.25 for the acyl methylene protons, in the region found for η^2-acyl complexes (δ 3.1 for complex **1**). It seems likely that **3a**, the preferred isomer in solution, is a η^2-acyl complex, Mo(η^2-$COCH_2SiMe_3$)(S_2CNMe_2)(CO)(PMe_3)$_2$, possibly with *trans*-PMe_3 ligands. We would, however, postpone a definite proposal on the structures of these two complexes until the results of detailed IR, NMR, and X-ray studies, presently under way, are available.

To gain more information on the above systems we have carried out the preparation of other Mo(COR)(S_2CNMe_2)(CO)(PMe_3)$_2$ complexes containing R groups such as Me_3CCH_2 and Me_2PhCCH_2, where a hydrolytic cleavage similar to the C–Si heterolysis observed for complex **3** could not be feasible. The reaction of the chloro complexes MoCl(η^2-COR)(CO)(PMe_3)$_3$ with NaS_2CNMe_2 takes place readily with formation of the expected Mo(COR)(S_2CNMe_2)(CO)(PMe_3)$_2$ derivatives in eq 4.

$$\mathrm{MoCl(COR)(CO)(PMe_3)_3 + NaS_2CNMe_2 \xrightarrow{THF} Mo(COR)(S_2CNMe_2)(CO)(PMe_3)_2 + NaCl} \quad (4)$$

η^2-Acyl formulations, with *trans*-PMe_3 ligands, are proposed for these complexes since the IR spectrum shows a band at ca. 1500 cm^{-1} due to ν(C–O) acyl and the ^1H NMR displays a pseudotriplet for the phosphine ligands. The dithiocarbamate methyl protons give rise to a broad unresolved singlet, indicating that exchange of the Me groups is slow on the NMR time scale.

As with the Mo(η^2-COR)X(CO)(PMe_3)$_3$ complexes we were interested in determining whether the η^2-acyl linkage in the related dithiocarbamate derivatives would remain intact upon reaction with carbon monoxide. This interest was further enhanced by the isolation of complex **2**. Since it is expected that the interacting C–H bond can be displaced from the metal center by action of other donor ligands, we had the opportunity of carrying out the migratory insertion reaction of carbon monoxide into the Mo–C bond of the as yet unknown methyl complex "Mo(CH_3)(S_2CNMe_2)(CO)$_2$(PMe_3)$_2$" to give an η^1-acetyl Mo($COCH_3$)(S_2CNMe_2)(CO)$_2$(PMe_3)$_2$ or a related η^2-acyl complex

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[24] Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1968**, *7*, 953–959.

[25] Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Carmona, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1519–1523.

[26] Jones, R. A.; Chiu, K. W.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1980**, 408–409.

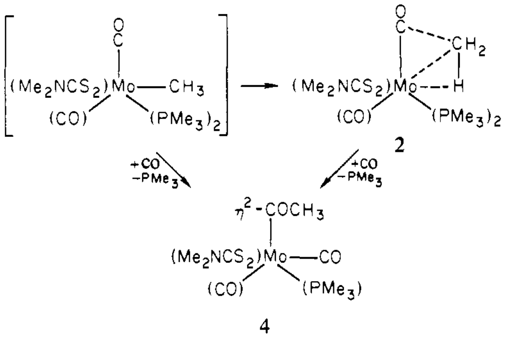
[27] Cotton, F. A.; Day, V. W. *J. Chem. Soc., Chem. Commun.* **1974**, 415–416.

[28] Butler, G.; Chatt, J.; Leigh, G. J.; Smith, A. R. P. *Aust. J. Chem.* **1980**, *33*, 717.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	$Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)(PMe_3)_3$	$[Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2]$
mol wt	502.9	425.4
space group	$P2_12_12_1$	$P2_1/c$
cell constants		
a, Å	10.747 (3)	11.633 (5)
b, Å	12.511 (3)	9.962 (4)
c, Å	18.897 (4)	17.266 (6)
β, deg		95.80 (3)
cell vol, $Å^3$	2540.8	1990.6
molecules/unit cell	4	4
ρ(calcd), g cm^{-3}	1.31	1.42
μ(calcd), cm^{-1}	8.48	10.04
radiation	Mo K	Mo Kα
max crystal dimensions, mm	0.43 × 0.40 × 0.80	0.45 × 0.65 × 0.65
scan width	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ
standard reflections	(10,0,0) (0,0,14)	(0,0,–10) (600)
decay of standards	±2%	±2%
reflections measured	2619	1603
2θ range, deg	50	≤36
reflections collected	2141	1116
no. of parameters varied	208	193
GOF	0.86	2.00
R	0.025	0.029
R_w	0.028	0.034

Scheme I



having only one PMe_3 or CO ligand, via an agostic acyl intermediate **2**, as shown in Scheme I. As expected the reaction takes place under very mild conditions (1–2 min, 20 °C), affording yellow crystals of a complex of composition $Mo(COCH_3)(S_2CNMe_2)(CO)_2(PMe_3)$ (**4**), for which a η^2-acyl coordination of the acetyl group is proposed since $\nu(C–O)_{acyl}$ appears at ca. 1580 cm^{-1}, and the acetyl methyl protons give rise to a singlet at δ 2.88 (2.82 in $MoCl(\eta^2\text{-}COCH_3)(CO)(PMe_3)_3$ and 2.85 in $MoCl(\eta^2\text{-}COCH_3)(CO)_2(PMe_3)_2$; see above). Two strong carbonyl absorptions are found at 1920 and 1820 cm^{-1}, indicating a cis distribution of the carbon monoxide ligands. No definite stereochemical proposal can be given with the available data.

The remaining $Mo(\eta^2\text{-}COR)(S_2CNMe_2)(CO)_2(PMe_3)$ (R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph) complexes can be similarly obtained by carbonylation of the corresponding monocarbonyl derivatives. They exhibit spectral properties close to those of **4**, and therefore the occurrence of η^2-acyl linkages in these complexes is highly likely (cf. Table 2 of the supplementary material).

Concluding Remarks

While the results of recent X-ray studies[21] on the complex $Fe(\eta^5\text{-}C_5H_5)(COC_2H_5)(PMe_3)_2$ question the possibility of distinguishing between η^1- and η^2-acyl structures with the aid of IR data and suggest that the range of ν(C–O) in σ-bonded acyls should be extended to much lower wavenumbers than previously envisaged, the results reported in this paper clearly demonstrate the validity of such assignments when based on IR and NMR data for series of closely related derivatives and supported by an X-ray structural determination on a prototype complex. The wide range over which $\nu(C–O)_{acyl}$ spans for the compounds studied in this work and the strong dependence of the energy of this absorption on the nature of the metal atom and the coligands clearly indicate that the position of this band can only be used as a qualitative indication of the type of acyl bonding and not as a measure of the strength of the M–O bond. As a striking confirmation of the above, the results found for the $MCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3$ (M = Mo, W) complexes can be quoted. The molybdenum complex shows $\nu(C–O)_{acyl}$ at ca. 1500 cm^{-1} and $\Delta_{(Mo–O)-(Mo–C)} = 0.30$ Å, while the tungsten analogue[8a] has $\nu(C–O)_{acyl}$ at 1460 cm^{-1} and $\Delta_{(W–O)-(W–C)} = 0.32$ Å.

Finally, the isolation of the unprecedented acetyl complex **2**, $Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2$, showing a strong Mo-$\beta$-C-H interaction, provides, for the first time, evidence on the possible occurrence of intermediates of this type in the carbonyl migratory insertion reaction. Work is in progress in order to ascertain the occurrence of similar $\overline{\mathrm{M{-}C{-}H}}$ interactions in other related complexes.

Experimental Section

Microanalyses were by Pascher Microanalytical Laboratory, Bonn. Molecular weights were measured cryoscopically, under nitrogen. Infrared spectra were recorded on a Perkin-Elmer Model 577. ^1H NMR spectra were run on a Perkin-Elmer R 12 A (35 °C). ^{31}P NMR were recorded on a Nicolet NT-200 at the University of Alabama. ^{31}P NMR shifts are reported in ppm, referenced to external 85% H_3PO_4.

All preparations and other operations were carried out under oxygen-free nitrogen, following conventional Schlenk techniques. Solvents were rigorously dried under nitrogen by standard techniques and degassed before use. The light petroleum had a bp of 40–60 °C. NaS_2CNMe_2 was dried by heating at 90 °C under vacuum for 6–7 days. $MoCl_2(CO)_2(PMe_3)_3$[10] and PMe_3[29] were prepared by literature methods.

Preparations. $MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3$ (1) and Other $MoCl(\eta^2\text{-}COR)(CO)(PMe_3)_3$ Complexes. To a stirred suspension of yellow $MoCl_2(CO)_2(PMe_3)_3$ (0.90 g, ca. 2 mmol) in 50 mL of diethyl ether, at –60 °C, was added $Mg(CH_2SiMe_3)Cl$ (2.3 mL of a ca. 0.90 M Et_2O solution). The cold bath was then removed and the mixture stirred at room temperature for 5–6 h. The solvent was evaporated in vacuo and the residue was treated with 20 mL of petroleum ether. Et_2O was syringed with stirring until the red color of the precipitate completely disappeared (usually ca. 20 mL of Et_2O). The mixture was centrifuged and the title product crystallized by cooling overnight at –35 °C; yield 60–70%. The reaction can be scaled up without any appreciable change in the yield.

Other related complexes, $MoCl(\eta^2\text{-}COR)(CO)(PMe_3)_3$ (R = CH_2CMe_3, CH_2CMe_2Ph), can be obtained in similar yields by using analogous procedures. Longer reaction times (ca. 12 h) and larger excess of the Grignard reagent (usually 2 equiv) are however required.

$MoBr(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3$. Complex **1** (0.5 g, ca. 1 mmol) and KBr (4 mmol, a large excess) were stirred at room temperature in 20 mL of THF over a period of 12 h. The resulting mixture was then evaporated to dryness and the residue extracted with 40 mL of a 1:1 mixture of petroleum ether–ether. After centrifugation and cooling

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(29) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149–156.

Table II. Final Fractional Coordinates for $Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)(PMe_3)_3$

atom	*x*/*a*	*y*/*b*	*z*/*c*
Mo	0.35481 (4)	0.00440 (4)	0.11539 (2)
Cl	0.5608 (1)	0.1036 (1)	0.10244 (7)
P(1)	0.4608 (1)	−0.0883 (1)	0.21472 (8)
P(2)	0.2810 (2)	0.1331 (1)	0.02300 (8)
P(3)	0.4283 (2)	−0.1396 (1)	0.03664 (8)
Si	−0.0174 (2)	0.0758 (2)	0.2331 (1)
O(1)	0.1221 (5)	−0.1333 (4)	0.0858 (3)
O(2)	0.2853 (4)	0.1311 (3)	0.1961 (2)
C(1)	0.2090 (6)	−0.0818 (4)	0.0984 (3)
C(2)	0.2385 (5)	0.0411 (4)	0.1960 (3)
C(3)	0.1376 (5)	0.0081 (5)	0.2448 (2)
C(4)	−0.1220 (7)	0.0252 (8)	0.3034 (4)
C(5)	0.007 (1)	0.2207 (6)	0.2412 (7)
C(6)	−0.0856 (7)	0.0454 (8)	0.1461 (4)
C(7)	0.4893 (6)	0.0028 (7)	0.2885 (3)
C(8)	0.3816 (7)	−0.1977 (5)	0.2584 (4)
C(9)	0.6167 (6)	−0.1450 (6)	0.2044 (4)
C(10)	0.3831 (8)	0.1581 (7)	−0.0513 (4)
C(11)	0.1325 (8)	0.1107 (6)	−0.0220 (4)
C(12)	0.2617 (9)	0.2662 (5)	0.0563 (4)
C(13)	0.3533 (9)	−0.1535 (6)	−0.0487 (3)
C(14)	0.4212 (8)	−0.2783 (5)	0.0665 (4)
C(15)	0.5889 (7)	−0.1264 (6)	0.0091 (4)
H(1)[C(3)]	0.1654	0.0100	0.2948
H(2)[C(3)]	0.1299	−0.0748	0.2479
H(3)[C(4)]	−0.0876	0.0373	0.3414
H(4)[C(4)]	−0.2001	0.0552	0.3050
H(5)[C(4)]	−0.0747	−0.0615	0.3203
H(6)[C(5)]	0.0733	0.2453	0.2789
H(7)[C(5)]	−0.0562	0.2534	0.2160
H(8)[C(5)]	0.0567	0.2788	0.2166
H(9)[C(6)]	−0.1875	0.0618	0.1371
H(10)[C(6)]	−0.0148	0.0598	0.1129
H(11)[C(6)]	−0.1305	−0.0147	0.1430
H(12)[C(7)]	0.4056	0.0392	0.3198
H(13)[C(7)]	0.5424	0.0674	0.2819
H(14[C(7)]	0.5435	−0.0332	0.3325
H(15)[C(8)]	0.3150	−0.1612	0.2746
H(16)[C(8)]	0.3566	−0.2455	0.2283
H(17)[C(8)]	0.4166	−0.2185	0.2924
H(18)[C(9)]	0.6311	−0.2005	0.1686
H(19)[C(9)]	0.6606	−0.1664	0.2459
H(20)[C(9)]	0.6811	−0.0903	0.1746
H(21)[C(10)]	0.3695	0.2153	−0.0795
H(22)[C(10)]	0.3870	0.0935	−0.0861
H(23)[C(10)]	0.4650	0.1668	−0.0456
H(24)[C(11)]	0.1518	0.0601	−0.0448
H(25)[C(11)]	0.1110	0.1587	−0.0562
H(26)[C(11)]	0.0565	0.0927	0.0226
H(27)[C(12)]	0.2196	0.2741	0.0952
H(28)[C(12)]	0.2412	0.3225	0.0404
H(29)[C(12)]	0.3553	0.2725	0.0936
H(30)[C(13)]	0.3511	−0.2128	−0.0787
H(31)[C(13)]	0.2762	−0.1552	−0.0450
H(32)[C(13)]	0.3381	−0.0874	−0.0726
H(33)[C(14)]	0.3445	−0.2962	0.0837
H(34)[C(14)]	0.4400	−0.3351	0.0272
H(35)[C(14)]	0.4668	−0.2998	0.1117
H(36)[C(15)]	0.5863	−0.0599	−0.0192
H(37)[C(15)]	0.6368	−0.1607	0.0525
H(38)[C(15)]	0.6310	−0.1614	−0.0182

Table III. Bond Distances (Å) and Angles (deg) for $Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)(PMe_3)_3$

atoms	distance	atoms	distance
M–Cl	2.550 (1)	P(2)–C(11)	1.830 (8)
M–P(1)	2.483 (1)	P(2)–C(12)	1.792 (7)
M–P(2)	2.504 (2)	P(3)–C(13)	1.811 (7)
M–P(3)	2.467 (2)	P(3)–C(14)	1.826 (6)
M–O(2)	2.324 (4)	P(3)–C(15)	1.810 (7)
M–C(1)	1.929 (6)	Si–C(3)	1.882 (6)
M–C(2)	2.024 (6)	Si–C(4)	1.851 (8)
P(1)–C(7)	1.827 (7)	Si–C(5)	1.839 (8)
P(1)–C(8)	1.811 (7)	Si–C(6)	1.839 (8)
P(1)–C(9)	1.830 (7)	O(1)–C(1)	1.160 (7)
P(2)–C(10)	1.809 (8)	O(2)–C(2)	1.234 (6)
		C(2)–C(3)	1.481 (7)

atoms	angle	atoms	angle
Cl–M–P(1)	84.34 (5)	C(7)–P(1)–C(9)	99.8 (3)
Cl–M–P(2)	83.98 (5)	C(8)–P(1)–C(9)	100.7 (3)
P(1)–M–P(2)	166.58 (6)	M–P(2)–C(10)	117.4 (3)
Cl–M–P(3)	91.11 (5)	M–P(2)–C(11)	120.1 (2)
P(1)–M–P(3)	88.18 (6)	C(10)–P(2)–C(11)	101.2 (4)
P(2)–M–P(3)	98.65 (5)	M–P(2)–C(12)	112.9 (2)
Cl–M–O(2)	90.6 (1)	C(10)–P(2)–C(12)	100.5 (4)
P(1)–M–O(2)	88.3 (1)	C(11)–P(2)–C(12)	101.8 (4)
P(2)–M–O(2)	85.3 (1)	M–P(3)–C(13)	117.7 (3)
P(3)–M–O(2)	175.9 (1)	M–P(3)–C(14)	119.6 (2)
Cl–M–C(1)	164.0 (2)	C(13)–P(3)–C(14)	99.5 (3)
P(1)–M–C(1)	103.7 (2)	M–P(3)–C(15)	114.3 (3)
P(2)–M–C(1)	89.2 (2)	C(13)–P(3)–C(15)	100.2 (4)
P(3)–M–C(1)	75.9 (2)	C(14)–P(3)–C(15)	102.5 (4)
O(2)–M–C(1)	103.3 (2)	C(3)–Si–C(4)	107.4 (3)
Cl–M–C(2)	119.9 (2)	C(3)–Si–C(5)	108.0 (4)
P(1)–M–C(2)	79.6 (1)	C(4)–Si–C(5)	111.3 (5)
P(2)–M–C(2)	100.6 (1)	C(3)–Si–C(6)	111.4 (3)
P(3)–M–C(2)	144.9 (2)	C(4)–Si–C(6)	109.2 (4)
O(2)–M–C(2)	32.0 (2)	C(5)–Si–C(6)	109.6 (5)
C(1)–M–C(2)	75.6 (2)	M–O(2)–C(2)	60.5 (3)
M–P(1)–C(7)	111.3 (2)	M–C(1)–O(1)	177.7 (5)
M–P(1)–C(8)	118.8 (3)	M–C(2)–O(2)	87.5 (4)
C(7)–P(1)–C(8)	101.7 (3)	M–C(2)–C(3)	149.0 (4)
M–P(1)–C(9)	121.4 (2)	O(2)–C(2)–C(3)	123.5 (5)
		Si–C(3)–C(2)	116.7 (4)

at −35 °C the compound was obtained as dark red crystals in ca. 70% yield. Starting with the appropriate chloroacyls and KX salts the following compounds were obtained by the above procedure: $MoBr(\eta^2\text{-}COCH_2CMe_2Ph)(CO)(PMe_3)_3$, $Mo(NCO)(\eta^2\text{-}COR)(CO)(PMe_3)_3$ (R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph). They were isolated as dark red crystalline solids from Et_2O–petroleum mixtures with the exception of the less soluble NCO–CH_2CMe_2Ph derivative, which requires ether–acetone mixtures.

$MoCl(\eta^2\text{-}COCH_3)(CO)(PMe_3)_3$. Methyllithium (1.5 mL, 1.8 M Et_2O solution, 2.7 mmol) was added to a suspension of $MoCl_2(CO)_2(PMe_3)_3$ (1.25 g, 2.5 mmol) in 70 mL of Et_2O, at −10 °C. After a few minutes the reaction mixture was allowed to reach room temperature and then stirred for 6 more h. The solid became syrupy and a red solution was slowly formed. When the reaction was complete a red solution and a white, finely divided solid resulted. This suspension was evaporated to dryness and the residue extracted with a 1:1 petroleum ether–diethyl ether mixture; further centrifugation and cooling at −35 °C overnight produced the desired product as red crystals in ca. 50% yield.

$MoI(\eta^2\text{-}COCH_3)(CO)(PMe_3)_3$. This complex is the only product isolated in the reaction of $MoCl_2(CO)_2(PMe_3)_3$ and 2 equiv of CH_3MgI after 24 h of stirring at room temperature. The product crystallized from ether–petroleum ether at −35 °C in ca. 50% yield. For reasons still unknown, this preparation is not completely reliable, and in some instances very low yields of the title complex have been obtained. The compound can, however, be easily prepared by metathesis of $MoCl(\eta^2\text{-}COCH_3)(CO)(PMe_3)_3$ with KI in acetone or tetrahydrofuran.

$MoCl(\eta^2\text{-}COCH_2CMe_3)(CO)_2(PMe_3)_2$. Through a solution of $MoCl(\eta^2\text{-}COCH_2CMe_3)(CO)(PMe_3)_3$ (0.5 g, ca. 1 mmol) in 40 mL of Et_2O carbon monoxide was slowly bubbled at room temperature until the color of the solution changed from red to pale yellow (ca. 1 h). The solvent was then stripped in vacuo and the residue extracted with petroleum ether–ether. Centrifugation and cooling at −35 °C afforded the desired product as yellow microcrystals in ca. 70% yield.

The complexes $MoCl(\eta^2\text{-}COCH_2CMe_2Ph)(CO)_2(PMe_3)_2$ and $MoI(\eta^2\text{-}COCH_3)(CO)_2(PMe_3)_2$ have been obtained by the same procedure, as yellow crystals from ether–petroleum ether. We have been unable to isolate the complex $MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)_2(PMe_3)_2$ by reaction of **1** with CO. Instead, and doubtless due to the presence of adventitious water, the acetyl complex $MoCl(\eta^2\text{-}COCH_3)(CO)_2(PMe_3)_2$ was isolated in ca. 50% yield.

$Mo(COCH_2SiMe_3)(S_2CNMe_2)(CO)(PMe_3)_2$ (3a, 3b). Thirty milliliters of THF was syringed onto a mixture of $MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3$ (0.5 g, ca. 1 mmol) and anhydrous NaS_2CNMe_2 (2 mmol, excess). The reaction mixture was stirred at room temperature for ca. 6 h, the solvent was then removed in vacuo, and the residue was extracted with 30 mL of petroleum ether. The expected product was obtained in ca. 70% yield upon cooling at 0 °C for several hours. In most cases the title complex was obtained as orange prisms, **3b**, although in some instances, dark red crystals of **3a** were also collected.

Table IV. Final Fractional Coordinates for $[Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2]$

atom	*x/a*	*y/b*	*z/c*
Mo	0.76202 (7)	−0.22062 (7)	0.91007 (4)
S(1)	0.7619 (2)	0.0096 (2)	0.9742 (1)
S(2)	0.6428 (2)	−0.2266 (2)	1.0247 (1)
P(1)	0.8655 (2)	−0.1113 (2)	0.8118 (1)
P(2)	0.7034 (2)	−0.4541 (2)	0.8953 (2)
O(1)	0.5870 (6)	−0.2122 (7)	0.7666 (4)
O(2)	0.9781 (6)	−0.3957 (7)	0.8782 (4)
N	0.6239 (7)	0.0137 (8)	1.0902 (4)
C(1)	0.6552 (8)	−0.2157 (9)	0.8251 (6)
C(2)	0.9145 (9)	−0.324 (1)	0.9114 (6)
C(3)	0.950 (1)	−0.280 (2)	0.9980 (8)
C(4)	0.6708 (8)	−0.0559 (9)	1.0374 (5)
C(5)	0.6472 (9)	0.156 (1)	1.1008 (6)
C(6)	0.5391 (9)	−0.047 (1)	1.1374 (6)
C(7)	0.8835 (9)	−0.206 (1)	0.7257 (5)
C(8)	1.0111 (9)	−0.053 (1)	0.8425 (6)
C(9)	0.8005 (9)	0.039 (1)	0.7702 (7)
C(10)	0.7516 (9)	−0.548 (1)	0.8152 (6)
C(11)	0.5495 (8)	−0.4833 (9)	0.8829 (6)
C(12)	0.747 (1)	−0.560 (1)	0.9779 (7)
H(1)[C(3)]	0.877 (8)	−0.234 (9)	1.009 (5)
H(2)[C(3)]	0.963 (7)	−0.348 (8)	1.026 (5)
H(3)[C(3)]	1.021 (8)	−0.236 (8)	0.999 (5)
H(4)[C(5)]	0.5840	0.2069	1.0640
H(5)[C(5)]	0.7210	0.1830	1.0837
H(6)[C(5)]	0.6016	0.2143	1.1412
H(7)[C(6)]	0.4952	−0.0067	1.1798
H(8)[C(6)]	0.5491	−0.1468	1.1536
H(9)[C(6)]	0.4884	−0.0178	1.0883
H(10)[C(7)]	0.9267	−0.1613	0.6878
H(11)[C(7)]	0.8084	−0.2348	0.6868
H(12)[C(7)]	0.9282	−0.2865	0.7373
H(13)[C(8)]	1.0139	0.0103	0.8920
H(14)[C(8)]	1.0491	−0.0227	0.7893
H(15)[C(8)]	1.0492	−0.1622	0.8444
H(16)[C(9)]	0.7067	0.0355	0.7506
H(17)[C(9)]	0.8558	0.0835	0.7425
H(18)[C(9)]	0.7788	0.1109	0.8098
H(19)[C(10)]	0.7098	−0.6383	0.7998
H(20)[C(10)]	0.8428	−0.5717	0.8230
H(21)[C(10)]	0.7302	−0.4809	0.7677
H(22)[C(11)]	0.5027	−0.4409	0.9190
H(23)[C(11)]	0.5294	−0.5790	0.8773
H(24)[C(11)]	0.5149	−0.4335	0.8285
H(25)[C(12)]	0.7282	−0.5281	1.0294
H(26)[C(12)]	0.7236	−0.6426	0.9643
H(27)[C(12)]	0.8394	−0.5594	0.9926

The two forms exhibit different IR spectra but have identical ^1H NMR (see text). Upon attempted recrystallization, **3a** afforded orange prisms of **3b**.

The complexes $Mo(\eta^2\text{-}COR)(S_2CNMe_2)(CO)(PMe_3)_2$ (R = CH_2CMe_3, CH_2CMe_2Ph) were obtained by the same method, in similar yields. Both crystallized from petroleum ether at −35 °C as dark red crystals.

$Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2$ (2). (a) To a solution of complex **3** (0.5 g, 1 mmol) in acetone two drops of water were added. After being stirred at room temperature for 2 h, the solution was evaporated to dryness, and the yellow-orange microcrystalline residue was washed with petroleum ether and dried in vacuo; yield ca. 100%. The complex was recrystallized from ether–petroleum or from EtOH at −35 °C.

(b) Complex **2** can also be obtained by the reaction of the halo derivatives $Mo(\eta^2\text{-}COCH_3)X(CO)(PMe_3)_3$ (X = Cl, I), with dried NaS_2CNMe_2, by a procedure analogous to that used for synthesis of other dithiocarbamate complexes; yield ca. 70%.

$Mo(\eta^2\text{-}COCH_3)(S_2CNMe_2)(CO)_2(PMe_3)$ (4). (a) A solution of the trimethylsilylmethyl complex $Mo(\eta^2\text{-}COCH_2SiMe_3)(S_2CNMe_2)(CO)_2(PMe_3)$ in acetone was treated with water as above. Crystallization from ether–petroleum affords yellow crystals of the compound in ca. 30% yield.

(b) Carbon monoxide was bubbled through a solution of complex **2** in Et_2O, for ca. 2 min. The color of the solution changed to pale yellow, and from the reaction mixture the dicarbonyl complex was obtained in ca. 70% yield. The complexes $Mo(\eta^2\text{-}COR)(S_2CNMe_2)(CO)_2(PMe_3)$ (R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph) were similarly obtained by carbonylation of the corresponding monocarbonyl derivatives $Mo(\eta^2\text{-}COR)(S_2CNMe_2)(CO)(PMe_3)_2$.

Table V. Bond Distances (Å) and Angles (deg) for $[Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2]$

atoms	distance	atoms	distance
Mo–S(1)	2.547 (2)	Mo–S(2)	2.529 (2)
Mo–P(1)	2.435 (2)	Mo–P(2)	2.430 (3)
Mo–C(1)	1.83 (1)	Mo–C(2)	2.05 (1)
Mo–C(3)	2.60 (1)	Mo–H(1)	2.06 (9)
S(1)–C(4)	1.724 (9)	S(2)–C(4)	1.74 (1)
P(1)–C(7)	1.79 (1)	P(1)–C(8)	1.82 (1)
P(1)–C(9)	1.80 (1)	P(2)–C(10)	1.81 (1)
P(2)–C(11)	1.80 (1)	P(2)–C(12)	1.80 (1)
O(1)–C(1)	1.219 (9)	O(2)–C(2)	1.21 (1)
N–C(4)	1.31 (1)	N–C(5)	1.46 (1)
N–C(6)	1.47 (1)	C(2)–C(3)	1.57 (2)
C(3)–H(1)	1.00 (9)		
atoms	angle	atoms	angle
S(1)–Mo–S(2)	69.91 (8)	S(1)–Mo–P(1)	85.56 (8)
S(2)–Mo–P(1)	154.80 (9)	S(1)–Mo–P(2)	153.50 (9)
S(2)–Mo–P(2)	83.63 (9)	P(1)–Mo–P(2)	120.55 (9)
S(1)–Mo–C(1)	107.2 (3)	S(2)–Mo–C(1)	104.3 (3)
P(1)–Mo–C(1)	76.8 (3)	P(2)–Mo–C(1)	77.3 (3)
S(1)–Mo–C(2)	119.1 (3)	S(2)–Mo–C(2)	121.5 (3)
P(1)–Mo–C(2)	75.1 (3)	P(2)–Mo–C(2)	75.8 (3)
C(1)–Mo–C(2)	122.7 (4)	S(1)–Mo–C(3)	89.3 (3)
S(2)–Mo–C(3)	91.9 (3)	P(1)–Mo–C(3)	93.6 (4)
P(2)–Mo–C(3)	93.1 (3)	C(1)–Mo–C(3)	160.0 (4)
C(2)–Mo–C(3)	37.2 (4)	S(1)–Mo–H(1)	74 (3)
S(2)–Mo–H(1)	73 (2)	P(1)–Mo–H(1)	106 (2)
P(2)–Mo–H(1)	100 (3)	C(1)–Mo–H(1)	176 (2)
C(2)–Mo–H(1)	58 (3)	C(3)–Mo–H(1)	21 (2)
Mo–S(1)–C(4)	87.8 (3)	Mo–S(2)–C(4)	88.0 (3)
Mo–P(1)–C(7)	116.8 (3)	Mo–P(1)–C(8)	116.8 (3)
C(7)–P(1)–C(8)	103.1 (5)	Mo–P(1)–C(9)	115.7 (3)
C(7)–P(1)–C(9)	100.8 (5)	C(8)–P(1)–C(9)	101.2 (5)
Mo–P(2)–C(10)	118.0 (3)	Mo–P(2)–C(11)	115.6 (3)
C(10)–P(2)–C(11)	101.9 (5)	Mo–P(2)–C(12)	115.1 (4)
C(10)–P(2)–C(12)	102.7 (5)	C(11)–P(2)–C(12)	101.1 (5)
C(4)–N–C(5)	121.2 (8)	C(4)–N–C(6)	121.3 (8)
C(5)–N–C(6)	117.3 (8)	Mo–C(1)–O(1)	177.7 (7)
Mo–C(2)–O(2)	149.2 (8)	Mo–C(2)–C(3)	90.9 (8)
O(2)–C(2)–C(3)	120 (1)	Mo–C(3)–C(2)	51.9 (6)
Mo–C(3)–H(1)	48 (5)	C(2)–C(3)–H(1)	99 (5)
S(1)–C(4)–S(2)	114.1 (6)	S(1)–C(4)–N	124.6 (7)
S(2)–C(4)–N	121.3 (7)		

X-ray Data Collection, Structure Dtermination, and Refinement for $Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)(PMe_3)_3$. Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($2\theta > 40$) accurately centered on the diffractometer are given in Table I. The space group was determined as $P2_12_12_1$ from systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. The method has been previously described.[30] A summary of the data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[31] Neutral atom scattering factors for Mo, Cl, P, O, and C were taken from Cromer and Waber,[32] and the scattering for molybdenum was corrected for real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[33] Scattering factors for H were from ref 34.

The position of the molybdenum atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the Mo atom readily revealed the positions of the remaining non-H atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.064$. The hydrogen atoms were located with the aid of a difference Fourier map and were not refined. Refinement of the

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non-H atoms with anisotropic thermal parameters led to an R value of 0.035. Conversion to the inverse configuration led to final values of $R = 0.025$ and $R_w = 0.028$. A final difference Fourier showed no feature greater than 0.3 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

X-ray Data Collection, Structure Determination, and Refinement for $Mo(COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2$. Data collection was carried out as for complex **1**. Final lattice constants and a summary of the data collection parameters are given in Table I.

The structure was solved by a combination of Patterson and Fourier techniques. Least-squares isotropic refinement of the non-hydrogen atoms led to an R value of 0.081 at convergence. The methyl hydrogen atoms were located with the aid of a difference Fourier map, but only the hydrogens on C(3) (H(1)–H(3)) were varied. Refinement of the non-hydrogen atoms with anisotropic temperature factors and of the positional and isotropic thermal parameters of the three hydrogens atoms on C(3) led to final R values of 0.029 (R) and 0.034 (R_w). A final difference Fourier map showed no feature greater than 0.3 e/Å^3. The weighting scheme was based on unit weights and no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table IV.

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Supplementary Material Available: Thermal parameters and observed and calculated structure factor amplitudes for $Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)(PMe_3)_3$ and $Mo(\eta^2\text{-}COCH_3)(S_2CNMe_2)(CO)(PMe_3)_2$ (Tables A–D), and analytical and spectroscopic data for the new compounds $Mo(\eta^2\text{-}COCH_2R)X(CO)_n(PMe_3)_{4-n}$ and $Mo(\eta^2\text{-}COCH_2R)(S_2CNMe_2)(CO)_n(PMe_3)_{3-n}$ (n = 1,2) (Tables 1 and 2) (24 pages). Ordering information is given on any current masthead page.

Oxidative Addition of Nitrosobenzene Fragments across the Triply Bonded Ditungsten Hexa-*tert*-butoxide Molecule. The Preparation and Structure of $[W(OCMe_3)_2(NPh)]_2(\mu\text{-}O)(\mu\text{-}OCMe_3)_2$

F. Albert Cotton* and Edwar S. Shamshoum

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843. *Received October 31, 1983*

Abstract: $W_2(OCMe_3)_6$ reacts with nitrosobenzene in toluene at 45 °C over a period of 12 h to give $[W(OCMe_3)_2(NPh)]_2(\mu\text{-}O)(\mu\text{-}OCMe_3)_2$ in 55–60% yield. The molecule consists of face-sharing octahedra with two *tert*-butoxide units and an oxygen atom as the bridging groups. The tungsten-to-tungsten distance is 3.059 (0) Å. The W–O distances for μ-O are 1.937 (4) and 1.937 (4) Å, while the W–O distances for the oxygen atoms of the bridging *tert*-butoxide groups are W(1)–O(6) = 2.078 (4) Å, W(2)–O(6) = 2.269 (4) Å and W(1)–O(7) = 2.264 (4) Å, W(2)–O(7) = 2.092 (4) Å. The W–N distances are 1.737 (5) and 1.738 (5) Å, and the W–N–C angles have an average value of 164.7 [3]°. The compound crystallizes in space group $C2/c$ with a = 27.57 (1) Å, b = 18.09 (1) Å, c = 18.36 (1) Å, β = 115.97°, V = 8231 (8) Å^3, and Z = 8. The tungsten atoms have formal oxidation numbers of VI and no W–W bond exists, the relatively short W–W separation being attributable to the presence of bridging ligands and the role of the ligated oxygen and nitrogen atoms in reducing the effective charge on the metal atoms through extensive π donation. From the bond lengths and angles it is concluded that the W–N bonds have an order of ca. 2.5, which includes about one-half of a $N \rightarrow W$ π donor bond over and above the basic W=N double bond. The oxygen atoms, especially those of the terminal alkoxy ligands, also contribute significant π density to the metal atoms.

The chemistry of compounds containing both metal–metal bonds and metal alkoxide groups, particularly their reactions with unsaturated or oxidizing organic groups to form new metal–carbon or metal–nitrogen bonds, is currently in a phase of extremely rapid growth.[1] In these reactions the metal atoms generally go to a higher formal oxidation state although there are a few cases where this is not so, or ambiguity arises depending on the sort of assumptions made about bonding. Several $Mo_2(OR)_6$ compounds are known and have been studied, but for tungsten work has necessarily been restricted to $W_2(OCMe_3)_6$ which is the only known $W_2(OR)_6$ compound.[1] Schrock, Listerman, and Sturgeoff,[2] Chisholm et al.,[3] and Cotton, Schwotzer, and Shamshoum[4] have found many diverse reactions of $W_2(OCMe_3)_6$ with C≡C and C≡N bonds, and for $Mo_2(OCMe_3)_6$ interesting reactions occur with CO.[5] Two of the most recently reported studies are those of Chisholm, Huffman, and Marchant,[6] who have observed the reaction of dimethylcyanamide, Me_2NCN, with $W_2(OCMe_3)_6$ and $Mo_2(OCH_2CMe_3)_6$, and of Cotton and Schwotzer, who studied the reaction of CO with $Mo_2(O\text{-}i\text{-}Pr)_6$ in pyridine.[7]

In this paper we report the first reaction of a nitroso compound, nitrosobenzene (C_6H_5NO), with $W_2(OCMe_3)_6$. This gives a product in which a remarkable double oxidative addition has occurred leading to the formation of W=N double bonds with concomitant loss of the W≡W bond.

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