A Thioketene Complex of Molybdenum(IV): Crystal Structure of [Mo{η^2-κ(C,S),σ-κ(S′)-S=C=CRC(=O)S}(=O){HB(pz)$_3$}] (R = C$_6$H$_4$Me-4, pz = Pyrazol-1-yl)

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Introduction

The interaction of carbon disulfide with alkylidyne complexes has attracted considerable attention recently (Scheme 2). Mayr has investigated the reactions of alkylidyne complexes of tungsten, in the presence of phosphines.[2] The results obtained have been interpreted as involving the coupling reactions of intermediate thiocarbonyl−alkylidyne complexes. Recently, we showed an alternative mode of reactivity for late transition metal alkylidyne complexes.[3] In this case cycloaddition is followed by cleavage of the resulting metallacycle into thiocarbonyl and thioacyl components.[3] These quite diverse reactions have prompted us to investigate in more detail the interactions of alkylidyne complexes with CS$_2$. Herein, we wish to report the formation of an unusual metallacyclic thioketene complex which results from the reactions of [Mo(≡CR)(CO)(L){HB(pz)$_3$}] [hereafter R = C$_6$H$_4$Me-4, pz = pyrazol-1-yl; L = CO (**1a**), PPh$_3$ (**1b**)] with CS$_2$.

Results and Discussion

The complex [Mo(≡CR)(CO)$_2${HB(pz)$_3$}] (**1a**) reacts slowly at room temperature (7 days) with excess CS$_2$ to provide a red complex (**2**) in low yield (10%) after chromatography. The same complex (**2**) also results from [Mo(≡CR)(CO)(PPh$_3$){HB(pz)$_3$}] (**1b**)[4] over a longer period (30 days), however, in substantially improved yield (45%). Infrared data for the complex indicate that it no longer contains *terminal* carbonyl ligands. The gross formulation follows from FAB-MS data for which a molecular ion is observed which is consistent with "Mo(CO)OCS$_2$(CR){HB(pz)$_3$}". ^{1}H and ^{13}C NMR data indicate three distinct pyrazolyl environments and the latter also include a low-field resonance at 204.8 ppm. Unfortunately, these data do not unequivocally indicate the nature of the complex formed. Accordingly, a crystallographic study was undertaken. The results are summarized in Tables 1 and 2 and identify the compound as [Mo{η^2-κ(C,S),σ-κ(S′)-S=C=CRC(=O)S}(=O){HB(pz)$_3$}] (**2**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex [Mo{η^2-κ(C,S),σ-κ(S′)-S=C=C(C$_6$H$_4$Me-4)C(=O)S}(O){HB(pz)$_3$}] (**2**)

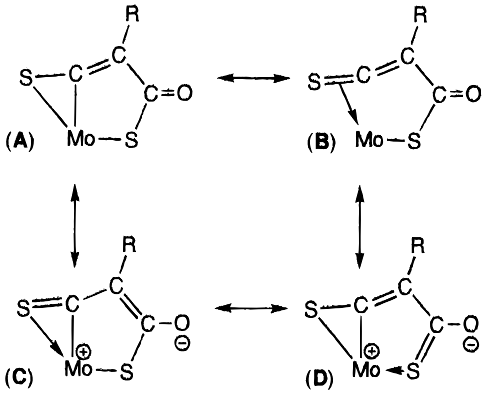
bond lengths		interbond angles	
Mo−C(3)	2.164(6)	S(2)−Mo−S(6)	115.2(1)
Mo−S(2)	2.413(2)	S(2)−Mo−C(3)	42.0(2)
Mo−S(6)	2.419(2)	S(2)−C(3)−C(4)	150.0(5)
C(3)−C(4)	1.324(8)	C(4)−C(5)−S(6)	113.8(4)
C(4)−C(5)	1.476(9)	Mo−S(6)−C(5)	105.9(2)
C(4)−C(8)	1.478(8)	S(6)−C(5)−O(7)	120.8(5)
C(3)−S(2)	1.658(6)	N(15)−Mo−O(1)	167.4(2)
C(5)−S(6)	1.781(7)	N(20)−Mo−S(2)	159.6(1)
C(5)−O(7)	1.208(8)	N(25)−Mo−S(6)	158.2(2)
Mo−O(1)	1.668(4)	O(1)−Mo−N(20)	93.3(2)
Mo−N(15)	2.304(5)	O(1)−Mo−N(25)	91.5(2)
Mo−N(20)	2.188(5)	O(1)−Mo−S(2)	99.3(2)
Mo−N(25)	2.211(5)	O(1)−Mo−S(6)	99.2(2)

Table 2. Crystallographic Data for [Mo{η^2-κ(C,S),σ-κ(S′)-S=C=C(C$_6$H$_4$Me-4)C(=O)S}(O){HB(pz)$_3$}] (**2**)

empirical formula: C$_{19}$H$_{17}$BMoN$_6$O$_2$S$_2$
$a = 9.417(3)$ Å
$b = 10.337(4)$ Å
$c = 11.554(4)$ Å
$\alpha = 83.38(3)°$
$\beta = 83.21(3)°$
$\gamma = 77.10(3)°$
$V = 1084.1(7)$ Å^3
$Z = 2$
$\rho_{\text{calc}} = 1.631$ g cm^{-3}
fw = 532.3
triclinic
space group $P\bar{1}$
$\lambda = 1.541\ 78$
μ(Cu Kα) = 7.00 mm^{-1}
$F(000) = 536$
$T = 293(2)$ K
$R_1 = 0.050^a$
$wR_2 = 0.127^b$

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$.

Scheme 1



The X-ray structure (Figure 1) reveals the formation of a novel metallacyclic thioketene ligand incorporating the elements of CS$_2$, one carbonyl ligand and the alkylidyne unit. The geometry around the molybdenum center is distorted octahedral (considering the thiocarbonyl unit as a unidentate ligand) with angles in the ranges 78.1(1)−102.3(2) and 158.2(2)−167.4(2)°. Although the Mo−N(20) and Mo−N(25) lengths are comparable and unexceptional [2.188(5) and 2.211(5) Å, respectively], the bond to the remaining pyrazolyl group is significantly longer [Mo−N(15), 2.304(5) Å], reflecting the pronounced *trans* influence of the oxo ligand. The oxo ligand shows a typically short Mo−O distance [1.668(4) Å] but is noticeably displaced from being orthogonal to the equatorial coordination plane (*ca.* 6°), as is N(15) (*ca.* 7°). Both of these displacements are away from the metallacycle. Interest focuses on the metallacycle itself. It appears that electronic delocalization occurs within this ring as indicated by its planarity: the atoms Mo, S(2), C(3), C(4), C(5), and S(6) are coplanar to within 0.10 Å (by S(6)). There is, however, no conjugation between the tolyl group and the metallacycle, the average torsional twist being *ca.* 31°. The

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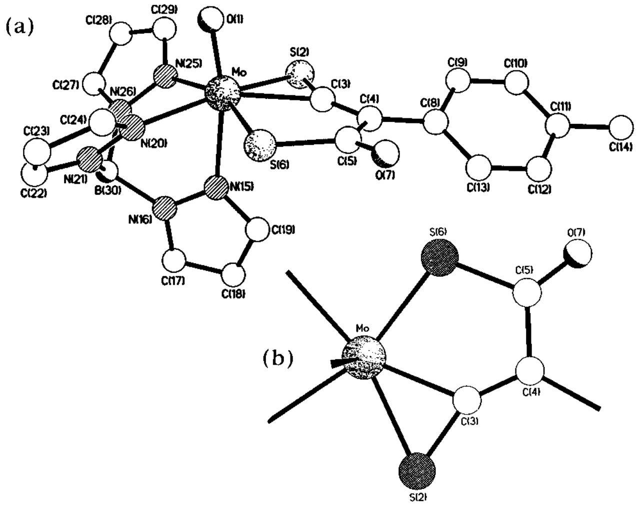
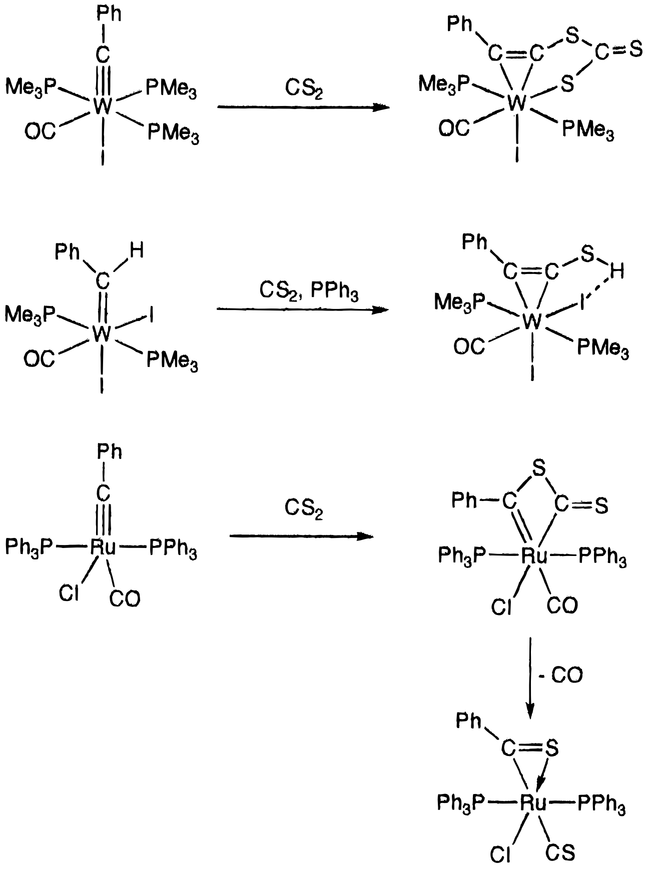


Figure 1. (a) Molecular geometry of $[Mo\{\kappa^3{:}\eta^2,\sigma'\text{-}S{=}C{=}CRC({=}O)S\}(O)\{\kappa^3\text{-}HB(pz)_3\}]$ (**2**). Pyrazolyl and tolyl H atoms were omitted for clarity. (b) Alternative view normal to plane of metallacycle.

molybdenum atom is displaced toward the oxo ligand relative to the plane of the five coordinated atoms, normal to this direction by 0.22 Å, a feature typical of molybdenum oxo complexes.[5] Within the metallacycle, the bond lengths are most consistent with the resonance forms **A** and **B** (Scheme 1). Thus, despite π-coordination to molybdenum, the C(3)−S(2) bond length [1.658(6) Å] clearly indicates multiple C−S bonding, being significantly shorter than for C(5)−S(6) [1.781(7) Å]. A substantial degree of multiple bonding is also evident between C(3) and C(4) [1.324(8) Å], as compared to the essentially single C(4)−C(5) and C(4)−C(8) bond lengths [1.476(9) and 1.478(8) Å, respectively]. The two Mo−S bond distances are identical despite the different binding modes and the geometric constraints of chelation, and pseudo-olefinic coordination of the thioketene group. This results in a "bend-back" angle of 150.0(5)° at C(3).

Given the already disparate results summarised in Scheme 2, the mechanism for the formation of **2** remains equivocal. The presence of an oxo ligand almost certainly results from adventitious oxidation during the chromatographic work-up. Perhaps the most surprising feature to be accommodated mechanistically is the cleavage of CS_2 into two ultimately remote components within the metallacycle. We favor that shown in Scheme 3: (i) cycloaddition of Mo≡C and C=S bonds; (ii) ring contraction and formation of a terminal sulfido ligand; (iii) coupling of sulfido and carbonyl ligands to provide coordinated carbonyl sulfide; (iv) coupling of thioketenyl and carbonyl sulfide ligands; (v) oxidative formation of the terminal oxo ligand. The initial cycloaddition, being the regiochemical reverse of that observed for late transition metal alkylidynes[3] is reminiscent of the addition of carbon dioxide to a tungsten aminomethylidyne complex described by Fischer.[6] Ring-contraction to afford a thioketenyl ligand also appears plausible, given that thioketenyl ligands now have ample, albeit recent, literature precedent for group 6 metals.[2,7,8]

Scheme 2. The Reactions of Alkylidyne Complexes with Carbon Disulfide[2,3]



It is perhaps noteworthy that the proposed mechanism does not involve terminal thiocarbonyl intermediates. This raises the question as to whether the results of Mayr[2] might also be accommodated by an alternative and related process involving direct alkylidyne/CS_2 cycloaddition and formation of sulfido/thioketenyl intermediates akin to intermediate (**A**) (Scheme 3). The abstraction of sulfur by PMe_3 or PPh_3, could thus be from a transient terminal sulfido ligand, rather than coordinated CS_2. Furthermore, a related imido/thioketenyl intermediate (**B**) (Scheme 1) has been proposed by Weiss to account for the products of the addition of alkyl isothiocyanates to high valent alkylidyne complexes.[9] This interpretation builds on and accommodates earlier observations for related processes involving isocyanates and carbodiimides.[8,10] Definitive results which would adequately discriminate between the mechanisms proposed previously[2] and here have yet to be obtained. Clearly, however, the reactivity of alkylidyne complexes toward CS_2 and related heterocumulenes[8−11] is complex and warrants further study.

Experimental Procedures

The compounds $[Mo({\equiv}CR)(CO)(L)\{HB(pz)_3\}]$ [R = C_6H_4Me-4, pz = pyrazol-1-yl; L = CO (**1a**), PPh_3 (**1b**)],[4] have been described previously. All manipulations were carried out under an atmosphere of prepurified dinitrogen using conventional Schlenk-tube and vacuum line techniques. Solvents were purified by distillation from an

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(5) For recent crystallographic studies of molybdenum oxo complexes see: Gresley, N. M.; Griffith, W. P.; Parkin, B. C.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans* **1996**, 2039 and references therein.

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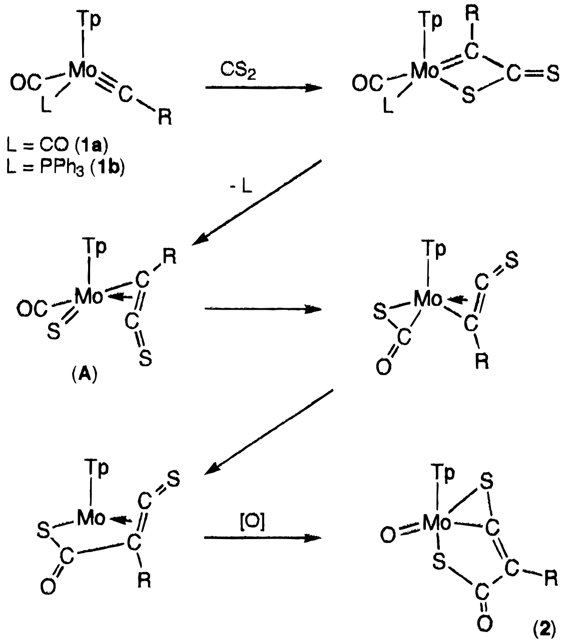
Scheme 3. Reaction of [Mo(≡CR)(CO)L{HB(pz)$_3$}] with CS$_2$ (L = CO, PPh$_3$; R = C_6H_4Me-4, Tp = HB(pz)$_3$; [O] = Oxidation)



appropriate drying agent and degassed prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Jeol JNM EX270 NMR spectrometer and calibrated against internal SiMe$_4$ (^{1}H) or CDCl$_3$ (^{13}C). Infrared spectra were recorded from dichloromethane solutions and Nujol mulls using a Perkin-Elmer 1725-X FT-IR spectrometer. FAB Mass spectrometry was carried out using an Autospec Q mass spectrometer with 3-nitrobenzyl alcohol as matrix. Abundances are given for the major peak of isotopic envelopes confirmed by simulation. Elemental microanalytical data were obtained from the ICSTM microanalytical service.

Preparation of [Mo{η^2-κ(C,S),σ-κ(S′)-S=C=C(C_6H_4Me-4)C(=O)S}(=O){HB(pz)$_3$}] (2). (a) [Mo(≡CC$_6$H$_4$Me-4)(CO)$_2${HB(pz)$_3$}] (**1a**) (0.47 g, 1.0 mmol) was dissolved in tetrahydrofuran (25 mL). Carbon disulfide (5 mL, excess) was added and the mixture stirred at room temperature for 7 days. The resulting red/brown solution was freed of volatiles *in vacuo*, and the residue was extracted with a minimum of dichloromethane. This extract was chromatographed (silica gel, 10 °C) eluting with diethyl ether. The major red/purple fraction which eluted was freed of volatiles and the residue crystallized from a mixture of chloroform and hexane at −40 °C. Yield 0.053 g (10%). (b) [Mo(≡CC$_6$H$_4$Me-4)(CO)(PPh$_3$){HB(pz)$_3$}] (0.70 g, 1.0 mmol) was treated as in (a) above with the exception that the mixture was stirred for 30 d. Yield 0.240 g (45%). ^{1}H NMR (CDCl$_3$, 25 °C): δ 2.43 [s, 3 H, CH$_3$], 6.2 [s(br), 1 H, BH], 5.83, 6.55, 6.60 [t × 3, 1 H × 3, H^4(pz), J(HH) = 2 Hz], 7.36, 8.13 [(**AB**)$_2$, 4 H, C$_6$H$_4$, J(**AB**) = 8 Hz], 6.74, 7.41, 7.87, 7.90, 8.65, 8.72 [d × 6, 1 H × 6, H^{3,5}(pz), J(HH) = 2 Hz] ppm. ^{13}C{^{1}H} NMR: δ 204.8 [OCS], 146.0, 145.1, 144.1, 141.8, 137.0, 134.6 [C^{3,5}(pz)], 130.8 [C^4(C$_6$H$_4$)], 137.4, 136.1, 120.6 [S=$\underline{\text{C}}$=C, S=C=$\underline{\text{C}}$, and C^1(C$_6$H$_4$), unequivocal assignment precluded], 129.4, 127.3 [C^{2,3,5,6}(C$_6$H$_4$)], 107.5, 107.4, 105.5 [C^4(pz)], 21.3 [CH$_3$] ppm. FAB-MS (NBA matrix) *m/z* (%) = 700 (0.8) [M + NBA − H$_2$O]$^+$, 684 (1.5) [M + NBA]$^+$, 533 (34) [M]$^+$, 466 (3) [M − pz]$^+$, 207 (9) [SCCRCOS]$^+$, 147 (56) [H$_2$B(pz)$_2$]$^+$, 91(36) [R]$^+$. Anal. Found: C, 42.1; H, 3.0; N, 14.8. Calcd for $C_{19}H_{17}BMoN_6O_2S_2$: C, 42.7; H, 3.2; N, 15.7.

Crystal Structure Determination of [Mo{η^2-κ(C,S),σ-κ(S′)-S=C=C(C_6H_4Me-4)C(=O)S}(O){HB(pz)$_3$}] (2). Thin red plates were obtained by slow diffusion of hexane into a solution of the complex in chloroform at −40 °C. A crystal of approximate dimensions 0.19 × 0.10 × 0.02 mm was used for the diffraction study. Intensity data were collected in the ω scan mode on a Siemens P4/PC diffractometer using Cu Kα radiation to a maximum 2θ value of 124°. Table 2 provides a summary of the crystal data, data collection, and refinement parameters for **2**. The structure was solved by the heavy-atom method and all the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2. The methyl hydrogen atoms were located from a ΔF map, optimized, assigned isotropic thermal parameters [U(H) = 1.5U_{eq}(C)], and allowed to ride on their parent carbon. The remaining hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters [U(H) = 1.2U_{eq}(C/B)], and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system (Version 5.03) with absorption corrected data (empirical, max/min transmission factors 0.62 and 0.27, respectively) to give R_1 = 0.050, wR_2 = 0.127 for 2764 independent, observed reflections [$|F_o| > 4\sigma(|F_o|)$] and 281 parameters. Selected bond lengths and angles are given in Table 1.

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Supporting Information Available: An X-ray crystallographic file in CIF format for complex [Mo{η^2-κ(C,S),σ-κ(S′)-S=C=C(C_6H_4Me-4)C(=O)S}(=O){HB(pz)$_3$}] (**2**) is available on the Internet only. Access information is given on any current masthead page.

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