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Halogenation and Alkylation at a $\mathrm{Mo^{III}_2(\mu\text{-}S)}$ Site. Crystal Structure of the Metal−Sulfenyl Halide Complex $[\mathrm{Mo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}SMe)_2(\mu\text{-}SI)(CO)_2}]\mathrm{I_5}$

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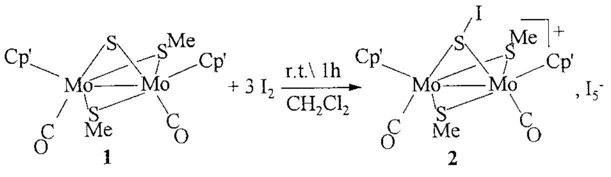
Introduction

Bridging sulfide (S^{2-}), hydrosulfide (SH^-), and thiolate (SR^-) anions are useful ligands in polymetallic sulfur chemistry since they usually help to stabilize the metallic framework. They may also model the sulfur environment found in some natural metalloenzymes.[1] The reactivity of metal−sulfur sites is often determined by the Lewis and/or Brönsted base behavior of the available lone pairs and may be focused on either the metal or sulfur atoms. A wide range of reactions involving the bridging sulfur atoms of bimetallic complexes has been described.[1a,b,2−5] In many of these reactions it is thought that the sulfur atom undergoes transient protonation or halogenation, respectively modeling reduction of dinitrogen by metalloenzymes[1b,c] and the formation of metal−halide bonds.[2a,4,5] Recently, we have shown that the decarbonylation of compounds of the general class $[\mathrm{Mo_2Cp'_2(CO)}_n]$ (n = 4 or 6) in the presence of dimethyl disulfide is controlled by the electron density on the metal, varying with the substitution pattern of the Cp′ cyclopentadienyl groups.[6] When Cp′ = C_5Me_5 (η^5-C_5Me_5) the dicarbonyl μ-sulfido complex $[\mathrm{Mo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}S)(\mu\text{-}SMe)_2(CO)_2}]$ **1** is obtained. Since **1** possesses an attractive $\{\mathrm{Mo^{III}_2(\mu\text{-}S)}\}$ site whose reactivity has been little explored, it seemed interesting to study electrophilic attack on it by halogens. Here we show that the sulfide ligand in **1** readily forms sulfur−halide bonds whose stability depends on the halide. Reactions of **1** with various functionalized alkyl halides are also reported.

Scheme 1



Cp′ = C_5Me_5

Results and Discussion

The reaction of the μ-sulfido dimolybdenum complex $[\mathrm{Mo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}S)(\mu\text{-}SMe)_2(CO)_2}]$ **1** with an excess of I_2 in CH_2Cl_2 gave a green solution of a novel dinuclear complex $[\mathrm{Mo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}SMe)_2(\mu\text{-}SI)(CO)_2}]\mathrm{I_5}$ **2** (Scheme 1). **2** was characterized by IR and ^{1}H NMR spectroscopy. Its ^{1}H NMR spectrum in CD_2Cl_2 exhibits a resonance for the (η^5-C_5Me_5) rings at 2.01 ppm and one for the SMe bridges at 2.34 ppm. The IR spectrum displays a strong band at 1960 cm^{-1} (KBr pellets) which is attributable to terminal CO vibrations. A single-crystal X-ray diffraction study revealed that **2** does indeed contain a sulfenyl−halide ligand. Crystals of **2** are built from more or less discrete $[\mathrm{Mo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}SMe)_2(\mu\text{-}SI)(CO)_2}]^+$ cations (Figure 1a) and V-shaped I_5^- anions (Figure 1b). The cation lies across a mirror plane defined by the three bridging sulfur atoms so that the (η^5-C_5Me_5) rings are equivalent by symmetry. It is structurally closely analogous to the previously reported complexes $[\mathrm{Mo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}SMe)_2(\mu\text{-}SH)(CO)_2}]^+$ and $[\mathrm{Mo_2Cp_2(\mu\text{-}SMe)_3(CO)_2}]^+$ (Cp = C_5H_5).[6,7] Thus, two eclipsed (η^5-C_5Me_5)Mo(CO) units are linked by a Mo−Mo bond whose length [2.7735(12) Å] is typical of the values found in dimeric Mo^{III} complexes containing three bridging groups.[1d,6,7] The resulting metal coordination can be described as a distorted four-legged piano stool supplemented by a metal−metal bond. In addition, the molybdenum atoms are nearly coplanar with the methane thiolate sulfur atoms [S(2)−Mo(1)−S(3)−Mo(1^i) = 2.6(1)°] and the carbonyl ligands and the thiolate methyl groups lie on the same side of this plane.

Although sulfenyl complexes have occasionally been proposed as intermediates in reactions of metallosulfur compounds with halogen, little is known about their structures. The iodosulfide bridge unit is therefore an important and unusual feature of **2**. The Mo−SI and Mo−SMe distances are indistinguishable. The S−I distance [2.504(2) Å] is longer than either the sum of covalent radii (2.37 Å) or the values [2.386(2) and 2.406(4) Å] found in aryl sulfenyl iodides.[8] However, it compares well with the S−I distances in the trihalide polymer $[\mathrm{Mo_2(NTo)_2\{S_2P(OEt)_2\}_2(\mu\text{-}S)(\mu\text{-}O_2CMe)(\mu\text{-}SI_3)}]_n$ [2.498(2) and 2.544(2) Å] where the dimolybdenum units are linked by V-shaped S−I···I···I−S bridges reminiscent of the I_5^- anion (see below) in that they involve relatively weak central I···I

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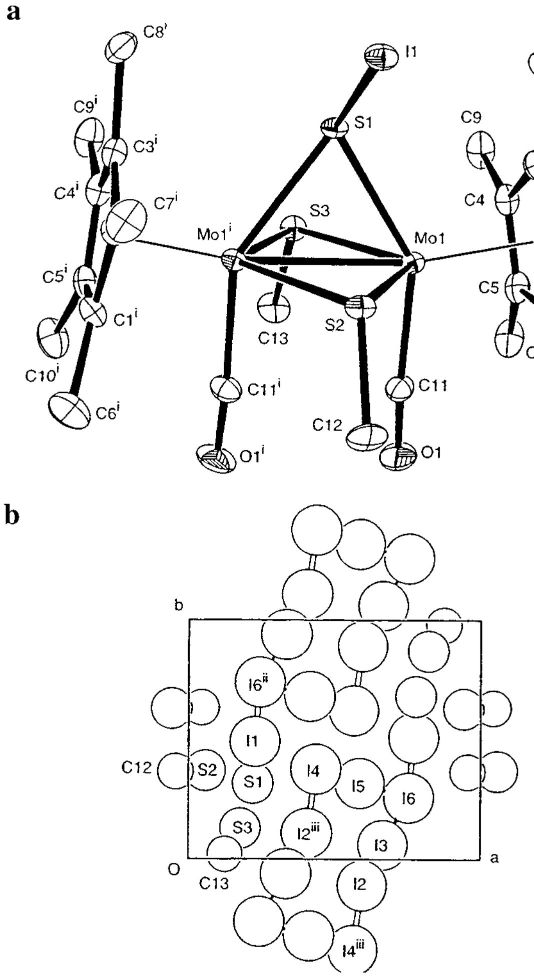

Figure 1. (a) An ORTEP drawing (20% thermal ellipsoids) of the cation $[\{(\eta^5\text{-}C_5Me_5)Mo(CO)\}_2(\mu\text{-}SMe)_2(\mu\text{-}SI)]^+$ **2**$^+$. Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(1^{i}) 2.7735(12), Mo(1)−C(11) 2.007(8), Mo(1)−S(1) 2.454(2), Mo(1)−S(2) 2.477(2), Mo(1)−S(3) 2.457(2), S(1)−I(1) 2.504(2), C(11)−Mo(1)−Mo(1^{i}) 89.6(3), C(11)−Mo(1)−S(1) 145.1(3), C(11)−Mo(1)−S(2) 87.3(3), C(11)−Mo(1)−S(3) 89.8(2), Mo(1)−S(1)−Mo(1^{i}) 68.8(1), Mo(1)−S(1)−I(1) 115.4(1), Mo(1)−S(2)−Mo(1^{i}) 68.1(1), Mo(1)−S(3)−Mo(1^{i}) 68.7(1), S(1)−Mo(1)−S(2) 74.9(1), S(3)−Mo(1)−S(2) 111.5(1), S(1)−Mo(1)−S(3) 70.2(1). (b) A view down the *c*-axis of the packing of the I_5^- anions and the SMe and SI units bridging units in **2**. All atoms shown lie on the mirror plane at $z = 0$. Atomic radii shown are ca. 75% of the van der Waals radii. Weak I···I interactions in the range 3.60−4.00 Å are indicated by open bonds. Selected bond lengths (Å) and angles (deg): I(2)−I(3) 2.749(2), I(4)−I(5) 2.796(2), I(5)−I(6) 3.106(2), I(3)−I(6) 3.275(2), I(1)···S(2) 3.495(3), I(1)···I(6^{ii}) 3.600(1), I(2)···I(4^{iii}) 3.902(2), I(2)−I(3)−I(6) 178.1(1), I(4)−I(5)−I(6) 178.4(1), I(5)−I(6)−I(3) 77.3(1). Symmetry codes: (i) *x*, *y*, −*z*; (ii) 1 − *x*, 1 − *y*, *z*; (iii) 1 − *x*, −*y*, *z*.

bonds of 3.036(1) and 3.158(1) Å and the S−I···I units are nearly linear.[2a] All other reported S−I bond lengths, including those in the few structurally characterized M_2SI metallosulfur complexes,[4,5] are greater than 2.60 Å.[8c] Among the rare metallic compounds with S−I bonds in the range 2.6−2.9 Å are $[\{(en)_2Co(SCH_2CH_2NH_2)\}_2I]^{5+}$ [S−I = 2.619(2) Å],[9] $[CpMo(N^tBu)(\mu\text{-}S)\cdot I_2]_2$ [S−I = 2.720(1) Å],[5d] and $[Co(py)_4(NCS\cdot I_2)_2]$ [S−I = 2.797(2) Å].[10] Nonmetallic compounds with S−I bonds in the range 2.6−2.9 Å are more common[11] and have been successfully used as templates to build polyiodide arrays.[11e] The chemical significance of these longer S−I bonds emphasizes the strength of the shorter S−I bond in **2**.

The anions in **2** are aggregated into continuous planar ribbons of polyiodide which run parallel to the *b*-axis (Figure 1b). The atoms I(2)−I(6) define a V-shaped pentaiodide anion formed by relatively weak interactions of two I_2 molecules with an I^- anion: the central I(6)−I(3) and I(6)−I(5) bonds are both fairly long [3.275(2) and 3.106(2) Å] while the terminal I(2)−I(3) and I(4)−I(5) distances [2.749(2) and 2.796(2) Å] are only slightly greater than the bond length in solid iodine [2.715(6) Å].[12a] The I−I bond lengths in **2** are broadly consistent with values in other I_5^- structures (see, e.g., refs 12b−d), but the central I(5)−I(6)−I(3) angle [77.3(1)°] is unusually acute. The pentaiodide ions associate through I(2)···I(4^{iii}) interactions of 3.902(2) Å to give I_{10}^{2-} rectangles which were also recently found in the structure of H_3O[dibenzo-18-crown-6]I_5.[12d] The sulfenyl iodine atom interacts with the polyiodide array mainly through an I(1)···I(6^{ii}) contact of 3.600(1) Å which is 0.36 Å shorter than the van der Waals diameter of iodine.

Similar experiments were performed with Br_2 and Cl_2. A moderately stable, green complex **3** was isolated from reaction of **1** with Br_2 and was identified as the bromo analogue of **2** by comparison of the spectral data of its cation with those of the iodine derivative. The ^1H NMR spectrum displays two resonances at 2.09 and 2.34 ppm in CD_2Cl_2 assignable to the C_5Me_5 rings and the SMe bridges, respectively. The IR spectrum (KBr pellets) shows a strong band at 1980 cm^{-1} characteristic of carbonyl vibrations. On monitoring the reaction of **1** with excess chlorine by IR at room temperature one short-lived carbonyl species was detected by the appearance of a strong band at 1965 cm^{-1}, close to the position of bands observed in the carbonyl stretching region for the iodine **2** and bromine **3** derivatives. This strongly suggests that the structure of the transient chloro complex **[4]**$^+$ is similar to those of [**2**]$^+$ and [**3**]$^+$. The orange dichloromethane solution of the intermediate **4** evolved quickly to give finally a pink solution from which only one well-defined product could be identified, on the basis of a single-crystal diffraction study and spectral data, as the aqua compound $[Mo(\eta^5\text{-}C_5Me_5)Cl_4(H_2O)]$ **6**. Evidently, complex **4** was first readily oxidized by an excess of chlorine and then hydrolyzed in wet conditions to form the monometallic compound **6**. However, when the reaction was conducted in dry CH_2Cl_2 a bimetallic complex was formed. On the basis of elemental analysis it was formulated as $[(Mo(\eta^5\text{-}C_5Me_5)Cl)_2(\mu\text{-}Cl)_3(\mu\text{-}S)]Cl$ **5**, a logical intermediate in the conversion of **4** to **6**, and it was indeed observed that crystallization of **5** in wet CH_2Cl_2−hexane gave a clean conversion to **6**. Further attempts at spectroscopic characterization of **5** failed because of its low stability. Complex **6** is air-stable and soluble in THF and

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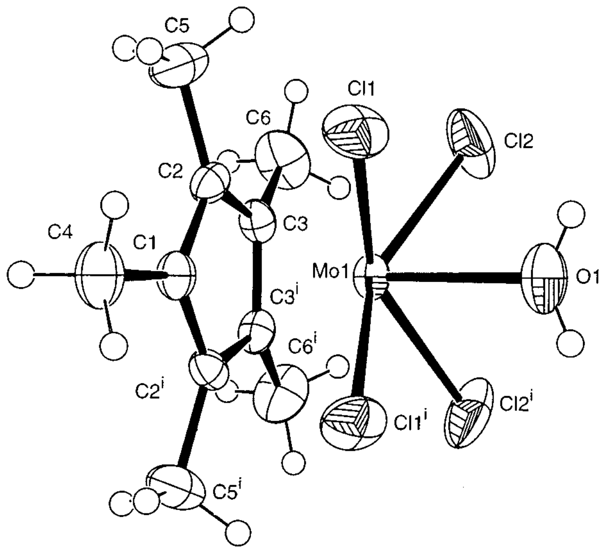
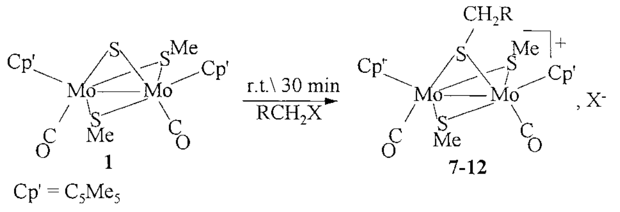


Figure 2. An ORTEP drawing (20% thermal ellipsoids) of a molecule of $[(\eta^5\text{-}C_5Me_5)MoCl_4(OH_2)]$ **6**. Selected bond lengths (Å) and angles (deg): Mo(1)−O(1) 2.222(7), Mo(1)−C(Cp) 2.356(6)−2.461(5), Mo(1)−Cl(1) 2.408(2), Mo(1)−Cl(2) 2.416(2), O(1)−Mo(1)−C(Cp) 149.7(3)−150.4(2), O(1)−Mo(1)−Cl(1) 75.4(2), O(1)−Mo(1)−Cl(2) 76.2(2). Symmetry code: (i) −*x*, *y*, *z*.

dichloromethane. Its ^1H NMR spectrum showed very broad resonances indicative of a paramagnetic species. This precludes the formation of the diamagnetic (d^0) Mo(VI)−hydroxo compound as a possible hydrolysis product and supports the formulation of **6** as a 17-electron molybdenum(V) complex.

Molecules of **6** (Figure 2) straddle a crystallographic mirror plane and contain an octahedrally coordinated molybdenum atom; the centroid of the $\eta^5\text{-}C_5Me_5$ ring occupies a single coordination vertex trans to the oxygen atom. An equatorial plane around the metal is formed by the four chlorine atoms. The metal atom is displaced from the equatorial plane toward the $\eta^5\text{-}C_5Me_5$ ring centroid, so that the O−Mo−Cl angles are 75.4(2)−76.2(2)°. The long Mo(1)−O(1) distance of 2.222(7) Å is an immediate indication of the lack of the multiple bonding between these two atoms since Mo═O distances involving terminal oxo ligands are typically 1.678−1.707 Å.[13] The formulation of **6** as an aqua rather than hydroxo complex is also consistent with our location of the water hydrogen atoms and with the Mo(1)−O(1) bond length. The longest Mo−OH bond length we have found[8c] is that of 2.080(3) Å in $[CpMo(OH)(PMe_3)_3][BF_4]$[14] whereas the mean of 316 $Mo-OH_2$ distances is 2.184 Å (80% lie in the range 2.112−2.220 Å)[8c] and values of 2.225(7) and 2.245(8) Å have been recently reported for a molybdenum(III) complex.[15] The conclusion from the diffraction study that **6** is an aqua derivative is confirmed by IR bands at 3420 (br) and 1570 (s) cm^{-1}, which correspond to typical vibrations of H_2O, and by the EPR spectrum of a dichloromethane solution containing **6**. It showed a single resonance flanked by satellites due to the low abundance (ca. 25%) of molybdenum isotopes (^{95}Mo and ^{97}Mo) both with $I = {}^5/_2$, at $g = 1.911$ ($a_{Mo} = 39.3$ G). A similar EPR pattern was previously observed by Poli et al. in the octahedral molybdenum(V) complex $[CpMoCl_4\{S(Me)(CH_2)_2PPh_2\}]$.[16] A significant aspect of this study is the demonstration that aqua ligands can be readily introduced into organometallic complexes. Similar aqua derivatives have already been postulated as intermediates in hydrolysis reactions,[14,17] but only a few, such as $[Mo\{{=}C(Et)\text{-}\eta^3\text{-}(C(Et)C(Et)CHEt)\}Br(OH_2)(\eta^5\text{-}C_5H_5)][BF_4]$,[15] have been structurally characterized.

Scheme 2



The functionalization of the sulfido bridge in the dimolybdenum complex $[Mo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}S)(\mu\text{-}SMe)_2(CO)_2]$ **1** can be also easily achieved at room temperature: dissolving **1** in various alkyl halides (CH_2Cl_2, CH_2Br_2, $ClCH_2CN$, $BrCH_2CCH$, $BrCH_2CO_2Me$, $ClCH_2CHCH_2$) gives red solutions of complexes of general formula $[Mo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}SMe)_2(\mu\text{-}SR)(CO)_2]X$ **7**−**12** (Scheme 2). All the complexes **7**−**12** have been characterized by spectroscopy and by elemental analyses. The IR spectra of all the complexes exhibited a strong ν(CO) band at ca. 1970−1960 cm^{-1}. ^1H and ^{13}C NMR spectra displayed a set of resonances fully consistent with a bimetallic core *cis*-$[Mo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}SMe)_2(CO)_2]$ bridged by a third alkanethiolate ligand: one resonance for the two equivalent C_5Me_5 ligands, two peaks for the two inequivalent SMe bridges, one signal for the two equivalent CO groups (^{13}C NMR), and the expected resonance pattern for the various SR bridges. These reactions illustrate the nucleophilic character of the sulfido ligand in **1**[6] and give a pathway for introducing a functionalized organic chain into the metallic framework. The sulfur-based nucleophilicity is also shown in the reactions of **1** with halogens X_2 (X = I, Br, Cl) by affording the stable (**2**) or moderately stable (**3**) sulfenyl halide derivatives in preference to direct oxidation of the molybdenum atoms. It has been reported that the electron-releasing C_5Me_5 groups could increase the reducing power of organometallic complexes[6,18] and promote oxidation of the molybdenum atoms. It has also been shown that permethylated groups inhibit decarbonylation reactions and the presence of carbonyl ligands tends to remove the electronic density from the metal atoms.[6] These effects would prevent direct oxidation of the metallic atoms and favor the formation of sulfenyl−metal species.

Experimental Section

General Procedures. The reactions were performed under nitrogen using standard Schlenk techniques, and solvents were deoxygenated and dried by standard methods. IR spectra were obtained with a Perkin-Elmer 1430. Both ^1H and ^{13}C NMR spectra were recorded on a Bruker AC300 spectrophotometer. Shifts are relative to tetramethylsilane as an internal reference. EPR spectra were recorded on a JEOL FE 3X apparatus. Chemical analyses were performed by the Centre de

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Microanalyses du CNRS, Vernaison. Literature methods were used for the preparation of [(η^5-C_5Me_5)$_2$$Mo_2$($\mu$-SMe)$_3$($\mu$-S)(CO)$_2$].[6]

Synthesis of [Mo$_2$(η^5-C$_5$Me$_5$)$_2$(μ-SMe)$_2$(μ-SI)(CO)$_2$]I$_5$ 2. A mixture of **1** (100 mg, 0.155 mmol) and I_2 (118 mg, 0.466 mmol) in CH_2Cl_2 (10 mL) was stirred for 1 h at room temperature. The solvent was then evaporated in vacuo. The residue was washed twice with pentane (5 mL) and recrystallized from methylene chloride/ethyl ether to give green crystals. Yield: 161 mg, 75%. Anal. Calcd for $C_{22}H_{36}I_6Mo_2O_2S_3$: C, 20.5; H, 2.6. Found: C, 21.0; H, 2.7.

Spectroscopic Data for 2. IR (KBr pellets): ν(CO) 1960(s) cm^{-1}.^{1}H NMR (CD_2Cl_2): δ 2.34 (6H, s, SMe), 2.01 (30H, s, C_5Me_5).

Synthesis of [Mo$_2$(η^5-C$_5$Me$_5$)$_2$(μ-SMe)$_2$(μ-SBr)(CO)$_2$]Br$_3$ 3. Bromine was added (25 μL, 0.50 mmol) to a dichloromethane solution of **1** (100 mg, 0.155 mmol). The solvent was then evaporated in vacuo. The residue was washed with pentane (3 × 5 mL) to give a dark-green powder **3**. Yield: 123 mg, 85%. Poor analytical results were obtained for **3** because of its low stability. Anal. Calcd for $C_{24}H_{36}Br_4Mo_2O_2S_3$: C, 29.9; H, 3.8; Br, 33.1. Found: C, 27.5; H, 3.6; Br, 35.9.

Spectroscopic Data for 3. IR (KBr pellets): ν(CO) 1980(s) cm^{-1}.^{1}H NMR (CD_2Cl_2): δ 2.34 (6H, s, SMe), 2.09 (30H, s, C_5Me_5).

Reaction of 1 with Chlorine. Chlorine gas was bubbled through a CH_2Cl_2 (10 mL) solution of **1** (100 mg, 0.155 mmol) in a Schlenk tube until the color changed from green to orange. IR control of the solution then showed the formation of the carbonyl complex [**4**]$^+$. Additional bubbling of chlorine through the stirred reaction mixture quickly turned it pink ($\approx$5 min). The solvent was then removed under vacuum, and the residue was washed with pentane (3 × 5 mL) to give a pink powder **5**. Yield: 98 mg, 90%. Anal. Calcd for $C_{20}H_{30}Cl_6Mo_2S$: C, 33.9; H, 4.2; Cl, 30.0. Found: C, 32.8; H, 4.1; Cl, 29.3.On cooling at −15 °C for a few days solutions of **5** in CH_2Cl_2/hexane (1:1) afforded orange single crystals of **6**.

Preparation of [Mo$_2$(η^5-C$_5$Me$_5$)$_2$(μ-SMe)$_2$(μ-SR)(CO)$_2$]X Complexes 7−12. The following procedure is applicable to the synthesis of all these complexes. Complex **1** (100 mg, 0.155 mmol) was dissolved in the appropriate alkyl halide (2 mL, excess). The solution was stirred for 30 min at room temperature (when CH_2Cl_2 was used, the solution was warmed overnight). During this time the reaction mixture changed from green to red. Addition of diethyl ether precipitated the alkylated complexes **7**−**12** as red powders, which were washed twice with pentane (5 mL).

7 (R = CH$_2$Cl, X = Cl). Yield: 91 mg, 80%. Anal. Calcd for $C_{25}H_{38}Cl_2Mo_2O_2S_3$: C, 41.1; H, 5.2; Cl, 9.7. Found: C, 40.1; H, 5.3; Cl, 9.5.

Spectroscopic Data for 7. IR (KBr pellets): ν(CO) 1960(s) cm^{-1}.^{1}H NMR (CD_3CN): δ 4.12 (s, 2H, SCH_2Cl), 2.35 (s, 3H, SCH_3), 2.28 (s, 3H, SCH_3), 2.03 (s, 30H, C_5Me_5).^{13}C NMR (CD_3CN): δ 237.7 (*C*O), 107.3 (*C*$_5$(CH$_3$)$_5$), 46.2 (S*C*H$_2$Cl), 25.9, 24.3 (S*C*H$_3$), 12.1 (C$_5$(*C*H$_3$)$_5$).

8 (R = CH$_2$Br, X = Br). Yield: 108 mg, 85%. Anal. Calcd for $C_{25}H_{38}Br_2Mo_2O_2S_3$: C, 36.7; H, 4.7; Br, 19.5. Found: C, 36.4; H, 4.8; Br, 18.7.

Spectroscopic Data for 8. IR (KBr pellets): ν(CO) 1960(s) cm^{-1}.^{1}H NMR (CD_3CN): δ 3.93 (s, 2H, SCH_2Br), 2.35 (s, 3H, SCH_3), 2.28 (s, 3H, SCH_3), 2.04 (s, 30H, C_5Me_5).^{13}C NMR (CD_3CN): δ 237.7 (*C*O), 107.4 (*C*$_5$(CH$_3$)$_5$), 32.6 (S*C*H$_2$Br), 25.9, 24.1 (S*C*H$_3$), 12.2 (C$_5$(*C*H$_3$)$_5$).

9 (R = CH$_2$CN, X = Cl). Yield: 92 mg, 82%. Anal. Calcd for $C_{26}H_{38}NClMo_2O_2S_3$: C, 43.3; H, 5.3; N, 1.9; Cl, 4.9. Found: C, 43.1; H, 5.2; N, 1.9; Cl, 5.2.

Spectroscopic Data for 9. IR (KBr pellets): ν(CN) 2240(w), ν(CO) 1965(s) cm^{-1}.^{1}H NMR (CD_3CN): δ 2.72 (s, 2H, SCH_2CN), 2.37 (s, 3H, SCH_3), 2.33 (s, 3H, SCH_3), 2.02 (s, 30H, C_5Me_5).^{13}C NMR (CD_3CN): δ 237.2 (*C*O), 119.5 (SCH$_2$*C*N), 107.4 (*C*$_5$(CH$_3$)$_5$), 26.1, 23.8 (S*C*H$_3$), 12.1 (C$_5$(*C*H$_3$)$_5$), 10.8 (S*C*H$_2$CN).

10 (R = CH$_2$CCH, X = Br). Yield: 95 mg, 80%. Anal. Calcd for $C_{27}H_{39}BrMo_2O_2S_3$: C, 42.5; H, 5.1; Br, 10.5. Found: C, 42.5; H, 5.1; Br, 10.3.

Spectroscopic Data for 10. IR (KBr pellets): ν(CO) 1970(s), ν(C≡C) 2100(w) cm^{-1}.^{1}H NMR (CD_3CN): δ 2.80 (t, *J* = 2.8 Hz, 1H, SCH$_2$C≡C*H*), 2.70 (d, *J* = 2.8 Hz, 2H, SC*H*$_2$C≡CH), 2.34 (s, 3H, SCH_3), 2.29 (s, 3H, SCH_3), 2.01 (s, 30H, C_5Me_5).^{13}C NMR (CD_3CN): δ 238.2 (*C*O), 107.0 (*C*$_5$(CH$_3$)$_5$), 82.6 (SCH$_2$*C*≡CH), 77.6 (SCH$_2$C≡*C*H), 25.9, 24.1 (S*C*H$_3$), 14.8 (S*C*H$_2$C≡CH),12.1 (C$_5$(*C*H$_3$)$_5$).

11 (R = CH$_2$CO$_2$Me, X = Br). Yield: 98 mg, 79%.

Table 1. Crystallographic Data for [Mo$_2$(η^5-C$_5$Me$_5$)$_2$(μ-SMe)$_2$(μ-Si)(CO)$_2$]I$_5$ **2** and [Mo(η^5-C$_5$Me$_5$)Cl$_4$(H$_2$O)] **6**

	2	**6**
empirical formula	$C_{24}H_{36}I_6Mo_2O_2S_3$	$C_{10}H_{17}Cl_4MoO$
fw	1405.99	390.96
space group	*Pnnm*	*Cmc*2$_1$
a (Å)	17.7079(3)	13.974(1)
b (Å)	14.4213(2)	11.9079(4)
c (Å)	14.5978(2)	8.4183(5)
V (Å^3)	3727.9(1)	1400.8(2)
Z	4	4
ρ_{calc}, g/cm^3	2.505	1.854
μ (Mo Kα),mm^{-1}	5.831	1.676
R1^a [$I > 2\sigma(I)$, all]	0.052, 0.083	0.033, 0.042
wR2^b [$I > 2\sigma(I)$, all]	0.114, 0.138	0.079, 0.084

^{a} $R1 = \sum||F_{obs}| - |F_{calc}||/\sum|F_{obs}|$. ^{b} $wR2 = \{\sum[w(F_{obs}{}^2 - F_{calc}{}^2)^2]/\sum[w(F_{obs}{}^2)^2]\}^{1/2}$.

Spectroscopic Data for 11. IR (KBr pellets): ν(CO) 1960(s), ν(C═O) 1735(m) cm^{-1}. ^{1}H NMR (CD_3CN): δ 3.65 (s, 3H, SCH$_2$CO$_2$C*H*$_3$), 2.68 (s, 2H, SC*H*$_2$CO$_2$CH$_3$), 2.36 (s, 3H, SCH_3), 2.31 (s, 3H, SCH_3), 1.98 (s, 30H, C_5Me_5).^{13}C NMR (CD_3CN): δ 238.1(*C*O), 171.9 SCH$_2$*C*O$_2$CH$_3$),106.9 (*C*$_5$(CH$_3$)$_5$), 53.4 (SCH$_2$CO$_2$*C*H$_3$), 28.0 (S*C*H$_2$CO$_2$CH$_3$), 26.2, 23.8 (S*C*H$_3$), 11.9 (C$_5$(*C*H$_3$)$_5$).

12 (R = CH$_2$CHCH$_2$, X = Cl). Yield: 84 mg, 75%.

Spectroscopic Data for 12. IR (KBr pellets): ν(CO) 1960(s) cm^{-1}. ^{1}H NMR (CD_3CN): δ 5.81 (qt, J_1 = 17.0 Hz, J_2 = 10.2 Hz, J_3 = 6.7 Hz, 1H, SCH$_2$C*H*═CH$_2$), 5.20 ("dq", J_1 = 17.0 Hz, J_4 = 1.4 Hz, 1H, SCH$_2$CH═C*H*$_2$), 5.11 ("dq", J_1 = 10.2 Hz, J_4 = 1.4 Hz, 1H, SCH$_2$CH═C*H*$_2$), 2.72 ("dt", J_3 = 6.7 Hz, J_4 = 1.4 Hz, 2H, SC*H*$_2$CH═CH$_2$), 2.34 (s, 3H, SCH_3), 2.31 (s, 3H, SCH_3), 1.98 (s, 30H, C_5Me_5).^{13}C NMR (CD_3CN): δ 238.8 (*C*O), 138.4, 119.0 (SCH$_2$*C*H═*C*H$_2$), 106.7 (*C*$_5$(CH$_3$)$_5$), 29.6 (S*C*H$_2$CH═CH$_2$), 26.5, 24.1 (S*C*H$_3$), 12.2 (C$_5$(*C*H$_3$)$_5$).

X-ray Crystallographic Analyses of 2 and 6. Information concerning the structure analyses is presented in Table 1. Measurements were made at 20 °C with Mo X-rays, λ = 0.71073 Å, using a Bruker SMART diffractometer for **2** and a CAD4 diffractometer for **6**. Both structures were solved by Patterson methods and refined by least squares on F^2 using anisotropic U_{ij} values for all non-hydrogen atoms.[19]

Structure Analysis of 2. 28463 intensity measurements with θ(Mo Kα) < 28°, after application of empirical transmission factors of 0.5063−0.7298, yielded 4796 unique F^2 with R_{int} = 0.073. These were used to refine 184 parameters. Hydrogen parameters were not refined. The idealized disordered methyl group model (HFIX 123)[19a] was used for (η^5-C$_5$Me$_5$) hydrogen atoms. In the final difference synthesis function values ranged from 2.64 to −3.00 e Å^{-3} but virtually all regions with $|\Delta\rho| > 1$ e Å^{-3} were within 1 Å of I or Mo atoms. The high value of R_{int} and the noisy final difference synthesis are attributed to inadequacies in the absorption correction (μ = 5.8 mm^{-1}) and poor crystal quality. Attempts to improve the absorption correction or to get better data were not successful.

Structure Analysis of 6. 2653 absorption-corrected intensity measurements with θ(Mo Kα) < 30° gave 1251 unique F^2 values (R_{int} = 0.031) from which 87 parameters were refined. The single independent water H atom was freely refined, as were the orientations of the methyl groups. Final $|\Delta\rho|$ values were < 0.75 e Å^{-3}.

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Supporting Information Available: An X-ray crystallographic file in CIF format for complexes **2** and **6**. This material is avalaible free of charge via the Internet at http://pub.acs.org.

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(19) Programs used: (a) *SHELXL-97*—*Programs for Crystal Structure Analysis* (Release 97-2). Sheldrick, G. M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998. (b) WinGX—A Windows Program for Crystal Structure Analysis. Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.