bridged intermediate in the case of CNBu^t. The failure of the CNBu^t ligand to bridge the Os–Os dative bond in 1 also accounts for why the carbonyl trans to this ligand does not undergo ready exchange with the rest of the carbonyls in the molecule.

As can be seen from Figure 5 all the carbonyls of the $Os_3(CO)_{11}$ unit undergo exchange at 19 °C. Terminal-bridge carbonyl exchange in the perpendicular plane that contains Os(3) and Os(4) can account for the collapse of the signals attributed to carbonyls e, f, and j. There must, however, be an additional rearrangement in **2** in order that the signal assigned to carbonyl g can collapse. This may be a 3-fold twist at Os(3) that exchanges carbonyls e, f, and g. This type of exchange has been proposed for $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1–5).[23,29] There was some evidence that such an exchange occurs at Os(4) in that the signal assigned to carbonyl j collapsed to the base line at a rate faster than expected if this carbonyl were only involved in the CO exchange in the perpendicular plane containing Os(3) and Os(4). This is apparent in the spectrum at −8 °C (Figure 5) since the signals f and j should collapse at the same rate if they are only involved in one rearrangement.

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Registry No. 1, 123724-38-9; 2, 123724-39-0; $Os_4(CO)_{15}$, 110698-51-6; $Os_4(CO)_{14}$, 115227-28-6; Os, 7440-04-2.

Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic thermal parameters for 1 (2 pages); a listing of observed and calculated structure factors for 1 (14 pages). Ordering information is given on any masthead page.

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(29) Alex, R. F.; Pomeroy, R. K. *J. Organomet. Chem.* **1985**, *284*, 379.

Chemistry of η^2-CS_2 Metal Complexes. Comparison of the Reactivities of the Two Isomeric Heterometallacycles MoC(S)SC(R)=CR and MoSC(S)C(R)=CR. Unexpected Formation of a Carbon–Carbon Bond between the Five-Membered Metalla Ring and an η^5-Cyclopentadienyl Ligand

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Two aspects of the chemistry of the two isomeric heterometallacycles arising from 1:1 addition of alkynes to [$Cp_2Mo(\eta^2$-$CS_2)$], i.e. [Cp_2MoC(S)SC(R)=CR] (**1a**, R = CO_2Me; **1b**, R = CF_3) and [Cp_2MoSC(S)C(R)=CR] (**2a**, R = CO_2Me), have been studied: (i) their reactions with methyl iodide and (ii) the subsequent reactions with sodium tetrahydroborate. While CH_3I reacts with **1a** and **2a** to give the corresponding S-methylated cationic complexes [Cp_2MoC(SCH_3)SC(R)=CR]I (**3a**, R = CO_2Me) and [Cp_2MoSC(SCH_3)C(R)=CR]I (**4a**, R = CO_2Me), respectively, the reaction with **1b** affords the molecular complex [CpMo(η^7-$C_5H_4C(SCH_3)SC(R)$=CR)] (**5b**, R = CF_3). Complex **3a** reacts with sodium tetrahydroborate to give **5a**, the CO_2Me analogue of **5b**, and [Cp_2MoCH(SCH_3)SC(R)=CR] (**6a**, R = CO_2Me). Complex **4a** reacts with sodium tetrahydroborate to afford [CpMo(η^7-C_5H_4C(R)C(R)=C(SCH_3)S)] (**7a**, R = CO_2Me) and [Cp_2MoSCH_2C(R)=CR] (**8a**, R = CO_2Me). Possible mechanisms for these reactions are discussed. The structure of **5b** has been determined by single-crystal X-ray diffraction analysis. The crystals are monoclinic, space group $P2_1/c$, with a = 11.861 (3) Å, b = 9.839 (3) Å, c = 15.075 (4) Å, β = 106.28 (2)°, V = 1688.7 (5) Å^3, Z = 4 and D_c = 1.88 g·cm^{-3}. The structure was solved by using 2953 unique reflections ($I > 3\sigma(I)$) and refined to R = 0.027 and R_w = 0.024. This study clearly shows the unexpected formation of a carbon–carbon bond between a cyclopentadienyl group and the heterometallacyclic fragment (C–C = 1.454 (3) Å).

Introduction

The η^2-coordinated CS_2 ligand exhibits nucleophilic behavior, which began to be exploited in organometallic and organic synthesis a few years ago.[2] Among the different aspects of its reactivity which have been examined, the reaction with acetylenes bearing electron-withdrawing groups is one of the most investigated.[2-8] In most cases

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(1) (a) Université de Bretagne Occidentale. (b) Université de Rennes I.

(2) For review see: Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1986; Vol. 1, pp 146–254.

(3) Wakatsuki, Y.; Yamazaki, H.; Iwasaki, H. *J. Am. Chem. Soc.* **1973**, *95*, 5781.

(4) (a) Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1978**, 573. (b) *J. Am. Chem. Soc.* **1978**, *100*, 3946. (c) *Inorg. Chem.* **1981**, *20*, 2486.

(5) Le Marouille, J. Y.; Lelay, C.; Benoit, A.; Grandjean, D.; Touchard, D.; Le Bozec, H.; Dixneuf, P. H. *J. Organomet. Chem.* **1980**, *191*, 133.

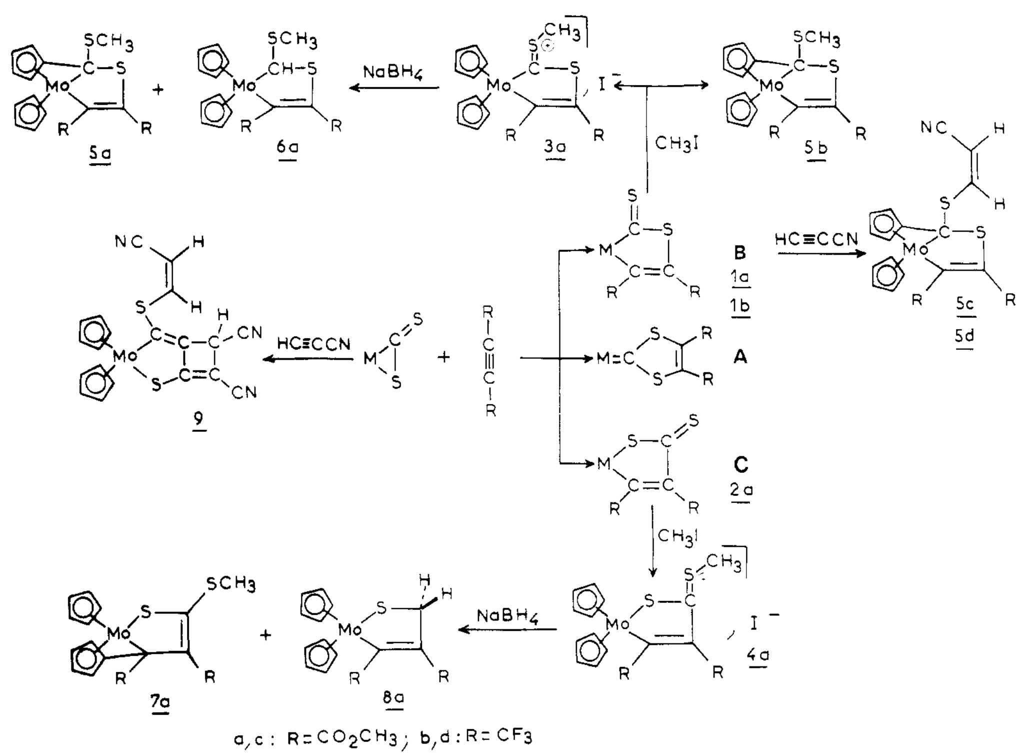

Figure 1. Addition reactions between alkynes and $[M(\eta^2\text{-}CS_2)]$ complexes and related reactions. Complexes **1** and **2** with M = $[Mo(\eta^5\text{-}C_5H_5)_2]$, complexes **5c** (R = CO_2Me), **5d** (R = CF_3), and **9** have been previously described.[10] In all this work, **a** refers to R = CO_2Me and **b** to R = CF_3.

this reaction affords the type A metalladithioalkylidene complex (Figure 1), which is an interesting precursor of various sulfur-containing products such as substituted tetrathiafulvalenes and 1,3-dithiole-2-thiones.[2,7-9] We recently reported that with $[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CS_2)]$ the activated alkynes RC≡CR (R = CO_2Me, CF_3) reacted to afford type B or type C heterometallacyclic complexes; while dimethyl acetylenedicarboxylate (R = CO_2Me) afforded both isomers **1a** and **2a**, hexafluorobut-2-yne (R = CF_3) only gave the $[\overline{Cp_2MoC(S)SC(R)=C}R]$ derivative (**1b**)[10] (Figure 1).

The reactivities of such metallacyclic complexes clearly depend on steric and electronic properties that themselves depend on the structure of the cycle (type B or type C) and the nature of the substituents R initially bound to the alkyne. The above three complexes allow an evaluation of the importance of these two contributions. Consideration of the behavior of the two isomers with R = CO_2Me, **1a** and **2a**, will allow a comparison of the reactivity of the two types of metallacycles while comparative studies of **1a** and **1b**, which have identical metal–carbon type B skeletons, may reveal the influence of the substituents R.

As an example of the reactivity of these metallacyclic complexes, we recently reported that cyanoethyne, HC≡CCN, reacted with the type B complexes **1a** and **1b** to afford 1:1 adducts (**5**) with unexpected structures (Figure 1) while it does not react with the type C complex **2a**.[10]

We report here further examples of the reactivity of these five-membered metalla ring complexes, describing their reactions with methyl iodide and the subsequent reactions with sodium tetrahydroborate. Possible mechanisms for these reactions will also be discussed.

Results and Discussion

Reactions of Complexes 1 and 2 with Methyl Iodide.

Treatment of the two isomers $[\overline{Cp_2MoC(S)SC(R)=C}R]$ (**1a**, R = CO_2Me) and $[\overline{Cp_2MoSC(S)C(R)=C}R]$ (**2a**, R = CO_2Me) with an excess of methyl iodide in THF at room temperature caused precipitation of green powders in almost quantitative yield. These complexes, **3a** and **4a**, respectively, were characterized by elemental analyses and ^1H NMR spectroscopy. In both cases the data were consistent with the formation of cationic complexes arising from methylation of the uncoordinated sulfur atom of the starting complex (Figure 1). To our knowledge, only one example of such S-alkylation of the exocyclic sulfur atom of a type C complex has been reported previously.[3]

Curiously, when a similar reaction with methyl iodide was conducted with **1b**, the CF_3 analogue of **1a**, no precipitation was observed, while the initially green solution turned orange. Chromatography on a silica gel column afforded orange microcrystals of **5b**, for which analytical data clearly indicate the absence of iodine. Although the ^1H NMR data clearly showed the methylation of the exocyclic sulfur atom ($\delta(SCH_3)$ = 2.42 ppm), the most pertinent feature of this spectrum was the presence of peaks consistent with the transformation of one of the two η^5-C_5H_5 ligands into a substituted η^5-C_5H_4 group. This transformation was confirmed by the ^{13}C NMR spectrum, in which five different peaks assignable to the carbon atoms of the η^5-C_5H_4 ligand were present. Since these data revealed an unprecedented reaction with methyl iodide,

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(6) Frazier, C. C.; Magnussen, N. D.; Osuji, L. N.; Parker, K. O. *Organometallics* **1982**, *1*, 903.

(7) Schenk, W. A.; Schwietzke, T.; Müller, H. *J. Organomet. Chem.* **1982**, *232*, C41. Schenk, W. A.; Kuemmerle, D.; Burschka, C. *J. Organomet. Chem.* **1988**, *349*, 183.

(8) Bianchini, C.; Meli, A. *J. Chem. Soc., Chem. Commun.* **1983**, 1309. Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* **1985**, *4*, 264. Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M.; Silvestre, J.; Hoffmann, R. *Organometallics* **1986**, *5*, 1733.

(9) Le Bozec, H.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1462. Ngounda, M.; Le Bozec, H.; Dixneuf, P. H. *J. Org. Chem.* **1982**, *47*, 4000. Khasnis, D. V.; Le Bozec, H.; Dixneuf, P. H.; Adams, R. D. *Organometallics* **1986**, *5*, 1772.

(10) (a) Conan, F.; Guerchais, J. E.; Mercier, R.; Sala-Pala, J.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1988**, 345. (b) Conan, F.; Sala-Pala, J.; Guerchais, J. E.; Li, J.; Hoffmann, R.; Mealli, C.; Mercier, R.; Toupet, L. *Organometallics* **1989**, *8*, 1929.

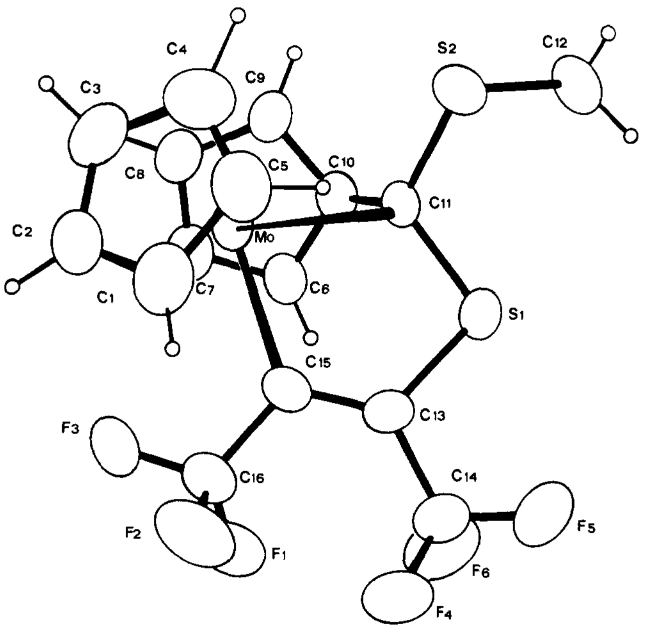


Figure 2. Molecular structure of **5b** (50% probability ellipsoids).

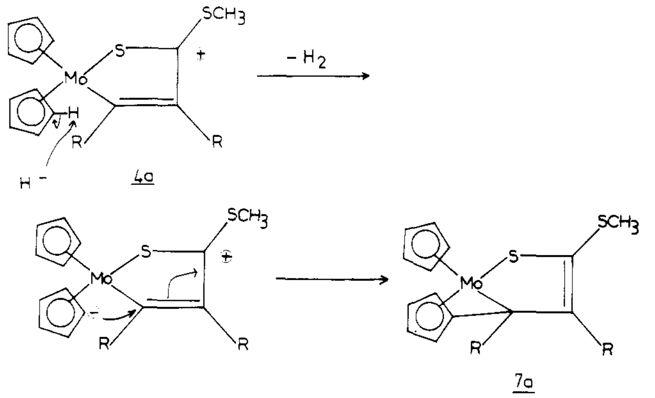
it appeared important to carry out an X-ray structural study of **5b**. This analysis unambiguously showed the unexpected coupling of the metallacycle fragment with a cyclopentadienyl group and indicated that **5b** must be formulated as $[(\eta^5\text{-}C_5H_5)\overline{Mo(\eta^7\text{-}C_5H_4C(SCH_3)C(CF_3)}\text{=}CCF_3)]$ (Figures 1 and 2).

Although we were unable to isolate, from the reaction of **1b** with methyl iodide, the cationic complex **3b** analogous to **3a**, intermediate formation of this derivative seemed likely. The nonprecipitation of this complex, in contrast to the case for **3a**, may be due to the CF_3 groups, which usually induce an increase in solubility. Formation of **5b** from this intermediate might arise from either an electrophilic substitution of a hydrogen atom of the Cp ligand by the carbocation (hypothesis i) or a nucleophilic attack of iodide on the Cp ligand, with cleavage of a CH bond and formation of the new carbon–carbon bond (hypothesis ii) (Figure 3). While hypothesis i is in agreement with the usual reactivity of ferrocene derivatives,[11] hypothesis ii conforms with the results recently reported by Cooper et al.,[12] which show that nucleophilic reagents react with the cationic complex $[(\eta^5\text{-}C_5H_5)_2WBr(SMe_2)]^+$ to afford $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Nu)WBrH]$ (Nu = $OCMe_3$, PPh_2, SR, ...) via nucleophilic attack on a cyclopentadienyl ligand and cleavage of a C–H bond.

Reaction of Complexes 3a and 4a with Sodium Tetrahydroborate. In order to elucidate further the chemistry of the two types of heterometallacycles 1 and 2, the reactions of their methylated derivatives **3a** and **4a** were investigated. The cationic structure of these complexes seemed to be especially appropriate for investigating their reactivity toward nucleophilic reagents, and their reactions with the tetrahydroborate anion were first studied. It is noteworthy that previous work in this and other laboratories[13,14] has shown the ability of the tetrahydroborate anion to transform some $[L_nM(\eta^2\text{-}C(S)SMe)]^+$ cationic complexes into $[L_nM(\eta^2\text{-}CH(S)SMe)]$ molecular complexes via nucleophilic attack by the hydride anion on the *exo*-CS_2 carbon atom (L_nM = Cp_2NbBu,[13] $Fe(CO)_2(PMe_3)_2$[14]). However, the reaction of tetrahydroborate with such cations has been also shown to markedly depend on the nature of the L_nM moiety. Such a reaction may in fact follow different paths; in some cases hydrido or thiocarbonyl complexes are formed while in others dimerization of the η^2-C(S)SR ligand is observed.[15]

Chart I

Scheme I



Sodium tetrahydroborate reacted at room temperature with **3a**, affording after further workup two new complexes.

Although the elemental analysis and mass spectrum of the first complex established the chemical purity, the ^1H NMR spectrum was complicated (see Experimental Section). In this spectrum, which was in agreement with the formula $[(\eta^5\text{-}C_5H_5)\overline{Mo(\eta^7\text{-}C_5H_4C(SCH_3)SC(R)\text{=}C}R)]$ (**5a**, R = CO_2Me), analogous to that of **5b**, every type of proton emerged as a pair of resonances, indicating the presence of two isomeric species. Attribution of each signal to the corresponding isomer was possible since modification of the experimental conditions induced modifications of the isomer ratio.

The formation of **5a** from **3a** might arise by a mechanism similar to that already discussed for **5b** (Figure 3).

The existence of **5a** in two isomeric forms may be easily explained by the inequivalence of the two cyclopentadienyl ligands of **5a** induced by the nonplanarity of the heterometallacycle (Chart I). It is noteworthy that, for unknown reasons, for other complexes **5** (**5b**, this work; **5c**, **5d**, see ref 10 and Figure 1) the existence of such isomers is not detected spectroscopically.

The second complex, **6a**, obtained in the reaction of **3a** with sodium tetrahydroborate in ca. 30% yield, gave analytical, mass, and spectroscopic data in agreement with the formula $[Cp_2\overline{MoCH(SCH_3)SC(R)\text{=}C}R]$ (R = CO_2Me). The presence of a Mo–CH(SCH_3)S unit, arising from nucleophilic attack of hydride on the *exo*-CS_2 carbon atom, was clearly revealed by peaks at δ 38.4 ppm in the ^{13}C NMR spectrum.

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[11] Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G. Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 8, Chapter 59, p 1019.

[12] McNally, J. P.; Glueck, D.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 4838.

[13] Amaudrut, J.; Kadmiri, A.; Sala-Pala, J.; Guerchais, J. E. *J. Organomet. Chem.* **1984**, *266*, 53.

[14] Touchard, D.; Dixneuf, P. H.; Adams, R. D.; Segmüller, B. E. *Organometallics* **1984**, *3*, 640.

[15] See for instance: (a) Touchard, D.; Fillaut, J. L.; Khasnis, D. V.; Dixneuf, P. H.; Mealli, C.; Masi, D.; Toupet, L. *Organometallics* **1988**, *7*, 67 and references therein. (b) Schenk, W. A.; Kuemmerle, D.; Schwietzke, T. *J. Organomet. Chem.* **1988**, *349*, 163 and references therein.

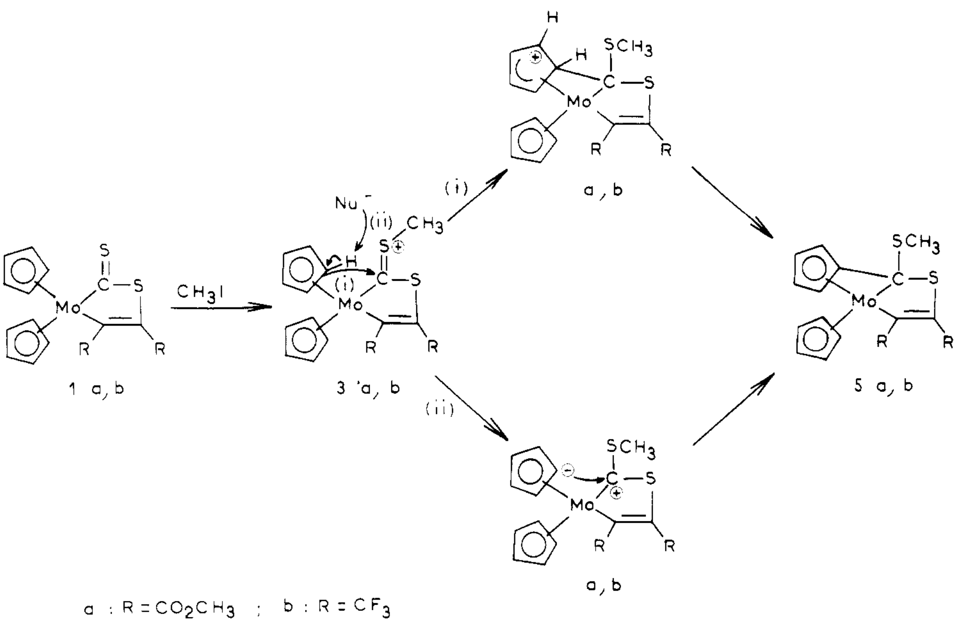


Figure 3. Possible mechanism of formation of complexes **5** from complexes **1** via the S-methylated carbocationic complexes **3**. The second step may correspond to (i) an electrophilic substitution or (ii) a nucleophilic attack with $Nu^- = H^-$ for complex **a** ($R = CO_2Me$) and $Nu^- = I^-$ for complex **b** ($R = CF_3$).

Sodium tetrahydroborate also reacted with the cationic complex **4a** in THF at room temperature to give two new products: **7a** as a yellow-brown powder in very low yield (ca. 3%) and **8a** as red microcrystals in ca. 15% yield.

The tentative formulation of **7a** as $[(\eta^5\text{-}C_5H_5)Mo(\eta^7\text{-}C_5H_4C(R)C(R){=}C(SCH_3)S)]$ ($R = CO_2Me$) was deduced from analytical, mass, and ^1H NMR data. It is noteworthy that the C_5H_4 resonances in the ^1H NMR spectrum were similar to those of **5b**. They clearly indicated cleavage of one of the C–H bonds and strongly suggested formation of a new carbon–carbon bond with dihydrogen evolution and migration of the carbon–carbon double bond according to the mechanism given in Scheme I.

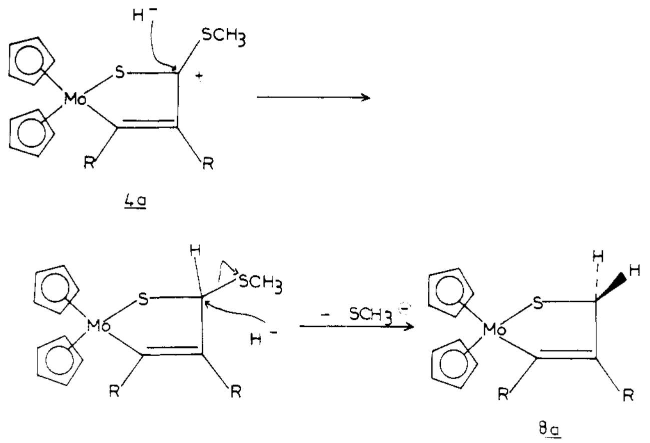
Unfortunately, it was not possible to confirm this structural hypothesis by an X-ray study since all attempts to obtain suitable crystals of **7a** for a crystallographic analysis failed.

^1H NMR data for complex **8a** clearly indicate (i) the absence of a SCH_3 group, (ii) the presence of a CH_2 group, and (iii) the presence of an "intact" $[Mo(\eta^5\text{-}C_5H_5)_2]$ unit. Accordingly, in agreement with analytical and mass spectroscopic data, **8a** was formulated as $[Cp_2MoSCH_2C(R){=}CR]$ ($R = CO_2Me$). Thus, formation of **8a** involves the cleavage of the $C\text{–}SCH_3$ bond. An example of the cleavage of a carbon–exocyclic sulfur bond in a η^2-methyl dithioester cationic complex has been previously reported by Dixneuf et al.,[14] who obtained $[Fe(\eta^2\text{-}CH_2S)(CO)_2(PMe_3)_2]$ upon treatment of $[Fe(\eta^2\text{-}C(S)SMe)(CO)_2(PMe_3)_2]^+$ with $NaBH_4$.

We presume that formation of **8a** from **4a** proceeds via an intermediate arising from an initial nucleophilic attack of hydride on the *exo*-CS_2 carbon atom, although no experimental evidence is available for the existence of such species (Scheme II).

In a second step, this intermediate, which is an isomer of **6a**, would undergo a second nucleophilic attack by hydride on the same carbon atom with subsequent cleavage of the $C\text{–}SCH_3$ bond. This second attack would be possible for this complex, and not for **6a**, since the electrophilic character of the carbon atom must be weaker in the latter due to back-bonding from filled metal orbitals to an acceptor π^* orbital of the ligand.

Scheme II



It is noteworthy that in the course of the reaction of **3a** and **4a** with $NaBH_4$, we were unable to isolate any intermediate containing coordinated BH_x species. Such intermediates have been previously reported in reactions of $[M(\eta^2\text{-}C(S)SR)]$ derivatives with $NaBH_4$.[13,16]

Crystal Structure of $[(\eta^5\text{-}C_5H_5)Mo(\eta^7\text{-}C_5H_4\text{—}C(SCH_3)\text{—}S\text{—}C(CF_3){=}C(CF_3))]$ (5b). The X-ray diffraction study of **5b** unequivocally established the formation of a carbon–carbon bond between the cyclopentadienyl group and the heterocyclic fragment and clearly revealed that this complex may be formulated as $[(\eta^5\text{-}C_5H_5)Mo(\eta^7\text{-}C_5H_4C(SCH_3)SC(CF_3){=}C(CF_3))]$ (Figures 1 and 2; Tables I and II).

The following are the principal features of the structure.

(i) The heterometallacyclic skeleton MoC(11)S(1)C-

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[16] Khasnis, D. V.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1987**, 230.

Table I. Atom Coordinates and Temperature Factors B ($Å^2$) in 5b

atom	x	y	z	B
Mo	0.74142 (2)	0.18860 (2)	0.75643 (1)	2.801 (4)
S(1)	0.63232 (5)	−0.00700 (6)	0.90192 (4)	3.43 (1)
S(2)	0.46729 (5)	0.19155 (7)	0.78819 (5)	3.77 (1)
F(1)	1.0010 (1)	−0.0997 (2)	0.8933 (1)	6.17 (5)
F(2)	0.9155 (2)	−0.1657 (2)	0.7568 (1)	7.17 (5)
F(3)	0.9871 (1)	0.0340 (2)	0.7815 (1)	6.89 (4)
F(4)	0.8449 (2)	−0.2927 (2)	0.8897 (2)	6.96 (5)
F(5)	0.7021 (2)	−0.2683 (2)	0.9459 (1)	5.76 (4)
F(6)	0.8667 (2)	−0.1798 (2)	1.0140 (1)	6.96 (6)
C(1)	0.7337 (3)	0.0442 (3)	0.6286 (2)	4.58 (6)
C(2)	0.7984 (3)	0.1595 (3)	0.6220 (2)	4.64 (6)
C(3)	0.7256 (3)	0.2739 (3)	0.6149 (2)	5.06 (7)
C(4)	0.6127 (3)	0.2258 (4)	0.6177 (2)	5.32 (7)
C(5)	0.6186 (3)	0.0861 (4)	0.6269 (2)	5.00 (7)
C(6)	0.8229 (2)	0.2351 (3)	0.9103 (2)	3.48 (5)
C(7)	0.8823 (2)	0.3201 (3)	0.8637 (2)	4.12 (6)
C(8)	0.7981 (2)	0.4055 (3)	0.8048 (2)	4.22 (6)
C(9)	0.6859 (2)	0.3759 (3)	0.8144 (2)	3.66 (5)
C(10)	0.6988 (2)	0.2616 (3)	0.8773 (1)	3.13 (4)
C(11)	0.6169 (2)	0.1509 (2)	0.8429 (2)	2.94 (4)
C(12)	0.4037 (3)	0.1901 (4)	0.8831 (2)	5.49 (7)
C(13)	0.7574 (2)	−0.0736 (3)	0.8767 (2)	3.22 (5)
C(14)	0.7936 (3)	−0.2029 (3)	0.9308 (2)	4.36 (6)
C(15)	0.8113 (2)	−0.0065 (2)	0.8225 (2)	3.25 (5)
C(16)	0.9258 (2)	−0.0597 (3)	0.8138 (2)	4.65 (6)
H(1)	0.756 (3)	−0.049 (4)	0.632 (2)	4*
H(2)	0.864 (3)	0.163 (3)	0.611 (2)	4*
H(3)	0.743 (3)	0.360 (4)	0.603 (2)	4*
H(4)	0.559 (3)	0.270 (4)	0.612 (2)	4*
H(5)	0.563 (3)	0.020 (3)	0.633 (2)	4*
H(6)	0.843 (3)	0.162 (3)	0.943 (2)	4*
H(7)	0.970 (3)	0.326 (3)	0.870 (2)	4*
H(8)	0.787 (3)	0.474 (4)	0.766 (2)	4*
H(9)	0.609 (3)	0.411 (3)	0.778 (2)	4*
H(12A)	0.437 (3)	0.272 (4)	0.918 (2)	4*
H(12B)	0.411 (3)	0.108 (4)	0.896 (2)	4*
H(12C)	0.340 (3)	0.202 (3)	0.853 (2)	4*

[a] Starred atoms denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent parameter, defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table II. Selected Interatomic Distances (Å) and Angles (deg) in $[(\eta^5\text{-}C_5H_5)Mo(\eta^7\text{-}C_5H_4C(SCH_3)SC(CF_3)=C(CF_3))]$ (5b)[a]

Interatomic Distances

Metallacycle

Mo–C(11)	2.258 (3)	C(13)–C(14)	1.507 (4)
C(11)–S(1)	1.774 (2)	C(15)–C(16)	1.495 (4)
S(1)–C(13)	1.758 (3)	C(16)–F(1)	1.337 (3)
C(13)–C(15)	1.343 (4)	C(16)–F(2)	1.335 (4)
Mo–C(15)	2.214 (2)	C(16)–F(3)	1.348 (4)
C(11)–S(2)	1.780 (2)	C(14)–F(4)	1.322 (4)
S(2)–C(12)	1.795 (4)	C(14)–F(5)	1.335 (4)
C(10)–C(11)	1.454 (3)	C(14)–F(6)	1.329 (3)

Cp Rings

C(1)–(5) Cp ring		C(6)–(10) Cp ring	
C(1)–C(2)	1.389 (5)	C(6)–C(7)	1.402 (4)
C(2)–C(3)	1.405 (5)	C(7)–C(8)	1.412 (4)
C(3)–C(4)	1.432 (5)	C(8)–C(9)	1.409 (4)
C(4)–C(5)	1.381 (5)	C(9)–C(10)	1.451 (3)
C(1)–C(5)	1.420 (5)	C(6)–C(10)	1.439 (3)
av	1.405		
Mo–C(1)	2.375 (3)	Mo–C(6)	2.295 (2)
Mo–C(2)	2.327 (3)	Mo–C(7)	2.360 (3)
Mo–C(3)	2.251 (3)	Mo–C(8)	2.294 (3)
Mo–C(4)	2.248 (3)	Mo–C(9)	2.218 (3)
Mo–C(5)	2.314 (3)	Mo–C(10)	2.146 (2)
av	2.303		

Bond Angles

Mo–C(10)–C(11)	74.9 (4)	C(9)–C(10)–C(11)	114.2 (2)
C(15)–Mo–C(11)	79.65 (9)	S(1)–C(13)–C(14)	109.1 (2)
Mo–C(11)–S(1)	116.2 (4)	C(14)–C(13)–C(15)	129.2 (2)
C(11)–S(1)–C(13)	101.1 (1)	S(1)–C(13)–C(15)	121.5 (2)
C(11)–S(2)–C(12)	102.5 (1)	C(13)–C(15)–C(16)	118.7 (2)
C(6)–C(10)–C(9)	106.0 (2)	Mo–C(15)–C(13)	121.2 (3)
C(6)–C(10)–C(11)	120.2 (2)		

[a] Esd's in parentheses refer to the least significant digit.

(13)C(15) is planar within 0.04 Å. This plane approximately bisects the Cp_2Mo unit (at an angle of 34.05 (1)° with the C(1)–C(5) Cp ring and 30.7 (1)° with the C(6)–C(10) Cp ring). It is noteworthy that the C(10) and S(2) atoms are clearly out of this plane (−1.278 (2) Å for C(10); 1.000 (7) Å for S(2)).

The overall geometry of this skeleton resembles that found in the starting complex $[Cp_2MoC(S)SC(CF_3)=C(CF_3)]$ (**1b**).[10b] The most important differences concern the Mo–C(11) bond (2.258 (3) Å in **5b**; 2.185 (6) Å in **1b**) and the C(11)–S(1) bond (1.774 (2) in **5b**; 1.735 (6) Å in **1b**). The lengthening of these two bonds from **1b** to **5b** indirectly results from the methylation of the S(2) atom, since in **1b** delocalization of the π electron system over all of the metallacyclic fragment is favored by the presence of the exocyclic carbon–sulfur double bond. Other distances and angles in this fragment are very similar to those in **1b**[10] (bond lengths (Å) and bond angles (deg) with the corresponding value in **1b** given in brackets: S(1)–C(13) = 1.758 (3) [1.765 (6)]; C(13)–C(15) = 1.343 (4) [1.331 (8)]; C (15)–Mo = 2.214 (2) [2.201 (6)]; C(11)–Mo–C(15) = 79.65 (9) [80.4 (2)]).

(ii) The new carbon–carbon bond between the C(10) atom of the cyclopentadienyl ring and the *exo*-CS_2 carbon atom C(11) shows a slight multiple-bond character (C(10)–C(11) = 1.454 (3) Å). Its formation perturbs the geometry of the cyclopentadienyl ligand in the following way (Figure 4): (a) the two carbon–carbon bond lengths involving C(10) are significantly longer (C(6)–C(10) = 1.439 (3) Å, C(10)–C(9) = 1.451 (3) Å) than the other three (from 1.402 (4) to 1.412 (4) Å; mean value 1.408 (4) Å) and than the average C–C bond length (1.405 (5) Å) in the "normal" η^5-C_5H_5 ligand;(b) the Mo–C(10) bond length (2.146 (2) Å) is significantly shorter than the other four (from 2.218 (3) to 2.360 (3) Å; mean value 2.292 Å) and than the Mo–C bond length (from 2.248 (3) to 2.375 (3) Å; mean value 2.303 Å) for the η^5-C_5H_5 ligand.

Figure 4 clearly shows that these features are in good agreement with those previously reported for two other molybdenum complexes containing a $[Mo(C_5H_4C-)]$ moiety, $[(\eta^6\text{-}C_6H_6)Mo(\eta^6\text{-}C_5H_4CPh_2)]$[17] and $[(\eta^5\text{-}C_5H_5)Mo(\eta^7\text{-}C_5H_4C(SCHCHCN)SCR=CR)]$ (**5c**; R = CO_2Me).[10]

(iii) The carbon–sulfur C(12)–S(2) bond of the thiomethyl group (1.795 (4) Å) appears to be an almost pure σ C–S bond, as does the C(11)–S(2) bond (1.780 (2) Å), while the C–F bond lengths in the CF_3 groups (from 1.322 (4) to 1.348 (4) Å; mean value 1.334 Å) are normal.

Concluding Remarks

The results reported here show that the two metallacyclic isomers $[Cp_2MoC(S)SC(R)=CR]$ and $[Cp_2MoSC(S)C(R)=CR]$ have rich reactivities, which include

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[17] Bandy, J. A.; Mtetwa, V. S. B.; Prout, K.; Green, J. C.; Davies, C. E.; Green, M. L. H.; Hazel, N. J.; Izquierdo, A.; Martin-Polo, J. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2037.

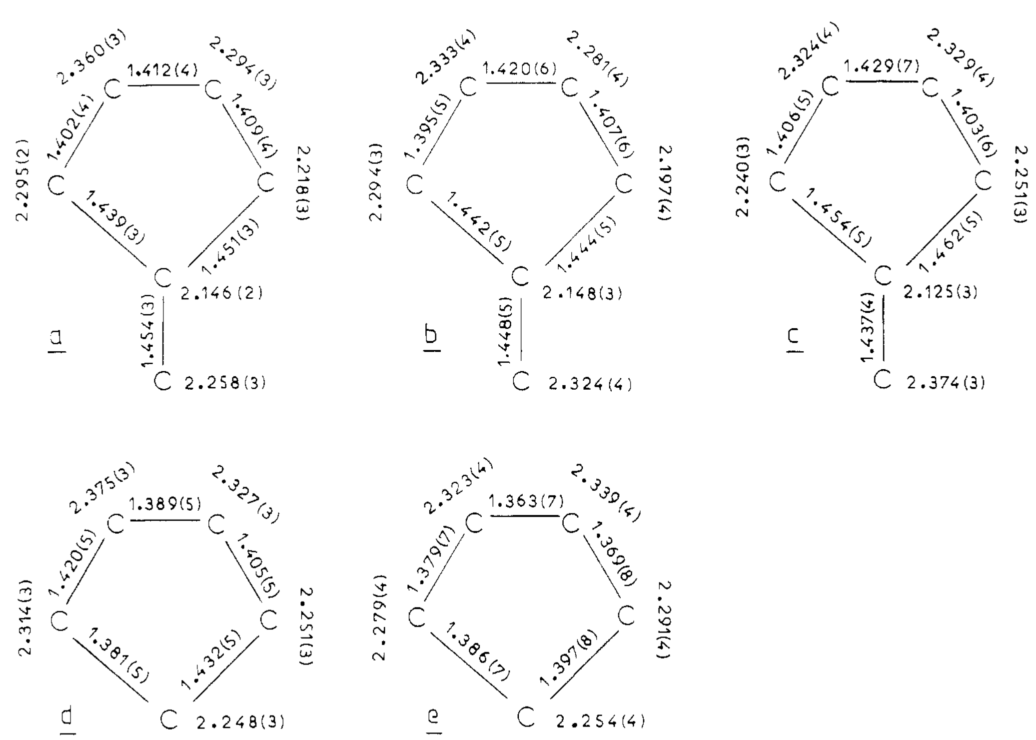

Figure 4. Carbon–carbon and molybdenum–carbon bond lengths (Å) for the $\overline{[Mo-(C_5H_4-C)]}$ unit in (a) **5b** (this work) (b) $[(\eta^5\text{-}C_5H_5)\overline{Mo(\eta^7\text{-}C_5H_4C(SCHCHCN)SCR{=}CR)}]$ (R = CO_2Me)[10] and (c) $[(\eta^6\text{-}C_6H_6)\overline{Mo(\eta^6\text{-}C_5H_4CPh_2)}]$.[17] Also given for comparison in (d) and (e) are the corresponding distances for the unsubstituted η^5-C_5H_5 ligand in the first two complexes.

unexpected coupling between one of the cyclopentadienyl rings and the five-membered heterometallacyclic fragment by three different pathways: (i) reaction of methyl iodide (**5b**), (ii) reaction of methyl iodide followed by treatment with sodium tetrahydroborate (**5a**), and (iii) reaction with cyanoethyne (**5c** and **5d**)[10] (Figure 1). It is noteworthy that these reactions correspond to the formation in situ of a fulvene-like ligand that, by adopting the observed coordination mode, acts as a six-electron donor. The reactivities of these metallacycles, which clearly depend on the nature of the metallacycle and on the nature of the R substituents, are currently under further investigation, since novel organic products may be generated via reaction of CS_2 in the coordination sphere of the molybdenum.

Experimental Section

General Procedures and Physical Measurements. All reactions were performed in Schlenk flasks under a dry, oxygen-free dinitrogen atmosphere. All solvents were distilled by standard techniques and thoroughly deoxygenated before use. All elemental analyses were performed by "Service Central d'Analyse du CNRS" (Vernaison, France). ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained on JEOL FX 100 and Bruker AC 300 spectrometers operating in the FT mode ($SiMe_4$ as internal standard for ^{1}H and ^{13}C; CF_3CO_2H as external standard for ^{19}F). Mass spectra were obtained with a Varian MAT 311 spectrophotometer ("Centre de Mesures Physiques", Rennes, France). The IR spectra were measured on a Perkin-Elmer 1430 spectrometer.

Complexes **1a**, **1b**, and **2a** were prepared from $[Cp_2Mo(\eta^2\text{-}CS_2)]$ as previously described.[10] $NaBH_4$ was dried in vacuo prior to use (80 °C, 10^{-1} mmHg; 15 h).

Reactions of Complexes 1 and 2 with Methyl Iodide: Preparation of Complexes 3a, 4a, and 5b. Complex 3a. A THF solution of **1a** (0.65 g, 1.5 mmol) containing a large excess of CH_3I (0.5 mL, 8 mmol) was stirred at room temperature for ca. 16 h. The resulting precipitate was filtered, washed with THF, and dried in vacuo. Recrystallization from dichloromethane–hexane afforded bright green microcrystals in almost quantitative yield. Anal. Calcd for $C_{18}H_{19}IMoO_4S_2\cdot 0.66CH_2Cl_2$: C, 34.9; H, 3.2; S, 10.0; I, 19.8. Found: C, 34.9; H, 3.1; S, 9.7; I, 19.3. Mass spectrum: *m/e* 459.972 (M^+ − HI; calcd 459.970). ^{1}H NMR ($CDCl_3$, δ): 3.07 (3 H, s, SCH_3); 3.79 (3 H, s, OCH_3); 3.80 (3 H, s, OCH_3); 5.51 (10 H, s, C_5H_5). IR (KBr, cm^{-1}): ν_{CO} 1700, 1730 (CO_2CH_3).

Complex 4a. **4a** was prepared from **2a** by using a procedure similar to that described for the preparation of **3a** and obtained in almost quantitative yield as brown-green crystals. Anal. Calcd for $C_{18}H_{19}IMoO_4S_2$: C, 36.9; H, 3.3; S, 10.9; Mo, 16.4. Found: C, 37.0; H, 3.4; S, 10.6; Mo, 16.3. Mass spectrum: *m/e* 459.968 (M^+ − HI; calcd 459.970). ^{1}H NMR ($CDCl_3$, δ): 2.98 (3 H, s, SCH_3); 3.81 (3 H, s, OCH_3); 3.84 (3 H, s, OCH_3); 5.60 (10 H, s, C_5H_5). IR (KBr, cm^{-1}): ν_{CO} 1690, 1700 (CO_2CH_3).

Complex 5b. A THF solution of **1b** (0.5 g, 1.1 mmol) containing an excess of CH_3I (0.4 mL, 6.4 mmol) was stirred at room temperature for ca. 72 h. The solvent was then removed under reduced pressure to give a brown oil, which was dried in vacuo and then dissolved in the minimum amount of dichloromethane. The resulting solution was chromatographed on a silica gel column made up with hexane. Elution with a 1:1 dichloromethane–hexane mixture afforded, after evaporation to dryness, orange microcrystals of **5b** in ca. 75% yield. Anal. Calcd for $C_{16}F_6H_{12}MoS_2$: C, 40.2; H, 2.5; F, 23.8; S, 13.4. Found: C, 40.4; H, 2.4; F, 23.4; S, 13.0. Mass spectrum: *m/e* 479.9 (M^+; calcd 479.9). ^{1}H NMR (CD_2Cl_2, δ): 2.42 (3 H, s, SCH_3); 4.28 (1 H, ddd), 4.92 (2 H, m), 6.14 (1 H, ddd) (C_5H_4); 5.13 (5 H, s, C_5H_5). ^{13}C NMR (CD_2Cl_2, δ): 23.0 (s, SCH_3); 77.4 (s), 86.1 (s), 87.9 (s), 116.2 (s) (CH of C_5H_4); 91.6 (s, C_5H_5); 102.9 (s, C of C_5H_4); 118.4 (q, $^1J_{CF}$ = 280 Hz, CF_3); 126.2 (q, $^1J_{CF}$ = 274 Hz, CF_3); 145.1 (q, $^2J_{CF}$ = 32 Hz, C=C); 146.2 (q, $^2J_{CF}$ = 37 Hz, C=C). ^{19}F NMR (CD_2Cl_2, δ): 20.6 (q, $^5J_{FF}$ = 14.6 Hz, CF_3); 32.5 (q, $^5J_{FF}$ = 14.6 Hz, CF_3).

Reactions of Complexes 3a and 4a with Sodium Tetrahydroborate: Preparation of Complexes 5a, 6a, 7a, and 8a. Complexes 5a and 6a. A solution of **3a** (0.65 g, 1.1 mmol) was stirred in dichloromethane with an excess of $NaBH_4$ (room temperature for ca. 120 h). After filtration on Celite, the resulting red solution was concentrated and then chromatographed on a silica gel column made up with hexane. Elution with dichloromethane gave an orange solution from which, after evaporation of the solvent under reduced pressure and recrystallization (dichloromethane–hexane), orange crystals of **5a** were obtained in low yield (ca. 4%). Further elution with a 95:5 dichloro-

Table III. Crystallographic Data for the Structural Analysis for Compound 5b

	A. Crystal Data
compd	$[(\eta^5\text{-}C_5H_5)Mo(\eta^7\text{-}C_5H_4C(SCH_3)SC(CF_3){=}C(CF_3))]$
formula	$C_{16}F_6H_{12}S_2Mo$
mol wt	478.3
color	orange
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	11.861 (3)
b, Å	9.839 (3)
c, Å	15.075 (4)
β, deg	106.28 (2)
V, Å^3	1688.7 (5)
Z	4
ρ_{calc}, g·cm^{-3}	1.88
$F(000)$	944
	B. Measurement of Intensity Data
radiatn, Å	λ(Mo Kα) = 0.71069
cryst size, mm	0.12 × 0.15 × 0.17
temp, K	296 (±1)
max 2θ, deg	54
scan	$\omega/2\theta = 1$
t_{max} (for one measure), s	60
octants collected	$+h,+k,\pm l$ ($h \leq 15$; $k \leq 12$; $l \leq 19$)
no. of rflns measd	4089
no. of data used ($I > 3\sigma(I)$)	2953
R_{INT}	0.011
	C. Treatment of Data
linear abs coeff, cm^{-1}	8.8 (no abs cor)
R(isotropic)	0.087
R(anisotropic)	0.043
final R (including H's)	0.027
R_w	0.024
w	$1/\sigma(F_o)^2 = \lvert\sigma^2(I) + (0.04F_o^2)^2\rvert^{-1/2}$

methane–THF mixture gave a red solution from which, after recrystallization (dichloromethane–hexane), **6a** was obtained as red microcrystals in 25–30% yield. Analytical and spectral data for **5a**: Anal. Calcd for $C_{18}H_{18}MoO_4S_2$: C, 47.2; H, 4.0; Mo, 20.9. Found: C, 47.0; H, 4.0; Mo, 20.6. Mass spectrum: m/e 460.1 (M$^+$; calcd 460.0). ^{1}H NMR (CDCl$_3$, δ, isomer I): 2.43 (3 H, s, SCH$_3$); 3.64 (6 H, m, OCH$_3$); 4.38 (1 H, m), 4.74 (1 H, m), 4.99 (1 H, m), 6.06 (1 H, m)) (C$_5$H$_4$); 5.12 (5 H, s, C$_5$H$_5$). ^{1}H NMR (CDCl$_3$, δ, isomer II): 2.42 (3 H, s, SCH$_3$); 3.64 (6 H, m, OCH$_3$); 3.60 (1 H, m), 4.56 (1 H, m), 4.99 (1 H, m), 5.98 (1 H, m) (C$_5$H$_4$); 5.11 (5 H, s, C$_5$H$_5$). Analytical and spectral data for **6a**: Anal. Calcd for $C_{18}H_{20}MoO_4S_2$: C, 47.0; H, 4.4. Found: C, 46.2; H, 4.2. Mass spectrum: m/e 462.0 (M$^+$; calcd 462.0). ^{1}H NMR (CDCl$_3$, δ): 2.12 (3 H, s, SCH$_3$); 3.67 (3 H, s, OCH$_3$); 3.74 (3 H, s, OCH$_3$); 4.92 (5 H, s, C$_5$H$_5$); 5.12 (1 H, s, CH); 5.21 (5 H, s, C$_5$H$_5$). ^{13}C NMR (CDCl$_3$, δ): 21.4 (SCH$_3$); 38.4 (CH); 50.9, 52.0 (OCH$_3$); 92.7, 93.5 (C$_5$H$_5$); 144.8, 160.1 (C=C); 163.9, 177.3 (COO).

Complexes 7a and 8a. These complexes were prepared from **4a** by using a procedure similar to that described for the syntheses of **5a** and **6a**. Elution with dichloromethane and recrystallization (dichloromethane–hexane) gave **7a** as an orange powder in ca. 3% yield. Further elution with a 98:2 dichloromethane–THF mixture gave, after recrystallization (dichloromethane–hexane), **8a** as red microcrystals in ca. 15% yield. Analytical and spectral data for **7a**: Anal. Calcd for $C_{18}H_{18}MoO_4S_2$: C, 47.2; H, 4.0. Found: C, 47.2; H, 3.9. Mass spectrum: m/e 459.6 (M$^+$; calcd 460.0). ^{1}H NMR (CDCl$_3$, δ): 2.45 (3 H, s, SCH$_3$); 3.64 (3 H, s, OCH$_3$); 3.72 (3 H, s, OCH$_3$); 4.44 (1 H, m), 4.72 (1 H, m), 4.95 (1 H, m), 6.31 (1 H, m) (C$_5$H$_4$); 5.04 (5 H, s, C$_5$H$_5$). Analytical and spectral data for **8a**: Anal. Calcd for $C_{17}H_{18}MoO_4S$: C, 49.3; H, 4.4; S, 7.7. Found: C, 49.9; H, 4.4; S, 7.3. Mass spectrum: m/e 415.6 (M$^+$; calcd 416.0). ^{1}H NMR (CDCl$_3$, δ): 3.66 (3 H, s, OCH$_3$); 3.68 (2 H, s, CH$_2$); 3.78 (3 H, s, OCH$_3$); 5.14 (10 H, s, C$_5$H$_5$).

Crystallographic Analysis of 5b. Single crystals were grown from dichloromethane–hexane solutions stored under dinitrogen. The data were collected with an Enraf-Nonius CAD-4 automatic four-circle diffractometer. The intensities were corrected for Lorentz and polarization effects, but no absorption corrections were applied. The scattering factors were taken from ref 18. The structure was solved by a combination of Patterson function and Fourier differences. After anisotropic refinement, the hydrogen atoms were located from difference Fourier maps and refined with isotropic temperature factors $B = 4$ Å^2. The best full-matrix least-squares refinement of the structure[19] (x, y, z, β_{ij} for non-hydrogen atoms and x, y, z for hydrogen atoms) converged to $R_w = 0.024$ ($S = 1.04$). Details of the crystal data, experimental conditions, and solution and refinement are given in Table III, while atomic coordinates are provided in Table I and selected bond distances (Å) and angles (deg) are given in Table II.

Supplementary Material Available: A table of general temperature factor expressions (B's) (1 page); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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(18) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(19) Sheldrick, G. M. "SHELX 76, Program for Crystal Structure Determinations"; University of Cambridge: Cambridge, England, 1976.