acetylene (0.6 g, 5 mmol) or (trimethylsilyl)acetylene (10 mL, 7 mmol). The mixture was heated to 70 °C and stirred there for 6 h. The solution was concentrated by evaporation, and hexane (10 mL) was added to induce the precipitation of the red-brown insertion product (35–41%), $Cp_2NbC(CH_3){=}CHPh(CH_3C{\equiv}CPh)$. EIMS: *m/z* (species, relative intensity) 456 (M^+, 0.5), 340 ($M^+ - C_2MePh$, 21), 224 (Cp_2NbH^+, 100), 223 (Cp_2Nb^+, 59). ^1H NMR (C_6D_6): δ 6.96 (CH=, d), 4.61 (Cp, s), 1.86, 1.94 (Me, s), 7.2–8.9 (C_6H_5, m). $Cp_2NbCH{=}CHSiMe_3(HC{\equiv}CSiMe_3)$. EIMS: *m/z* (species, relative intensity) 420 (M^+, 4), 322 ($M^+ - CHCSiMe_3$, 72), 224 (Cp_2NbH^+, 100), 223 (Cp_2Nb^+, 61). ^1H NMR (C_6D_6): δ 7.57 (CH≡, s), 4.73, 4.80 (CH=CH, d), 4.50 (Cp, s), 1.47, 1.49 ($SiMe_3$, s).

Reaction of Alkyne Complexes with CO, CO_2, $P(CH_3)_3$, and Carbonyl Compounds. Alkyne complexes 1 and 7 were used to examine their reactivity toward donor molecules. Gaseous CO and CO_2 (>20 mmol) were bubbled in a benzene solution (10 mL) of 1 and 7 (2.0 mmol) at 60 °C for 2 h, but no change was observed in their ^1H NMR spectra. A 1:2 mixture of 1 or 7 and $P(CH_3)_3$ or pyridine in toluene-d_8 sealed in a NMR tube was heated to 100 °C for 3 h. No spectral or color change was observed during this procedure. The complexes 1 and 7 were also inert to acetone and propanal (charged in a 1:3 ratio) even at 80 °C in toluene. Further heating to 120 °C resulted in the production of a complex mixture containing mesityl oxide derived from aldol type condensation of the carbonyl compound.

Structure Determination of 5–7. Single crystals of 5–7 sealed in a thin-walled glass capillary under argon were mounted on a Rigaku automated four-circle diffractometer. Relevant crystal and data statistics are summarized in Table III. The unit cell parameters at 20 °C were determined by a least-squares fit to 2θ values of 25 strong high-angle reflections. Each sample showed no significant intensity decay over the duration of data collection. The crystal structures of the above complexes were all solved by the heavy-atom method and refined by full-matrix least squares as implemented in the XRAY-76 system utilizing the observed reflections [$|F_o| > 3\sigma(F_o)$]. In the subsequent refinements, the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the amplitudes of observed and calculated structure factors, respectively. After the anisotropic refinement of non-hydrogen atoms for 5–7, all hydrogen atoms were located in the difference Fourier maps with the help of geometrical calculations and were refined isotropically.

Acknowledgment. We are indebted to a Grant-in-Aid for scientific research (No. 1490012) from the Ministry of Education, Science, and Culture, Japan.

Registry No. 1 (exo isomer), 136736-44-2; 1 (endo isomer), 136780-80-8; 2 (exo isomer), 136736-45-3; 2 (endo isomer), 136780-81-9; 3 (exo isomer), 136736-46-4; 3 (endo isomer), 136780-82-0; 4 (exo isomer), 136736-47-5; 4 (endo isomer), 136780-83-1; 5, 136736-48-6; 6, 136736-49-7; 7, 136736-50-0; 8, 136736-51-1; 9, 136736-52-2; 10, 136736-53-3; 11, 77299-70-8; 12, 136736-54-4; $Cp_2NbC(CH_3){=}CHPh(CH_3C{\equiv}CPh)$, 136736-55-5; $Cp_2NbCH{=}CHSiMe_3(HC{\equiv}CSiMe_3)$, 136736-56-6; $Cp_2NbH(C_2H_4)$, 11105-70-7; $Cp_2TaH(C_2H_4)$, 66786-38-7; Cp_2NbH(propene), 123620-30-4; Cp_2NbH(styrene), 123620-31-5.

Supplementary Material Available: Listings of additional bond lengths and angles, hydrogen atom parameters, and anisotropic thermal parameters for 5–7 (9 pages); tables of the observed and calculated structure factors (82 pages). Ordering information is given on any current masthead page.

Notes

Role of $[Cp^*Mo(\mu\text{-}S)]_2S_2CH_2$ in Dichloromethane Hydrogenolysis

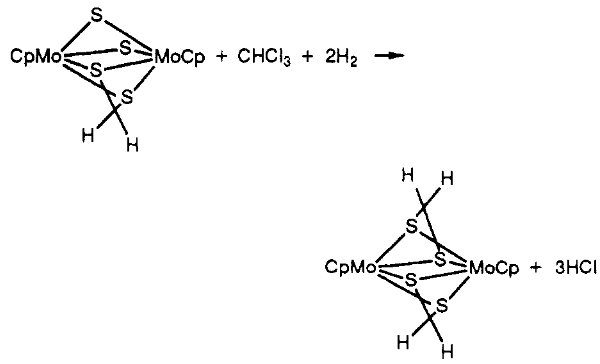
M. Maciejewski Farmer, R. C. Haltiwanger, F. Kvietok, and M. Rakowski DuBois*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Received March 13, 1991

Summary: The reaction of $(Cp^*MoS)_2S_2CH_2$ ($Cp^* = C_5Me_5$) with dichloromethane under 1–2 atm of H_2 at 50 °C led to the hydrogenolysis of dichloromethane and the formation of $(Cp^*MoS_2CH_2)_2$ (**1**). Complex **1** crystallized in space group $P\bar{1}$ with unit cell dimensions $a = 7.992$ (2) Å, $b = 8.354$ (3) Å, $c = 10.624$ (5) Å, $\alpha = 88.11$ (3)°, $\beta = 74.15$ (3)°, $\gamma = 62.83$ (2)°, and $V = 603.6$ (4) Å^3. The X-ray diffraction study of **1** verified that the two Cp*Mo units were symmetrically bridged by two η^2 methanedithiolate ligands. When $(Cp^*MoS)_2S_2CH_2$ was reacted with dichloromethane under nitrogen rather than hydrogen pressure, the cationic product $[(Cp^*Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]Cl$ (**2**) was formed. Complex **2** reacted with hydrogen to form **1** and is, therefore, a likely intermediate in the dichloromethane hydrogenolysis.

Several years ago we reported that the dinuclear molybdenum(IV) complex $[CpMo(\mu\text{-}S)]_2S_2CH_2$ reacted slowly with chloroform under 1–3 atm of hydrogen to form $[CpMoS_2CH_2]_2$ and HCl as shown in eq 1.[1,2] In recent



(1)

studies of the analogous (pentamethylcyclopentadienyl)molybdenum(IV) complex, $[Cp^*Mo(\mu\text{-}S)]_2S_2CH_2$, we observed that the bis(methanedithiolate) product was formed in good yield in reactions with dichloromethane under hydrogen. We report here the characterization of a probable intermediate in this unusual hydrogenolysis reaction and some novel reaction chemistry of these deriv-

(1) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

(2) Weberg, R. T. Ph.D. Thesis, University of Colorado, Boulder, CO, 1986.

Table I. Selected Bond Distances (Å) and Angles (deg) for $[Cp^*MoS_2CH_2]_2$ (1)

Distances			
Mo(1)-Mo(1A)	2.621 (2)	Mo(1A)-S(1)	2.449 (2)
Mo(1)-S(1)	2.449 (2)	Mo(1A)-S(2)	2.445 (3)
Mo(1)-S(1A)	2.449 (2)	S(1)-C(1)	1.797 (14)
Mo(1)-S(2)	2.457 (2)	S(2)-C(1)	1.811 (11)
Mo(1)-S(2A)	2.445 (3)	Mo(1)-$C_{cp(av)}$	2.305 (23)
Angles			
Mo(1)-S(1)-Mo(1A)	64.7 (1)	S(1)-Mo(1)-S(2)	67.0 (10
Mo(1)-S(2)-Mo(1A)	64.7 (1)	Mo(1)-S(1)-C(1)	90.9 (4)
S(1)-Mo(1)-S(1A)	115.3 (1)	Mo(1)-S(2)-C(1)	90.4 (3)
S(2)-Mo(1)-S(1A)	79.4 (10	S(1)-C(1)-S(2)	97.3 (4)

atives, which reveals unexpected electronic properties of the ligands. When the catalytic and stoichiometric reactions of quadruply bridged $[Cp^*MoS_2]_2$ derivatives were studied previously in chlorinated solvents,[3,4] competing reactions with the solvents were observed to lead to unidentified products. This study establishes the nature of the reaction of one of these derivatives with dichloromethane and further identifies additional products that are formed under hydrogen pressures and under acidic conditions.

Results and Discussion

Reaction of $[Cp^*Mo(\mu\text{-}S)]_2S_2CH_2$ with Hydrogen and Dichloromethane. When the complex $(Cp^*Mo(\mu\text{-}S))_2S_2CH_2$ was heated in dichloromethane under a hydrogen atmosphere at 50 °C for ~6 days, the blue color of the solution changed to brown and a brown crystalline precipitate appeared. The product was tentatively characterized as $[Cp^*MoS_2CH_2]_2$ (1) by mass spectroscopic data. The solubility of the complex was very low in most organic solvents but was quite good in carbon disulfide. ^1H NMR data in this solvent showed two singlets at 2.05 and 6.12 ppm with relative intensities of 15:2.

Because of our initial difficulties in finding an effective NMR solvent, the tentative structural assignment was confirmed by an X-ray diffraction study. Single crystals were obtained from the reaction solution. The complex crystallized in space group $P\bar{1}$ with one molecule per unit cell. A perspective view of the molecule is given in Figure 1. Positional parameters are presented in Table I, and selected bond distances and angles, in Table II. The molecule consists of two Cp*Mo units bridged by two η^2-methanedithiolate ligands. The two halves of the molecule are related by an inversion center that lies along the metal–metal vector. The bond distances and angles of the methanedithiolate ligands are similar to those characterized previously for a related dimer containing the same ligand, $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)_2$.[1] Most of the molybdenum–sulfide distances and angles are also very similar to those observed in the previous study. The short distance between the two sulfur atoms in the methanedithiolate ligands (S_1- - -S_2 = 2.72 Å) appears to lead to an opening up of the Mo–S–Mo(1A) angles. Values of 64.7° are observed in this structure compared to an average value of 64.1° for the same angle in several related molybdenum(III) dimers that have been characterized previously.[5] The Mo–Mo distance of 2.621 (2) Å is ca. 0.03 Å longer than the metal–metal distances observed in the previously studied complexes.

Synthesis and Characterization of $[(Cp^*Mo)_2(S_2CH_2)(\mu\text{-}SCH_2Cl)]Cl$. In order to obtain information on how the reaction with dichloromethane and hydrogen proceeded, we examined the stepwise reaction of $[Cp^*Mo(\mu\text{-}S)]_2S_2CH_2$ with these reagents. Reaction of the latter complex with dichloromethane at 50 °C for 2 days under nitrogen resulted in the formation of a blue violet solution. The product was isolated by evaporation of solvent and recrystallization from CH_2Cl_2/hexanes and characterized by spectroscopic data as $[(Cp^*Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]Cl$ (2). The FAB mass spectrum of the product showed a parent ion that was consistent with the formulation of the cation. In the ^1H NMR spectrum in $CDCl_3$, a singlet at 3.45 ppm was assigned to the methylene group of the chloromethanethiolate ligand. The intensity of this resonance was significantly decreased in the spectrum of the complex prepared from CD_2Cl_2. Singlets at 2.42 and 4.55 ppm were assigned to the Cp* and methanedithiolate ligands, respectively.

(3) Kubas, G. J.; Ryan, R. R.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1989**, *111*, 7823.
(4) Farmer, M.; Rakowski DuBois, M. Unpublished work.
(5) Miller, W. K.; Haltiwanger, R. C.; VanDerveer, M. C.; Rakowski DuBois, M. *Inorg. Chem.* **1983**, *22*, 2973.

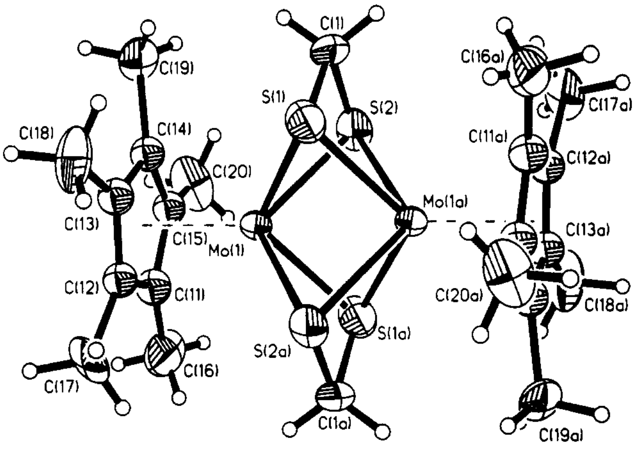


Figure 1. ORTEP plot of $[Cp^*MoS_2CH_2]_2$ (1). Thermal ellipsoids are shown at the 50% probability level. For clarity one of the disordered orientations (50% occupancy) of the Cp* ligands has been omitted.

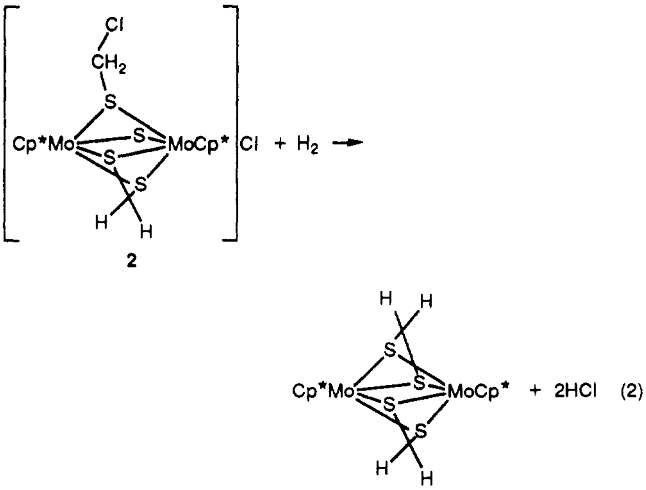
Table II. Atomic Coordinates[a] ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for $[Cp^*MoS_2CH_2]_2$ (1)

	x/a	y/b	z/c	U(eq)[b]
Mo(1)	−130 (1)	−195 (1)	−1183 (1)	24 (1)**
S(1)	2813 (3)	−2147 (3)	−526 (2)	51 (1)**
S(2)	−717 (3)	−2063 (3)	544 (2)	48 (1)**
C(1)	1860 (19)	−3706 (11)	19 (9)	81 (6)**
C(11)*	−1584 (33)	852 (32)	−2821 (18)	37 (4)
C(12)*	222 (39)	582 (30)	−3375 (20)	32 (5)
C(13)*	1589 (29)	−1201 (31)	−3416 (16)	35 (4)
C(14)*	454 (46)	−2128 (30)	−2882 (19)	35 (5)
C(15)*	−1515 (34)	−901 (42)	−2515 (19)	33 (6)
C(16)*	−3642 (32)	2416 (28)	−2637 (19)	76 (10)**
C(17)*	616 (42)	2155 (27)	−3881 (17)	75 (13)**
C(18)*	3783 (23)	−2002 (31)	−4030 (15)	61 (9)**
C(19)*	1471 (27)	−4259 (22)	−2992 (16)	49 (8)**
C(20)*	−3135 (31)	−1475 (34)	−2065 (19)	66 (11)**
C(21)*	−909 (30)	78 (33)	3384 (15)	34 (9)**
C(22)*	−1008 (26)	1889 (39)	3212 (21)	51 (9)**
C(23)*	986 (36)	1545 (29)	2632 (15)	27 (8)**
C(24)*	2225 (20)	−354 (22)	2481 (14)	29 (6)**
C(25)*	1007 (36)	−1253 (22)	2931 (17)	37 (9)**
C(26)*	−2579 (30)	−288 (34)	4092 (18)	69 (11)**
C(27)*	−2745 (36)	3648 (27)	3692 (20)	82 (11)**
C(28)*	1578 (36)	3021 (25)	2383 (18)	63 (12)**
C(29)*	4477 (24)	−1136 (28)	1964 (19)	62 (8)**
C(30)*	1944 (32)	−3241 (22)	3116 (18)	57 (9)**

[a] Atoms have occupancies of 1.0 except as those marked with an asterisk, in which case the occupancies are 0.50. [b] For atoms marked with two asterisks, the equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

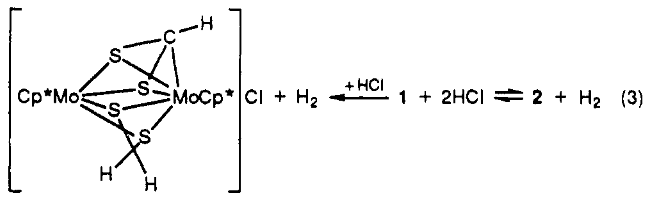
Alkylation of sulfido ligands by organic halides has been observed previously for related cyclopentadienyl- and (methylcyclopentadienyl)molybdenum complexes.[6-8] The latter derivatives, however, appear to be unreactive in dichloromethane. The increased reactivity of the permethylcyclopentadienyl complex can be attributed to the higher electron density in the Mo_2S_4 core and enhanced nucleophilicity of sulfido ligands as a result of the electron-donating Cp* ligands. Displacement of a chloride from dichloromethane has been observed previously in reactions with nucleophilic sulfido ligands in metal complexes.[9-11]

Reaction of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]Cl$ (2) with Hydrogen. Complex 2 reacted cleanly with hydrogen at ambient temperature in $CDCl_3$ to form the neutral derivative 1 (eq 2). Unstirred NMR tube reactions required 2 weeks to reach completion at room temperature, but even under these mild conditions, a significant amount of 1 was detected after 6 days. The result is consistent with the proposal that the chloromethanethiolate cation is an intermediate in the observed hydrogenolysis of dichloromethane discussed above. The reactions of hydrogen with cationic alkanethiolate complexes similar to 1 have been studied previously.[12] In many cases, the reactions proceeded to form a neutral complex $(CpMo)_2(S_2CH_2)(\mu\text{-}SR)(\mu\text{-}SH)$ and 1 equiv of protons. It seems likely that a similar intermediate $(Cp^*Mo)_2(S_2CH_2)(\mu\text{-}SCH_2Cl)(\mu\text{-}SH)$ (I) is formed in the reaction of 2 with hydrogen. However, no spectroscopic information is available on whether or how such an intermediate might eliminate HCl to form the final observed product, 1.



2 1

Further attempts were made to detect the intermediate I by reacting the neutral complex 1 with HCl. When an isolated sample of 1 was reacted with excess HCl at room temperature for 5 days, evidence was, in fact, observed for the partial conversion of 1 back to 2 (eq 3). However evidence for intermediate I was not detected by NMR spectroscopy. The reaction of 1 with protic acid proved to be quite complex. For example in this reaction with HCl, in addition to the formation of 2 in ca. 20% yield, a second cationic derivative was observed in the ^1H NMR spectrum in ~80% yield. This major product has been identified as $[(Cp^*Mo)_2(S_2CH_2)(S_2CH)]Cl$ (3) by comparison of NMR data with that of an authentic sample of the BF_4 salt (see below). Spectroscopic data and structural features of a closely related cyclopentadienyl derivative with an η^3-dithioacetate ligand have been reported in a previous study.[8] Complex 3 did not undergo a further reaction with an additional 1 equiv of HCl to form the chloromethanethiolate cation 2. Nor did 3 react with hydrogen to re-form 1. The complex, therefore, does not appear to be an intermediate in the interconversion of 1 and 2.



3

The formation of 3 from 1 is a result of the formal addition of 1 equiv of HCl and the elimination of 1 equiv of H_2. The net reaction involves the abstraction of a hydride ion by a proton. Although the mechanism of hydride abstraction is not known, the hydridic nature of the protons in the methanedithiolate ligand has been confirmed. The reaction of 1 with triphenylcarbenium ion proceeded to form cationic 3 in high yield.

The complexity of the reactions of 1 with acids was further demonstrated when alternate acids were employed. As expected, when 1 was reacted with acids with less nucleophilic counterions, e.g. trifluoroacetic or triflic acid, products analogous to 2 were not observed. The cation of 3 was a major product, but in addition we observed the formation of variable amounts of yet another cation $[Cp^*Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]^+$, which resulted from protonolysis of a C–S bond in a dithiolate ligand. The latter product was readily identified because it has been prepared previously by an independent route.[4] We have not further explored the factors that control product formation in this system. However, recent studies of reactions of related neutral molybdenum(III) dimers with electrophiles have suggested that both the metal ion and a sulfur ligand can undergo electrophilic attack,[12b] and such a dual pathway may contribute to the variable products observed in the present system.

Experimental Section

Materials and Procedures. $(Cp^*MoS)_2S_2CH_2$ was prepared as reported previously.[13] Dichloromethane was distilled from CaH_2. Acids and other reagents were purchased from commercial sources and used without purification.

^1H NMR spectra were recorded at 200 MHz on a Chemagnetics A-200 instrument or at 300 MHz on a Varian Gemini-300 spectrometer. Chemical shifts (ppm) were referenced to $SiMe_4$ by using the solvent signal as a secondary reference. Mass spectra (FAB and EI) were obtained on a VG Analytical 7070 EQ-HF mass spectrometer. Elemental analyses were provided by Spang Laboratories.

X-ray Diffraction Study of $[Cp^*MoS_2CH_2]_2$ (1). Crystals of 1 were isolated from dichloromethane at room temperature. The dark brown plates were often twinned. A suitable crystal

(6) Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119.
(7) Weberg, R. T.; Haltiwanger, R. C.; Laurie, J. C. V.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6242.
(8) Coons, D. E.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1987**, *6*, 2417.
(9) Lizano, A. C.; Noble, M. E. *Inorg. Chem.* **1988**, *27*, 747.
(10) Gukathasan, R. R.; Morris, R. H.; Walker, A. *Can. J. Chem.* **1983**, *61*, 2490.
(11) Briant, C. E.; Gardner, C. J.; Andy Hor, T. S.; Howells, N. D.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1984**, 2645.
(12) (a) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234. (b) Lopez, L. L.; Bernatis, P.; Haltiwanger, R. C.; Rakowski DuBois, M. Submitted for publication.

(13) Birnbaum, J.; Godziela, G.; Maciejewski, M.; Tonker, T. L.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1990**, *9*, 394.

Table III. Crystallographic Data for $[Cp^*MoS_2CH_2]_2$ (1)

formula	$C_{22}H_{34}S_4Mo_2$
fw	618.6
space group	$P\bar{1}$
cryst system	triclinic
a, Å	7.992 (2)
b, Å	8.354 (3)
c, Å	10.624 (5)
α, deg	88.11 (3)
β, deg	74.15 (3)
γ, deg	62.83 (2)
V, Å^3	603.6 (4)
Z	1
d_{calc}, g cm^{-3}	1.702
F(000), e	314
μ, cm^{-1}	13.55
radiation (λ, Å)	Mo Kα (0.71073)
temp, K	294–298
transm coeff	0.638, 0.326
R, R_w	0.063, 0.076

obtained by cleaning one of the plates was mounted on a glass fiber by using epoxy resin. Crystal data for 1 are given in Table III. Complete details of the experimental conditions and structural refinement are included in the supplementary material. The structure was determined by using direct methods and Fourier techniques. The compound crystallized with one independent half-molecule, positioned about a crystallographic inversion center. The pentamethylcyclopentadienes were disordered by a rotation of approximately 40°. The ring centroids were displaced by 0.2 Å. The structures were refined by using full-matrix, least-squares techniques with hydrogen atoms included on fixed idealized positions. The methylene hydrogens were refined with individual isotropic displacement parameters, and the MeCp hydrogens, with two group isotropic displacement parameters, one for each pentamethylcyclopentadienyl moiety. Full tables of the derived results are included in the supplementary materials.

Synthesis of $[Cp^*MoS_2CH_2]_2$. In a 50-mL flask equipped with a Teflon stopcock was dissolved $[Cp^*Mo(\mu\text{-}S)]_2S_2CH_2$ (0.043 g, 0.071 mmol) in 10 mL of CH_2Cl_2, and the resulting solution was degassed by three freeze–pump–thaw cycles. With the solution at ambient temperature, 1 atm of H_2 was added, and the solution was heated for 6 days at 50 °C. During this time, the color of the solution changed from blue to golden, and a dark brown crystalline precipitate appeared. The solution was then allowed to cool to ambient temperature and was filtered. The crystalline product was washed with CH_3CN and air-dried. Yield: 0.037 g, 0.060 mmol, 85%. ^1H NMR (CS_2): δ 6.12 (s, S_2CH_2, 4 H), 2.05 (s, Me_5Cp, 30 H). FAB-MS: m/e 618 (P), 573 (P – SCH_2), 559 (P – SCH_2 – CH_2).

Synthesis of $[(Cp^*Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]Cl$ (2). In a 50-mL Schlenk tube was dissolved $[Cp^*Mo(\mu\text{-}S)]_2S_2CH_2$ (0.050 g, 0.083 mmol) in 10 mL of CH_2Cl_2, and the resulting solution was degassed by three freeze–pump–thaw cycles. With the solution at ambient temperature, 1 atm of N_2 was added; the solution was heated for 3 days at 50 °C. During this time, the color of the solution changed from blue to violet. The solution was allowed to cool to ambient temperature and was reduced in volume. Hexane was added to precipitate the product, which was then recrystallized from CH_2Cl_2 and hexanes as dark purple microcrystals. ^1H NMR ($CDCl_3$): δ 5.32 (s, CH_2Cl_2, 2 H) 4.55 (s, S_2CH_2, 2 H), 3.45 (s, SCH_2Cl, 2 H), 2.42 (s, Me_5Cp, 30 H). ^{13}C NMR (CD_3CN): δ 118.4 (C_5Me_5), 13.7 (CH_3). Methylene carbons were not observed in the dilute solutions studied. FAB-MS: m/e 653 (P of cation), 617 (P – Cl), 573 (P – SCH_2Cl), 558 (P – SCH_2Cl – CH_2). Anal. Calcd for $C_{22}H_{34}Cl_2Mo_2S_4$ and 1 mol of CH_2Cl_2: C, 35.66; H, 4.69; S, 16.56. Found: C, 35.32; H, 5.03; S, 15.96. Both the ^1H NMR data and the elemental analyses indicated that the compound crystallized with 1 mol of CH_2Cl_2/mol of compound.

Reaction of $[(Cp^*Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]Cl$ (2) with H_2. A solution of 2 and $CDCl_3$ in a thin-wall 5-mm NMR tube was degassed by three freeze–pump–thaw cycles. While the solution was at ambient temperature, 1 atm of H_2 was added. The solution was then cooled to –196 °C, and the NMR tube was flame-sealed. The solution remained at ambient temperature for 15 days, and the reaction was monitored by ^1H NMR spectroscopy. During the course of the reaction, the solution changed from purple to golden brown, and a brown crystalline solid appeared. Slightly soluble 1 could be detected in the NMR spectra of the $CDCl_3$ solution during the reaction; a spectrum of the precipitate in CS_2 showed clean formation of 1.

Reaction of $[Cp^*MoS_2CH]_2$ (1) with HCl. A slurry of $[Cp^*MoS_2CH_2]_2$ and CD_2Cl_2 in a thin-wall 5-mm NMR tube was degassed by three freeze–pump–thaw cycles. HCl was admitted to 30 Torr while the slurry was at –196 °C, and the tube was flame-sealed. After 5 days at ambient temperature, there was no solid present in the tube and the solution was a reddish purple color. The ^1H NMR spectrum of this solution showed clean formation of $[(Cp^*Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]Cl$ (2) and $[(Cp^*Mo)(S_2CH)(S_2CH_2)(MoCp^*)]Cl$ (3) (see below for NMR data) in a ratio of 1 to 4, respectively.

Synthesis of $[(Cp^*Mo)(S_2CH_2)(S_2CH)(MoCp^*)]^+$ (Cation of 3). (a) CD_2Cl_2 (0.7 mL) was vacuum-transferred to a thin-wall 5-mm NMR tube that contained $(Cp^*MoS_2CH_2)_2$ (0.005 g, 8 × 10^{-3} mmol) and Ph_3CBF_4 (0.004 g, 12 × 10^{-3} mmol) at –196 °C. $(Cp^*MoS_2CH_2)_2$ dissolved upon warming to yield a golden solution. The ^1H NMR spectrum of the solution showed clean formation of $[(Cp^*Mo)(S_2CH)(S_2CH_2)(MoCp^*)]BF_4$. ^1H NMR: δ 2.22, 1.92, (2 s, Cp*); 4.90, 6.72 (2 d, J = 9 Hz, S_2CH_2); 6.33 (s, S_2CH).

(b) $[Cp^*Mo(\mu\text{-}S)]_2S_2CH_2$ (0.088 g, 0.15 mmol) was dissolved in $CHCl_3$, and CH_2I_2 (0.2 mL, 2.3 mmol) was added to the solution. The solution was freeze–pump–thaw degassed and stirred under vacuum at room temperature for 1 week. The solvent was removed, and the remaining solid was chromatographed on acidic alumina with acetonitrile. The first gold fraction was collected and dried to give the iodide salt of the desired cation. Yield: approximately 0.032 g, 30%. ^1H NMR: see above; evidence for CH_3CN was also observed in the spectrum. FAB-MS: m/e 617 (P of cation), 604 (P – CH), 558 (P – CH – SCH_2). Anal. Calcd for $C_{22}H_{33}Mo_2S_4I$ plus 1 mol of CH_3CN: C, 36.72; H, 4.63; S, 16.34. Found: C, 35.99; H, 4.87; S, 16.12.

Reaction of $[Cp^*MoS_2CH_2]_2$ (1) with Triflic Acid. Complex 1 (0.010 g, 1.6 × 10^{-2} mmol) was dissolved in CD_2Cl_2 in an NMR tube, and CF_3SO_3H (25 μL, 2.5 × 10^{-2} mmol) was added. The solution was degassed twice at –77 °C, and the tube was sealed under vacuum. The reaction was kept at room temperature and followed by ^1H NMR spectroscopy. After 2 days the following products were identified by their NMR spectra: $[(Cp^*Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]^+$ (δ 2.36 (s, Cp*), 1.38 (s, SMe), 3.84 (s, S_2CH_2)) and $[(Cp^*Mo)(S_2CH_2)(S_2CH)MoCp^*]^+$ (cation of 3). Relative ratio of the two products was ~1:2. The following resonances for a third, possibly intermediate, product were observed at early reaction times: δ 2.16, 1.94 (2 s, Cp*); 3.8, 5.4 (2 d, S_2CH_2); 3.1, 2.5 (d and t, S_2CH_2); –1.2 (d, S–H or Mo–H).

Attempted Reaction of $[(Cp^*Mo)_2(S_2CH_2)(S_2CH)]^+$ (Cation of 3) with H_2. A solution of $[(Cp^*Mo)_2(S_2CH_2)(S_2CH)]CF_3SO_3$ in CD_2Cl_2 in a thin-wall 5-mm NMR tube was degassed by three freeze–pump–thaw cycles. While the solution was at ambient temperature, 1 atm of H_2 was added. The solution was cooled to –196 °C, and the tube was flame-sealed. By ^1H NMR spectroscopy, no reaction was observed after 2 days at ambient temperature and after 3 days at 50 °C.

Attempted Reaction of $[(Cp^*Mo)_2(S_2CH_2)(S_2CH)]^+$ (Cation of 3) with HCl. A solution of $[(Cp^*Mo)_2(S_2CH_2)(S_2CH)]I$ in CD_2Cl_2 in a thin-wall 5-mm NMR tube was degassed by three freeze–pump–thaw cycles. While the solution was at –196 °C, HCl was admitted to 30 Torr and the tube was flame-sealed. By ^1H NMR spectroscopy, no reaction was observed after 2 days at ambient temperature and after 4 days at 50 °C.

Acknowledgment. This work was supported by the Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy.

Registry No. 1, 136630-16-5; 2, 136630-17-6; 3, 136630-18-7; $[(Cp^*Mo)(S_2CH)(S_2CH_2)(MoCp^*)]BF_4$, 136630-20-1; $[(Cp^*Mo)(S_2CH)(S_2CH_2)(MoCp^*)]CF_3SO_3$, 136630-21-2; [(Cp*-

Mo)(S_2CH)(S_2CH_2)(MoCp*)]I, 136630-22-3; [(Cp*Mo)$_2$-(S_2CH_2)(μ-S)(μ-SCH_3)]CF_3SO_3, 136630-24-5; [Cp*Mo(μ-S)]$_2S_2CH_2$, 124944-97-4; CH_2Cl_2, 75-09-2.

Supplementary Material Available: Complete listings of crystallographic data, bond distances and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for 1 (9 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

C–H Cleavage versus N–N Cleavage in μ_3-η^2-Azoalkane Ligands on the $M_3(CO)_9$ Clusters of Iron, Ruthenium, and Osmium

B. Hansert,[†] M. Tasi,[†] A. Tiripicchio,[‡] M. Tiripicchio Camellini,[‡] and H. Vahrenkamp*[,†]

Institut für Anorganische und Analytische Chemie, Universität Freiburg, D-7800 Freiburg, Germany, and Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, I-43100 Parma, Italy

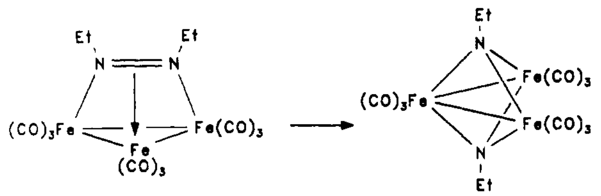
Received February 22, 1991

Summary: While thermal treatment of the cluster $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}N_2Et_2)$ leads to N–N cleavage and formation of the isomeric cluster $Fe_3(CO)_9(\mu_3\text{-NEt})_2$, the new ruthenium cluster $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}N_2Et_2)$ undergoes a different thermal rearrangement. One hydrogen atom of an *N*-ethyl group is transferred to the metal core, and the isomeric cluster $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-EtN—N=CH—CH}_3)$ containing a hydrazone-type ligand is formed. Both isomeric ruthenium clusters can be hydrogenated to yield $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-EtN-NHEt})$ containing a hydrazine-type ligand. $Os_3(CO)_{12}$ and azoethane yield only the hydrazone derivative $HOs_3(CO)_9(\mu_3\text{-}\eta^2\text{-EtN—N=CH—CH}_3)$. The crystal structures of the Os_3–hydrazone and of the Ru_3–hydrazine-type clusters have been determined.

If clusters are to become synthons in preparative chemistry it will have to be demonstrated that they can activate organic substrates efficiently and in a new fashion. Accordingly, ligand sphere reactivity of organometallic clusters is of current interest.[1] A prominent substrate for investigations of this kind is the alkyne ligand.[2] Less well investigated objects for such studies are the related ligand systems with C–N and N–N multiple bonds (nitriles,[3] isonitriles,[4] azoalkanes[5]).

We have demonstrated isoelectronic relations between clusters with face-bridging alkyne, nitrile, and azoalkane ligands,[6] and we have used cluster expansion methods for the synthesis of all three compound types.[7] For reactivity investigations we have focused on the cluster-bound azoalkane ligand. We could show that it can behave like an alkyne ligand in its N–N cleavage reaction[8] as well as in its combination with other organic fragments to form organic products.[9] We have now tried to extend these investigations, previously done on the $Fe_3(CO)_9$ cluster, to corresponding ruthenium and osmium clusters with azoalkane ligands. This paper reports our first results of these studies.

Prior to us Bruce[10] and Gladfelter[11] had shown that azoarenes in contact with ruthenium carbonyls are cleaved to form nitrene-bridged clusters, similar to the azoalkane → nitrene cleavage 1 → 2 observed by us on the iron cluster.[8] This cleavage occurs so easily that azoalkane-



1 2

or azoarene-bridged ruthenium clusters were unknown until recently.[7] It was therefore not unexpected for us to find that the azoethane Ru_3 cluster **3** is rather labile. However, to our surprise, the lability of **3**, is not due to its N–N cleavage but to alternative C–H cleavage, and so far we have not been able to make the ethylnitrene-bridged ruthenium cluster analogous to **2**.

† Universität Freiburg.
‡ Università di Parma.

(1) Lavigne, G. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: Weinheim, 1990. Shriver, D. F.; Sailor, M. F. *Acc. Chem. Res.* **1988**, *21*, 374. Kaesz, H. D. *J. Organomet. Chem.* **1990**, *383*, 413. Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. Adams, R. D.; Horvath, I. *Prog. Inorg. Chem.* **1985**, *33*, 127. Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1. Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41. Vahrenkamp, H. *Pure Appl. Chem.* **1989**, *61*, 1777. Vahrenkamp, H. *Pure Appl. Chem.* **1990**, *63*, 643.

(2) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113. Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169.

(3) Andrews, M. A.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7260 and papers cited therein. Bernhardt, W.; Vahrenkamp, H. *Z. Naturforsch.* **1988**, *43B*, 643.

(4) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209. Bruce, M. I.; Hambley, T. W.; Nicholson, B. H. *J. Chem. Soc., Chem. Commun.* **1983**, 353.

(5) *Eisen-Organische Verbindungen*; Gmelin Handbuch der Anorganischen Chemie, Vol. C1; Springer Verlag: Heidelberg, 1979; pp 127–163. Albini, A.; Kisch, H. *Top. Curr. Chem.* **1976**, *105*. Kisch, H.; Krüger, C.; Marcolin, H. E.; Trautwein, A. X. *Z. Naturforsch.* **1987** *42B*, 1435 and references cited therein.

(6) Vahrenkamp, H. *J. Organomet. Chem.* **1990**, *400*, 107.

(7) Bantel, H.; Hansert, B.; Powell, A. K.; Tasi, M.; Vahrenkamp, H. *Angew. Chem.* **1989**, *101*, 1084; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1059.

(8) Wucherer, E. J.; Tasi, M.; Hansert, B.; Powell, A. K.; Garland, M. T.; Halet, J. F.; Saillard, J. Y.; Vahrenkamp, H. *Inorg. Chem.* **1989**, *28*, 3564.

(9) Tasi, M.; Powell, A. K.; Vahrenkamp, H. *Chem. Ber.* **1991**, *124*, 1549.

(10) Bruce, M. I.; Humphrey, M. G.; bin Shawkataly, O.; Snow, M. R.; Tiekink, R. T. *J. Organomet. Chem.* **1987**, *336*, 199.

(11) Smieja, J. A.; Gozum, J. E.; Gladfelter, W. L. *Organometallics* **1987**, *6*, 1311.

0276-7333/91/2310-4070$02.50/0