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Unusual Ligand Formation in CS_2 Chemistry: Synthesis, Structure, and Reactivity of $Mo_2(S_2CNEt_2)_3(\mu\text{-}CSC(S)S)(\mu\text{-}S_3C_2NEt_2)$

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The complex reaction of CS_2 with $Mo(CO)_2(S_2CNEt_2)_2$ in the presence of 2 equiv of triphenylphosphine forms the dinuclear complex $Mo_2(S_2CNEt_2)_3(\mu\text{-}CSC(S)S)(\mu\text{-}S_3C_2NEt_2)$ (**1**) in 95% yield. The identity of **1** was determined by a single-crystal X-ray study. Two molecules of **1** crystallize in space group $P\bar{1}$ with $a = 15.749$ (6) Å, $b = 16.013$ (7) Å, $c = 9.740$ (6) Å, $\alpha = 107.26$ (3)°, $\beta = 105.92$ (4)°, and $\gamma = 71.14$ (2)°. The structure reveals that one molecule of carbon disulfide and two thiocarbonyl units have been incorporated in two new ligands. One ligand results from CS coupling with CS_2 to form a $-CSC(=S)S-$ unit where the carbon bridges both metals and the sulfide terminus chelates to one molybdenum. The second ligand appears to form by thiocarbonyl insertion into a molybdenum–sulfide bond of a dithiocarbamate (S_2CNEt_2) to give a $-SC(SC(S)NEt_2)$ moiety. The thiocarbonyl–C–S unit perpendicularly bridges the metal–metal axis and is reminiscent of a bridging alkyne. This ligand also chelates to one metal through a dithiocarbamate sulfur. The similarity of the structure of **1** to that of $Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(S_2CNMe_2)_3(SCNMe_2)$ (**4**) encourages development of a qualitative molecular orbital scheme for **1** from the analysis presented for the dinuclear alkyne derivative **4**. Both of these dinuclear compounds have formal Mo(III) centers in roughly conlateral-bioctahedral geometries. Addition of Me^+ using the $[Me_3O][BF_4]$ reagent yields a cation that may be subsequently reduced with use of $K[HB(O\text{-}i\text{-}Pr)_3]$. Cyclic voltammetry and visible spectroscopy data are compared for these dinuclear species.

Introduction

The expansive organometallic chemistry of carbon disulfide with transition metals has created a wide variety of carbon- and sulfur-containing ligands.[1] The fruits of these studies include examples of η^2-bound and bridged CS_2 ligands.[2] Regardless of one's viewpoint concerning CS_2 as a model for CO_2, carbon disulfide is a versatile synthetic reagent for the preparation of thiocarbonyl,[3] thioacyl,[2a,4] dithiocarbene,[4d,5] and dithiolate ligands.[4d,6]

Our initial goal was to generate $M(CS)_2(dtc)_2$ from $M(CO)_2(dtc)_2$ (dtc = S_2CNR_2 is a general abbreviation for any dithiocarbamate ligand, while detc will designate diethyldithiocarbamate, S_2CNEt_2, and dmtc will designate dimethyldithiocarbamate, $S_2CNMe)_2$) by the common method of CS_2 addition in the presence of triphenylphosphine.[7] The unusual stability of 16-electron $Mo(CO)_2(dtc)_2$ complexes has been discussed,[8] and their usefulness as precursors to Mo(II) dithiocarbamate derivatives such as Mo(CO)(alkyne)$(dtc)_2$, $Mo(CO)_2L(dtc)_2$, and $Mo(CO)(N_2R)(dtc)_2$ is well documented.[9]

The reaction of $M(CO)_2(dtc)_2$ with CS_2 and 2 equiv of PPh_3 does not, however, give $M(CS)_2(dtc)_2$ for either molybdenum or tungsten. The peculiar flexibility of CS_2 as a ligand building block is evident in the product obtained with $Mo(CO)_2(detc)_2$. $Mo_2(detc)_3(S_3C_2NEt_2)(S_3C_2)$ provides the first examples of (i) thiocarbonyl insertion into a coordinated dithiocarbamate and (ii) the coupling of CS and CS_2. Herein we report the structure of $Mo_2(detc)_3(S_3C_2NEt_2)(S_3C_2)$ (**1**), its reactivity with electrophiles, and spectral and electrochemical data for all products. From the surprising structural similarity between **1** and $Mo_2(dmtc)_3(SCNMe_2)(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)$ we infer that the $Mo_2(\mu\text{-}\pi\text{-}base)(\mu\text{-}\pi\text{-}acid)$ dimeric linkage is particularly favored. Bonding properties and spectral data for these dinuclear compounds will be compared.

Experimental Section

Materials and Methods. All manipulations were done under purified nitrogen on a vacuum line using standard Schlenk techniques. $Mo(CO)_2(detc)_2$ was prepared as reported.[10] Carbon disulfide, triphenylphosphine, trimethyloxonium tetrafluoroborate, and potassium triisopropoxyborohydride in THF were used as received. Methylene chloride and tetrahydrofuran were distilled from sodium–benzophenone ketyls. Infrared spectra were recorded on a Beckman IR 4250 instrument. ^1H and ^{13}C NMR data were obtained with a Bruker 250-MHz spectrometer; chemical shifts are reported downfield of Me_4Si in ppm. Cyclic voltammograms were obtained with a Bioanalytical Systems CV-27 cyclic voltammograph. Visible spectroscopy experiments were performed on a Hewlett-Packard 8450A spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Syntheses. $\mathbf{Mo_2(detc)_3(S_3C_2NEt_2)(S_3C_2)}$ **(detc =** $\mathbf{S_2CNEt_2}$**) (1).** $Mo(CO)_2(detc)_2$ (2.73 g, 6.09 mmol) was charged into a 300-mL flask in the drybox. After removal from the drybox triphenylphosphine (3.19 g, 12.2 mmol) was added under a nitrogen flush and the two solids were purged with four evacuation/nitrogen refill cycles. CH_2Cl_2 (50 mL) was then added, and both reagents dissolved. CS_2 (20 mL) was deaerated and added via syringe. The deep red-purple solution was refluxed for 1 h during which time a subtle color change to dark burgundy occurred. An equivalent volume of Et_2O promoted precipitation of the crude product, which was contaminated with $SPPh_3$. The phosphine sulfide was removed by washing with toluene (2 × 50 mL), leaving a dark brick red crystalline solid in 95% yield. The solid is air stable for indefinite periods of time. IR (cm^{-1}, KBr): ν_{CS} 1038, 995; ν_{CN} 1510 sh, 1490; ν_{Mo-S} 345; other absorptions 2960, 2920, 1427, 1352, 1270, 1207, 1142, 841. ^1H NMR (CD_2Cl_2): δ 3.3–4.2 (m, 16 H, $-CH_2-$); 1.0–1.5 (m, 24 H, $-CH_3$). ^{13}C NMR (CD_2Cl_2): δ 363.5 (s, $Mo_2(\mathit{C}SC(=S)S)$); 259.3 (s, $-S\mathit{C}(=S)S$); 209.0, 202.8, 201.5 (s, $S\mathit{C}S(detc)$); 171.6 (s, $Mo_2(S\mathit{C}detc)$); 45.3–44.7 (m, $-CH_2-$); 12.8–11.7 (m, $-CH_3$).

$\mathbf{[Mo_2(detc)_3(S_3C_2NEt_2)(S_2C_2(SMe))]^+[BF_4]^-}$ **(2).** **1** (1.00 g, 1.05 mmol) was dissolved in CH_2Cl_2 (50 mL) and chilled to −78 °C in an *i*-PrOH/dry ice bath. This solution was transferred through stainless steel tubing into a second flask containing $[Me_3O][BF_4]$ (0.13 g, 1.05 mmol), also chilled to −78 °C. Within minutes the deep burgundy of **1** changed to an orange-red. The solution was warmed to ambient tem-

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perature and stirred until all the solid oxonium salt had disappeared (1 h). The solvent volume was reduced in vacuo to 20 mL, and precipitation of a crude oily orange solid was induced by addition of Et_2O (20 mL). The product was extracted from the tar with THF (20 mL), reprecipitated with an equal volume of Et_2O, and triturated with more ether (2 × 50 mL) to yield a dark orange-brown solid in 80–85% yields. IR (cm^{-1}, KBr): ν_{BF} 1040 br; ν_{CN} 1525 sh, 1495; other absorptions 2960, 2920, 1352, 1270, 1203, 1142, 837. ^1H NMR (CD_2Cl_2): δ 3.22 (s, 3 H, –SMe); 3.3–4.2 (m, 16 H, $-CH_2-$); 1.0–1.5 (m, 24 H, $-CH_3$). ^{13}C NMR (CD_2Cl_2): δ 353.3 (s, $Mo_2(\mathit{C}SC(=S)S)$); 247.8 (s, $CS\mathit{C}(SMe)S$); 208.0, 201.5, 200.9, 199.5 (s, $S\mathit{C}S(detc)$); 176.2 (s, $Mo_2(S\mathit{C}detc)$; 45.9–45.1 (m, $-CH_2$); 23.3 (q, J_{CH} = 140 Hz, –SMe); 13–11 (m, $-CH_3$). Anal. Calcd for $C_{24}H_{43}B_1N_4F_4S_{12}Mo_2$: C, 27.43; H, 4.12; S, 36.60; Mo, 18.26. Found: C, 27.66; H, 4.26; S, 36.51; Mo, 17.97.

$Mo_2(detc)_3(S_3C_2NEt_2)(S_2C_2(H)(SMe))$ (3). **2** (0.80 g, 0.80 mmol) was dissolved in CH_2Cl_2 (30 mL) and chilled to –78 °C. $K[B(OPr)_3H]$ (1 mL, 1 M in THF) was dripped in via syringe. After 3–4 min the solution was a deep plum purple. Stirring was continued 5 min, and then the solution was allowed to warm to ambient temperature. Removal of solvent in vacuo left a dark solid, from which **3** was extracted into methylene chloride (30 mL) while leaving the potassium borohydride salts. Addition of Et_2O (30 mL) caused precipitation of purple crystals in yields of ca. 75%. IR (cm^{-1} KBr): ν_{CN} 1510, 1490; other absorptions 2960, 2918, 1428, 1352, 1270, 1209, 1141, 843. ^1H NMR (CD_2Cl_2): δ 7.87, 7.62, 7.50 (s, 1 H, HC(SMe)); 3.3–4.2 (m, 16 H, $-CH_2-$); 2.56, 2.52, 2.38 (s, 3 H, –SMe); 1.0–1.5 (m, 24 H, $-CH_3$). ^{13}C NMR: (CD_2Cl_2): δ 375.6, 375.2 (s, $Mo_2(\mathit{C}SC(=S)S)$); 209.3, 208.9, 203.6, 203.3, 201.7, 201.2 (s, $S\mathit{C}S(detc)$); 169.4, 167.7 (s, $S\mathit{C}detc$); 91.7, 89.2 (d, J_{CH} = 170 Hz, $\mathit{C}(H)SMe$); 47.7–42.2 (m, $-\mathit{C}H_2(detc)$); 29.9 (m, SMe); 15.6–10.5 (m, $-CH_3$). Anal. Calcd for $C_{24}H_{44}N_4S_{12}Mo_2$: C, 29.87; H, 4.59; S, 39.85; Mo, 19.88. Found: C, 30.10; H, 4.62; S, 40.06; Mo, 19.67.

Single-Crystal Structure Determination of $Mo_2(detc)_3(S_3C_2NEt_2)(S_3C_2)$ (1). Single crystals were grown from slow diffusion of methanol into a methylene chloride solution of **1**. The crystal selected, of approximate dimensions 0.25 × 0.40 × 0.60 mm, was mounted on a glass fiber and coated with epoxy. Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer.[11] Twenty-five reflections in the region $14.5° < \theta < 17.9°$ indicated a triclinic lattice having a = 15.749 (6) Å, b = 16.013 (7) Å, c = 9.749 (6) Å, α = 107.26 (4)°, β = 105.92 (4)°, and γ = 71.14 (3)° defining a cell volume of 2176 (3) $Å^3$. From the complexity of the ^1H NMR spectrum, we expected this molecule to be dinuclear. The calculated density of 1.45 g/cm^3 is appropriate for two dinuclear molecules per triclinic cell. A total of 6063 unique data in octants $+h,\pm k,\pm l$ were collected with $2° < 2\theta < 46°$. No reorientation of the crystal was required throughout data collection, and no decay in the standard reflection intensities was observed. Six low-angle reflections were chosen to measure absorptivity.

Our initial attempt to solve the Patterson map in space group $P\bar{1}$ was successful; the positions of the two molybdenum atoms in the dimer were identified and refined to a reasonable separation of 2.6 Å. All other non-hydrogen atoms were located in subsequent Fourier calculations. During refinement a twofold disorder in ethyl carbons (C12 and C13) of one dithiocarbamate was identified from a difference Fourier map. On the basis of the heights of the two peaks, each of the two positions for C12 and C13 was set at 0.5 occupancy and was refined as an isotropic sphere. When the refinement of the 43 non-hydrogen atoms had converged, the 40 hydrogen positions were calculated (C–H = 0.95 Å) and entered. Full-matrix least-squares refinement of the structural model converged with a largest parameter shift of 1.32 with R_1 = 4.7% and R_2 = 5.5%.[12a] The data were corrected for Lorentz polarization and absorption during the later stages of refinement. A final difference Fourier calculation showed a featureless map whose maximum peak height was 0.49 $e/Å^3$.

Results

Syntheses. The clean reaction of $Mo(CO)_2(detc)_2$ with excess carbon disulfide (30% solution in methylene chloride) and 2 equiv of triphenylphosphine occurs within 1 h at 40 °C to form **1** in high yields (95%). This diethyldithiocarbamate derivative (**1**) has appreciable solubility in methylene chloride, from which it is routinely obtained as deep burgundy red crystals. Compound **1** is indefinitely stable to the atmosphere.

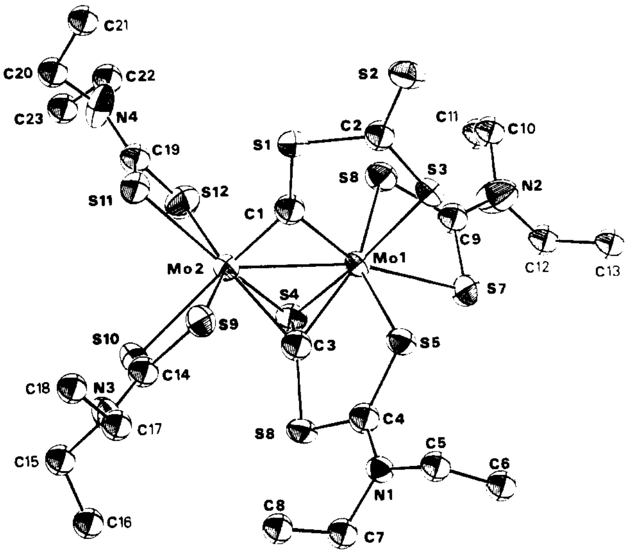

Figure 1. ORTEP drawing of $Mo_2(S_2CNEt_2)_3(S_3C_2NEt_2)(S_3C_2)$ showing the atomic labeling scheme. Thermal ellipsoids are drawn at the 40% probability level except for the carbon atoms, which have been arbitrarily drawn with β = 5 to clarify the molecular geometry.

Formation of **1** results from a net addition of two thiocarbonyl fragments and one molecule of carbon disulfide to two $Mo(CO)_2(detc)_2$ molecules with concomitant dimerization and loss of all carbonyl ligands (eq 1). As anticipated, the triphenylphosphine served to abstract sulfur atoms from CS_2 to generate $SPPh_3$. The resultant CS moieties have been incorporated into two new ligands. One CS has apparently inserted into a Mo–S bond of a dithiocarbamate chelate to form an $S_3C_2NR_2$ unit where the –CS moiety positions itself to perpendicularly bridge the Mo–Mo axis. The second CS has coupled with carbon disulfide to form an –SC(=S)SC– group which binds to one Mo through the sulfide terminus and simultaneously bridges both metals through the carbyne carbon on the other end. Three normal dithiocarbamate chelates complete the coordination spheres of the metals.

$$2Mo(CO)_2(detc)_2 + 2CS + CS_2 \rightarrow \underset{\mathbf{1}}{Mo_2(detc)_3(S_3C_2NEt_2)(S_3C_2)} + 4CO(g) \quad (1)$$

While formation of an η^2-CS_2 molybdenum carbonyl complex is a likely first step in the reaction, no evidence for such an intermediate was observed in infrared spectra of the reacting solution. Likewise, treatment of $Mo(CO)_2(detc)_2$ with a 30% CS_2/CH_2Cl_2 solution in the absence of phosphine did not produce any detectable carbonyl–(η^2-CS_2) complexes, but slow (36 h) loss of the CO ligands produced a brown solid in 70% yields. No distinguishing ν_{CS} stretches were observed that could be associated with $M(\eta^2\text{-}CS_2)$, $M_2(\eta^2\text{-}CS_2)$, $M(\eta^2\text{-}CS_3)$, or molybdenum sulfide vibrations. Reaction to form an analogue of **1** does not proceed for tungsten. Rather, reaction of $W(CO)_2(PPh_3)(dtc)_2$ with CS_2 in CH_2Cl_2 in the presence of a second equivalent of phosphine yields a black solid which does not display the characteristic ν_{CS} of **1**.

Description of the Structure of $Mo_2(detc)_3(S_3C_2NEt_2)(S_3C_2)$ (1). An ORTEP drawing illustrating the molecular structure of **1** is given in Figure 1. Tables II–IV list atomic positions, bond distances, and intramolecular angles, respectively. Of the four dithiocarbamates available from the reagent monomers, three are retained intact in the dinuclear product. These three chelates are defined by coordinating atoms S7, S8 at Mo1 and by S9, S10 and S11, S12 at Mo2. The fourth dithiocarbamate is bound to Mo1 through only one slfur (S5); the second sulfur of this dithio-

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(11) Programs were utilized during solution and refinement as provided in the Enraf-Nonius Structure Determination Package. Scattering factors are taken from: Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Ibers, J. A.; Hamilton, W., Eds.; Kynoch Press: Birminghan, England, 1974; Vol. IV.

(12) (a) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [2F_o/\sigma(F_o^2)]^2$ and $\sigma(F_o^2) = [\sigma^2(I) + p^2I^2]$ with p assigned a value of 0.01. Expressions for the residuals are $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. (b) $I = S(C + RB)$ and $\sigma(I) = (2S^2(C + R^2B) + (pI)^2)^{1/2}$, where S = scan rate, C = total integrated peak count, R = ratio of scan time to background count time, B = total background count time, and p = 0.01, a correction factor.

Table I. Collection and Refinement Parameters for $Mo_2(S_2CNEt_2)_3(S_3C_2NEt_2)(S_3C_2)$

mol formula	$C_{23}H_{40}MoN_4S_{12}$
fw	949.25
space group	$P\bar{1}$
a, Å	15.749 (6)
b, Å	16.013 (7)
c, Å	9.740 (6)
α, deg	107.26 (3)
β, deg	105.92 (4)
γ, deg	71.14 (2)
V, Å^3	2176 (3)
Z	2
D(calcd), g/cm^3	1.449
μ, cm^{-1}	11.354
radiation	Mo Kα (0.71073 Å)
monochromator	graphite cryst
data collected	$+h,\pm k,\pm l$ in $1.0° < \theta < 23.0°$
scan width, deg	1.0 + (0.35 tan θ)
bkgd	25% full peak width on each side
no. of unique data	6063
no. of data $I > 3\sigma(I)$	2955
no. of variables	368
largest parameter shift	1.32
R_1, %	4.7
R_2, %	5.5
highest peak in Fourier map, e/Å^3	0.49
error in observn of unit wt	2.06

Table II. Final Fractional Positions for $Mo_2(S_2CNEt_2)_3(S_3C_2NEt_2)(SC(S)SC)$ (**1**)

atom	x	y	z
Mo1	0.35395 (7)	0.25182 (7)	0.3051 (1)
Mo2	0.19465 (7)	0.21601 (7)	0.1996 (1)
S1	0.2353 (2)	0.3049 (2)	0.5730 (4)
S2	0.3527 (3)	0.3707 (2)	0.8465 (4)
So	0.4217 (2)	0.3024 (2)	0.5679 (4)
S4	0.2800 (2)	0.2352 (2)	0.0458 (4)
S5	0.4699 (2)	0.1172 (2)	0.3653 (4)
S6	0.3796 (2)	0.0375 (2)	0.0660 (4)
S7	0.4865 (2)	0.2911 (2)	0.2559 (4)
S8	0.3144 (2)	0.4169 (2)	0.3042 (4)
S9	0.2188 (2)	0.0745 (2)	0.2779 (4)
S10	0.1278 (2)	0.0977 (2)	−0.0104 (4)
S11	0.0490 (2)	0.2574 (2)	0.2986 (4)
S12	0.0820 (2)	0.3434 (2)	0.1088 (4)
N1	0.5198 (5)	−0.0535 (5)	0.2252 (9)
N2	0.4522 (7)	0.4655 (6)	0.2699 (12)
N3	0.1546 (7)	−0.0531 (6)	0.0722 (12)
N4	−0.0629 (7)	0.4094 (8)	0.2307 (13)
C1	0.2521 (7)	0.2688 (6)	0.392 (1)
C2	0.3394 (7)	0.3277 (6)	0.667 (1)
C3	0.3203 (7)	0.1511 (7)	0.135 (1)
C4	0.4630 (7)	0.0276 (6)	0.220 (1)
C5	0.5982 (8)	−0.0695 (8)	0.347 (1)
C6	0.6817 (9)	−0.0544 (9)	0.323 (1)
C7	0.5071 (7)	−0.1341 (7)	0.107 (1)
C8	0.4362 (8)	−0.1725 (8)	0.129 (1)
C9	0.4203 (8)	0.3993 (7)	0.276 (1)
C10	0.3998 (10)	0.5608 (8)	0.299 (1)
C11	0.3695 (14)	0.6008 (11)	0.183 (2)
C14	0.1658 (8)	0.0291 (7)	0.107 (1)
C15	0.1114 (9)	−0.0929 (9)	−0.071 (2)
C16	0.1740 (12)	−0.1412 (12)	−0.171 (2)
C17	0.1876 (9)	−0.1089 (8)	0.176 (2)
C18	0.1237 (13)	−0.1086 (12)	0.260 (2)
C19	0.0135 (7)	0.3450 (8)	0.215 (2)
C20	−0.1277 (11)	0.4046 (12)	0.313 (2)
C21	−0.1099 (12)	0.4492 (11)	0.457 (2)
C22	−0.0853 (12)	0.4881 (17)	0.168 (2)
C23	−0.1335 (14)	0.4681 (13)	0.038 (3)
C12A	0.524 (2)	0.450 (1)	0.195 (2)
C13A	0.619 (2)	0.430 (2)	0.313 (3)
C12B	0.562 (1)	0.454 (1)	0.300 (2)
C13B	0.577 (2)	0.422 (2)	0.163 (3)

Table III. Intramolecular Bond Distances (Å) in $Mo_2(S_2CNEt_2)_3(S_3C_2NEt_2)(CSC(S)S)$ (**1**)

Mo1–Mo2	2.616 (1)	Mo2–S4	2.406 (3)
Mo1–S3	2.486 (3)	Mo2–S9	2.484 (3)
Mo1–S4	2.449 (3)	Mo2–S10	2.587 (3)
Mo1–S5	2.438 (3)	Mo2–S11	2.547 (3)
Mo1–S7	2.562 (3)	Mo2–S12	2.441 (3)
Mo1–S8	2.515 (2)	Mo2–C1	1.917 (9)
Mo1–C1	1.922 (9)	Mo2–C3	2.086 (9)
Mo1–C3	2.026 (8)		
S1–C1	1.749 (9)	S4–C3	1.680 (8)
S1–C2	1.740 (9)	S5–C4	1.697 (9)
S2–C2	1.658 (9)	S6–C3	1.776 (9)
S3–C2	1.701 (9)	S6–C4	1.711 (9)
C5–C6	1.500 (12)	C13A–C13B	1.42 (3)
C7–C8	1.524 (11)	C15–C16	1.450 (16)
C10–C11	1.356 (15)	C17–C18	1.45 (2)
C12A–C13A	1.63 (3)	C20–C21	1.37 (2)
C12B–C13B	1.34 (3)	C22–C23	1.29 (4)
C12A–C12B	1.03 (3)		
S7–C9	1.694 (10)	S10–C14	1.677 (11)
S8–C9	1.685 (10)	S11–C19	1.693 (12)
S9–C14	1.706 (10)	S12–C19	1.676 (12)
N1–C4	1.325 (9)	N3–C14	1.317 (11)
N1–C5	1.472 (11)	N3–C15	1.429 (15)
N1–C7	1.478 (10)	N3–C17	1.430 (16)
N2–C9	1.334 (10)	N4–C19	1.320 (12)
N2–C10	1.465 (14)	N4–C20	1.49 (2)
N2–C12A	1.43 (3)	N4–C22	1.46 (3)
N2–C12B	1.63 (3)		

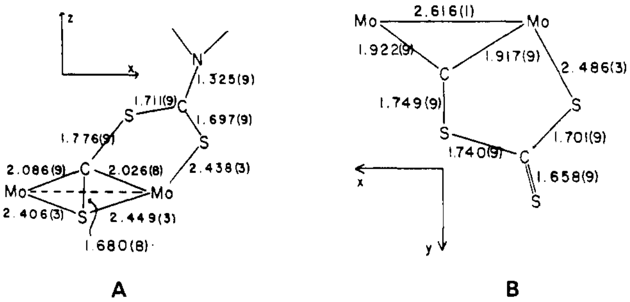

Figure 2. Schematic diagram of the S_3C_2 and $S_3C_2NEt_2$ bridging ligands in $Mo_2(S_2CNEt_2)_3(S_3C_2NEt_2)(S_3C_2)$.

carbamate is linked to C3 of the inserted thiocarbonyl group by a single bond (1.776 (9) Å).[13] A schematic view of this group is provided in Figure 2A. Note that S6 is 3.5 Å from Mo1. The thiocarbonyl group –C3S4 bridges Mo1 and Mo2 and is twisted only 3° from the plane perpendicular to the metal–metal axis. The C3–S4 distance of 1.680 (8) Å indicates a high degree of unsaturation[13] consistent with a μ,η^2-CS bonding formalism. While no examples of this unusual bonding mode for CS exist,[14] one may relate it via the –C≡S: resonance form to perpendicularly bridging alkynes in metal dimers. From this perspective, the Mo1–C3 and Mo2–C3 distances of 2.03 and 2.09 Å are unusually short and indicate strong Mo–C bonds (cf. average Mo–C distances to bridging alkyne ligands in $Mo_2(\mu\text{-}S)(\mu\text{-}EtC_2Et)(dmtc)_3(SCNMe_2)$ (2.17 Å), $Mo_2(\mu\text{-}HC_2H)(\mu\text{-}O\text{-}i\text{-}Pr)_2(O\text{-}i\text{-}Pr)_4(py)_2$[15a] (2.08 Å), $Mo_2(\mu\text{-}EtC_2Et)(\pi\text{-}C_5H_5)_2(CO)_4$ (2.20 Å[15b])). The S6–C3–S4 angle of 126° can also be understood in terms of rehybridization of C3 as observed in $M_2(\mu\text{-}RC{\equiv}CR)$

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(13) Compare with S—C = 1.81 Å and S=C = 1.71 Å: Ondik, H.; Smith, D. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, p 276.

(14) A related example of similar bonding through the ligand π-system for CO is found in $Cp_3Nb_3(CO)_9$: Hermann, W. A.; Biersack, H.; Ziegler, M. L.; Wiedenhammer, K.; Siegel, R.; Rehder, D. *J. Am. Chem. Soc.* **1981**, *103*, 1692.

(15) (a) Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1981**, *103*, 4245. (b) Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

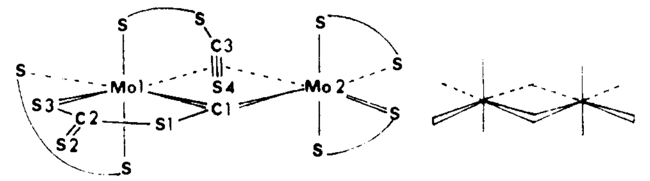
Table IV. Intramolecular Angles (deg) in $Mo_2(S_2CNEt_2)_3(S_3C_2NEt_2)(CSC(S)S)$ (**1**)

Mo2–Mo1–S3	126.67 (7)	S4–Mo1–S7	90.72 (9)
Mo2–Mo1–S4	56.60 (7)	S4–Mo1–S8	83.96 (9)
Mo2–Mo1–S5	109.97 (7)	S4–Mo1–C1	100.8 (3)
Mo2–Mo1–S7	147.22 (8)	S4–Mo1–C3	42.8 (2)
Mo2–Mo1–S8	101.83 (7)	S5–Mo1–S7	84.66 (9)
Mo2–Mo1–C1	47.0 (3)	S5–Mo1–S8	148.17 (9)
Mo2–Mo1–C3	51.5 (2)	S5–Mo1–C1	107.6 (2)
S3–Mo1–S4	168.11 (9)	S5–Mo1–C3	77.2 (2)
S3–Mo1–S5	75.86 (9)	S7–Mo1–S8	68.84 (9)
S3–Mo1–S7	84.71 (9)	S7–Mo1–C1	157.3 (2)
S3–Mo1–S8	84.15 (9)	S7–Mo1–C3	107.6 (2)
S3–Mo1–C1	80.1 (3)	S8–Mo1–C1	92.8 (2)
S3–Mo1–C3	149.1 (2)	S8–Mo1–C3	126.6 (2)
S4–Mo1–S5	114.70 (9)	C1–Mo1–C3	93.9 (3)
Mo1–Mo2–S4	58.18 (7)	S4–Mo2–S11	150.97 (10)
Mo1–Mo2–S9	102.43 (7)	S4–Mo2–S12	81.59 (10)
Mo1–Mo2–S10	136.79 (8)	S4–Mo2–C1	102.4 (3)
Mo1–Mo2–S11	134.33 (8)	S4–Mo2–C3	43.2 (2)
Mo1–Mo2–S12	110.42 (8)	S9–Mo2–S10	69.48 (9)
Mo1–Mo2–C1	47.1 (3)	S9–Mo2–S11	80.86 (10)
Mo1–Mo2–C3	49.5 (2)	S9–Mo2–S12	145.75 (11)
S4–Mo2–S9	125.57 (9)	S9–Mo2–C1	90.2 (2)
S4–Mo2–S10	91.79 (9)	S9–Mo2–C3	84.2 (2)
S10–Mo2–S11	87.35 (9)	S11–Mo2–C1	87.8 (3)
S10–Mo2–S12	92.77 (10)	S11–Mo2–C3	165.1 (2)
S10–Mo2–C1	158.6 (12)	S12–Mo2–C1	105.0 (2)
S10–Mo2–C3	87.3 (2)	S12–Mo2–C3	124.7 (2)
S11–Mo2–S12	69.48 (11)	C1–Mo2–C3	92.1 (3)
C1–S1–C2	101.2 (4)	Mo1–S7–C9	86.5 (4)
Mo1–S3–C2	108.0 (3)	Mo1–S8–C9	88.2 (3)
Mo1–S4–Mo2	65.21 (7)	Mo2–S9–C14	89.6 (4)
Mo1–S4–C3	55.0 (3)	Mo2–S10–C14	86.8 (4)
Mo2–S4–C3	58.2 (3)	Mo2–S11–C19	85.4 (4)
Mo1–S5–C4	109.2 (3)	Mo2–S12–C19	89.3 (4)
C3–S6–C4	95.9 (4)		
C4–N1–C5	122.8 (8)	C10–N2–C12B	112.5 (11)
C4–N1–C7	121.1 (8)	C14–N3–C15	122.7 (12)
C7–N1–C7	116.1 (8)	C14–N3–C17	121.2 (11)
C9–N2–C10	122.1 (10)	C15–N3–C17	116.0 (11)
C9–N2–C12A	123.4 (13)	C19–N4–C20	121.4 (14)
C9–N2–C12B	120.5 (12)	C19–N4–C22	120.2 (15)
C10–N2–C12A	112.1 (12)	C20–N4–C22	118.4 (15)
Mo1–C1–Mo2	85.9 (4)	Mo2–C1–S1	140.4 (5)
Mo1–C1–S1	133.2 (5)	Mo2–C1–C2	174.8 (4)
Mo1–C1–C2	94.0 (4)	S1–C1–C2	39.3 (3)
S1–C2–S2	118.4 (6)	S2–C2–S3	124.4 (6)
S1–C2–S3	117.2 (5)		
Mo1–C3–Mo2	79.0 (3)	Mo2–C3–S4	78.6 (3)
Mo1–C3–S4	82.2 (4)	Mo2–C3–S6	136.0 (4)
Mo1–C3–S6	133.8 (5)		
S5–C4–S6	121.5 (5)	N1–C5–C6	112.0 (8)
S5–C4–N1	120.8 (7)	N1–C7–C8	111.1 (8)
S6–C4–N1	117.7 (7)		
S7–C9–S8	116.3 (6)	N1–C10–C11	116.4 (14)
S7–C9–N2	120.6 (9)	N1–C12A–C13A	106 (2)
S8–C9–N2	123.1 (9)	N1–C12B–C13B	100 (2)
S9–C14–S10	115.0 (6)	N3–C15–C16	113.7 (13)
S9–C14–N3	121.8 (10)	N3–C17–C8	116.5 (12)
S10–C14–N3	123.2 (10)		
S11–C19–S12	115.2 (6)	N4–C20–C21	111 (2)
S11–C19–N4	122.6 (11)	N4–C22–C23	106 (3)
S12–C19–N4	122.3 (10)		

structures where the C–C–R angles are near 135°.[15] All four S_2CNEt_2 groups have normal bond lengths and angles with the exception of the S5–C4–S6 angle of 121° found in the unique dithiocarbamate which has incorporated CS. This is roughly 6° larger than analogous angles in the three normal S_2CNEt_2 ligands. Similar distances for S5–C4 (1.697 (9) Å) and S6–C4 (1.711 (9) Å) point to retention of a delocalized system typical of dithiocarbamate chelates even in this transformed ligand. Note that Mo/S5/C4/S6 are coplanar to within ±0.02 Å.

The –SC(=S)SC– ring created by the coupled thiocarbonyl and carbon disulfide provides the second bridge linking the two metals and fills the remaining coordination site on Mo1 (Figure 2B). Bridging carbon atom C1 has short bonds to both Mo1 and Mo2 (1.922 (9), 1.917 (9) Å), which correlate with its carbyne character as inferred from ^{13}C NMR data. While the 1.658 (9) Å separation of C2 and S2 justifies its assignment as a double bond, the other carbon–sulfur distances of this group are intermediate between those typical of single and double C–S bonds. The planarity of atoms S3/C2/S2/S1/C1 (±0.02 Å) supports the hypothesis that π-electron density is conjugated around this ring. The slightly shortened Mo1–S3 distance of 2.486 (3) Å also hints at multiple bonding relative to the four Mo–S distances exceeded 2.50 Å, which average 2.55 Å (see the bonding discussion for clarification of these interactions).

If the unsaturated C3–S4 moiety is considered to occupy one coordination site and the Mo–Mo bond is neglected momentarily, both Mo1 and Mo2 are six-coordinate and roughly octahedral. The idealized geometry of this dinuclear compound may then be described as a colateral bioctahedron:



A metal–metal separation of 2.616 (1) Å is compatible with a Mo1–Mo2 bond. This point will be addressed in the Discussion as will short axial vs. equatorial Mo–S bond lengths.

Spectral Properties of 1. IR Spectrum. Two strong absorptions at 1038 and 995 cm^{-1} were diagnostic of a ν_{CS} vibration but too low in energy to be due to the expected ligands M–CS, $M_2(\mu\text{-}CS)$, or $M(\eta^2\text{-}CS_2)$.[1,2,16] Possible structures having comparable thiocarbonyl stretching frequencies are $M_2(\mu\text{-}CS_2)$, $M(\eta^2\text{-}CS_3)$, and $M(\eta^2\text{-}C_2S_4)$.[1,2,17,18] Subsequent to the structure determination of **1**, we assign the observed ν_{CS} bands to the exocyclic and endocyclic modes of the –CSC(=S)S– ligand by analogy to the reported absorptions for bidentate trithiocarbonate and C_2S_4 groups. The only other infrared absorptions that could be discerned in spectra of **1** were attributable to S_2CNEt_2 ligands.

^1H and ^{13}C NMR Spectra. The large number of signals under the broad envelope of $-CH_2$ and $-CH_3$ resonances in the proton NMR spectrum of **1** was consistent with a dinuclear molecule having diastereomeric ethyl protons. More informative was the ^{13}C NMR spectrum of **1**, where singlets at 363.5, 259.3 and 171.6 ppm and multiple signals between 200 and 210 ppm suggested a dinuclear complex with four dithiocarbamate ligands and three new carbon centers. Our assignment for this spectrum follows. The low-field singlet (363.5 ppm) is typical of bridging carbynes (cf. $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$, $\delta = 352.6$[19]) and is attributed to the bridging carbon C1. Bridging mercaptocarbyne ligands with $\delta = 400$ have been reported in iron dimers,[20] while terminal mercaptocarbyne carbons have been reported in the 250–260 ppm range.[21] The short Mo1–C1, Mo2–C1 distances verify multiple bonding character. Moving upfield, the signal at 259.3 ppm can be assigned to C2, a trigonal carbon bound to three sulfurs. This chemical shift is in excellent agreement with the resonance reported for a carbon in a similar environment.[18] The starred carbon in III (shown in the Discussion) appears at 251 ppm. Three signals

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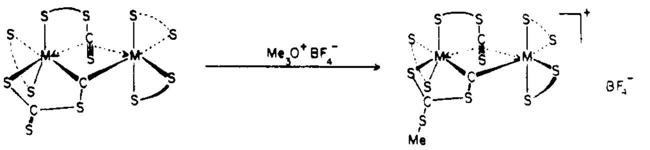
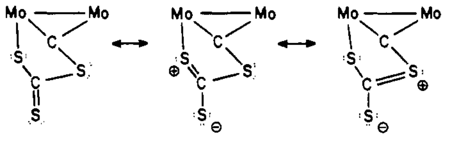
at 209.0, 202.8, and 201.5 ppm in the ratio 1:1:2 are assigned to the central carbons of the four dithiocarbamates. One might guess that the lowest field singlet belongs to C4 of the unique CS-inserted dithiocarbamate. Finally, the isolated singlet at 171.6 ppm is assigned to C3 of the detcCS bridge. The analogy of this π-bound CS group to an alkyne gains credence when chemical shifts for the bridgehead carbons are compared since in $Mo_2(\mu\text{-}RCCR')(\mu\text{-}S)(dmtc)_3(SCNMe_2)$ the alkyne carbons resonate in the 140–150 ppm[22] range. Signals near 45 and 12 ppm are in the normal region for dithiocarbamate ethyl carbons.

Reactions of 1. Methylation. The presence of a C=S moiety in **1** prompted us to probe its reactivity toward electrophiles. Addition of $[Me_3O][BF_4]$ to **1** at −78 °C results in methylation at the thioketone sulfur, S2, producing cationic **2**, a dark brick orange powder, in 85% yield (eq 2). The infrared spectrum of **2** shows a decrease in the relative intensity of the peak at 995 cm^{-1} (dithiocarbamate also has an absorption here[23]), while an intense, broad absorption due to the tetrafluoroborate counterion dominates the region near 1050 cm^{-1}. The ^1H NMR spectrum of **2** exhibits one singlet at 3.22 ppm in addition to complex patterns for the dithiocarbamate methylene and methyl protons that are nearly identical with those observed for **1**; integration verifies that one methyl group has been added per dinuclear unit. Only one isomer of **2** is observed in the ^{13}C spectrum, where the carbyne carbon resonates at 353.3 ppm (a shift of −10.2 ppm relative to **1**), the trigonal carbon at 247.8 ppm (−11.5 ppm), and the thiocarbonyl carbon, C3, has moved downfield to 176.1 ppm (+4.5 ppm). The methyl thiolate carbon was identified as a quartet in the proton-coupled ^{13}C spectrum at 23.3 ppm (J_{CH} = 140 Hz). A separate signal is evident for each of the four original dithiocarbamate carbons in the 200–210 ppm region. We were surprised that methylation at S2 did not substantially change the electronic environment at C2, as implied by the nominal 12 ppm shift upfield. The modest electronic change at C2 may be rationalized by consideration of other resonance structures for the –SC(=S)SC– group:

$$\underset{\mathbf{1}}{Mo_2(detc)_3(S_3C_2NEt_2)(S_3C_2)} + [Me_3O][BF_4] \rightarrow \underset{\mathbf{2}}{[Mo_2(detc)_3(S_3C_2NEt_2)(CSC(SMe)S)][BF_4]} + Me_2O \quad (2)$$

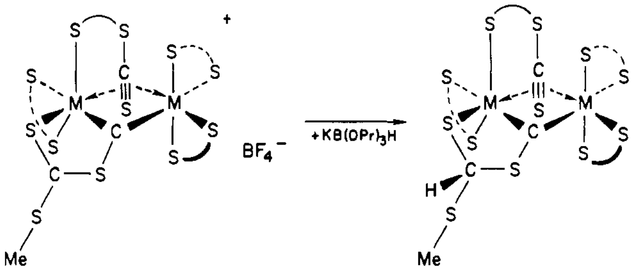




Methylation of a charge-separated structure to give **2** would be expected to cause little perturbation of the trigonal carbon environment. Dixneuf and co-workers have noted a similarly unresponsive carbon resonance when $L_2(CO)_2Fe(\mu\text{-}CS_2)$ is alkylated to form the thioacyl cation, $[L_2(CO)_2Fe(S_2CR)]^+$, where the chemical shifts for the CS_2-derived carbon are 288 and 293 ppm, respectively.[4b]

Hydride Addition to $[Mo_2(detc)_3(S_3C_2NEt_2)(S_2C_2(SMe))]^+$. The neutral complex **3** is generated by hydride addition to **2** at −78 °C and marks the complete functionalization of CS_2 to a trithio-substituted saturated carbon (eq 3). **3** is easily crystallized from methylene chloride and diethyl ether to give dark plum crystals. Both **2** and **3** are stable in air. The infrared spectrum of **3** shows only normal dithiocarbamate absorptions. The ^1H NMR spectrum of **3** revealed three isomers. While the $-CH_2$ and $-CH_3$ regions were complex and relatively uninformative, three distinct singlets were observed in the region 7.5–7.9 ppm (ratio 10:5:1) whose integrated intensities were approximately one-third of a corresponding set of singlets between 2.4 and 2.6 ppm. We assign the low-field signals to the unique hydrogen which we believe has added to C2, while the higher field set centered at 2.5 ppm are attributed to the methyl thiolate group on C2. The unusually large deshielding of the unique proton derived from the hydride reagent is comparable to the chemical shift observed in coordinated $\eta^2\text{-}S_2C(PPhMe_2)H$ (6.25 ppm);[24] substitution of –SMe for $PPhMe_2$ would predictably lower the resonance. The $^{13}C\{^1H\}$ NMR spectrum of **3** also suggests three isomers are present although the smallest set of peaks are difficult to distinguish from base line noise. For carbons C1 and C3, three singlets are observed near 375 and near 179 ppm, respectively, in the 10:5:1 ratio seen in the ^1H spectrum. Carbon C2, now tetrahedral, has moved upfield to 90 ppm where three doublets manifest three isomers, each with J_{CH} = 170 Hz. The methyl thiolate carbon is expected to appear as a quartet, but overlapping signals centered at 29 ppm result in a complex spectrum in this region.

$$\underset{\mathbf{2}}{Mo_2(detc)_3(S_3C_2NEt_2)(S_2C_2(SMe))^+} + H^- \rightarrow \underset{\mathbf{3}}{Mo_2(detc)_3(S_3C_2NEt_2)(CSC(H)(SMe)S)} \quad (3)$$

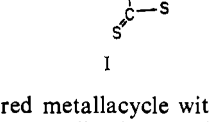


2 **3**

Possible diastereomers of **1**–**3** are shown in Figure 3. The sole difference between sets A and B is the relative orientation of the two dithiocarbamate chelates on Mo2. Of the four possible isomers (**3A**, **3A′**, **3B**, and **3B′**) we observe only three. Two of these three signals are present in a 2:1 ratio and constitute greater than 80% of the total material, leaving less than 20% for the third and fourth isomers. Since only a single unsplit methyl signal is seen in the ^1H NMR spectrum of **2** (a small shoulder in the ^1H spectrum of **2** is the only possible indication of a second isomer), we believe the major isomers of **3** originate from a common isomer of **2**, and are thus either **3A** and **3A′** or **3B** and **3B′**.

Discussion

The new ligands $-S_3C_2-$ and $-S_3C_2NR_2$ are assembled in nearly quantitative yield according to reaction 1. Reports of related transformations exist in the literature. The geometry and bonding within the $-S_3C_2-$ group is reminiscent of the C_2S_4 group obtained by dimerization of CS_2. A monomeric rhodium complex (I) with



I

a planar five-membered metallacycle with two exocyclic thiocarbonyls has been structurally characterized by Werner[25] that displays vibrations attributed to ν_{CS} at 1060, 1034, 1000, and 911

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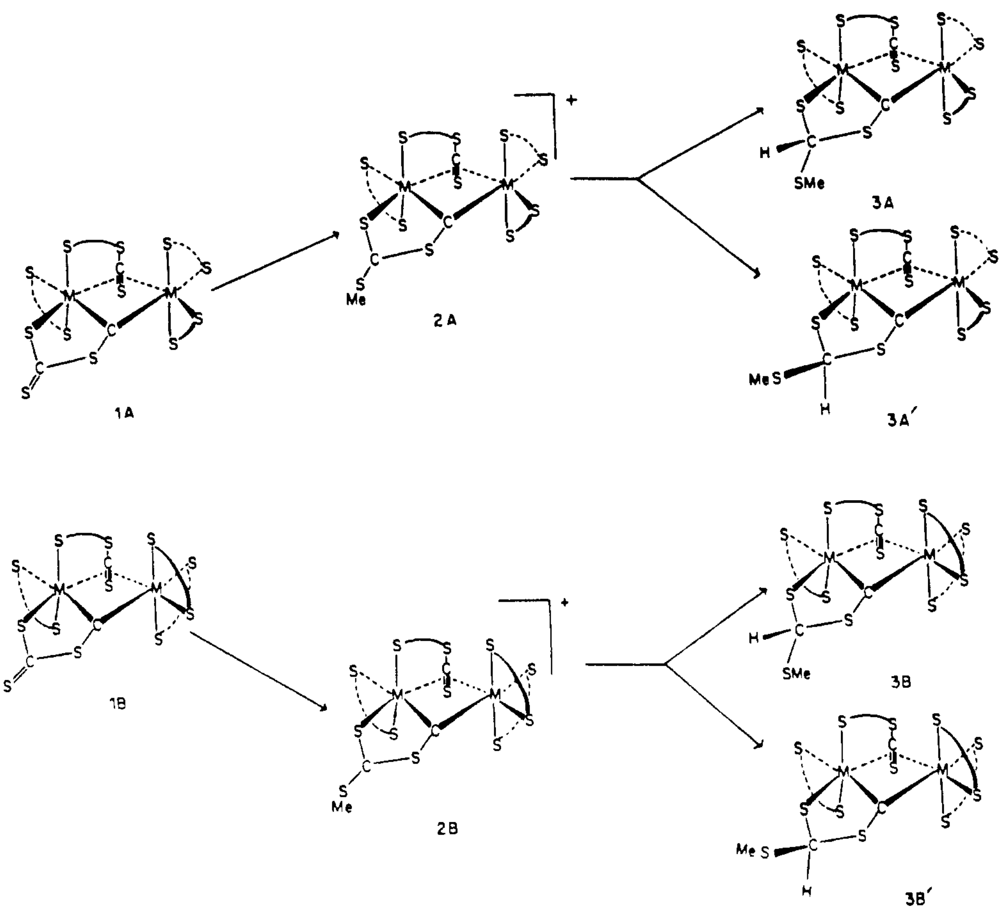
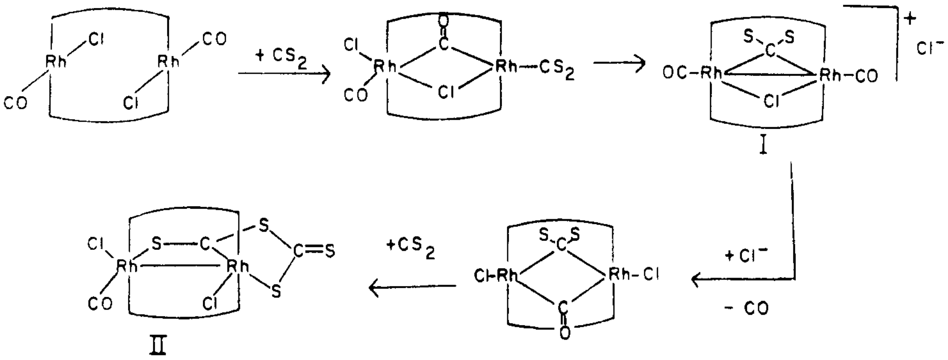
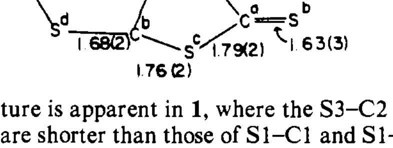


Figure 3. Possible isomers of **1**–**3** (only one enantiomer of each pair is illustrated).

Scheme I

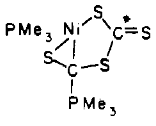


cm^{-1}. Another model is a rhodium dimer containing C_2S_4, II[26] (see Scheme I). Although the C_2S_4 ring is planar and suggests extensive conjugation, distances S^a–C^a and C^a–S^b are shorter than C^a–S^c or C^b–S^c, indicating partial retention of S=C=S bonding character in that fragment:

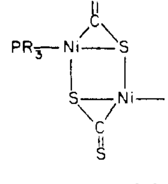


A similar feature is apparent in **1**, where the S3–C2 and C2–S2 bond lengths are shorter than those of S1–C1 and S1–C2. Three ν_{CS} vibrations observed for II at 1050, 995, and 980 cm^{-1} are comparable to values of 1038 and 995 cm^{-1} assigned to ν_{CS} in **1**. Conversion of II to the connectivity of S_3C_2 observed in **1** can be visualized by phosphine abstraction of S^d to leave C^b to bridge both metals. Reactions of CS_2 and metal carbonyl clusters with loss of sulfur have been reported to form M–CSSC–M bridges and $M_2(\mu$-CS) ligands.[27]

Electronic effects of different phosphines can also influence reaction pathways in the presence of carbon disulfide. Ibers and co-workers have recently determined the product resulting from addition of CS_2 and 2 equiv of PR_3 (R = Me, Et) to $Ni(COD)_2$ to be III, the first example of a CS_2 condensation product that



III



IV, R = Ph, *p*-tolyl, C_6H_{11}

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has retained a phosphine bound to that group.[18] Use of triphenyl-, tritolyl-, or tricyclohexylphosphine in the reaction gives only dimeric IV. Note that in this nickel system the small phosphine binds to carbon and forms III rather than abstracting a sulfur to form an $-S_3C_2-$ fragment as found in **1**, which would in this case generate an unfavorable nickel–terminal carbyne moiety.

Though CS_2 or CS insertion into a M–S bond of a dithiocarbamate complex has not been reported, both CS_2 insertions into M–X bonds and dithiocarbamate M–S bond scission by electrophiles are known. Representative examples are

$$(PMe_3)_2Pd(Me)(I) + CS_2 \rightarrow (PMe_3)_2IPd(\eta^2\text{-}S_2CH)$$ [6]

$$(PMe_3)_2Pd(I)(acyl) + CS_2 \rightarrow (PMe_3)(acyl)Pd(\eta^2\text{-}S_2CPMe_3)$$ [6]

$$(PMe_3)_3PdH^+ + CS_2 \rightarrow (PMe_3)_2Pd(\eta^2\text{-}S_2C(H)PMe_3)^+$$ [6]

$$(PMe_2Ph)_5RuH^+ + CS_2 \rightarrow (PMe_2Ph)_4Ru(\eta^2\text{-}S_2CH)$$ [6]

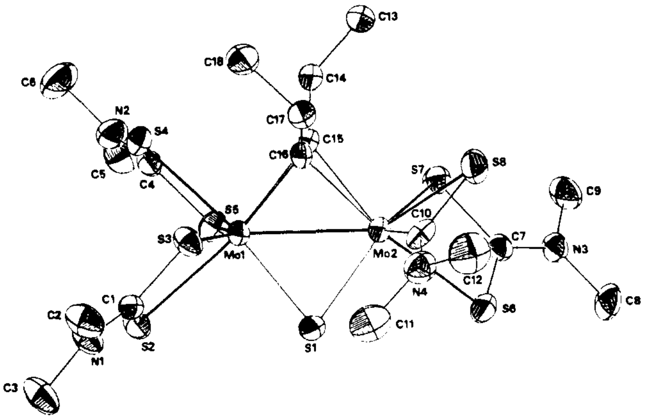
$$\rightarrow (PMe_2Ph)_3Ru(\eta^2\text{-}S_2C(H)PMe_2Ph)$$ [24]

$$(CO)_3HRe(dppe) + CS_2 \rightarrow (CO)_3Re(dppe)(S_2CH)$$ [28]

$$Mo(S_4)_2S^{2-} + CS_2 \rightarrow SMo(\text{-}SSC(S)S\text{-})_2{}^{2-}$$ [29]

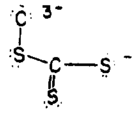
$$(dppe)CpFe\text{-}CCMe + CS_2 \rightarrow (dppe)CpFe(\text{-}C{=}C(Me)C(S)S\text{-})$$ [30]

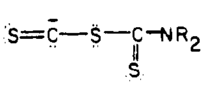
The high-yield preparations of the bizarre ligands present in complexes **1**–**3** are conceptually simplified by recognizing their structural kinship to a previously reported molybdenum dimer. $Mo_2(S_2CNR_2)_3(SCNR_2)(\mu\text{-}S)(\mu\text{-alkyne})$ is formed in the thermal reaction of $Mo(alkyne)_2(S_2CNR_2)_2$ and 1 equiv of phosphine; the structure of $Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(S_2CNMe_2)_3(SCNMe_2)$ (**4**) has been determined.[22] The net reaction forming **4** is an oxidative addition of a dithiocarbamate C–S bond to Mo(II), yielding a sulfide bridge and a bidentate thiocarboxamido ligand ($SCNMe_2$) on a Mo(III) dimer. Both **1** and **4** contain two six-coordinate metals (neglecting metal–metal bonding) with dinuclear geometries resembling conlateral bioctahedra. Metal atom separations in each dimer are suggestive of a Mo–Mo single bond, 2.647 Å in **4** and 2.616 Å in **1**. All four terminal equatorial sites in **1** are occupied by sulfur atoms. In both **1** and **4** one of the bridging ligands is a π-base with an electron pair in a p orbital perpendicular to the Mo–X–Mo plane (X = S in **4** or the carbyne carbon C1 in **1**). The other bridging ligand (alkyne in **4** or $Et_2NCSSC{\equiv}S$: in **1**) functions as a π-acid to both metal centers.



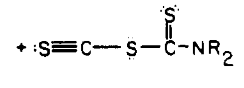
4

With use of conventional electron-counting methods (thiocarboxamido is monoanionic, alkyne ligands are considered neutral) the two metals of **4** are unequivocally Mo(III). Assigning oxidation states to the molybdenum atoms **1** is not as straightforward. We can formally consider the $-S_3C_2-$ unit a tetraanion where the terminal sulfur S3 has a 1− charge and carbon C1 has a 3− charge in keeping with its carbyne character (see below). It is less clear how to assign an overall charge to the $-S_3C_2NR_2$ ligand. Two choices are as follows: (i) consider it anionic, the result of deprotonation of a thioformaldehyde; (ii) assign it as a cationic ligand where the positive charge resides on the thiocarbonyl sulfur:




$S{=}C{-}S{-}C({=}S){-}NR_2$

i


$^{+}S{\equiv}C{-}S{-}C({=}S){-}NR_2$

ii

We favor formalism ii because it simplifies the bonding description. With a cationic charge allocated to the latter ligand, the formal oxidation state of each molybdenum is 3+, and the relationship to compound **4** is apparent (use of anionic structure i is not incorrect but would lead to a Mo(IV) formalism).

The qualitative molecular orbital scheme constructed for $Mo_2(S_2CNR_2)_3(SCNR_2)(\mu\text{-}S)(\mu\text{-alkyne})$ clarified the role of metal–ligand π-bonding, the orbital origin of the metal–metal single bond, and the diamagnetism of that Mo(III) dimer. Figure 4 illustrates the important molecular orbital features of **4**. Note that the relative order of the orbitals has not been determined by calculation.

Adopting an octahedral coordination geometry for each metal generates a 2 above 3 d-orbital arrangement; only the dπ levels are pertinent to the discussion (see Figure 4). Symmetric and antisymmetric combinations of dπ pairs from the two metals produce the six orbitals on the left side, which are occupied by a total of six electrons from the two Mo(III) ions. Metal–metal σ-bonding and σ-antibonding orbitals result from the symmetric ($xy + xy'$) and antisymmetric ($xy - xy'$) combinations, respectively. The four remaining dπ orbitals are split in energy by π-interactions with ligand orbitals shown on the right of the diagram. Both $yz + yz'$ and $yz - yz'$ are stabilized by back-donation into alkyne C–C π* orbitals, while each of the xz combinations is raised in energy through π-donation from either bridging sulfide or terminal dithiocarbamate filled sulfur p orbitals. The symmetric ($xz + xz'$) combination matches the p_z orbital of the sulfide bridge. Partners for the antisymmetric ($xz - xz'$) orbital are found in the p_x orbitals of two axial dithiocarbamate sulfurs (starred in Figure 4). Placement of the six metal-based electrons in this MO picture nicely fills only dπ stabilized levels, accounting for the single Mo–Mo bond and the diamagnetic behavior of **4**.

The structural similarity of **1** and **4** provides a conceptual framework for considering the bonding in **1**. Three sets of Mo–S bond distances can be discerned in **1**: longest are the four equatorial bonds (average 2.55 Å), followed by axial Mo–S bonds to S8 and S9 (average 2.50 Å), with axial Mo–S5 and Mo–S12 the shortest set (average 2.44 Å). The length of the equatorial distances may result from the strong trans influence of the bridging ligands. Variation in axial bond lengths can be explained by consideration of π interactions predicted with use of the qualitative MO scheme. The only axial sulfurs properly oriented to achieve S p_x → Mo donation into the antisymmetric ($xz - xz'$) combination are identified as S5 and S12. Thus, their shorter bond distances reflect partial multiple Mo–S bonding. A similar effect was noted in the structure of **4**.

The importance of bridging ligand π-interactions to the stability of d^3 dimers with conlateral geometries is suggested by the simple MO scheme outlined above. Indeed, the basic M_2(π-base)(π-acid)

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Table V. Visible Electronic Data

complex	λ_{max},[a] nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})	
$Mo_2(detc)_3(S_3C_2NEt_2)(S_3C_2)$ (**1**)	482 (4.78)	526 (4.79)
$[Mo_2(detc)_3(S_3C_2NEt_2)(S_2C_2(SMe))][BF_4]$ (**2**)	470 (3.84)	510 (2.63)
$Mo_2(detc)_3(S_3C_2NEt_2)(S_2C_2(H)(SMe))$ (**3**)		546 (1.56)
$Mo_2(dmtc)_3(SCNMe_2)(S)(1\text{-}Hxn)$ (**5**)[b]	683 (4.07)	839 (7.59)

[a] Measured in 1-cm cells with methylene chloride as solvent. [b] 1-Hxn = 1-hexyne.

Table VI. Cyclic Voltammetric Data[a]

complex	redns, V[b]	oxidns, V
$Mo_2(detc)_3(S_3C_2NEt_2)(S_3C_2)$ (**1**)	−1.10	+0.88,[d] +1.30[d]
$[Mo_2(detc)_3(S_3C_2NEt_2)(S_2C_2(SMe))][BF_4]$ (**2**)	−0.75, −1.28[c]	+0.61,[d] +1.28[d]
$Mo_2(detc)_3(S_3C_2NEt)(S_2C_2(H)(SMe))$ (**3**)	−1.31	+0.60,[d] +1.28[d]
$Mo_2(dmtc)_3(SCNMe_2)(S)(1\text{-}Hxn)$ (**5**)	−1.36	+0.29, +0.79,[d] +0.91[d]
$Mo_2(dmtc)_3(SCNMe_2)(S)(HCCPh)$ (**6**)	−1.27	+0.33, +0.69,[d] +0.81[d]

[a] All data were recorded with a 200 mV/s scan rate in CH_2Cl_2/0.2 M TBAP. [b] Referenced to Ag/Ag$^+$. [c] Quasi-reversible, $i_{pc}/i_{pa} > 1$. [d] Irreversible; potential listed is E_{pa}.

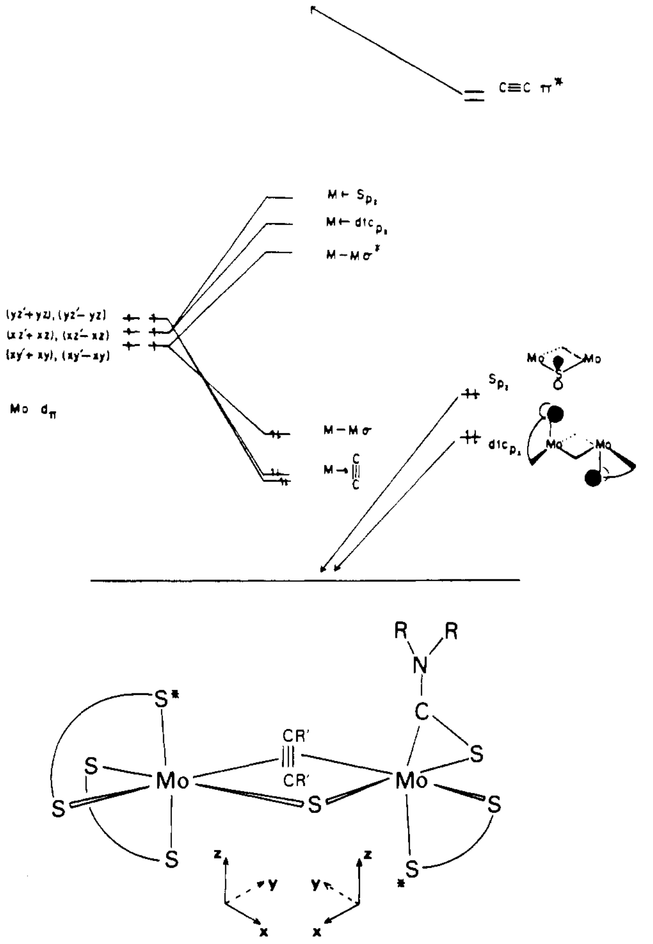

Figure 4. Qualitative dπ–ligand π molecular orbital diagram for $Mo_2(S_2CNR_2)_3(SCNR)(\mu\text{-}S)(\mu\text{-alkyne})$.

bridging frame is retained throughout the preparations of **2** and **3**.

The compatibility of **1** to the bonding model constructed for **4** makes the Mo(III) assignment attractive even though it remains arbitrary. In order to probe the relationship between **1** and **4** further, electronic spectra and cyclic voltammograms of the compounds listed in Tables V and VI were recorded. Dimers **1**, **2**, and **5** show two visible transitions with absorptivities of similar magnitude. The separation between absorption maxima in **5** shrinks for complexes **1** and **2**; dimer **3** exhibits only one distinct absorption in the same region. Energy differences between an unsaturated η^2-CS and an η^2-alkyne and between a bridging carbyne and a sulfide are manifested here in considerable blue shifts for the transitions of complexes **1**–**3**. The relatively low extinction coefficients for these transitions suggest that they are of d → d character.

Electrochemical data for the five dimers (Table VI) reflects similar redox behavior. All four neutral dimers (**1**, **3**, **5**, and **6**) have reversible reductive waves in the region −1.1 to −1.3 V. The first reduction process is easier for cationic **2**, as expected, and occurs at −0.75 V. A second reduction is observed for **2** at −1.28 V. Assuming a comparable $\Delta(E_R{}^1 - E_R{}^2)$ value of 500 mV for the neutral compounds, the second reduction for these complexes is probably outside the solvent potential window. Both alkyne-bridged dimers **5** and **6** have one-electron reversible oxidations near +0.3 V that are absent in the other dimers. However, all of these dinuclear compounds exhibit similar electrochemistry between +0.60 and +1.50 V, where two irreversible waves appear. The second of these is less positive by 300–400 mV for **5** and **6**.

In summary, we have described the preparation of the novel ligands −CSC(=S)S− and −SCS$_2$CNEt$_2$ and defined their connectivity in the structure of **1**. Although their binding mode is unprecedented, these ligands choose to occupy coordination sites such that specific π-interactions with the metals are analogous to those filled by bridging sulfide and alkyne ligands in **4**. The robust d^3, d^3 $M_2(\mu\text{-}\pi\text{-base})(\mu\text{-}\pi\text{-acid})$ bridging framework may promote the quantitative formation of these unusual CS$_2$-derived ligands.

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Supplementary Material Available: Thermal parameters of non-hydrogen atoms (Table VII), positional parameters of hydrogen atoms (Table VIII), and observed and calculated structure factors (Tables IX) (25 pages). Ordering information is given on any current masthead page.