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Transition-Metal Complexes with Sulfur Ligands. 113.[1] Syntheses, X-ray Crystal Structures, and Reactivity of Molybdenum(II) Complexes with Thioetherthiolate Ligands Having XS$_4$ Donor Atom Sets (X = S, O, NH)

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In quest of molybdenum complexes that have sulfur donors in their coordination sphere and exhibit reactivity toward small molecules such as CO, NO, NO$^+$, N$_3^-$, and above all N$_2$, the chemistry of [Mo("^{R}XS$_4$")] complexes has been investigated. Mo(II) complexes of the type [Mo(CO)$_2$("^{R}XS$_4$")] (R = H, X = S, **1a**; R = *tert*-butyl, X = S, **1b**; R = H, X = NH, **2**; R = H, X = O, **3**) formed by reaction of [Mo(CO)$_4$(Cl)$_2$] or [Mo(CO)$_3$(PPh$_3$)$_2$(Cl)$_2$] and the thiols "^{R}XS$_4$"−H$_2$ or corresponding thiolates. Complex **1a** served as a structural reference and proved the Mo center to be seven-coordinate. The [Mo("S$_5$")] fragment approximately forms a square pyramid at the base of which the two *cis* CO ligands are coordinated. Crystal data of **1a**·0.5Et$_2$O: monoclinic space group $P2_1/c$; a = 14.182(7) Å, b = 14.525(11) Å, c = 11.421(15) Å, β = 108.98(7)°, Z = 4, R/R_w = 6.0/5.6. The [Mo("S$_5$")] fragment of **1a** exhibits the *meso*-configuration, and NMR spectra indicate the same configuration for the [Mo("^{R}XS$_4$")] fragments of the other CO complexes. Oxidation of **1**−**3** yielded the C_s symmetrical Mo(IV) oxo complexes [Mo(=O)("^{R}XS$_4$")] (R = H, X = S, **4a**; R = *tert*-butyl, X = S, **4b**; R = H, X = NH, **5**; R = H, X = O, **6**). Complex **4a** was characterized by X-ray structure analysis (orthorhombic space group $P2_12_12_1$; a = 10.872(2), b = 14.502(5), c = 11.324(2) Å; Z = 4; R/R_w = 4.4/3.7%). When treated with PMe$_3$, **1a**, **1b** and **2** yielded the thermolabile phosphine derivatives *meso*-[Mo(CO)(PMe$_3$)("^{R}XS$_4$")] (R = H, X = S, **7**; R = *tert*-butyl, X = S, **9**; R = H, X = NH, **8**) whereas the reaction of **3** gave [Mo(CO)(PMe$_3$)$_2$("OS$_4$")] (**10**). Reaction of **7** with an excess of PMe$_3$ resulted in cleavage of the bridging S(C$_2$H$_4$)$_2$ unit from the "S$_5$"$^{2-}$ ligand and formation of the Mo(IV) complex [Mo(PMe$_3$)$_2$("S$_2$")$_2$] (**11**). Complex **11** was characterized by X-ray structure analysis (monoclinic space group $P2_1/c$, a = 16.857(4) Å, b = 17.742(4) Å, c = 7.569(2) Å, β = 93.53(2)°, Z = 4, R/R_w = 2.8/2.6) and contains a Mo center surrounded by four S and two *cis* P donors in a pseudo-trigonal prismatic arrangement. Complexes **1a** and **1b** reacted with NO$^+$ or NO gas to give the NO complexes [Mo(NO)("^{R}S$_5$")]BF$_4$ (R = H, **12**; R = *tert*-butyl, **13**) and [Mo(NO)$_2$("^{bu}S$_5$")] (**14**). NMR and IR spectra and reactivity suggest that **13** contains dinuclear cations which reversibly dissociate into mononuclear C_1 symmetrical [Mo(NO)("^{bu}S$_5$")]$^+$ ions in solution. Complexes **13** and **14** added PMe$_3$ or N$_3^-$ to give [Mo(NO)(PMe$_3$) ("^{bu}S$_5$")] (**15**), [Mo(NO)(N$_3$)("^{bu}S$_5$")] (**16**), and (NEt$_4$)[Mo(NO)$_2$(N$_3$)("^{bu}S$_5$")] (**17**). Although all complexes contain small molecules as ligands which are substrates or inhibitors for nitrogenase and **16** and **17** even molecules which theoretically can conproportionate to give N$_2$, attempts to obtain N$_2$ complexes with [Mo("^{R}XS$_4$")] fragments remained unsuccessful.

Introduction

Molybdenum in sulfur dominated coordination spheres is found in industrial catalysts for hydrodesulfurization such as MoS$_2$ [2] as well as in the active centers of numerous oxidoreductases,[3] and the importance of sulfur ligation for molybdenum atoms in oxidoreductases has recently been substantiated by the X-ray structural model for the nitrogenase FeMo cofactors.[4] Even if currently the iron atoms of these cofactors are favored as binding site(s) of the N$_2$ molecule,[5] the molybdenum atom cannot yet be excluded to perform this function[6a] such that suitable model N$_2$ complexes of molybdenum are still of high interest.[6b] However, transition metal complexes which exhibit sulfur dominated coordination spheres, bear no abiological ligands such as phosphines, and nevertheless coordinate N$_2$ are extremely rare.

In fact, to the best of our knowledge, the thioether complex [Mo(N$_2$)$_2$(octamethyl-1,5,9,13-tetrathiacyclohexadecane)][7] appears to be the sole example fulfilling these requirements, and it happens to be a molybdenum species. Even this complex, however, does not meet other important requirements. It does not form under mild (reducing) conditions, but its synthesis requires strongly reducing reagents such as sodium metal, and

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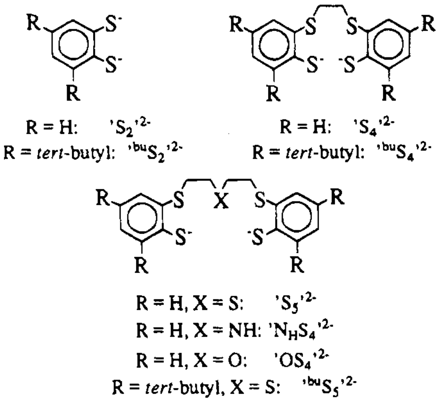
Chart 1. Ligands and Abbreviations



it has a metal(0) center in contrast to the FeMo cofactors whose molybdenum (as well as iron) centers probably exhibit nonzero oxidation states.

In quest of molybdenum complexes fulfilling all these requirements, we have tried to synthesize molybdenum(II) complexes of pentadentate thioetherthiolate ligands binding nitrogenase relevant small molecules and ions which can serve as precursors of N_2 ligands. In numerous cases, seven-coordinate complexes were obtained which can theoretically form many diastereomers.[8] Their unambiguous structural characterization also became an important point.

Ligands and abbreviations used are summarized in Chart 1; preliminary results on [Mo(CO)$_2$(“S_5”)] (**1a**) and [Mo(CO)$_2$(“OS_4”)] (**2**) were reported elsewhere.[9,10]

Experimental Section

General Methods. Unless noted otherwise, all reactions were carried out under an atmosphere of dinitrogen at room temperature in dried N_2-saturated solvents by using standard Schlenk techniques. IR spectra of solutions were recorded in CaF_2 cuvettes with compensation of the solvent bands; solids were measured in KBr pellets. Physical measurements were carried out with the following instruments: IR spectra, Perkin-Elmer IR 983 and Perkin-Elmer 1600 series FT; NMR spectra, Jeol FT-NMR JNM-GX 270.

“S_5”$-H_2$,[9] “N_HS_4”$-H_2\cdot HCl$,[10] “OS_4”$-H_2$,[10] “$^{bu}S_5$”$-H_2$,[11] NEt_4N_3,[12] PMe_3,[13] [Mo(CO)$_4$ (Cl)$_2$],[14] and [Mo(CO)$_3$(PPh$_3$)$_2$(Cl)$_2$][15] were prepared as described in the literature.

X-ray Structure Determinations of [Mo(CO)$_2$(“S_5”)]·0.5Et$_2$O (1a·0.5Et$_2$O), [Mo(=O)(“S_5”)] (4a), and [Mo(PMe$_3$)$_2$(“S_2”)$_2$] (11). Brown single crystals of [Mo(CO)$_2$(“S_5”)] ·0.5Et$_2$O (**1a**·0.5Et$_2$O) were grown from a DMF solution which was layered with Et$_2$O. Purple single crystals of [Mo(=O)(“S_5”)] (**4a**) and red-black single crystals of [Mo(PMe$_3$)$_2$(“S_2”)$_2$] (**11**) were obtained from the reaction mixtures. Suitable crystals were sealed in glass capillaries and mounted on a Siemens P4 diffractometer. Corrections for absorption were not applied. Data were collected with Mo Kα radiation (0.710 73 Å) in a 2θ range from 3 to 54°. The structures were solved by direct methods (SHELXTL-PLUS);[16] non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen positions were taken from the difference Fourier synthesis and fixed on their positions with a common isotropic thermal parameter.

Table 1. Selected Crystallographic Data of [Mo(CO)$_2$(“S_5”)]·0.5Et$_2$O (**1a**·0.5Et$_2$O), [Mo=O)(“S_5”)] (**4a**), and [Mo(PMe$_3$)$_2$(“S_2”)$_2$] (**11**)

	1a·0.5Et$_2$O	**4a**	**11**
formula	$C_{20}H_{21}MoO_{2.5}S_5$	$C_{16}H_{16}MoOS_5$	$C_{18}H_{26}MoP_2S_4$
fw	557.65	480.57	528.55
cryst dimen (mm^3)	0.8 × 0.4 × 0.3	0.4 × 0.4 × 0.2	0.4 × 0.4 × 0.4
space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
cryst syst	monoclinic	orthorhombic	monoclinic
a (Å)	14.182(7)	10.872(2)	16.857(4)
b (Å)	14.525(11)	14.502(5)	17.742(4)
c (Å)	11.421(15)	11.324(2)	7.569(2)
β (deg)	108.98(7)		93.53(2)
hkl value scanned	$-18 \le h \le +18$ $-18 \le k \le +3$ $-14 \le l \le +14$	$-13 \le h \le +7$ $0 \le k \le +18$ $-14 \le l \le +14$	$-21 \le h \le +21$ $-22 \le k \le 0$ $-9 \le l \le +3$
cell vol (Å^3)	2225(3)	1785(1)	2259(1)
Z	4	4	4
ϱ_{calcd} (g cm^{-3})	1.66	1.79	1.55
$F(000)$	1132	968	1080
μ(cm^{-1})	10.76	13.16	10.93
measd temp (K)	200	293	293
reflcns, collecd	10459	6819	6652
reflecns, independ	4820	3936	4968
reflcns, obsd	3290	2979	3475
params, refined	248	208	226
R/R_w[a]	6.0/5.6	4.4/3.7	2.8/2.6

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sum[\omega||F_o| - |F_c||]^{1/2}/\sum[\omega|F_o|]^{1/2}$; $\omega = 1/\sigma^2(F_o)$.

Tables 1 and 2 list selected crystallographic data, fractional atomic coordinates, and equivalent isotropic thermal parameters of **1a**·0.5Et$_2$O, **4a**, and **11**.

Syntheses. [Mo(CO)$_2$(“S_5”)] (1a). NaOMe (13.4 mmol, 13.4 mL of a 1 M solution in MeOH) was added to a solution of “S_5”$-H_2$ (2.46 g, 6.7 mmol) in 40 mL of THF. [Mo(CO)$_3$(PPh$_3$)$_2$(Cl)$_2$] (5.19 g, 6.7 mmol) and 30 mL of MeOH were added. Within the course of 1.5 h, gas evolved, the color of the suspension changed from yellow to brown, and a microcrystalline brown solid precipitated. It was separated, rinsed with 150 mL of MeOH and 150 mL of Et$_2$O, and dried *in vacuo*; yield 2.74 g (79%). Anal. Calcd for **1a**·0.5Et$_2$O, $C_{20}H_{21}MoO_{2.5}S_5$ (557.65): C, 43.08; H, 3.79; S, 28.75. Found: C, 43.14; H, 3.79; S, 29.01. IR (KBr, cm^{-1}): 1952, 1879 (vs, ν_{CO}). ^{1}H NMR (DMSO-d_6, ppm, 270 MHz): δ 7.60 (d, 2 H, C_6H_4), 7.43 (d, 2 H, C_6H_4), 7.10 (t, 2 H, C_6H_4), 6.97 (t, 2 H, C_6H_4), 4.0−1.85 (m, 8 H, C_2H_4). ^{13}C{^{1}H} NMR (DMSO-d_6, ppm, 67.94 MHz): δ 152.4, 132.2, 130.8, 130.4, 124.4 (C_6H_4), 49.6, 35.4 (C_2H_4). Signals in the range of carbonyl C atoms could not be detected.

[Mo(CO)$_2$(“$^{bu}S_5$”)] (1b). A filtered solution of [Mo(CO)$_4$(Cl)$_2$] (1.64 g, 5.87 mmol) in 30 mL of CH_2Cl_2 was added dropwise to a suspension of “$^{bu}S_5$”$-H_2$ (3.49 g, 5.87 mmol) and $NaHCO_3$ (1.97 g, 23.45 mmol) in 20 mL of CH_2Cl_2. Gas evolved from the mixture which was stirred for 1 h and filtered over SiO_2. The filtrate was evaporated to dryness, the residue was redissolved in a minimum of acetone (~20 mL), and the resulting solution was cooled to −30 °C. A yellow powder precipitated which was collected after 1 d, washed with 10 mL of cold acetone, and dried *in vacuo*, yield 1.71 g (39%). Anal. Calcd for $C_{34}H_{48}MoO_2S_5$ (745.02): C, 54.81; H, 6.49; S, 21.52. Found: C, 54.14; H, 6.77; S, 21.30. IR (KBr, cm^{-1}): 1953, 1873 (vs, ν_{CO}). ^{1}H NMR (CD_2Cl_2, ppm, 270 MHz): δ 7.33 (d, 2 H, C_6H_2), 7.28 (d, 2 H, C_6H_2), 3.65−2.45 (m, 8 H, C_2H_4), 1.63 (s, 18 H, C_4H_9), 1.30 (s, 18 H, C_4H_9). ^{13}C{^{1}H} NMR (CD_2Cl_2, ppm, 67.94 MHz): δ 148.8, 146.2, 144.8, 131.3, 125.3, 125.0 (C_6H_2), 37.0, 34.0, 30.4, 28.5 (alkyl C). Signals in the range of carbonyl C atoms could not be detected.

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Table 2. Selected Fractional Atomic Coordinates [$\times 10^4$] and Isotropic Thermal Parameters [$pm^2 \times 10^{-1}$] for (a) [Mo(CO)$_2$(“S$_5$”)]·0.5Et$_2$O (**1a**·0.5Et$_2$O), (b) [Mo(═O)(“S$_5$”)] (**4a**), and (c) [Mo(PMe$_3$)$_2$(“S$_2$”)$_2$] (**11**)

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
				(a) **1a**·0.5Et$_2$O					
Mo(1)	1544(1)	8873(1)	2408(1)	23(1)	C(10)	4085(6)	8593(5)	4018(9)	33(3)
C(1)	1775(6)	10199(5)	2473(9)	34(3)	C(16)	2546(6)	6746(5)	1979(8)	32(3)
O(1)	1912(5)	10990(4)	2552(7)	47(3)	C(17)	2390(6)	6586(5)	3196(10)	37(3)
C(2)	1409(6)	9369(4)	742(7)	25(3)	C(25)	−1035(6)	8585(5)	1750(9)	31(3)
O(2)	1303(5)	9665(4)	−206(6)	39(2)	C(24)	−2019(6)	8359(6)	1173(9)	37(3)
S(1)	3048(2)	9125(1)	4284(2)	33(1)	C(23)	−2733(6)	8598(6)	1711(10)	43(4)
S(2)	2809(1)	7963(1)	1765(2)	27(1)	C(22)	−2443(6)	9064(6)	2850(10)	43(4)
S(3)	1447(1)	7323(1)	3473(2)	24(1)	C(21)	−1480(6)	9307(5)	3398(9)	35(3)
S(4)	−137(1)	8307(1)	1023(2)	29(1)	C(20)	−742(6)	9056(4)	2892(8)	25(2)
S(5)	501(1)	9410(1)	3647(2)	28(1)	C(26)	−95(6)	7054(5)	1228(9)	39(3)
C(15)	3994(5)	8091(5)	2983(8)	31(3)	C(27)	280(6)	6781(5)	2573(10)	37(3)
C(14)	4835(6)	7692(6)	2775(10)	41(3)	O(3)	5000	0	0	100(5)
C(13)	5754(7)	7808(6)	3658(12)	49(4)	C(3A)	4339(22)	−181(19)	749(30)	81(8)
C(12)	5852(6)	8318(6)	4719(10)	45(4)	C(3B)	5040(21)	292(19)	898(29)	82(8)
C(11)	5032(7)	8712(6)	4886(10)	43(3)	C(4)	4278(16)	202(14)	1559(22)	133(7)
				(b) **4a**					
Mo(1)	1106(1)	9472(1)	7830(1)	31(1)	C(10)	−1555(7)	10193(4)	9025(7)	37(2)
O(1)	739(4)	8763(3)	6702(4)	42(2)	C(16)	518(7)	11833(4)	7245(7)	41(2)
S(1)	−465(2)	9291(1)	9271(2)	43(1)	C(17)	924(8)	11985(4)	8510(7)	43(3)
S(2)	−219(2)	10716(1)	7076(2)	35(1)	C(25)	4235(6)	9231(4)	7635(6)	33(2)
S(3)	1768(2)	11040(1)	9184(2)	40(1)	C(24)	5422(7)	9277(4)	7207(8)	47(3)
S(4)	3089(2)	9933(1)	6940(2)	34(1)	C(23)	6347(7)	8777(5)	7763(9)	53(3)
S(5)	2383(2)	8613(1)	9144(2)	40(1)	C(22)	6036(9)	8217(5)	8703(7)	46(3)
C(15)	−1447(6)	10823(4)	8115(6)	37(2)	C(21)	4846(8)	8151(5)	9104(7)	45(3)
C(14)	−2310(6)	11524(5)	7963(8)	44(3)	C(20)	3893(8)	8676(4)	8580(6)	36(2)
C(13)	−3284(8)	11593(6)	8745(8)	50(3)	C(26)	3569(6)	11072(4)	7449(7)	42(3)
C(12)	−3393(8)	10976(6)	9665(8)	53(3)	C(27)	3351(8)	11231(5)	8730(7)	48(3)
C(11)	−2532(8)	10274(5)	9808(7)	45(3)					
				(c) **11**					
Mo(1)	7552(1)	131(1)	1912(1)	27(1)	C(15)	6798(2)	−1463(2)	3621(5)	36(1)
S(1)	6317(1)	−16(1)	3221(1)	37(1)	C(14)	6728(3)	−2213(2)	4189(6)	50(2)
S(2)	7637(1)	−1162(1)	2571(1)	37(1)	C(13)	6059(3)	−2431(3)	4983(6)	58(2)
S(3)	7543(1)	1355(1)	3120(1)	35(1)	C(12)	5454(3)	−1919(3)	5262(6)	56(2)
S(4)	8902(1)	211(1)	2889(1)	35(1)	C(11)	5526(2)	−1177(3)	4742(5)	48(1)
P(1)	6593(1)	742(1)	−318(1)	39(1)	C(10)	6203(2)	−944(2)	3897(5)	36(1)
C(1)	6945(3)	1275(3)	−2161(6)	65(2)	C(25)	9097(2)	1068(2)	3959(5)	32(1)
C(2)	5894(3)	1419(3)	525(7)	62(2)	C(24)	9858(2)	1236(2)	4697(5)	40(1)
C(3)	5928(2)	65(3)	−1427(6)	57(2)	C(23)	9990(2)	1911(3)	5552(6)	50(2)
P(2)	8273(1)	−341(1)	−680(1)	36(1)	C(22)	9380(3)	2415(2)	5719(6)	53(2)
C(4)	9006(2)	−1083(2)	−254(6)	50(2)	C(21)	8627(2)	2259(2)	5006(6)	46(1)
C(5)	7712(2)	−757(2)	−2582(6)	55(2)	C(20)	8481(2)	1583(2)	4098(5)	33(1)
C(6)	8871(2)	385(3)	−1682(6)	57(2)					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[Mo(CO)$_2$(“N$_H$S$_4$”)] (2). Under stirring, [Mo(CO)$_3$(PPh$_3$)$_2$(Cl)$_2$] (5.0 g, 6.4 mmol) was added to a solution of NaOMe (19.0 mmol, 19.0 mL of a 1 M solution in MeOH) and “N$_H$S$_4$”−H$_2$·HCl (2.54 g, 6.5 mmol) in 30 mL of THF/MeOH (1:1). Gas evolved from the resulting suspension, and its color deepened from yellow to orange in the course of 2 h. The orange solid material was collected, washed with 150 mL of MeOH and 150 mL of Et$_2$O, and dried *in vacuo*; yield 2.72 g (84%). Anal. Calcd for $C_{18}H_{17}MoNO_2S_4$ (503.54): C, 42.94; H, 3.40; N, 2.78; S, 25.47. Found: C, 43.07; H, 3.50; N, 2.77; S, 25.17. IR (KBr, cm^{-1}): 3189 (w, ν_{NH}), 1955, 1858 (s, ν_{CO}). ^{1}H NMR (DMSO-d_6, ppm, 270 MHz): δ 7.60 (d, 2 H, C$_6$*H*$_4$), 7.48 (d, 2 H, C$_6$*H*$_4$), 7.13 (t, 2 H, C$_6$*H*$_4$), 6.96 (t, 2 H, C$_6$*H*$_4$), 5.25 (m, 1 H, N*H*), 3.3−2.4 (m, 8 H, C$_2$*H*$_4$). ^{13}C-{^{1}H} NMR (DMSO-d_6, ppm, 67.9 MHz): δ 152.4, 132.3, 131.4, 129.7, 129.5, 123.1 (*C*$_6$H$_4$), 50.8, 46.1 (*C*$_2$H$_4$). Signals in the range of carbonyl C atoms could not be detected.

[Mo(CO)$_2$(“OS$_4$”)] (3). NaOMe (9.2 mL, 9.2 mmol of a 1 M solution in MeOH) was added to a solution of “OS$_4$”−H$_2$ (1.63 g, 4.6 mmol) in 40 mL of THF. After addition of [Mo(CO)$_3$(PPh$_3$)$_2$(Cl)$_2$] (3.55 g, 4.6 mmol), evolution of gas started, the color of the suspension changed from yellow to red in the course of 3 h, and a microcrystalline red solid separated. After addition of 30 mL of MeOH, the red solid was collected, rinsed with 150 mL of MeOH and 150 mL of Et$_2$O, and dried *in vacuo*; yield 1.52 g (65%). Anal. Calcd for $C_{18}H_{16}MoO_3S_4$ (504.52): C, 42.85; H, 3.20; S, 25.42. Found: C, 43.01; H, 3.36; S, 24.97. IR (KBr, cm^{-1}): 1943, 1886 (s, ν_{CO}). ^{1}H NMR (DMSO-d_6, ppm, 270 MHz): δ 7.64 (d, 2 H, C$_6$*H*$_4$), 7.51 (d, 2 H, C$_6$*H*$_4$), 7.15 (t, 2 H, C$_6$*H*$_4$), 6.98 (t, 2 H, C$_6$*H*$_4$), 4.4−2.9 (m, 8 H, C$_2$*H*$_4$).

[Mo(═O)(“^{R}S$_5$”)] (R = H (4a), *tert*-butyl (4b)). Within the course of 2 days in the presence of air, purple crystals of [Mo(═O)(“^{R}S$_5$”)] (R = H (**4a**), *tert*-butyl (**4b**)) precipitated from a yellow solution of [Mo(CO)$_2$(“^{R}S$_5$”)] (R = H (**1a**), *tert*-butyl (**1b**)) in a minimum of CH$_2$Cl$_2$, THF, acetone, or DMSO. IR (KBr, cm^{-1}): R = H (**4a**), 920 (s, $\nu_{Mo═O}$); R = *tert*-butyl (**4b**), 925 (s, $\nu_{Mo═O}$). ^{1}H NMR (CD$_2$Cl$_2$, ppm, 270 MHz): R = *tert*-butyl (**4b**), δ 7.70 (d, 2 H, C$_6$*H*$_2$), 7.57 (d, 2 H, C$_6$*H*$_2$), 4.10−1.90 (m, 8 H, C$_2$*H*$_4$), 1.75 (s, 18 H, C$_4$*H*$_9$), 1.39 (s, 18 H, C$_4$*H*$_9$).

[Mo(═O)(“XS$_4$”)] (X = NH (5), O (6)). Purple crystals of [Mo(═O)(“N$_H$S$_4$”)] (**5**) precipitated from yellow solutions or suspensions of [Mo(CO)$_2$(“N$_H$S$_4$”)] (**2**) in DMSO or THF/CH$_2$Cl$_2$ in the presence of air in the course of 14 days. In contrast, the color of solutions of [Mo(CO)$_2$(“OS$_4$”)] (**3**) in DMSO first turned from yellow to purple within 1 day, and subsequently purple crystals of [Mo(═O)(“OS$_4$”)] (**6**) precipitated within another day. When the crystallizations were complete, the supernatant mother liquors had become colorless in all cases. IR (KBr, cm^{-1}): X = NH (**5**), 925 (s, $\nu_{Mo═O}$); X = O (**6**), 945 (s, $\nu_{Mo═O}$). ^{1}H NMR (DMSO-d_6, ppm, 270 MHz): δ X = O (**6**), 8.0 (d, 2 H, C$_6$*H*$_4$), 7.76 (d, 2 H, C$_6$*H*$_4$), 7.34 (t, 2 H, C$_6$*H*$_4$), 7.19 (t, 2 H, C$_6$*H*$_4$), 3.7−2.6 (m, 8 H, C$_2$*H*$_4$).

[Mo(CO)(PMe$_3$)(“N$_H$S$_4$”)] (8). PMe$_3$ (0.6 mL, 6.0 mmol) was added to an orange suspension of [Mo(CO)$_2$(“N$_H$S$_4$”)] (**2**) (300 mg, 0.6 mmol) in 30 mL of THF. When the mixture was heated under reflux for 2 h, a yellow solution resulted which was cooled to room temperature. Yellow needles precipitated which were collected, washed with 10 mL of Et_2O, and dried *in vacuo*; yield 280 mg (85%). Anal. Calcd for $C_{20}H_{26}MoNOPS_4$ (551.61): C, 43.55; H, 4.75; N, 2.54; S, 23.25. Found: C, 43.52; H, 4.78; N, 2.65; S, 23.63. IR (KBr, cm^{-1}): 3243 (w, ν_{NH}), 1807 (s, ν_{CO}), 952 (m, δ_{PCH}). ^1H NMR (DMSO-d_6, ppm, 270 MHz): δ 7.54 (m, 4 H, C_6H_4), 7.02 (t, 2 H, C_6H_4), 6.87 (t, 2 H, C_6H_4), 4.97 (m, 1 H, N*H*), 2.95−2.25 (m, 8 H, C_2H_4), 1.3 (d, 9 H, $P(CH_3)_3$).

[Mo(CO)(PMe₃)(“^buS₅”)] (9). PMe_3 (0.4 mL, 4.0 mmol) was added to a solution of [Mo(CO)$_2$(“$^{bu}S_5$”)] (**1b**) (280 mg, 0.38 mmol) in 20 mL of CH_2Cl_2, whereupon gas evolved and the color of the solution changed from yellow to red-brown. When the solution was layered with 50 mL of *n*-hexane, a red-brown powder precipitated which was collected, washed with 30 mL of *n*-hexane, and dried *in vacuo*; yield 190 mg (63%). Anal. Calcd for $C_{36}H_{57}MoOPS_5$ (793.09): C, 54.52; H, 7.27; S, 20.22. Found: C, 54.46; H, 7.27; S, 19.25. IR (KBr, cm^{-1}): 1796 (vs, ν_{CO}), 951 (m, δ_{PCH}). ^1H NMR (CD_2Cl_2, ppm, 270 MHz): δ 7.42 (d, 2 H, C_6H_2), 7.32 (d, 2 H, C_6H_2), 3.6−2.0 (m, 8 H, C_2H_4), 1.68 (s, 18 H, C_4H_9), 1.50 (d, 9 H, $P(CH_3)_3$), 1.32 (s, 18 H, C_4H_9). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, ppm, 109.38 MHz): δ 22.5 (s, *P*Me$_3$). $^{13}C\{^1H\}$ NMR spectra could not be obtained, because **9** decomposes rather rapidly in solution.

[Mo(CO)(PMe₃)₂(“OS₄”)] (10). PMe_3 (0.5 mL, 5.0 mmol) was added to a suspension of [Mo(CO)$_2$(“OS_4”)] (**3**) in 20 mL of THF. The color of the suspension changed from red-violet to red in the course of 2 h, and microcrystalline pink **10** separated. Addition of 30 mL of Et_2O completed precipitation of **10**, which was collected as red powder, washed with 30 mL of Et_2O, and dried *in vacuo*; yield 205 mg (74%). Anal. Calcd for $C_{23}H_{34}MoO_2P_2S_4$ (628.67): C, 43.94; H, 5.45; S, 20.40. Found: C, 44.32; H, 5.71; S, 20.27. IR (KBr, cm^{-1}): 1815 (s, ν_{CO}), 945 (m, δ_{PCH}). ^1H NMR (CD_2Cl_2, ppm, 270 MHz): δ 8.1−7.0 (m, 8 H, C_6H_4), 4.2−3.0 (m, 8 H, C_2H_4), 1.15 (s, 18 H, $P(CH_3)_3$).

[Mo(PMe₃)₂(“S₂”)₂] (11). Red crystals of **11** precipitated from a solution of PMe_3 (0.5 mL, 5.0 mmol) and [Mo(CO)(PMe$_3$)(“S_5”)] (**7**) (110 mg, 0.19 mmol) in 20 mL of THF in the course of 2 weeks. They were collected and washed with 5 mL of THF, crystals suitable for X-ray analysis were separated, and the remaining material was pulverized and dried *in vacuo*; yield 75 mg (74%). Anal. Calcd for $C_{18}H_{26}MoP_2S_4$ (528.55): C, 40.90; H, 4.96; S, 24.27. Found: C, 40.95; H, 4.39; S, 24.13. IR (KBr, cm^{-1}): 949, 937 (s, δ_{PCH}). ^1H NMR (CD_2Cl_2, ppm, 270 MHz): δ 8.1 (m, 4 H, C_6H_4), 7.2 (m, 4 H, C_6H_4), 1.75 (d, 18 H, $P(CH_3)_3$).

[Mo(NO)(“S₅”)]BF₄ (12). At −78 °C, $NOBF_4$ (140 mg, 1.2 mmol) was added to a yellow-brown suspension of [Mo(CO)$_2$(“S_5”)] (**1a**) (625 mg, 1.2 mmol) in 30 mL of CH_2Cl_2. When the mixture was warmed, a purple solution resulted at −35 °C which was evaporated to dryness. The red-purple residue was stirred with 30 mL of *n*-hexane, collected, washed with 20 mL of *n*-hexane, and dried *in vacuo*; yield 570 mg (82%). Anal. Calcd for $C_{16}H_{16}NBF_4MoOS_5$ (581.38): C, 33.06; H, 2.77; N, 2.41. Found: C, 33.66; H, 2.95; N, 2.19. IR (KBr, cm^{-1}): 1689 (s, ν_{NO}). ^1H NMR (CD_2Cl_2, ppm, 270 MHz): δ 8.1−6.9 (m, 8 H, C_6H_4), 4.5−1.5 (m, 8 H, C_2H_4).

[Mo(NO)(“^buS₅”)]BF₄ (13). $NOBF_4$ (130 mg, 1.11 mmol) was added to a solution of [Mo(CO)$_2$(“$^{bu}S_5$”)] (**1b**) (750 mg, 1.0 mmol) in 70 mL of CH_2Cl_2. Gas evolved, and the color of the solution turned from yellow to purple in the course of 30 min. The solution was evaporated to dryness, and the resulting red-purple residue was stirred with 20 mL of *n*-hexane, collected, washed with 10 mL of *n*-hexane, and dried *in vacuo*; yield 645 mg (80%). Anal. Calcd for $BC_{32}F_4H_{48}MoNOS_5$ (805.81): C, 47.70; H, 6.00; N, 1.74; S, 19.90. Found: C, 47.81; H, 6.16; N, 1.49; S, 19.81. IR (KBr, cm^{-1}): 1701 (s, ν_{NO}). The ^1H NMR (CD_2Cl_2, (ppm), 270 MHz) spectrum showed that **13** yielded two species **13a** and **13b** in the ratio 4:1 in solution. ^1H NMR: δ 7.85 (d, 2 H, C_6H_2, **13b**), 7.83 (d, 2 H, C_6H_2, **13b**), 7.70 (d, 2 H, C_6H_2, **13a**), 7.55 (d, 2 H, C_6H_2, **13a**), 7.53 (d, 2 H, C_6H_2, **13a**), 7.26 (d, 2 H, C_6H_2, **13b**), 7.22 (d, 2 H, C_6H_2, **13a**), 4.45−2.25 (m, 16 H, C_2H_4, **13a** and **13b** superimposed), 1.55 (s, C_4H_9, **13b**), 1.54 (s, 9 H, C_4H_9, **13a**), 1.53 (s, C_4H_9, **13b**), 1.42 (s, 9 H, C_4H_9, **13a**), 1.38 (s, C_4H_9, **13b**), 1.31 (s, 18 H, C_4H_9, **13a**).

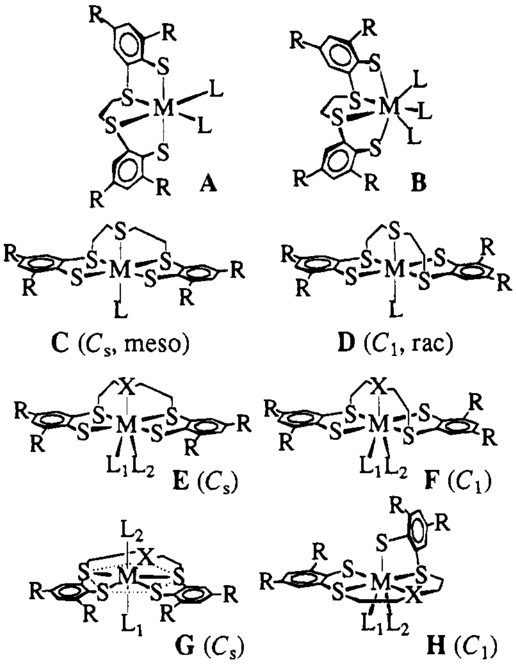
[Mo(NO)₂(“^buS₅”)] (14). When NO was bubbled through a suspension of [Mo(CO)$_2$(“$^{bu}S_5$”)] (**1b**) (1.36 g, 1.83 mmol) in 40 mL of THF for 15 min, the yellow suspension changed into an emerald-green solution which was evaporated to dryness. The residue was redissolved in 10 mL of CH_2Cl_2; the resulting solution was combined with 40 mL of *n*-hexane and reduced in volume to one third. The precipitated emerald-green powder was collected, washed with 30 mL of *n*-hexane, and dried *in vacuo*; yield 1.22 g (89%). Anal. Calcd for $C_{32}H_{48}MoN_2O_2S_5$ (749.01): C, 51.31; H, 6.46; N, 3.74; S, 21.41. Found: C, 51.40; H, 6.67; N, 3.52; S, 21.03. IR (KBr, cm^{-1}): 1774, 1672 (s, ν_{NO}). ^1H NMR (CD_2Cl_2, ppm, 270 MHz): δ 7.49 (d, 2 H, C_6H_2), 7.45 (d, 2 H, C_6H_2), 7.42 (d, 2 H, C_6H_2), 7.34 (d, 2 H, C_6H_2), 4.55−2.80 (m, 8 H, C_2H_4), 1.68 (s, 9 H, C_4H_9), 1.48 (s, 9 H, C_4H_9), 1.33 (s, 18 H, C_4H_9). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm, 67.9 MHz): δ 151.4, 150.9, 149.7, 149.1, 147.4, 147.1, 134.8, 130.7, 128.6, 127.4, 126.5, 126.1 (C_6H_2), 38.2, 38.0, 35.0, 33.7 (C_2H_4), 31.6, 30.2, 30.0 ($C(CH_3)_3$). Due to the decomposition of **14**, the signals of the quartenary C atoms of the $C(CH_3)_3$ groups could not be detected.

[Mo(NO)(PMe₃)(“^buS₅”)]BF₄ (15). PMe_3 (0.01 mL, 0.12 mmol) was added to [Mo(NO)(“$^{bu}S_5$”)]BF$_4$ (**13**) (100 mg, 0.12 mmol) in 15 mL of THF, whereupon the color of the solution changed from purple to yellow-brown. The solution was stirred for 20 min and evaporated to dryness. The brown residue was stirred for 1 h with 40 mL of *n*-hexane, collected, washed with 20 mL of *n*-hexane, and dried *in vacuo*; yield 90 mg (85%). Anal. Calcd for $BC_{35}F_4H_{57}MoNOPS_5$ (881.89): C, 47.67; H, 6.51; N, 1.59; S, 18.18. Found: C, 47.17; H, 6.51; N, 1.33; S, 17.56. IR (KBr, cm^{-1}): 1676 (vs, ν_{NO}), 955 (m, δ_{PCH}). ^1H NMR (CD_2Cl_2, ppm, 270 MHz): δ 7.54 (d, 2 H, C_6H_2), 7.35 (d, 2 H, C_6H_2), 7.23 (d, 2 H, C_6H_2), 7.00 (d, 2 H, C_6H_2), 4.10−2.40 (m, 8 H, C_2H_4), 1.60 (d, 9 H, $P(CH_3)_3$), 1.59 (s, 9 H, C_4H_9), 1.58 (s, 9 H, C_4H_9), 1.36 (s, 9 H, C_4H_9), 1.26 (s, 9 H, C_4H_9). Due to rather rapid decomposition of **15** in solution, $^{13}C\{^1H\}$ NMR spectra could not be recorded.

[Mo(NO)(N₃)(“^buS₅”)] (16). NEt_4N_3 (140 mg, 0.81 mmol) was added to a solution of [Mo(NO)(“$^{bu}S_5$”)]BF$_4$ (**13**) in 40 mL of acetone. Within the course of 20 min, the color of the solution changed from purple to red-brown. Evaporation to dryness yielded a red-brown residue which was redissolved in 40 mL of THF. The solution was filtered and evaporated to dryness again, the resulting red-brown residue was stirred for 1 h with 30 mL of *n*-hexane, collected, washed with 30 mL of *n*-hexane, and dried *in vacuo*; yield 535 mg (88%). Anal. Calcd for $C_{32}H_{48}MoN_4OS_5$ (761.03): C, 50.50; H, 6.36; N, 7.36. Found: C, 49.93; H, 6.69; N, 6.28. IR (KBr, cm^{-1}): 2051 (vs, ν_{N3}), 1673 (vs, ν_{NO}). ^1H NMR (THF-d_8, +20 °C, ppm, 270 MHz): δ 7.45 (s, 4 H, C_6H_2), 3.50−2.60 (m, 8 H, C_2H_4), 1.65 (s, 18 H, C_4H_9), 1.30 (s, 18 H, C_4H_9). The ^1H NMR (THF-d_8, ppm, 270 MHz) spectrum at −50 °C showed that **16** yielded two species **16a** and **16b** in solution: δ 7.57−7.35 (m, 8 H, C_6H_2, **16a** and **16b** superimposed), 4.30−2.50 (m, 16 H, C_2H_4, **16a** and **16b** superimposed), 1.70−1.20 (m, 72 H, C_4H_9, **16a** and **16b** superimposed). Signals of the main product **16a**: δ 7.55 (d, 2 H, C_6H_2), 7.52 (d, 2 H, C_6H_2), 7.47 (d, 2 H, C_6H_2), 7.40 (d, 2 H, C_6H_2), 4.30−2.50 (m, 8 H, C_2H_4), 1.66 (s, 18 H, C_4H_9), 1.32 (s, 9 H, C_4H_9), 1.30 (s, 9 H, C_4H_9).

NEt₄[Mo(NO)₂(N₃)(“^buS₅”)] (17). NEt_4N_3 (190 mg, 1.10 mmol) was added to an emerald-green suspension of [Mo(NO)$_2$(“$^{bu}S_5$”)] (**14**) (800 mg, 1.07 mmol) in 20 mL of acetone. The reaction mixture was stirred for 10 min yielding a red-brown solution which was evaporated to dryness. The residue was redissolved in 40 mL of THF, and the solution was filtered and evaporated to dryness again. The red-brown residue was stirred with 40 mL of *n*-hexane for 30 min, collected, washed with 30 mL of *n*-hexane, and dried *in vacuo*; yield 870 mg (88%). Anal. Calcd for $C_{40}H_{68}MoN_6O_2S_5$ (921.29): C, 52.15; H, 7.44; N, 9.12; S, 17.40. Found: C, 52.42; H, 7.69; N, 8.59; S, 17.40. IR (KBr, cm^{-1}): 2062 (vs, ν_{N3}), 1743, 1636 (vs, ν_{NO}). ^1H NMR (THF-d_8, +35 °C, ppm, 270 MHz): δ 7.22 (s, 2 H, C_6H_2), 7.00 (s, 2 H, C_6H_2), 3.46 (q, 8 H, $N(CH_2CH_3)_4$), 3.20−2.75 (m, 8 H, C_2H_4), 1.61 (s, 18 H, C_4H_9), 1.35 (m, 12 H, $N(CH_2CH_3)_4$), 1.28 (s, 18 H, C_4H_9). ^1H NMR (THF-d_8, −40 °C, ppm, 270 MHz): δ 7.30 (d, 2 H, C_6H_2), 7.15 (d, 2 H, C_6H_2), 7.12 (d, 2 H, C_6H_2), 6.83 (d, 2 H, C_6H_2), 3.47 (q, 8 H, $N(CH_2CH_3)_4$), 3.40−2.25 (m, 8 H, C_2H_4), 1.62 (s, 9 H, C_4H_9), 1.60 (s, 9 H, C_4H_9), 1.38 (m, 12 H, $N(CH_2CH_3)_4$), 1.30 (s, 9 H, C_4H_9), 1.26 (s, 9 H, C_4H_9).

Chart 2



A **B**

C (C_s, meso) **D** (C_1, rac)

E (C_s) **F** (C_1)

G (C_s) **H** (C_1)

Caution! We could not observe any dangerous properties of compounds **16** and **17**, but azides may be explosive.

Results

Stereochemistry. In order to facilitate description of the results, the stereochemistry of six- and seven-coordinate complexes with tetra- and pentadentate ligands of the “^{R}S$_4$”$^{2-}$ and “^{R}XS$_4$”$^{2-}$ type is briefly to be discussed (Chart 2).

Six coordinate complexes of the “^{R}S$_4$”$^{2-}$ ligand nearly invariably contain [M(“^{R}S$_4$”)] fragments in which the “^{R}S$_4$”$^{2-}$ ligand coordinates the metal in a helical manner with *trans* thiolate donors, as depicted in **A**.[17] The resulting [M(L)$_2$(“^{R}S$_4$”)] complexes such as [Fe(CO)$_2$(“S$_4$”)][17a] or [Mo(NO)$_2$(“S$_4$”)][17b] adopt C_2 symmetry.

The same feature is maintained in seven-coordinate complexes **B** but the [M(“^{R}S$_4$”)] fragment is comparatively distorted and the trans SMS angles deviate 10−20 deg from 180°,[14] e.g., in [Mo(CO)$_2$(PMe$_3$)(“S$_4$”)].[17b]

In comparison, metal complexes with [M(“^{R}XS$_4$”)] fragments exhibit a more complicated pattern. Molecular models show that the number of strain free stereoisomers is much larger, even in the case of six-coordinate species.[8] Two of these stereoisomers are exemplified by **C** and **D** having C_s and C_1 symmetry. They differ with respect to the thiolate positions, and the C_1 symmetry of **D** is due to the positioning of the C$_2$H$_4$ bridges lying on one side of the plane going through the metal, X, and the thioether sulfur donors. It is noted that **C** is the sole isomer having C_s symmetry. With regard to all other C_1 symmetrical (and chiral) isomers, it therefore represents the *meso*-isomer. **C** is verified in complexes such as [Fe(CO)(“S$_5$”)][8] or [Fe(MeOH)(“N$_H$S$_4$”)],[10b,18] **D** is found in, for instance, [Fe(CO)(“N$_H$S$_4$”)][10a,18] or [Ru(PPh$_3$)(“^{bu}S$_5$”)].[11]

Because generally nonrigidity has to be expected for seven-coordinate species,[19] the number of possible stereoisomers is even larger in the case of [M(L)$_2$(“^{R}XS$_4$”)] complexes. In addition, the stereogenicity of the X and thioether S donors has to be taken into account. However, inspection of molecular models shows that strain-free [M(“^{R}XS$_4$”)] fragments can preferably be expected for the stereoisomers **E**−**H**. In contrast to the six-coordinate [M(L)(“^{R}XS$_4$”)] complexes of which only one exhibits C_s symmetry, there are two C_s stereoisomers of [M(L)$_2$(“^{R}XS$_4$”)] complexes (**E** and **G**).

In all cases, X-ray structure analyses proved [M(L)(“^{R}XS$_4$”)] complexes to have the structures **C** or **D** when NMR spectra had indicated C_s or C_1 symmetry.

Chart 2 and the preceding discussion show that for [M(L)$_2$(“^{R}XS$_4$”)] complexes such an unambiguous distinction of stereoisomers by NMR spectroscopy is no longer possible. Even in the case of [M(L)$_2$(“^{bu}S$_5$”)] complexes for which the tertiary butyl substituents are a very sensitive ^{1}H NMR probe in order to determine whether the complexes are C_1 symmetrical or have a 2-fold element of symmetry, there are two alternative C_s structures possible.

Syntheses of [Mo(CO)$_2$(“^{R}XS$_4$”)] Complexes. [Mo(CO)$_2$(“^{R}XS$_4$”)] complexes generally formed according to eq 1 in CH$_2$Cl$_2$ or THF/MeOH solutions.

$$\begin{array}{l}[\mathrm{Mo(CO)_3(PPh_3)_2(Cl)_2}] + {}^{\text{“R}}\mathrm{XS_4}^{\text{”}2-} \longrightarrow \\ \qquad\qquad \mathrm{R = H;\ X = S,\ NH,\ O} \\ \quad [\mathrm{Mo(CO)_2(\text{“}^{R}XS_4\text{”})}] + 2\,\mathrm{Cl^-} + 2\mathrm{PPh_3} + \mathrm{CO} \\ \mathrm{R = H;\ X = S}\ (\mathbf{1a}),\ \mathrm{NH}\ (\mathbf{2}),\ \mathrm{O}\ (\mathbf{3}) \end{array} \qquad (1)$$

The reactions took place at room temperature or at about 0 °C, CO evolved, and the complexes were obtained as yellow to red-brown species. Depending on the ligand, modifications had to be elaborated in order to isolate the resulting complexes in pure form. Brown [Mo(CO)$_2$(“S$_5$”)] (**1a**), for instance, was obtained by using [Mo(CO)$_3$(PPh$_3$)$_2$(Cl)$_2$] and the salt “S$_5$”−Na$_2$ in THF/MeOH according to eq 1; the analogous dark-yellow [Mo(CO)$_2$(“^{bu}S$_5$”)] (**1b**), however, could only be isolated when [Mo(CO)$_4$(Cl)$_2$] and the neutral “^{bu}S$_5$”−H$_2$ were reacted in the presence of NaHCO$_3$ according to eq 2.

$$\begin{array}{l}[\mathrm{Mo(CO)_4(Cl)_2}] + \text{“}^{bu}\mathrm{S_5}\text{”}-\mathrm{H_2} \xrightarrow[\mathrm{NaHCO_3}]{\mathrm{CH_2Cl_2,\ 0\ ^\circ C}} \\ \qquad [\mathrm{Mo(CO)_2(\text{“}^{bu}S_5\text{”})}] + \text{other products} \quad (2) \\ \qquad\qquad \mathbf{1b}\end{array}$$

Brown [Mo(CO)$_2$(“S$_5$”)] (**1a**), orange [Mo(CO)$_2$(“N$_H$S$_4$”)] (**2**), and red [Mo(CO)$_2$(“OS$_4$”)] (**3**) are moderately soluble; **1b** dissolves excellently in practically all common organic solvents.

X-ray Structure Analysis of [Mo(CO)$_2$(“S$_5$”)]·0.5Et$_2$O (1a·0.5Et$_2$O). Due to the numerous stereoisomers being possible for [M(L)$_2$(“^{R}XS$_4$”)] complexes, a reliable structural reference was of special importance. It was obtained with [Mo(CO)$_2$(“S$_5$”)]·0.5Et$_2$O (**1a**·0.5Et$_2$O), whose molecular structure could be determined by X-ray diffraction and is depicted in Figure 1a. Table 3 lists selected distances and angles.

The seven-coordinate molybdenum center of **1a** is surrounded by five S and two C donors. The [Mo(“S$_5$”)] fragment approximately forms a square pyramid at the base of which the two *cis* CO ligands are bound. The Mo atom lies ca. 37 pm below the plane being defined by the four S(aryl) donors such that the [MoC$_2$S$_5$] core geometry can alternatively be described as capped pseudo-trigonal prismatic, as depicted in Figure 1b. Crystallographically, **1a** has C_1 symmetry only, but in solution, the NMR spectra indicate C_s symmetry. Thus, the [Mo(“S$_5$”)]

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[17] (a) Sellmann, D.; Weiss, R.; Knoch, F.; Ritter, G.; Dengler, J. *Inorg. Chem.* **1990**, *29*, 4107. (b) Sellmann, D.; Keller, J.; Beck, H. P.; Milius, W. *Z. Naturforsch.* **1986**, *41B*, 1551. (c) Sellmann, D.; Keller, J.; Moll, M.; Campana, C. E.; Haase, M. *Inorg. Chim. Acta* **1988**, *141*, 243.

[18] Sellmann, D.; Hofmann, Th.; Knoch, F. *Inorg. Chim. Acta* **1994**, *224*, 61.

[19] Kepert, D. L. *Prog. Inorg. Chem.* **1979**, *25*, 41.

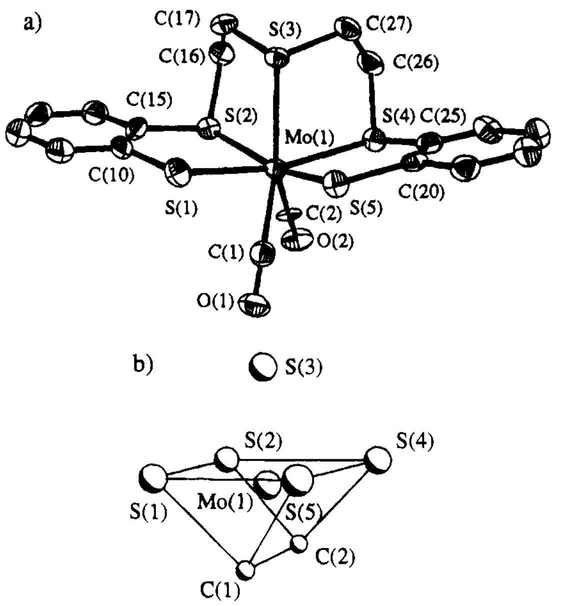


Figure 1. (a) Molecular structure of **1a**·0.5Et$_2$O drawn with 50% probability ellipsoids (H atoms and Et$_2$O solvate omitted); (b) capped pseudo-trigonal prismatic coordination around the Mo center.

Table 3. Selected Distances (pm) and Angles (deg) of [Mo(CO)$_2$(“S$_5$”)]·0.5Et$_2$O (**1a**·0.5Et$_2$O)

Mo(1)−S(1)	251.0(4)	C(1)−Mo(1)−C(2)	69.0(4)
Mo(1)−S(2)	252.2(4)	C(1)−Mo(1)−S(3)	151.2(3)
Mo(1)−S(3)	258.4(4)	C(2)−Mo(1)−S(3)	139.8(2)
Mo(1)−S(4)	253.2(4)	Mo(1)−C(1)−O(1)	177.8(9)
Mo(1)−S(5)	248.2(4)	Mo(1)−C(2)−O(2)	177.8(7)
Mo(1)−C(1)	195.1(8)	S(1)−Mo(1)−S(2)	80.6(1)
Mo(1)−C(2)	198.4(9)	S(2)−Mo(1)−S(4)	105.2(1)

core of **1a** corresponds to the *meso*-form of six-coordinate [ML(“^{R}S$_5$”)] complexes (**C** in Chart 2).

Distances and angles of **1a** show no anomalies and are also found in seven-coordinate Mo complexes of the related “S$_4$”$^{2-}$ ligand such as [Mo(CO)(μ-“S$_4$”)]$_2$,[20] [Mo(CO)$_2$(PMe$_3$) (“S$_4$”)],[17c] or [Mo(NO)(η^2-NH$_2$O)(“S$_4$”)],[21] which exhibit Mo−S(thiolate) and Mo−S(thioether) distances in the ranges of 246−253 pm and 251−259 pm.

IR and NMR Spectra of [Mo(CO)$_2$(“^{R}XS$_4$”)]. The complexes **1**−**3** each show two characteristic and nearly equally strong ν(CO) IR bands in the range of 1950−1850 cm^{-1} in KBr, indicating *cis* coordination of the CO ligands. In solution, the ν(CO) band at lower frequency is occasionally split. The splitting depends on solvent and temperature, indicating nonrigidity or even decoordination of “^{R}XS$_4$” donors of the [Mo(CO)$_2$(“^{R}XS$_4$”)] cores. In the case of **1b**, this is corroborated by the ^{1}H NMR spectrum, which shows two sharp tertiary butyl singlets indicating overall C_s symmetry but only poorly resolved C$_2$H$_4$ multiplets being atypical of *meso*-[M(“^{bu}S$_5$”)] fragments.

The ^{1}H NMR spectra of [Mo(CO)$_2$(“S$_5$”)] (**1a**), [Mo(CO)$_2$(“N$_H$S$_4$”)] (**2**), and [Mo(CO)$_2$ (“OS$_4$”)] (**3**) are very similar to each other. In addition to the C$_2$H$_4$ multiplets, they characteristically exhibit two doublets and two triplets for the aromatic protons, indicating that all three complexes have analogous structures and *meso*-[M(“XS$_4$”)] fragments as found for **1a** by X-ray structure analysis. The ^{1}H NMR spectrum of **2** additionally shows a NH multiplet. C_s symmetry of **1**−**3** in solution is also indicated by the number of signals in their ^{13}C NMR spectra.

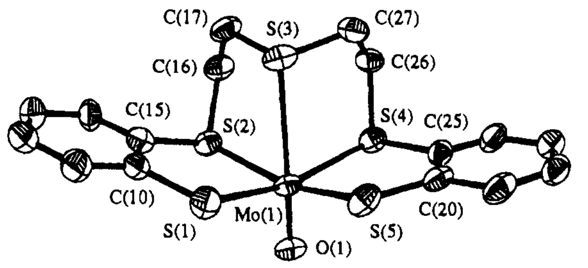


Figure 2. Molecular structure of [Mo(=O)(“S$_5$”)] (**4a**) drawn with 50% probability ellipsoids (H atoms omitted).

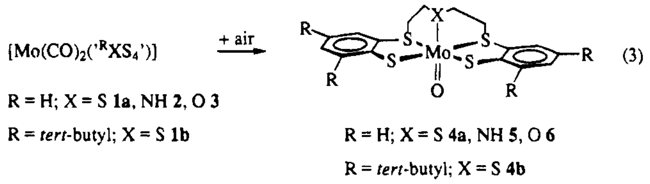
Table 4. Selected Distances (pm) and Angles (deg) of [Mo(=O)(“S$_4$”)] (**4a**)

Mo(1)−S(1)	237.7(2)	O(1)−Mo(1)−S(3)	163.3(2)
Mo(1)−S(2)	246.2(2)	S(2)−Mo(1)−S(3)	75.4(1)
Mo(1)−S(3)	283.5(2)	S(3)−Mo(1)−S(4)	77.4(1)
Mo(1)−S(4)	247.1(2)	S(1)−Mo(1)−S(3)	84.2(1)
Mo(1)−S(5)	238.6(2)	S(3)−Mo(1)−S(5)	86.2(1)
Mo(1)−O(1)	168.8(5)	S(1)−Mo(1)−S(2)	84.2(1)

Table 5. Comparison of Relevant Distances (pm) in [Mo(=O)(“XS$_4$”)] Complexes (X = S (**4a**), O (**6**), NH (**5**))

	4a	6	5
Mo(1)−S(1)	237.7(2)	237.7(2)	238.8(3)
Mo(1)−S(2)	246.2(2)	248.7(2)	247.9(4)
Mo(1)−S(3)/O/N	283.5(2)	251.0(4)	246.7(10)
Mo(1)−S(4)	247.1(2)	249.2(2)	249.0(4)
Mo(1)−S(5)	238.6(2)	238.7(2)	237.8(3)
Mo(1)−O(1)	168.8(5)	168.0(5)	169.4(8)

Oxidation of [Mo(CO)$_2$(“^{R}XS$_4$”)] to [Mo(=O)(“^{R}XS$_4$”)]. Molecular Structure of [Mo(=O)(“S$_5$”)] (4a). In solid state, the [Mo(CO)$_2$(“^{R}XS$_4$”)] complexes are stable toward air for longer periods of time, in solution; however, they are rapidly and quantitatively oxidized by air according to eq 3. The



resulting purple Mo(IV) oxo complexes [Mo(=O)(“S$_5$”)] (**4a**), [Mo(=O)(“^{bu}S$_5$”)] (**4b**), [Mo(=O)(“N$_H$S$_4$”)] (**5**), and [Mo(=O)(“OS$_4$”)] (**6**) are sparingly soluble in common solvents and were identified by spectroscopic means. Complexes **4a**, **5**, and **6** had been obtained previously from the reaction of [Mo(Cl)$_4$(THF)$_2$] with the respective ligands in presence of H$_2$O.[22] Complexes **5** and **6** had been characterized also by X-ray structure analyses such that, in the sequence of closely related **4a**, **5**, and **6**, only the molecular structure of **4a** was missing. It could now be determined, allowing analysis of the influence of the X donor upon the respective structures.

Figure 2 shows the molecular structure of **4a**, Table 4 lists selected distances and angles of **4a**, and Table 5 compares important parameters of **4a**, **5**, and **6**.

The Mo center in **4a** is surrounded pseudooctahedrally by the oxo ligand and five S donors. The four S(aryl) donors approximately form a plane, the Mo center lies 40 pm below this plane, and S(3) and O atoms are *trans* to each other. The structures of **4a**, **5**, and **6** are very similar to each other and exhibit nearly identical Mo−S and Mo=O distances[22] which are not influenced by the *trans* X donor (Table 5). The same

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[20] Sellmann, D.; Weiss, R.; Knoch, F. *Inorg. Chim. Acta* **1990**, *175*, 65.

[21] Sellmann, D.; Seubert, B.; Moll, M.; Knoch, F. *Angew. Chem.* **1988**, *100*, 1221; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1164.

[22] Sellmann, D.; Fünfgelder, S.; Knoch, F. *Z. Naturforsch.* **1992**, *47B*, 51.

holds for corresponding angles. Remarkable, however, is the Mo(1)−S(3) distance (283.5(2) pm) of **4a**. It reflects not only the strong *trans* influence of the oxo ligand but also falls outside the range of Mo−S(thioether) distances which are usually observed for this kind of complexes (268−280 pm).[23] In this respect, the distances of **4a** closely resemble those which were found by EXAFS investigations in Mo oxidases such as xanthine or sulfite oxidase.[24] They exhibit very long Mo−S distances of 284−285 pm, while their Mo=O and other Mo−S distances fall into the usual ranges (~170 and ~248 pm), which were also found in the model complexes [Mo(=O)$_2$(SCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$SCH$_3$][24a] (Mo=O, 169.5 pm, Mo−S(thiolate), 240 pm) and [Mo(=O)$_2$(“S$_4$”)][25] (Mo=O, 171.5 pm; Mo−S-(thiolate), 240 pm). The Mo−S(thioether) distances in these model complexes (269−277 pm) are longer than the Mo−S-(thiolate) distances but still significantly shorter than the long Mo(1)-S(3) distance in **4a**.

Phosphine Derivatives of [Mo(CO)$_2$(“^{R}XS$_4$”)]; X-ray Structure Determination of [Mo(PMe$_3$)$_2$(“S$_2$”)$_2$] (11). One reason for the synthesis of [Mo(CO)$_2$(“^{R}XS$_4$”)] complexes had been the wish to obtain precursors for coordinatively unsaturated species such as [Mo(CO)(“^{R}XS$_4$”)] in order to subsequently bind nitrogenase relevant small molecules. However, selective removal of one CO ligand was not possible. Selectively one CO ligand could only be substituted by phosphines according to eq 4.

$$\begin{array}{ll}
[\mathrm{Mo(CO)_2(“^{R}XS_4”)}] & + \mathrm{PMe_3} \rightarrow \\
\mathrm{R = H;\ X = S\ (\mathbf{1a}),\ NH\ (\mathbf{2})} & \\
\mathrm{R} = \textit{tert}\text{-butyl};\ \mathrm{X = S\ (\mathbf{1b})} & \\
 & [\mathrm{Mo(CO)(PMe_3)(“^{R}XS_4”)}] + \mathrm{CO} \quad (4) \\
 & \mathrm{R = H;\ X = S\ (\mathbf{7}),\ NH\ (\mathbf{8})} \\
 & \mathrm{R} = \textit{tert}\text{-butyl};\ \mathrm{X = S\ (\mathbf{9})}
\end{array}$$

The resulting red [Mo(CO)(PMe$_3$)(“S$_5$”)] (**7**),[9] yellow [Mo-(CO)(PMe$_3$)(“N$_H$S$_4$”)] (**8**), and red-brown [Mo(CO)(PMe$_3$)-(“^{bu}S$_5$”)] (**9**) show one ν(CO) IR band around 1800 cm^{-1} and a characteristic δ(PCH) band of the ligating PMe$_3$ around 950 cm^{-1} in KBr. They are thermolabile and decompose quite rapidly in solution at room temperature. Their ^{1}H NMR spectra indicate that the *meso*-[Mo(“^{R}XS$_4$”)] configuration of the precursor [Mo(CO)$_2$(“^{R}XS$_4$”)] complexes is retained and that only one stereoisomer forms. (The two CO ligands of *meso*-[Mo(CO)$_2$(“^{R}XS$_4$”)] complexes are stereochemically inequivalent such that theoretically two stereoisomers of *meso*-[Mo-(CO)(PMe$_3$)(“^{R}XS$_4$”)] complexes are possible.) For instance, the ^{1}H NMR spectrum of [Mo(CO)(PMe$_3$)(“N$_H$S$_4$”)] (**8**) shows two doublets and two triplets for the aromatic protons being characteristic of *meso*-[Mo(“N$_H$S$_4$”)] fragments and only one doublet for the PMe$_3$ ligand. The ^{1}H NMR spectrum of [Mo-(CO)(PMe$_3$)(“^{bu}S$_5$”)] (**9**) exhibits only two tertiary butyl singlets, two doublets for the aromatic protons, and, in addition, also only one PMe$_3$ doublet.

[Mo(CO)$_2$(“OS$_4$”)] (**3**) behaved slightly different. In order to achieve complete substitution of one CO ligand, an excess of PMe$_3$ had to be applied. Then, however, the red bis-(trimethylphosphine) complex [Mo(CO)(PMe$_3$)$_2$(“OS$_4$”)] (**10**) formed according to eq 5. The IR (KBr) spectrum of **10** also exhibits one ν(CO) band (1815 cm^{-1}), but the signals in the ^{1}H NMR spectrum, which show correct intensities, are broad and poorly resolved.

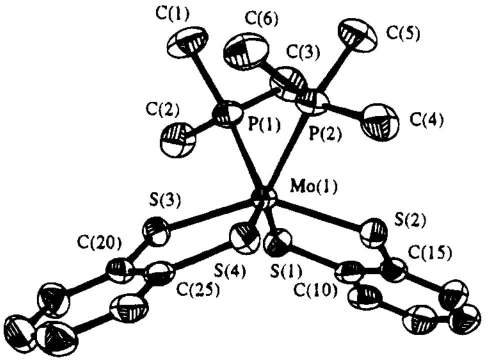
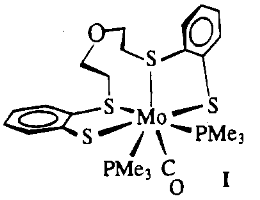


Figure 3. Molecular structure of [Mo(PMe$_3$)$_2$(“S$_2$”)$_2$] (**11**) drawn with 50% probability ellipsoids (H atoms omitted).

$$\begin{array}{ll}
[\mathrm{Mo(CO)_2(“OS_4”)}] + \mathrm{exc.\ PMe_3} \xrightarrow{\mathrm{THF}} & \\
\quad\mathbf{3} & \\
 & [\mathrm{Mo(CO)(PMe_3)_2(“OS_4”)}] + \mathrm{CO} \quad (5) \\
 & \qquad\qquad\mathbf{10}
\end{array}$$

This could be due to decoordination of one “OS$_4$” donor, as indicated by **I**, in order to avoid formation of a 20 valence electron species. The resulting structure can be expected to be highly fluxional. A similar decoordination of the O donor was assumed in [Fe(CO)(PR$_3$)(“OS$_4$”)].[26] Thermal decomposition of [Mo(CO)(PMe$_3$)(“^{R}XS$_4$”)] complexes and the nature of resulting species were investigated more closely with [Mo(CO)(PMe$_3$)(“S$_5$”)] (**7**) and [Mo(CO)(PMe$_3$) (“^{bu}S$_5$”)] (**9**). At room temperature, the ^{1}H NMR spectra of **9** in CD$_2$Cl$_2$ exhibit a rapidly growing signal at δ = 5.43 ppm, indicating the formation of ethylene which results from cleavage of the C$_2$H$_4$ bridges of the “^{bu}S$_5$”$^{2-}$ ligand. An analogous decomposition can be assumed for the parent compound [Mo(CO)(PMe$_3$)-(“S$_5$”)] (**7**), which loses the S(C$_2$H$_4$)$_2$ bridge of its “S$_5$”$^{2-}$ ligand to give [Mo(PMe$_3$)$_2$(“S$_2$”)$_2$] (**11**) when an excess of PMe$_3$ is added to solutions of **7**. Complex **11** had previously been obtained via different routes[27] and could now be characterized by X-ray structure analysis. Figure 3 shows the molecular structure; Table 6 lists selected distances and angles.



I

The Mo center is surrounded by four S and two P donors. Complex **11** exhibits only C_1 symmetry crystallographically, but the coordination geometry can best be described as pseudotrigonal prismatic, and the PMe$_3$ ligands (necessarily) occupy *cis* positions as had previously been concluded from NMR spectra. Complex **11** is closely related to the high-valent CO complex [Mo(CO)(PPh$_3$)(“^{bu}S$_2$”)$_2$].[28] In both complexes, the extraordinarily short Mo−S distances (~236 pm) can be traced back to π donor bonds from the thiolate donors to the Mo(IV) centers. Likewise short Mo−S(thiolate) distances are found in

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(23) Bruce, A.; Corbin, J. L.; Dahlstrom, P. L.; Hyde, J. R.; Minelli, M.; Stiefel, E. I.; Spence, J. T.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 917.

(24) (a) Berg, J. M.; Hodgson, K. O.; Cramer, S. P.; Corbin, J. L.; Elsberry, A.; Pariyadath, N.; Stiefel, E. I. *J. Am. Chem. Soc.* **1979**, *101*, 2774. (b) Cramer, S. P.; Gray, H. B.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1979**, *101*, 2772.

(25) Kaul, B. B.; Enemark, J. H.; Merbs, S. L.; Spence, J. T. *J. Am. Chem. Soc.* **1985**, *107*, 2885.

(26) Sellmann, D.; Kunstmann, H.; Moll, M.; Knoch, F. *Inorg. Chim. Acta* **1988**, *154*, 157.

(27) Sellmann, D.; Reisser, W. *J. Organomet. Chem.* **1985**, *294*, 333.

(28) (a) Sellmann, D.; Grasser, F. *Inorg. Chim. Acta* **1992**, *195*, 25. (b) Sellmann, D.; Grasser, F.; Knoch, F.; Moll, M. *Angew. Chem.* **1991**, *103*, 1346; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1311.

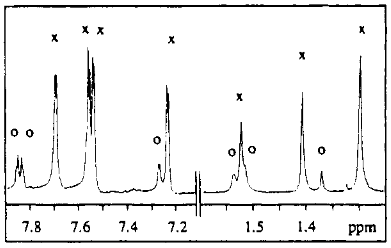


Figure 4. ^{1}H NMR spectrum of [Mo(NO)(“$^{bu}S_5$”)]BF$_4$ (**13**) (in CD$_2$Cl$_2$, 20 °C, × and ○ denote the two sets of observed signals).

Table 6. Selected Distances (pm) and Angles (deg) of [Mo(PMe$_3$)$_2$(“S$_2$”)$_2$] (**11**)

Mo(1)–S(1)	237.4(1)	P(1)–Mo(1)–S(1)	77.4(1)
Mo(1)–S(2)	234.9(1)	P(1)–Mo(1)–S(2)	126.3(1)
Mo(1)–S(3)	235.7(1)	P(2)–Mo(1)–S(2)	79.3(1)
Mo(1)–S(4)	235.3(1)	S(1)–Mo(1)–S(2)	81.3(1)
Mo(1)–P(1)	251.2(1)	S(1)–Mo(1)–S(3)	84.9(1)
Mo(1)–P(2)	251.5(1)	S(2)–Mo(1)–S(3)	145.0(1)

the Mo(IV) oxo complexes [Mo(=O)(“XS$_4$”)] (cf. Table 5). By contrast, the Mo–S(thiolate) distances in [Mo(CO)$_2$(“S$_5$”)] (**1a**) are noticeably longer (cf. Table 3).

NO Complexes with [Mo(“^{R}S$_5$”)] Fragments. While 16 valence electron (VE) complexes [M(L)(“^{R}XS$_4$”)] with L = CO had not been accessible, [Mo(NO)(“S$_5$”)]BF$_4$ (**12**) and [Mo(NO)(“$^{bu}S_5$”)]BF$_4$ (**13**) which at least formally have such an electron configuration, formed in straightforward reactions according to eq 6 and were isolated as red-purple powders. Their

$$[\mathrm{Mo(CO)_2(``RS_5")}] + \mathrm{NOBF_4} \xrightarrow{\mathrm{CH_2Cl_2}}$$

R = H (**1a**), *tert*-butyl (**1b**)

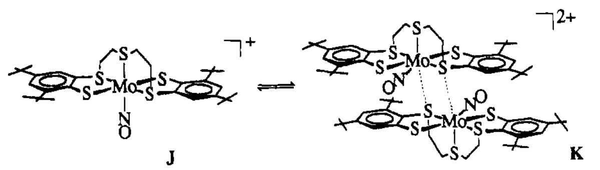
$$[\mathrm{Mo(NO)(``^{R}S_5")]BF_4} + 2\mathrm{CO} \quad (6)$$

R = H (**12**), *tert*-butyl (**13**)

characterization had to rely upon elemental analysis and spectroscopy because all attempts to grow single crystals remained unsuccessful. Complexes **12** and **13** each exhibit one characteristic, strong and sharp ν(NO) IR band in KBr at 1689 cm^{-1} (**12**) and 1701 cm^{-1} (**13**) but yielded NMR spectra which were compatible only with mixtures of at least two species. The ^{1}H NMR spectrum of **12** showed a splitting pattern which distinctly differed from that of typical *meso*-[M(L)(“S$_5$”)] complexes, such as [Fe(CO)(“S$_5$”)]. A likewise atypical ^{1}H NMR spectrum (Figure 4) was observed for **13** in which the tertiary butyl substituents and the splitting pattern of the aromatic protons of the “$^{bu}S_5$”$^{2-}$ ligand provide particularly sensitive probes for the symmetry of the [M(“$^{bu}S_5$”)] fragment.

Figure 4 shows in the tertiary butyl region a set of three signals of intensity 1:1:2 which is accompanied by a second smaller set of three signals and, correspondingly, two differently intensive sets of signals in the aromatic region.

The two sets of signals and their splitting suggest that **13** exists as a mixture of two species in solution, both of which cannot have C_s symmetry. It could not be determined whether **13** is mononuclear or dinuclear, but, with respect to reactivity, **13** behaves like a mononuclear species and generally yields mononuclear derivatives exhibiting C_1 symmetry. Therefore, we assume that the substitution of CO in *meso*-[Mo(CO)$_2$(“$^{bu}S_5$”)] (**1b**) by NO$^+$ leads to rearrangement of the [Mo(“$^{bu}S_5$”)] fragment, yielding C_1 symmetrical [Mo(NO)(“$^{bu}S_5$”)]$^+$ which subsequently and reversibly can dimerize to give centrosymmetrical {[Mo(NO)(“$^{bu}S_5$”)]$_2$}$^{2+}$ as depicted by **J** and **K** in eq 7. Both species **J** and **K** are expected to give rise to one of the observed sets of signals in the ^{1}H NMR spectrum.



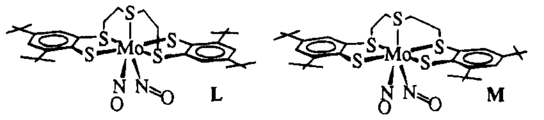
(7)

Attempts to obtain analogous nitrosyl complexes with [Mo(“N$_H$S$_4$”)] and [Mo(“OS$_4$”)] fragments yielded IR evidence for the formation of [Mo(NO)(“N$_H$S$_4$”)]BF$_4$ (ν(NO), 1694 cm^{-1} in KBr) which, however, could not be isolated in pure form.

When [Mo(CO)$_2$(“$^{bu}S_5$”)] (**1b**) was treated with an excess of NO gas instead of NOBF$_4$, the emerald-green dinitrosyl complex [Mo(NO)$_2$(“$^{bu}S_5$”)] (**14**) formed according to eq 8. The

$$\underset{\mathbf{1b}}{[\mathrm{Mo(CO)_2(``^{bu}S_5")}]} + 2\mathrm{NO} \xrightarrow{\mathrm{THF}} \underset{\mathbf{14}}{[\mathrm{Mo(NO)_2(``^{bu}S_5")}]} + 2\mathrm{CO} \quad (8)$$

^{1}H NMR spectrum of **14** shows three sharp singlets for the tertiary butyl residues in the intensity ratio 1:1:2 and, in addition to the C$_2$H$_4$ multiplets, four doublets for the aromatic protons. The number and splitting of these signals indicate C_1 symmetry of **14**, but they do not necessarily imply that the [Mo(“$^{bu}S_5$”)] fragment has become C_1 symmetrical. **14** exhibits two strong ν(NO) IR bands which appear at 1774 and 1672 cm^{-1} in KBr and at 1765 and 1661 cm^{-1} in THF solution indicating *cis* coordination of the NO ligands. The ν(NO) bands lie in the medium range of ν(NO) absorptions of metal nitrosyl complexes (2000–1500 cm^{-1}),[29] such that the [MoNO] units could be linear or bent. If both of them were linear, **14** would be a 20 VE complex and violate the 18 electron rule. Thus, it may be assumed that at least one [MoNO] unit is bent. Then structure **L** having a C_1 symmetrical [Mo(“$^{bu}S_5$”)] fragment would be compatible with the spectroscopic results but also structure **M** if one of the two NO ligands is not located in the mirror plane of the *meso*-[Mo(“$^{bu}S_5$”)] fragment.



L **M**

Addition Products of [Mo(NO)(“$^{bu}S_5$”)]BF$_4$ (13) and [Mo(NO)$_2$(“$^{bu}S_5$”)] (14). The major aim of these investigations was to find [Mo(“$^{bu}S_5$”)] complexes binding one or more nitrogen containing ligands whose intramolecular reaction in the coordination sphere possibly could result in the formation of N$_2$ ligands. As mentioned above, [Mo(NO)(“$^{bu}S_5$”)]BF$_4$ (**13**) behaves like a coordinatively unsaturated 16 VE species with respect to reactivity. It did not react with CO but rapidly added PMe$_3$ according to eq 9.

$$\underset{\mathbf{13}}{[\mathrm{Mo(NO)(``^{bu}S_5")]BF_4}} + \mathrm{PMe_3} \xrightarrow{\mathrm{CH_2Cl_2}} \underset{\mathbf{15}}{[\mathrm{Mo(NO)(PMe_3)(``^{bu}S_5")]BF_4}} \quad (9)$$

The ν(NO) IR band (1676 cm^{-1} in KBr) of resulting red-brown [Mo(NO)(PMe$_3$)(“$^{bu}S_5$”)]BF$_4$ (**15**) is clearly shifted to

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(29) (a) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53. (b) Eisenberg, R.; Meyer, C. D. *Acc. Chem. Res.* **1975**, *8*, 26. (c) Johnson, B. F. G.; McCleverty, J. A. *Prog. Inorg. Chem.* **1966**, *7*, 277. (d) Griffith, W. P. *Adv. Organometal. Chem.* **1968**, *7*, 211. (e) Bottomley, F. *Acc. Chem. Res.* **1978**, *11*, 158.

lower wavenumbers when compared to that of **13** (1701 cm^{-1}) and indicates an increase of electron density at the Mo center. Four singlets for the tertiary butyl groups and four doublets for the aromatic protons in the ^{1}H NMR spectrum prove that **15** has C_1 symmetry. The spectroscopic results further prove that only one species forms that is plausibly explained by the equilibrium of eq 7.

Monitored by IR spectroscopy, rapid reactions were also observed with σ ligands such as N_2H_4, NH_3, pyridine, and azide ions. However, the resulting complexes were labile, and only red-brown [Mo(NO)(N$_3$)(“^{bu}S$_5$”)] (**16**) could be isolated and characterized. Complex **16** formed according to eq 10.

$$\underset{\mathbf{13}}{[\mathrm{Mo(NO)}(\text{“}^{\mathrm{bu}}\mathrm{S_5}\text{”})]\mathrm{BF_4}} + \mathrm{NEt_4N_3} \xrightarrow{\text{acetone}} \underset{\mathbf{16}}{[\mathrm{Mo(NO)(N_3)}(\text{“}^{\mathrm{bu}}\mathrm{S_5}\text{”})]} + \mathrm{NEt_4BF_4} \quad (10)$$

The IR (KBr) spectrum of **16** shows characteristic ν(NO) and $\nu(N_3)$ bands at 1673 and 2051 cm^{-1}. The ^{1}H NMR spectra are temperature dependent. At room temperature, only two singlets for the tertiary butyl groups and only one singlet for the aromatic protons are observed, at −50 °C; however, the tertiary butyl groups give rise to three singlets of ratio 2:1:1, and the aromatic protons yield two superimposed sets of four doublets. This indicates that **16** is either highly fluxional or can easily isomerize, possibly *via* decoordination and recoordination of donors or ligands.

In contrast to expectations, azide ions were added also by [Mo(NO)$_2$(“^{bu}S$_5$”)] (**14**) which has at least an 18 valence electron configuration. According to eq 11, red-brown (NEt$_4$)[Mo(NO)$_2$(N$_3$)(“^{bu}S$_5$”)] (**17**) formed.

$$\underset{\mathbf{14}}{[\mathrm{Mo(NO)_2}(\text{“}^{\mathrm{bu}}\mathrm{S_5}\text{”})]} + \mathrm{NEt_4N_3} \xrightarrow{\text{acetone}} \underset{\mathbf{17}}{(\mathrm{NEt_4})[\mathrm{Mo(NO)_2(N_3)}(\text{“}^{\mathrm{bu}}\mathrm{S_5}\text{”})]} \quad (11)$$

Complex **17** dissolves in THF without any noticeable dissociation of the N_3^- ligand but slowly splits off NEt_4N_3 in CH_2Cl_2, acetone, or toluene, regenerating **14**. In the IR (KBr) spectrum, **17** exhibits a characteristic $\nu(N_3)$ (2063 cm^{-1}) and two ν(NO) bands (1743 and 1636 cm^{-1}) which are shifted to lower frequencies when compared with the ν(NO) bands of **14**.

Also **17** yields ^{1}H NMR spectra which are temperature dependent and very similar to the spectra of **16**. For instance, two singlets for the tertiary butyl residues indicate overall C_s symmetry at room temperature, but they are split into four singlets at −40 °C which are compatible only with a C_1 symmetrical species.

All attempts to achieve the formation of N_2 complexes from either **13**, **14**, **16**, or **17** remained unsuccessful so far. Thermolysis of [Mo(NO)(N$_3$)(“^{bu}S$_5$”)] (**16**) or (NEt$_4$)[Mo(NO)$_2$(N$_3$)(“^{bu}S$_5$”)] (**17**) in solid state or in solution yielded mixtures of products which contained nitrogen but could not be characterized more closely. $\nu(N_2)$ IR bands of intermediates such as [Mo(N$_2$)(“^{bu}S$_5$”)]$^+$ were not observed. Complexes **16** and **17** proved also relatively stable toward oxidation by O_2 or N_2O. With HBF_4 or $NOBF_4$, **16** reacted according to eqs 12 and 13.

Formation of HN_3 and N_2O was monitored by IR spectroscopy ($\nu(HN_3)$, 2137 cm^{-1}; $\nu(N_2O)$, 2220 cm^{-1}. (NEt$_4$)[Mo(NO)$_2$(N$_3$)(“^{bu}S$_5$”)] (**17**) proved inert toward O_2, PbO_2, and gaseous NO, its oxidation by I_2 or H_2O_2 gave mixtures containing **13**, **14**, and **16** among other products, and the reaction with $NOBF_4$ yielded **13**.

Table 7. ν(CO) and ν(NO) Frequencies of [Mo(“^{R}XS$_4$”)] Complexes (in KBr)

complex	ν(CO) or ν(NO) (cm^{-1})
[Mo(CO)$_2$(“S$_5$”)] (**1a**)	1952, 1879
[Mo(CO)$_2$(“^{bu}S$_5$”)] (**1b**)	1953, 1873
[Mo(CO)$_2$(“N$_H$S$_4$”)] (**2**)	1955, 1858
[Mo(CO)$_2$(“OS$_4$”)] (**3**)	1943, 1886
[Mo(CO)(PMe$_3$)(“S$_5$”)] (**7**)	1802
[Mo(CO)(PMe$_3$)(“^{bu}S$_5$”)] (**9**)	1796
[Mo(CO)(PMe$_3$)(“N$_H$S$_4$”)] (**8**)	1807
[Mo(CO)(PMe$_3$)$_2$(“OS$_4$”)] (**10**)	1815
[Mo(NO)(“S$_5$”)]BF$_4$ (**12**)	1689
[Mo(NO)(“^{bu}S$_5$”)]BF$_4$ (**13**)	1701
[Mo(NO)(PMe$_3$)(“^{bu}S$_5$”)]BF$_4$ (**15**)	1676
[Mo(NO)(N$_3$)(“^{bu}S$_5$”)] (**16**)	1673
[Mo(NO)$_2$(“^{bu}S$_5$”)] (**14**)	1774, 1672
(NEt$_4$)[Mo(NO)$_2$(N$_3$)(“^{bu}S$_5$”)] (**17**)	1743, 1636

$$\underset{\mathbf{16}}{[\mathrm{Mo(NO)(N_3)}(\text{“}^{\mathrm{bu}}\mathrm{S_5}\text{”})]} + \mathrm{HBF_4} \xrightarrow{\text{THF}} \underset{\mathbf{13}}{[\mathrm{Mo(NO)}(\text{“}^{\mathrm{bu}}\mathrm{S_5}\text{”})]\mathrm{BF_4}} + \mathrm{HN_3} \quad (12)$$

$$\underset{\mathbf{16}}{[\mathrm{Mo(NO)(N_3)}(\text{“}^{\mathrm{bu}}\mathrm{S_5}\text{”})]} + \mathrm{NOBF_4} \xrightarrow{\text{THF}} \underset{\mathbf{13}}{[\mathrm{Mo(NO)}(\text{“}^{\mathrm{bu}}\mathrm{S_5}\text{”})]\mathrm{BF_4}} + \mathrm{N_2O} + \mathrm{N_2} \quad (13)$$

Discussion of ν(CO) and ν(NO) Frequencies. The ν(CO) and ν(NO) bands in the vibrational spectra of the complexes described here allow discussion of influences of substituents in the aromatic rings or of changes of donors in the metal coordination sphere upon the electron density at the metal center (Table 7).

Comparison of **1a** and **1b** shows that tertiary butyl substituents do not influence significantly the electron density at the Mo center. Likewise, “S$_5$”, “N$_H$S$_4$” and “OS$_4$” complexes demonstrate that exchanging S for NH or O donors has little or no influence either. This allows two alternative conclusions. Either the S thioether donor in **1a** acts preferably as a σ donor only or the domination of the coordination sphere by sulfur donors cancels effects caused by substituting σ donors like NH or O for a thioether sulfur donor which is a potential π acceptor. The ν(CO) frequencies of [Mo(CO)(PMe$_3$)(“XS$_4$”)] behave likewise. Substitution of one CO by PMe$_3$ strongly influences the electron density causing the frequency of the remaining CO to decrease by ca. 100 cm^{-1}, but “S$_5$”, “N$_H$S$_4$”, and “OS$_4$” complexes show approximately identical ν(CO) frequencies.

Analogous effects are observed with the nitrosyl complexes, for instance, when [Mo(NO)(“^{bu}S$_5$”)]BF$_4$ (**13**) coordinates additional PMe$_3$ or N_3^- ligands, but in these cases the relative lowering of the ν(NO) bands is much smaller than that of the ν(CO) bands and amounts to about 25 cm^{-1} only. This may be due to the fact that **13** possibly contains dinuclear cations with seven-coordinate Mo centers (cf. eq 7) such that the addition reactions of **13** really represent substitutions of bridging thiolate donors by PMe$_3$ or N_3^-. A dinuclear structure of the cation and resulting seven-coordination of Mo could also explain the ν(NO) frequency of **13** at 1701 cm^{-1}, which is remarkably low for a cationic nitrosyl complex. It is considerably lower than the ν(NO) frequencies of mononuclear [Fe(NO)(“^{bu}S$_5$”)]$^+$ (1870 cm^{-1})[8,30] or [Ru(NO)(“^{bu}S$_5$”)]$^+$ (1852 cm^{-1})[31] which have 18 valence electron configurations. Even if, according to the

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(30) (a) Sellmann, D.; Höhn, K.; Moll, M. *Z. Naturforsch.* **1991**, *46B*, 665. (b) Sellmann, D.; Höhn, K.; Moll, M. *Z. Naturforsch.* **1991**, *46B*, 673.

molecular orbital scheme proposed by Enemark and Feltham[32] and others,[33] the ν(NO) frequency of six-coordinate mononitrosyl complexes is primarily determined by the relative metal and π^*(NO) character of the degenerate (2e) HOMO's, the low ν(NO) of **13** is thus a further strong hint for the dinuclearity of the cation in **13** in solid state.

Summary and Discussion. In quest of molybdenum complexes of higher oxidation states than zero which contain predominantly sulfur donors and no abiological ligands like phosphines and bind small molecules relevant to nitrogenase, we have investigated the chemistry of [Mo("^{R}XS$_4$")] complexes. X-ray structure determination of [Mo(CO)$_2$("S$_5$")] (**1a**) provided a structural reference for seven-coordinate complexes of the type [Mo(L)$_2$("^{R}XS$_4$")] (R = *tert*-butyl, X = S; R = H, X = S, O, NH) such as [Mo(CO)$_2$("^{bu}S$_5$")] (**1b**), [Mo(CO)$_2$("N$_H$S$_4$")] (**2**), [Mo(CO)$_2$("OS$_4$")] (**3**), [Mo(CO)(PMe$_3$)("^{bu}S$_5$")] (**9**), [Mo(CO)(PMe$_3$)("N$_H$S$_4$")] (**8**), and [Mo(CO)(PMe$_3$)("S$_5$")] (**7**). The ν(CO) frequencies of these complexes indicated that tertiary butyl substituents or the exchange of S for NH or O donors do not significantly influence the electron density at the Mo centers, although the corresponding complexes show different reactivities. This is evidenced, for instance, by the aerial oxidation becoming increasingly rapid in the series **2** < **1a** ≈ **1b** < **3**, yielding the six-coordinate C_s symmetrical Mo(IV) oxo complexes [Mo(=O)("S$_5$")] (**4a**), [Mo(=O)("^{bu}S$_5$")] (**4b**), [Mo(=O)("N$_H$S$_4$")] (**5**), and [Mo(=O)("OS$_4$")] (**6**). The corresponding molecular parameters of **4a**, **5**, and **6** are again nearly identical. CO substitution in **1a**, **1b**, and **2** by PMe$_3$ yielded the phosphine derivatives [Mo(CO)(PMe$_3$) ("^{bu}S$_5$")] (**9**), [Mo(CO)(PMe$_3$)("N$_H$S$_4$")] (**8**), and [Mo(CO)(PMe$_3$)("S$_5$")] (**7**), which are thermolabile and decompose in solution at room temperature. Decomposition of **9** could be monitored by ^{1}H NMR spectroscopy, indicating the formation of ethylene which results from cleavage of the C$_2$H$_4$ bridges of the "^{bu}S$_5$"$^{2-}$ ligand. Decomposition of [Mo(CO)(PMe$_3$)("S$_5$")] (**7**) in the presence of PMe$_3$ also results in loss of the C$_2$H$_4$ bridges, including one S donor, and yielded the Mo(IV) complex [Mo(PMe$_3$)$_2$("S$_2$")$_2$] (**11**), the structure of which was determined crystallographically. In contrast, the C$_2$H$_4$ bridges of the "OS$_4$"$^{2-}$ ligand in **3** were not cleaved when **3** was treated with an excess of PMe$_3$. Rather, presumably the O donor decoordinated and [Mo(CO)(PMe$_3$)$_2$("OS$_4$")] (**10**) formed.

The [Mo("^{R}S$_5$")] fragment is able to coordinate small N containing ligands such as NO$^+$ or NO, yielding [Mo(NO)("^{R}S$_5$")]BF$_4$ (R = H, **12**; R = *tert*-butyl, **13**) and [Mo(NO)$_2$("^{bu}S$_5$")] (**14**). These complexes further add PMe$_3$ or N$_3^-$, resulting in [Mo(NO)(PMe$_3$)("^{bu}S$_5$")]BF$_4$ (**15**), [Mo(NO)(N$_3$)("^{bu}S$_5$")] (**16**), or even (NEt$_4$)[Mo(NO)$_2$(N$_3$)("^{bu}S$_5$")] (**17**). Although **16** and **17** contain ligands which theoretically can symproportionate in order to yield N$_2$, the formation of N$_2$ complexes through either thermolysis or oxidation of **16** and **17** could not be observed. So far, none of the nitrosyl complexes could be characterized by X-ray structure determination, but NMR and IR spectra and reactivity suggest that **13** contains dinuclear cations which reversibly dissociate into mononuclear C_1 symmetrical [Mo(NO)("^{bu}S$_5$")]$^+$ ions. As can be concluded from NMR spectra, the addition products of **13**, **15**, and **16**, and the dinitrosyl complexes **14** and **17**, likewise exhibit C_1 symmetry.

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Supporting Information Available: Listings of crystallographic data and data collection parameters, all bond lengths and bond angles, anisotropic thermal parameters, and fractional coordinates of hydrogen atoms (8 pages). Ordering information is given on any current masthead page. Further details of the X-ray structure analyses have been deposited and can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen mbH, D-76344 Eggenstein-Leopoldshafen, by citing the depository numbers, CSD 401699 [Mo(CO)$_2$("S$_5$")]·0.5Et$_2$O ((**1a**)·0.5Et$_2$O), CSD 401700 [Mo(=O)("S$_5$")] (**4a**), and CSD 401698 [Mo(PMe$_3$)$_2$("S$_2$")$_2$] (**11**), the authors, and the reference.

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