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Transition-Metal Complexes with Sulfur Ligands. 37.[†] Iron, Molybdenum, and Ruthenium Complexes with Pentadentate OS_4 and N_HS_4 Ligands Combining Thiolato, Thioether, and Ether or Amine Donor Functions: Synthesis, Structures, and Reactivity of CO, NO, PMe_3, and N_2H_4 Derivatives

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In order to investigate specific properties of transition-metal sulfur complexes, $[Fe(CO)(XS_4)]$ compounds (X = O, NH) with the novel pentadentate ligands OS_4^{2-} = dianion of bis(2-((2-mercaptophenyl)thio)ethyl) ether and $N_HS_4^{2-}$ = dianion of bis(2-((2-mercaptophenyl)thio)ethyl)amine were synthesized by template alkylation of *cis*-$Na_2[Fe(CO)_2(S_2C_6H_4)_2]$ with bis(2-bromoethyl) ether and bis(2-bromoethyl)amine, respectively. $[Fe(CO)(OS_4)]$ crystallizes in the monoclinic space group $P2_1/c$ with $Z = 8$, $a = 2260.8$ (5) pm, $b = 2025.6$ (4) pm, $c = 794.7$ (1) pm, $\beta = 93.25$ (1)°, $R = 0.059$, and $R_w = 0.059$; $[Fe(CO)(N_HS_4)]$ crystallizes in the monoclinic space group $P2_1/c$ with $Z = 8$, $a = 2244.7$ (6), pm, $b = 2022.4$ (5) pm, $c = 805.2$ (2) pm, $\beta = 92.45$ (2)°, $R = 0.066$, and $R_w = 0.048$. In both complexes, the Fe centers are coordinated pseudooctahedrally by four S atoms in a plane and the C and X atoms occupy the trans positions; the $X(C_2H_4)_2$ entities bridge two trans S atoms of the $S_2C_6H_4$ units, thus generating the "trans" form of $[M(L)(XS_4)]$ complexes. This is unlike the meso form that has been found for the analogous $[Fe(CO)(S_5)]$ (S_5^{2-} = dianion of bis(2-((2-mercaptophenyl)thio)ethyl) sulfide), in which two cis S atoms of the $S_2C_6H_4$ units are connected. The X donors influence the length and reactivity of the trans Fe–CO bonds, making $[Fe(CO)(OS_4)]$ the most reactive species with respect to the substitution of CO, despite the fact that it has the shortest Fe–CO bond. A mechanism is proposed for the formation of meso and "trans" complexes from *cis*-$[Fe(CO)_2(S_2C_6H_4)_2]^{2-}$ based on an equilibrium between trigonal-bipyramidal and square-pyramidal structures of a five-coordinate intermediate. The discussion of the ^{13}C NMR spectra points out that a $[Fe(CO)(XS_4)]$ complex showing more than nine ^{13}C signals cannot have the meso structure. Reacting $[Fe(CO)(N_HS_4)]$ with L = PMe_3, N_2H_4 yields $[Fe(L)(N_HS_4)]$, reacting $[Fe(CO)(OS_4)]$ with the same reagents gives labile $[Fe(PMe_3)(OS_4)]$ but no hydrazine complex; in the latter case only $[Fe(OS_4)]_n$ is obtained. The NH function renders possible the synthesis of alkylation derivatives of the N_HS_4 ligand; the reaction of $[Fe(CO)(N_HS_4)]$ with $LiN(SiMe_3)_2$ and subsequently with MeI gives $[Fe(CO)(N_{Me}S_4)]$. The free ligands N_HS_4-H_2 and OS_4-H_2 were obtained by acid hydrolysis of $[Fe(CO)(XS_4)]$. The former, however, is better synthesized by direct reaction of 1,2-benzenedithiol, sodium methoxide, and bis(2-bromoethyl)amine in the ratio of 2:2:1. The free ligands react with $[MoCl_3(NO)(CH_3CN)_2]$, yielding $[Mo(Cl)(NO)(XS_4)]$, X = O, NH; the reaction of the lithium salt $Li_2[OS_4]$ with $[MoCl_2(CO)_3(PPh_3)_2]$ or $[RuCl_2(PPh_3)_2]$ yields $[Mo(CO)_2(OS_4)]$ or $[Ru(PPh_3)(OS_4)]$, respectively.

Introduction

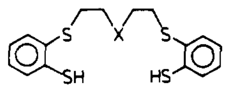
Transition metals in a coordination sphere of sulfur ligands form the active centers of many oxidoreductases, e.g. hydrogenase, xanthinoxidase, and nitrogenase;[1b] in some cases, e.g. nitrogenase, recent EXAFS data indicate the additional presence of nitrogen and oxygen atoms in the coordination sphere of the metal atoms.[2] The tacit understanding that the sulfur donors influence characteristically the reactivity of the metal centers, and thus the function of the enzymes, explains the current interest in transition-metal complexes with all kinds of sulfur ligands.[1b]

The search for specific properties of transition-metal sulfur complexes, as well as their designed modeling, is the objective of our investigations of metal complexes with thiolato as well as thioether ligands. Such specific properties that are basically due to the sulfur ligands may be found in the stabilization of uncommon coordination numbers and electron configurations as such as that of the Cr^0 center in the $[Cr(CO)_3(S_2C_6H_4)]^{2-}$ ion,[3] in the stabilization of unstable molecules such as diazene, NH=NH, in $[(\mu\text{-}N_2H_2)(Ru(dttd)(PPh_3))_2]$ ($dttd^{2-}$ = dianion of 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane),[4] or in the activation of NO toward nucleophilic attack by phosphines in $[Mo(NO)_2(dttd)]$.[5] Also, the drastically different substitution behavior of $[Ru(dttd)(PPh_3)_2]$ and $[Ru(bmae)(PPh_3)_2]$ ($bmae^{2-}$ = dianion of 1,2-bis(2-mercaptoanilino)ethane) can be traced back to the sulfur ligands. While in the former case, with a RuS_4 core, one PPh_3 ligand is substitutionally labile, in the latter case, with a RuS_2N_2 core, both PPh_3 ligands are inert.[6]

In order to achieve an even higher degree of sulfur ligation of hexacoordinate metal centers and to rule out completely any interference of phosphine ligands upon substitution, we synthesized complexes of the type $[M(L)(S_5)]$ (M = Fe, Ru; L = e.g. CO, NO^+, PMe_3; S_5^{2-} = dianion of bis(2-((2-mercaptophenyl)thio)ethyl) sulfide) (Figure 1). These complexes have MS_5 cores, and usually they form several isomers, which have to be separated and often render unambiguous spectroscopic characterization difficult.[7] Examples of the isomers I and II were characterized by X-ray structure analyses.

I and II differ mainly in the cis or trans connection of the $S_2C_6H_4$ entities by $S(C_2H_4)_2$ bridges. I contains a mirror plane and represents the meso form of all possible isomers; II possesses neither a mirror plane nor any other symmetry element. In the only invertomer (with respect to the S centers) which is free of steric strain, the C_2H_4 bridges are arranged asymmetrically; for the sake of simplicity and differentiation we termed the isomer II the "trans" form. In both isomers, the thioether S atom of the $S(C_2H_4)_2$ bridge is always found trans to the coligand L.

Anticipating that the replacement of this thioether S atom by O or NH donor atoms might change the properties of the metal center with respect to the M–L bond, we tried to synthesize corresponding compounds, leading to novel ligands of the type



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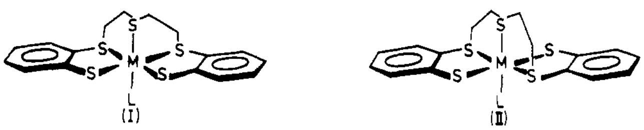

Figure 1. Meso (I) and "trans" forms (II) of $[ML(S_5)]$.

Table I. Summary of Crystallographic Data

compd	$[Fe(CO)(OS_4)]$	$[Fe(CO)(N_HS_4)]$
formula	$C_{17}H_{16}FeO_2S_4$	$C_{17}H_{17}FeNOS_4$
M_r	436.38	435.41
space group	$P2_1/c$	$P2_1/c$
cell dimens		
A, pm	2260.8 (5)	2244.7 (6)
b, pm	2025.6 (4)	2022.4 (5)
c, pm	794.7 (1)	805.2 (2)
β, deg	93.25 (1)	92.45 (2)
molecules/unit cell	8	8
cell vol, pm^3	3633 (2) × 10^6	3652 (2) × 10^6
d_{calcd}, g/cm^3	1.60	1.58
radiation wavelength, pm	71.073	71.073
temp. of meast, K	293	293
μ, cm^{-1}	12.4	12.3
R	0.059	0.066
R_w	0.059	0.048

For X = O, OS_4-H_2 = bis(2-((2-mercaptophenyl)thio)ethyl) ether; for X = NH, N_HS_4-H_2 = bis(2-((2-mercaptophenyl)thio)ethyl)amine; for X = NCH_3, $N_{Me}S_4$-H_2 = bis(2-((2-mercaptophenyl)thio)ethyl)methylamine. Fe, Ru, and Mo complexes thereof with CO, PMe_3, PPh_3, N_2H_4, and NO coligands will be reported.

Experimental Section

General Methods. All reactions were carried out under nitrogen by using the Schlenk technique at room temperature, if not noted otherwise; they were monitored routinely by IR spectroscopy. Solvents were dried and distilled under nitrogen before use. IR spectra (CaF_2 cuvettes or KBr disks) were recorded on a Zeiss IMR 16 infrared spectrometer; the solvent bands were compensated. Mass spectra were recorded on a Varian MAT 212 mass spectrometer and NMR spectra on JEOL PMS 60 (^{1}H) and JEOL FT-JNM-GX 270 spectrometers (^{1}H, ^{13}C). N_2H_4 was obtained by distilling N_2H_5OH (obtained from Fluka) from KOH at reduced pressure. $FeCl_2·4H_2O$, MeI, NaOMe, and *n*-butyllithium were purchased from Merck. *o*-Benzenedithiol,[8] bis(2-bromoethyl) ether,[9] bis(2-bromoethyl)amine hydrobromide,[10] PMe_3,[11] $LiN(SiMe_3)_2$,[12] $[MoCl_3(NO)(CH_3CN)_2]$,[13] $[MoCl_2(CO)_3(PPh_3)_2]$,[14] and $[RuCl_2(PPh_3)_3]$[15] were prepared by literature methods.

Caution! Bis(2-bromoethyl) ether and bis(2-bromoethyl)amine are mustard gas analogous and must be handled with care!

X-ray Data Collection, Structure Determination, and Refinement for [Fe(CO)(XS$_4$)] (X = O, NH). Single crystals were grown by covering CH_2Cl_2 solutions with a layer of diethyl ether. Single crystals of $[Fe(CO)(OS_4)]$ (0.60 × 0.20 × 0.04 mm^3) and $[Fe(CO)(N_HS_4)]$ (0.50 × 0.30 × 0.20 mm^3) were sealed under N_2 in a glass capillary. The structures were solved by direct methods; the non-hydrogen atoms were refined anisotropically, and the phenyl H atoms were placed at calculated positions and refined as rigid groups. The H atoms of the methylene groups were placed in ideal tetrahedral positions and rotated around their central C atom during refinement; the isotropic H atoms were refined with common temperature factors. Table I summarizes the data and information relating to data collection and structure refinement; the fractional atomic coordinates are given in Table II.

Preparation of Compounds. The synthesis of $[Fe(CO)_2(S_2C_6H_4)_2]^{2-}$ given in the literature[16] was slightly modified. To 2.83 g (2.36 mL, 20 mmol) of *o*-benzenedithiol in 30 mL of methanol are added 2.16 g (40 mmol) of NaOMe and 1.98 g (10 mmol) of $FeCl_2·4H_2O$. after the solution is stirred for 10 min, CO is bubbled through it for 2 h, and 70 mL of methanol is added, yielding a solution of 10 mmol of $[Fe(CO)_2(S_2C_6H_4)_2]^{2-}$.

(a) [Fe(CO)(OS$_4$)]. To a red solution of 10 mmol of $[Fe(CO)_2(S_2C_6H_4)_2]^{2-}$ in 100 mL of methanol is added 2.32 g (10 mmol) of bis(2-bromoethyl) ether in 20 mL of methanol, and the mixture is stirred for 15 h. The precipitating violet microcrystals are collected, washed with 3 × 15 mL of methanol and 10 mL of diethyl ether, and dried under vacuum. They are redissolved in CH_2Cl_2, and the solution is covered with a layer of methanol. Deep violet crystals form, which are collected and dried under high vacuum for 10 h; yield 2.0 g (45%). Anal. Calcd for $C_{17}H_{16}FeO_2S_4$ (M_r = 436.4): C, 46.79; H, 3.69. Found: C, 46.81; H, 3.71.

(b) [Fe(CO)(N$_H$S$_4$)]. A solution of 3.1 g (10 mmol) of bis(2-bromoethyl)amine hydrobromide and 540 mg (10 mmol) of NaOMe in 40 mL of methanol is added dropwise to the red solution of 10 mmol of $[Fe(CO)_2(S_2C_6H_4)_2]^{2-}$ in 100 mL of methanol. The mixture is stirred for 4 h, and a red precipitate forms. It is collected, washed with 3 × 10 mL of methanol, and dried under vacuum. Recrystallization from a CH_2Cl_2 solution, which is covered with a layer of methanol, yields dark red crystals after 2 days; yield 2.5 g (57%). Anal. Calcd for $C_{17}H_{17}FeNOS_4$ (M_r = 435.4): C, 46.89; H, 3.94; N, 3.22. Found: C, 46.99; H, 3.96; N, 3.23.

(c) [Fe(OS$_4$)]$_n$. A violet solution of 450 mg (1 mmol) of $[Fe(CO)(OS_4)]$ in 40 mL of CH_2Cl_2 is refluxed for 1.5 h, yielding a yellow precipitate. This is collected, washed with 3 × 8 mL of methanol, and dried under high vacuum for 10 h; yield 300 mg (70%). The precipitate occludes CH_2Cl_2 and is analyzed as $[Fe(OS_4)]_5·2CH_2Cl_2$. Anal. Calcd for $C_{82}Cl_4H_{84}Fe_5O_5S_{20}$ (M_r = 2350.4): C, 45.14; H, 3.87. Found: C, 44.99; H, 3.83.

(d) [Fe(PMe$_3$)(OS$_4$)]. A violet solution of 200 mg (0.49 mmol) of $[Fe(CO)(OS_4)]$ in 25 mL of THF is refluxed with 0.4 mL (4 mmol) of PMe_3 for 15 min. The green reaction mixture is filtered over filter pulp while hot and cooled slowly to −20 °C. After 12 h, the precipitating green microcrystals are collected, washed with diethyl ether, and dried under high vacuum for 8 h; yield 100 mg (42%). Anal. Calcd for $C_{19}H_{25}FeOPS_4$ (M_r = 484.5): C, 47.10; H, 5.20. Found: C, 47.06; H, 5.24.

(e) [Fe(PMe$_3$)(N$_H$S$_4$)]. A red solution of 400 mg (0.92 mmol) of $[Fe(CO)(N_HS_4)]$ in 60 mL of THF is refluxed with 2 mL (20 mmol) of PMe_3 for 5 h. The green reaction mixture is concentrated in volume to one-third, filtered over SiO_2, and covered with a layer of pentane. The green precipitate is collected and recrystallized from THF/pentane, yielding green microcrystals, which are collected and dried under high vacuum for 8 h; yield 200 mg (45%). Anal. Calcd for $C_{19}H_{26}FeNPS_4$ (M_r = 483.1): C, 47.24; H, 5.42; N, 2.90. Found: C, 47.15; H, 5.53; N, 2.57.

(f) [Fe(N$_2$H$_4$)(N$_H$S$_4$)]. A red solution of 300 mg (0.69 mmol) of $[Fe(CO)(N_HS_4)]$ in 30 mL of THF is refluxed with 0.5 mL of N_2H_4 for 24 h. The precipitating brown microcrystals are collected, washed with 5 mL of methanol, and dried under high vacuum for 8 h; yield 60 mg (20%). Anal. Calcd for $C_{16}H_{21}FeN_3S_4$ (M_r = 439.8): C, 43.69; H, 4.99; N, 9.56. Found: C, 42.82; H, 4.77; N, 9.52.

(g) [Fe(CO)(N$_{Me}$S$_4$)]. To a red solution of 845 mg (1.9 mmol) of $[Fe(CO)(N_HS_4)]$ in 100 mL of THF is added solid $LiN(SiMe_3)_2$ until the ν_{CO} band in the solution IR spectrum shifts from 1960 to 1940 cm^{-1} (about 1032 mg (6.2 mmol) $LiN(SiMe_3)_2$ is needed). To this solution, after it has changed to green, is added 1.15 mL (265 mg, 1.9 mmol) of MeI, restoring the red color. The solution is evaporated to dryness; the residue is redissolved in 30 mL of CH_2Cl_2 and filtered over 10 g of SiO_2, which is washed with 10 mL of CH_2Cl_2. The combined CH_2Cl_2 solutions are covered with a layer of 40 mL of diethyl ether. Within 2 days copper-colored needles separate out, which are collected and dried under high vacuum for 8 h; yield 250 mg (29%). Anal. Calcd for $C_{18}H_{19}FeNOS_4$ (M_r = 494.4): C, 48.10; H, 4.26; N, 3.12. Found: C, 48.36; H, 4.29; N, 2.88.

(h) OS$_4$-H$_2$. Method 1: Hydrolysis of [Fe(CO)(OS$_4$)]. A violet solution of 2.88 g (6.6 mmol) of $[Fe(CO)(OS_4)]$ in 150 mL of THF is refluxed with 2.7 mL of concentrated aqueous HCl for 15 min, yielding a clear yellow solution. It is evaporated to dryness, and the residue is extracted with 5 × 20 mL of diethyl ether. The combined extracts are dried over Na_2SO_4, filtered, and evaporated to dryness. The viscous residue is extracted with 4 × 20 mL of CCl_4. The CCl_4 extracts are filtered over SiO_2 and evaporated to dryness, yielding OS_4-H_2 as a colorless oil, yield 1.5 g (46%). Anal. Calcd for $C_{16}H_{18}OS_4$ (M_r = 354.5):

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Table II. Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($pm^2 \times 10^{-1}$) of the Non-Hydrogen Atoms

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
				(a) [Fe(CO)(OS_4)]					
Fe(1)	8730 (1)	5053 (1)	2376 (1)	30 (1)	Fe(2)	6234 (1)	5041 (1)	−2144 (1)	31 (1)
S(1)	9425 (1)	5838 (1)	1824 (3)	39 (1)	S(5)	5532 (1)	5809 (1)	−2944 (3)	42 (1)
S(2)	8126 (1)	5496 (1)	341 (3)	37 (1)	S(6)	6866 (1)	5558 (1)	−3744 (3)	42 (1)
S(3)	8028 (1)	4278 (1)	2948 (3)	39 (1)	S(7)	6949 (1)	4281 (1)	−1381 (3)	43 (1)
S(4)	9397 (1)	4495 (1)	4019 (3)	40 (1)	S(8)	5560 (1)	4421 (1)	−919 (3)	43 (1)
C(15)	8440 (4)	6282 (4)	−71 (10)	39 (3)	C(35)	6545 (4)	6353 (4)	−4151 (11)	42 (3)
C(14)	8125 (4)	6741 (5)	−1058 (12)	53 (3)	C(34)	6877 (5)	6852 (5)	−4787 (13)	60 (4)
C(13)	8366 (5)	7340 (5)	−1413 (13)	60 (4)	C(33)	6612 (5)	7445 (6)	−5173 (16)	77 (5)
C(12)	8940 (5)	7481 (4)	−787 (13)	60 (4)	C(32)	6022 (5)	7544 (5)	−4866 (14)	64 (4)
C(11)	9269 (4)	7030 (4)	198 (11)	47 (3)	C(31)	5690 (4)	7054 (4)	−4232 (11)	45 (3)
C(10)	9022 (3)	6414 (4)	582 (10)	35 (2)	C(30)	5949 (3)	6435 (4)	−3814 (10)	36 (2)
C(25)	9006 (3)	3808 (4)	4826 (10)	36 (2)	C(45)	5974 (4)	3760 (4)	74 (10)	36 (2)
C(24)	9310 (4)	3371 (4)	5924 (10)	43 (3)	C(44)	5692 (4)	3321 (4)	1097 (11)	46 (3)
C(23)	8999 (4)	2868 (4)	6641 (11)	49 (3)	C(43)	6011 (5)	2828 (4)	1922 (12)	53 (3)
C(22)	8392 (4)	2805 (4)	6248 (11)	52 (3)	C(42)	6609 (5)	2770 (4)	1714 (11)	55 (3)
C(21)	8097 (4)	3231 (4)	5154 (11)	45 (3)	C(41)	6894 (4)	3210 (4)	712 (11)	45 (3)
C(20)	8400 (3)	3744 (4)	4377 (10)	35 (2)	C(40)	6580 (3)	3721 (4)	−144 (10)	35 (2)
C(1)	8488 (4)	5565 (4)	3924 (11)	43 (3)	C(2)	6406 (4)	5526 (5)	−429 (11)	50 (3)
O(1)	8327 (4)	5919 (4)	4938 (9)	73 (3)	O(3)	6522 (4)	5866 (4)	722 (9)	82 (3)
C(16)	8379 (4)	5036 (5)	−1466 (10)	44 (3)	C(36)	6666 (5)	5153 (5)	−5754 (11)	56 (3)
C(17)	8587 (4)	4369 (4)	−918 (11)	46 (3)	C(37)	6469 (5)	4464 (5)	−5472 (12)	55 (3)
O(2)	9033 (2)	4475 (3)	448 (7)	37 (2)	O(4)	6004 (3)	4503 (3)	−4304 (7)	43 (2)
C(27)	9351 (4)	3888 (4)	938 (12)	46 (3)	C(47)	5723 (5)	3876 (4)	−4032 (13)	52 (3)
C(26)	9782 (4)	4088 (5)	2324 (13)	52 (3)	C(46)	5252 (4)	4003 (5)	−2845 (13)	56 (3)
				(b) [Fe(CO)(N_HS_4)]					
Fe(2)	3782 (1)	5018 (1)	2435 (2)	32 (1)	Fe(1)	1193 (1)	5009 (1)	−2222 (2)	36 (1)
S(8)	4433 (1)	4418 (1)	4003 (3)	43 (1)	S(4)	531 (1)	4348 (1)	−1012 (3)	46 (1)
S(7)	3044 (1)	4278 (1)	3045 (3)	39 (1)	S(3)	1939 (1)	4276 (1)	−1433 (3)	47 (1)
S(6)	3157 (1)	5503 (1)	560 (3)	41 (1)	S(2)	1847 (1)	5562 (1)	−3688 (3)	51 (1)
S(5)	4495 (1)	5794 (1)	1802 (3)	42 (1)	S(1)	478 (1)	5765 (1)	−3062 (3)	43 (1)
C(30)	4078 (4)	6407 (4)	728 (11)	38 (3)	C(10)	901 (4)	6431 (4)	−3801 (11)	35 (3)
C(31)	4331 (4)	7028 (4)	378 (12)	44 (4)	C(11)	647 (4)	7045 (4)	−4145 (12)	47 (4)
C(32)	3995 (6)	7482 (5)	−464 (13)	60 (5)	C(12)	976 (5)	7548 (5)	−4661 (15)	67 (5)
C(33)	3401 (6)	7365 (5)	−1037 (14)	69 (5)	C(13)	1591 (6)	7470 (5)	−4874 (16)	86 (6)
C(34)	3150 (5)	3777 (5)	−705 (14)	60 (4)	C(14)	1869 (5)	6884 (5)	−4533 (15)	69 (5)
C(35)	3473 (4)	6294 (4)	160 (12)	42 (4)	C(15)	1519 (4)	6371 (5)	−4015 (12)	45 (4)
C(40)	3381 (4)	3745 (4)	4493 (11)	30 (3)	C(20)	1590 (4)	3709 (4)	−136 (11)	36 (3)
C(41)	3056 (4)	3256 (4)	5318 (11)	42 (3)	C(21)	1916 (5)	3230 (4)	741 (12)	44 (4)
C(42)	3324 (5)	2827 (4)	6418 (12)	49 (4)	C(22)	1639 (5)	2810 (5)	1779 (11)	50 (4)
C(43)	3951 (5)	2871 (4)	6780 (11)	51 (4)	C(23)	1025 (5)	2835 (4)	1994 (12)	48 (4)
C(44)	4284 (4)	3340 (4)	6032 (11)	39 (3)	C(24)	705 (4)	3288 (4)	1135 (11)	44 (4)
C(45)	4000 (4)	3777 (4)	4918 (10)	33 (3)	C(25)	968 (4)	3730 (4)	54 (11)	33 (3)
C(2)	3563 (5)	5531 (5)	4041 (13)	52 (4)	C(1)	1325 (5)	5491 (5)	−435 (14)	58 (4)
O(3)	3418 (4)	5898 (4)	5082 (9)	94 (4)	O(1)	1415 (5)	5816 (4)	706 (9)	104 (4)
N(1)	4053 (3)	4438 (4)	479 (9)	36 (3)	N(2)	986 (3)	4471 (4)	−4360 (10)	44 (3)
C(46)	4777 (4)	3926 (5)	2381 (15)	57 (4)	C(26)	253 (4)	3868 (5)	−2794 (15)	59 (4)
C(47)	4314 (4)	3803 (4)	1002 (14)	48 (4)	C(27)	753 (5)	3799 (4)	−3998 (14)	49 (4)
C(36)	3363 (4)	5050 (5)	−1329 (12)	48 (3)	C(16)	1682 (5)	5168 (5)	−5780 (14)	62 (4)
C(37)	3571 (4)	4374 (5)	−853 (12)	46 (4)	C(17)	1483 (5)	4467 (5)	−5487 (14)	60 (4)

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

C, 54.20; H, 5.11. Found: C, 48.85; H, 4.61. OS_4-H_2 obstinately retains traces of CCl_4, causing unsatisfactory elemental analyses.

Method 2: Alkylation of *o*-Benzenedithiol. A 4.6-mL (5.66-g, 40-mmol) portion of *o*-benzenedithiol in 100 mL of methanol is refluxed with 2.16 g (40 mmol) of NaOMe and 4.64 g (20 mmol) of bis(2-bromoethyl) ether for 2 h. The reaction mixture is evaporated to dryness, and the viscous residue is extracted with 30 mL of CCl_4. The CCl_4 extract is filtered over SiO_2 and evaporated to dryness again, leading to 4 g (56%) of OS_4-H_2 as a colorless oil. Anal. Calcd for $C_{16}H_{18}OS_4$ (M_r = 354.5): C, 54.20; H, 5.11. Found: C, 41.08; H, 3.20.

(i) N_HS_4-H_2. To 2.36 mL (2.88 mg, 20 mmol) of *o*-benzenedithiol in 50 mL of methanol are added 1.08 g (20 mmol) of NaOMe. After addition of 3.1 g (10 mmol) of bis(2-bromoethyl)amine hydrobromide and 540 mg (10 mmol) of NaOMe in 15 mL of methanol, the mixture is refluxed for 45 min. Cooling to −30 °C yields colorless crystals, which are collected and redissolved in CH_2Cl_2/methanol (20 mL/50 mL). The solution is concentrated until it turns opaque and is stored at −30 °C. After 15 h the colorless precipitate is collected and dried under high vacuum for 8 h; yield 1.0 g (28%). Anal. Calcd for $C_{16}H_{19}NS_4$ (M_r = 353.6): C, 54.35; H, 5.41; N, 3.96. Found: C, 52.44; H, 5.63; N, 4.13.

(j) [Mo(NO)(Cl)(OS_4)]. To a green solution of 128 mg (0.40 mmol) of $[MoCl_3(NO)(CH_3CN)_2]$ in 20 mL of THF is added 145 mg (0.40 mmol) of OS_4-H_2 in 5 mL of THF. The mixture, after its color changes to red, is stirred for 3 h and concentrated in volume to one-third. Dropwise addition of 80 mL of diethyl ether yields a brown precipitate, which is collected and recrystallized from CH_2Cl_2, covered with a layer of diethyl ether; yield 150 mg (62%) of $[Mo(NO)(Cl)(OS_4)]\cdot CH_2Cl_2$. Anal. Calcd for $C_{17}Cl_3H_{18}MoNO_2S_4$ (M_r = 598.8): C, 34.09; H, 3.02; N, 2.43. Found: C, 34.13; H, 3.08; N, 2.52.

(k) [Mo(NO)(Cl)(N_HS_4)]. To 313 mg (1.0 mmol) of $[MoCl_3(NO)(CH_3CN)_2]$ in 30 mL of CH_2Cl_2 is added 353 mg (1 mmol) of N_HS_4-H_2. After being left to stand overnight, the solution is refluxed for 5 h, the color changing from green to red. It is filtered over filter pulp; the red filtrate is covered with a layer of methanol and stored at −30 °C. The precipitating red crystals are collected and dried under high vacuum for 10 h; yield: 50 mg (10%) of $[Mo(NO)(Cl)(N_HS_4)]\cdot CH_2Cl_2$. Anal. Calcd for $C_{17}Cl_3H_{19}MoN_2OS_4$ (M_r = 597.8): C, 35.98; H, 3.18; N, 4.66. Found: C, 33.49; H, 3.01; N, 4.33.

(l) $[Mo(CO)_2(OS_4)]$. To 185 mg (0.52 mmol) of OS_4-H_2 in 10 mL of THF is added 40 mg of LiOMe, and the resulting solution is evaporated to dryness. To the residue are added 30 mL of CH_2Cl_2 and 405 mg (0.52 mmol) of $[MoCl_2(CO)_3(PPh_3)_2]$, yielding a red suspension, which is stirred for 15 h. After filtration, the red filtrate is covered with a layer of methanol; the precipitating orange microcrystals are collected and dried under high vacuum for 8 h; yield 155 mg (59%). Anal. Calcd for $C_{18}H_{16}MoO_3S_4$ (M_r = 504.5): C, 42.85; H, 3.19. Found: C, 42.89; H, 3.35.

(m) $[Ru(PPh_3)(OS_4)]$. To 265 mg (0.75 mmol) of OS_4-H_2 in 10 mL

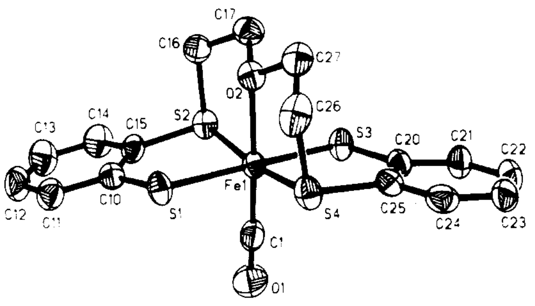
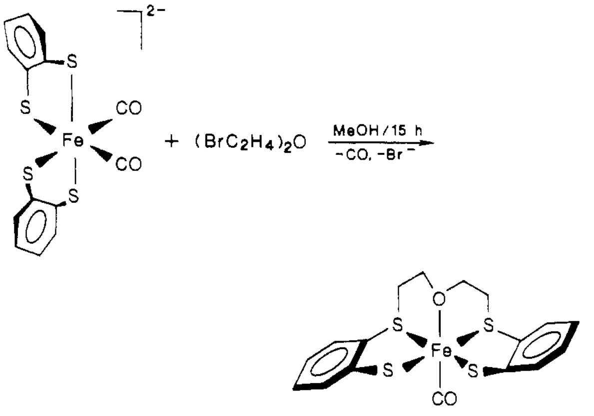


Figure 2. Molecular structure of $[Fe(CO)(OS_4)]$ (H atoms omitted).

of THF is added 1.5 mmol of *n*-butyllithium (0.90 mL of a 1.6 M solution of *n*-butyllithium in *n*-hexane) at −78 °C. The solution is heated to room temperature and added to 640 mg (0.75 mmol) of $[RuCl_2(PPh_3)_3]$ in 30 mL of THF, and the mixture is refluxed for 2.5 h. The red reaction mixture is evaporated to dryness, the viscous residue is dissolved in 30 mL of CH_2Cl_2, and this solution is filtered over SiO_2. The filtrate is evaporated to dryness again, and the residue, which is still viscous, is digested with diethyl ether, yielding an orange powder. This is collected and dried under high vacuum for 6 h; yield 360 mg (67%). Anal. Calcd for $C_{34}H_{31}OPRuS_4$ (M_r = 717.7): C, 54.64; H, 4.24. Found: C, 54.80; H, 4.34.

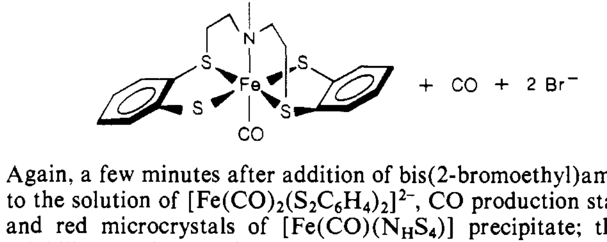
Results and Discussion

Synthesis of $[Fe(CO)(XS_4)]$ (X = O, NH). $[Fe(CO)(OS_4)]$ is obtained by template alkylation of dicarbonylbis(benzenedithiolato)ferrate(2−) (eq 1). A few minutes after the addition of bis(2-bromoethyl) ether to the deep red solution of $[Fe(CO)_2(S_2C_6H_4)_2]^{2-}$, violet microcrystals begin to precipitate with simultaneous evolution of carbon monoxide; the reaction is complete after the solution is left to stand overnight. $[Fe(CO)(OS_4)]$ dissolves much better in CH_2Cl_2, $CHCl_3$, THF, or DMSO than $[Fe(CO)(S_5)]$ and shows a characteristic ν_{CO} band at 1940 cm^{-1} and an intense band at 1070 cm^{-1} in the IR spectrum (KBr). This is assigned to the ν_{COC} band of the ether linkage.



(1)

In analogy to this process, $[Fe(CO)(N_HS_4)]$ is obtained (eq 2).



(2)

Again, a few minutes after addition of bis(2-bromoethyl)amine to the solution of $[Fe(CO)_2(S_2C_6H_4)_2]^{2-}$, CO production starts and red microcrystals of $[Fe(CO)(N_HS_4)]$ precipitate; their solubility equals that of $[Fe(CO)(OS_4)]$. The KBr IR spectrum of $[Fe(CO)(N_HS_4)]$ shows characteristic bands at 3180 cm^{-1} (ν_{NH}) and 1950 cm^{-1} (ν_{CO}).

Description and Discussion of the X-ray Structure Analyses for $[Fe(CO)(XS_4)]$ (X = O, NH). Since ^{13}C NMR spectra do not allow the unambiguous differentiation between meso and "trans" forms of $[Fe(CO)(XS_4)]$ complexes, as will be described in more detail below, the structures of $[Fe(CO)(OS_4)]$ and $[Fe(CO)(N_HS_4)]$ were determined by X-ray structure analyses. The unit cells of $[Fe(CO)(OS_4)]$ and $[Fe(CO)(N_HS_4)]$ both contain two independent molecules in the asymmetric units; however, since the respective molecules do not differ significantly, Figures 2 and 3 show views of only one of the molecules for each compound.

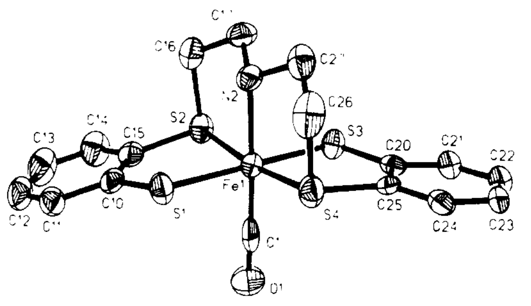


Figure 3. Molecular structure of $[Fe(CO)(N_HS_4)]$ (H atoms omitted).

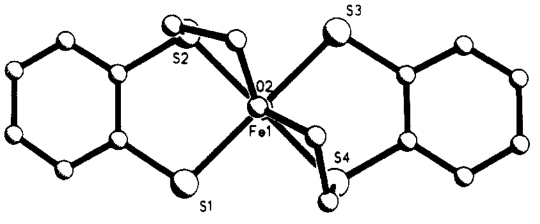


Figure 4. Top view along the X–Fe–CO axis of $[Fe(CO)(XS_4)]$ (H atoms omitted).

In both complexes the iron atoms are six-coordinate: Four S atoms, one C atom, and one O or N atom respectively form the pseudooctahedral coordination sphere. In each case, the CO ligand occupies the position trans to the O and N atoms, respectively. In contrast to the case for *meso*-$[Fe(CO)(S_5)]$, however, the $S_2C_6H_4$ entities are bridged in the trans manner, which had been found for $[Ru(PPh_3)(^tBu_4\text{-}S_5)]$ containing the *tert*-butyl derivative of $S_5\text{-}H_2$ ($^tBu_4\text{-}S_5^{2-}$ = dianion of 14,16,18,20-tetra-*tert*-butyl-2,3,11,12-dibenzo-1,4,7,10,13-pentathiatridecane).[7]

As in $[Ru(PPh_3)(^tBu_4\text{-}S_5)]$, the C_2H_4 groups of the $X(C_2H_4)_2$ bridges in $[Fe(CO)(OS_4)]$ and $[Fe(CO)(N_HS_4)]$ are arranged asymmetrically on one side of the Fe(1)S(2)S(4)X plane (X = O, N). Molecular models show this form to possess the minimal steric strain, which can be seen more clearly as one looks down the X–Fe–CO axis (Figure 4).[7]

The bond distances as well as the angles of $[Fe(CO)(OS_4)]$ and $[Fe(CO)(N_HS_4)]$, which are listed in Table III, cover the same range as found for other Fe(II) complexes of this type. Fe–S(thiolate) distances of 226–231 pm are also observed in $[Fe(CO)_2(^tBu_4\text{-}dttd)]$ ($^tBu_4\text{-}dttd^{2-}$ = dianion of 5,5,6,6-tetra-*tert*-butyl-2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane),[17] $[Fe(CO)_2(ttd)]$ (ttd^{2-} = dianion of 1,4,7,10-tetrathiadecane),[18] and *meso*-$[Fe(CO)(S_5)]$;[7] Fe–S(thioether) distances of these complexes cover the range between 222 and 225 pm.

It must be noted, however, that usually Fe–S(thiolate) distances are larger than Fe–S(thioether) distances; this may be contributed to the larger covalent radius of the thiolato S atom. Whereas in $[Fe(CO)(OS_4)]$ and $[Fe(CO)(N_HS_4)]$ the angles S(1)–Fe(1)–S(3) (S(5)–Fe(2)–S(7)) with 179.2 (1)° (178.9 (1)°) and 177.6 (1)° (177.8 (1)°) deviate only marginally from the ideal octahedral geometry, the angles S(2)–Fe(1)–S(4) (S(6)–Fe(2)–S(8)) with 169.3 (1)° (170.4 (1)°) and 172.4 (1)° (171.1 (1)°) are clearly distorted. This is certainly due to the bridging of these sulfur atoms and leads to a propellerlike twisting of the benzo rings with dihedral angles [S(1)–C(10)–C(15)–S(2)] ([S(4)–C(25)–C(20)–S(3)]) of −2.0 and 4.6° (0.9 and 5.7°). The Fe–S distances in the $Fe(S)_4$ plane of $[Fe(CO)(OS_4)]$ and $[Fe(CO)(N_HS_4)]$ as

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(17) Sellmann, D.; Freyberger, G.; Eberlein, R.; Böhlen, E.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1987**, *323*, 21.

(18) Sellmann, D.; Jonk, H.-E.; Pfeil, H.-R.; Huttner, G.; Seyerl, J. v. *J. Organomet. Chem.* **1980**, *191*, 171.

Table III. Selected Bond Distances (pm) and Bond Angles (deg)[a]

(a) $[Fe(CO)(OS_4)]$							
Fe(1)–S(1)	229.5 (2)	Fe(2)–S(5)	228.6 (2)	S(2)–C(16)	183.1 (9)	S(6)–C(36)	183.0 (10)
Fe(1)–S(2)	224.3 (2)	Fe(2)–S(6)	222.7 (2)	S(3)–C(20)	174.9 (8)	S(7)–C(40)	174.3 (8)
Fe(1)–S(3)	229.5 (2)	Fe(2)–S(7)	228.9 (2)	S(4)–C(25)	178.7 (8)	S(8)–C(45)	179.0 (8)
Fe(1)–S(4)	224.4 (2)	Fe(2)–S(8)	224.0 (2)	C(15)–C(10)	141.3 (11)	C(35)–C(30)	139.9 (11)
Fe(1)–C(1)	172.1 (9)	Fe(2)–C(2)	170.6 (10)	C(1)–O(1)	115.3 (10)	C(2)–O(3)	116.3 (11)
Fe(1)–O(2)	207.6 (5)	Fe(2)–O(4)	207.5 (6)	C(16)–C(17)	148.8 (12)	C(36)–C(37)	148.6 (14)
S(1)–C(10)	174.9 (8)	S(5)–C(30)	174.6 (8)	C(17)–O(2)	145.5 (10)	C(37)–O(4)	144.3 (11)
S(2)–C(15)	178.1 (8)	S(6)–C(35)	178.8 (8)	O(2)–C(27)	143.2 (9)	O(4)–C(47)	144.2 (10)
S(2)–Fe(1)–S(1)	88.9 (1)	S(6)–Fe(2)–S(5)	88.8 (1)	O(2)–Fe(1)–S(4)	84.6 (2)	O(4)–Fe(2)–S(8)	85.4 (2)
S(3)–Fe(1)–S(1)	179.2 (1)	S(7)–Fe(2)–S(5)	178.9 (1)	O(2)–Fe(1)–C(1)	177.3 (3)	O(4)–Fe(2)–C(2)	176.5 (3)
S(3)–Fe(1)–S(2)	91.0 (1)	S(7)–Fe(2)–S(6)	90.1 (1)	C(10)–S(1)–Fe(1)	103.3 (3)	C(30)–S(5)–Fe(2)	102.9 (3)
S(4)–Fe(1)–S(2)	169.3 (1)	S(8)–Fe(2)–S(6)	170.4 (1)	C(15)–S(2)–Fe(1)	104.9 (3)	C(35)–S(6)–Fe(2)	105.0 (3)
S(4)–Fe(1)–S(3)	89.4 (1)	S(8)–Fe(2)–S(7)	89.7 (1)	C(20)–S(3)–Fe(1)	103.9 (3)	C(40)–S(7)–Fe(2)	103.5 (3)
O(2)–Fe(1)–S(2)	84.7 (2)	O(4)–Fe(2)–S(6)	85.0 (2)	C(25)–S(4)–Fe(1)	105.7 (3)	C(45)–S(8)–Fe(2)	105.0 (3)
O(2)–Fe(1)–S(3)	91.2 (2)	O(4)–Fe(2)–S(7)	90.3 (2)	C(15)–C(10)–S(1)	121.6 (6)	C(35)–C(30)–S(5)	122.4 (6)
(b) $[Fe(CO)(N_HS_4)]$							
Fe(1)–S(4)	225.1 (3)	Fe(2)–S(8)	224.8 (3)	S(2)–C(15)	180.8 (9)	S(6)–C(35)	178.5 (9)
Fe(1)–S(3)	230.5 (3)	Fe(2)–S(7)	230.0 (3)	S(1)–C(10)	176.4 (9)	S(5)–C(30)	175.8 (9)
Fe(1)–S(2)	222.5 (3)	Fe(2)–S(6)	224.2 (3)	C(10)–C(15)	141.1 (12)	C(30)–C(35)	143.2 (13)
Fe(1)–S(1)	229.8 (3)	Fe(2)–S(5)	231.4 (3)	C(1)–O(1)	114.1 (12)	C(2)–O(3)	117.5 (11)
Fe(1)–C(1)	175.3 (12)	Fe(2)–C(2)	174.4 (11)	N(2)–C(27)	148.9 (12)	N(1)–C(47)	146.6 (11)
Fe(1)–N(2)	207.2 (8)	Fe(2)–N(1)	207.6 (7)	N(2)–C(17)	146.8 (13)	N(1)–C(37)	149.7 (12)
S(4)–C(25)	178.6 (8)	S(8)–C(45)	179.7 (9)	C(26)–C(27)	152.1 (15)	C(46)–C(47)	151.0 (15)
S(3)–C(20)	175.8 (9)	S(7)–C(40)	173.7 (9)	C(16)–C(17)	150.9 (14)	C(36)–C(37)	148.9 (13)
S(3)–Fe(1)–S(4)	89.1 (1)	S(7)–Fe(2)–S(8)	89.2 (1)	N(2)–Fe(1)–S(1)	88.7 (2)	N(1)–Fe(2)–S(5)	89.3 (2)
S(2)–Fe(1)–S(4)	172.4 (1)	S(6)–Fe(2)–S(8)	171.1 (1)	N(2)–Fe(1)–C(1)	176.4 (5)	N(1)–Fe(2)–C(2)	177.9 (4)
S(2)–Fe(1)–S(3)	88.9 (1)	S(6)–Fe(2)–S(7)	89.6 (1)	C(25)–S(4)–Fe(1)	105.3 (3)	C(45)–S(8)–Fe(2)	105.6 (3)
S(1)–Fe(1)–S(3)	177.6 (1)	S(5)–Fe(2)–S(7)	177.8 (1)	C(20)–S(3)–Fe(1)	104.2 (3)	C(40)–S(7)–Fe(2)	104.5 (3)
S(1)–Fe(1)–S(2)	88.7 (1)	S(5)–Fe(2)–S(6)	88.5 (1)	C(15)–S(2)–Fe(1)	104.9 (3)	C(35)–S(6)–Fe(2)	105.8 (4)
N(2)–Fe(1)–S(4)	85.4 (2)	N(1)–Fe(2)–S(8)	85.2 (2)	C(15)–C(10)–S(1)	121.4 (7)	C(35)–C(30)–S(5)	121.5 (7)
N(2)–Fe(1)–S(3)	91.5 (2)	N(1)–Fe(2)–S(7)	91.8 (2)	O(1)–C(1)–Fe(1)	178.5 (9)	O(3)–C(2)–Fe(2)	177.3 (8)
N(2)–Fe(1)–S(2)	87.3 (2)	N(1)–Fe(2)–S(6)	86.1 (2)	C(17)–N(2)–C(27)	113.5 (8)	C(37)–N(1)–C(47)	113.4 (7)

[a] Estimated standard deviations are given in parentheses.

well as *meso*-$[Fe(CO)(S_5)]$ are almost identical. In $[Fe(CO)(XS_4)]$, the Fe–X bonds trans to the CO ligand are practically equal with 207.6 (5) (207.5 (6)) pm for X = O and 207.2 (8) (207.6 (7)) pm for X = NH. In contrast, the Fe–C distances trans to the X atom appear to decrease from 176.4 (3) pm in *meso*-$[Fe(CO)(S_5)]$ to 175.3 (12) (174.4 (11)) pm in $[Fe(CO)(N_HS_4)]$ and to 172.1 (9) (170.6 (10)) pm in $[Fe(CO)(OS_4)]$. This could indicate an increase in bond strength of the Fe–CO bond. Though the standard deviations are rather large, this tendency is confirmed by the ν_{CO} frequencies, which drop from 1960 cm^{-1} ($[Fe(CO)(S_5)]$ and $[Fe(CO)(N_HS_4)]$) to 1940 cm^{-1} ($[Fe(CO)(OS_4)]$) (Table V). Nevertheless, of all three complexes $[Fe(CO)(OS_4)]$ is the one that is most easily thermally decarbonylated.

Differentiation between Meso and "Trans" Isomers of $[Fe(CO)(XS_4)]$ (X = S, O, NH) by ^{13}C NMR Spectroscopy. ^{13}C NMR spectra have proved to be a useful tool for observing geometrical rearrangements as well as for assigning the symmetry of benzenedithiolato and related complexes. They allow e.g. observation of the rearrangement of the $S_2C_6H_4^{2-}$ ligands from trans to cis positions when the square-pyramidal $[Ru(NO)(S_2C_6H_4)_2]^-$ is reacted with PMe_3 to give the pseudooctahedral $[Ru(NO)(PMe_3)(S_2C_6H_4)_2]^-$: The educt shows only three ^{13}C signals for the aromatic C atoms, but the product, which has only C_1 symmetry, gives 12 ^{13}C signals.[19] Corresponding observations were made for $[ML_1L_2(dttd)]$ complexes (M = Fe, Ru, Mo), which show six ^{13}C signals for the aromatic C atoms if $L_1 = L_2$ and 12 ^{13}C signals if $L_1 \neq L_2$, since in this case the molecular symmetry is lowered.[19b]

Since meso and "trans" isomers of $[M(L)(XS_4)]$ (Figure 1, I and II) also differ in symmetry (C_s and C_1), their ^{13}C NMR spectra should allow us to distinguish between them.

$[Fe(CO)(OS_4)]$, $[Fe(CO)(N_HS_4)]$, and $[Fe(CO)(N_{Me}S_4)]$ show one ν_{CO} band in the KBr IR spectra as well as in the solution IR spectra; they differ in this respect from $[Fe(CO)(S_5)]$, which shows only one ν_{CO} band in the solution IR spectrum at 1960 cm^{-1} but in KBr three ν_{CO} bands at 1980, 1970, and 1955 cm^{-1}, when recrystallized from DMF (140/−20 °C). After recrystallization from a mixture of DMF and methanol, crystals with one ν_{CO} band at 1950 cm^{-1} were obtained, and X-ray structure analysis proved them to consist of *meso*-$[Fe(CO)(S_5)]$. This species shows six ^{13}C signals for the benzo rings and two for the C_2H_4 groups, indicating C_s symmetry also in solution (cf. Table IV). Since the species with three ν_{CO} bands show exactly the same number of signals at identical chemical shifts, we were led to assume recrystallization conditions and solid-state effects were responsible for the occurrence of either one or three ν_{CO} bands in the KBr IR spectra of $[Fe(CO)(S_5)]$. In accordance with these observations and the X-ray structure analysis, "trans" $[Fe(CO)(N_HS_4)]$, having only C_1 symmetry, shows 12 $^{13}C_{arom}$ signals between 158.9 and 123.05 ppm and four ^{13}C signals for the C_2H_4 bridges. In contrast to our expectations, however, solutions of "trans" $[Fe(CO)(OS_4)]$ also show only six C_{arom} and two C_{bridge} signals, indicating C_s symmetry, i.e. the meso isomer.

In order to examine whether this unexpected spectrum was due to dynamic processes, spectra of $[Fe(CO)(OS_4)]$ were run at various temperatures down to −57 °C and spectra of [Fe-

Table IV. ^{13}C Chemical Shifts of $[Fe(CO)(XS_4)]$ Complexes (X = S, O, NH, NMe)[a]

complex	CO	C_6H_4	C_2H_4
$[Fe(CO)(S_5)]$[b]	215.97	156.27, 132.60, 131.39, 128.77, 128.65, 122.77	49.03, 35.61
$[Fe(CO)(OS_4)]$[c]	216.08	157.86, 135.12, 132.42, 131.64, 130.47, 123.10	67.20, 45.20
$[Fe(CO)(N_HS_4)]$[c]	215.65	158.69, 154.95, 138.20, 134.41, 132.39, 132.22, 131.96, 130.90, 130.52, 129.92, 123.05	48.45, 47.87, 47.11, 45.30
$[Fe(CO)(N_{Me}S_4)]$[b]	218.37	158.65, 134.31, 132.77, 130.60, 130.05, 123.25	60.82, 50.40, 43.92 (CH_3)

[a] δ is given in ppm relative to TMS. [b] In $CDCl_3$. [c] In DMSO-d_6.

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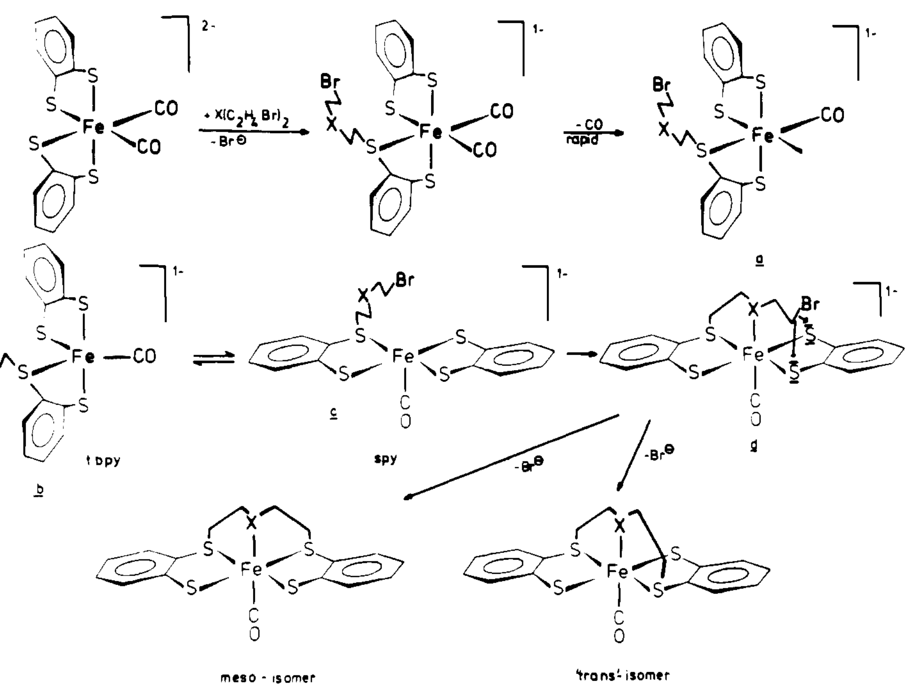
[19] (a) Sellmann, D.; Binker, G. *Z. Naturforsch.* **1987**, *42B*, 341. (b) Sellmann, D.; Keller, J.; Moll, M.; Campana, C. E.; Haase, M. *Inorg. Chim. Acta* **1987**, *141*, 243.

Scheme I. Formation of Meso and "Trans" Isomers of $[\mathrm{Fe(CO)(XS_4)}]$ Complexes (X = S, O, NH) from *cis*-$[\mathrm{Fe(CO)_2(S_2C_6H_4)_2}]^{2-}$



$(\mathrm{CO})(\mathrm{N_HS_4})]$ up to 100 °C. No clear change was observed in any of these cases. The question remains unanswered whether the unexpected $^{13}\mathrm{C}$ NMR spectrum of $[\mathrm{Fe(CO)(OS_4)}]$ is due to dynamic processes that are not frozen at −57 °C or maybe to a decoordination of the O donor in solution, causing equivalence of benzo rings as well as $\mathrm{C_2H_4}$ groups. We are also not able to explain why $[\mathrm{Fe(CO)(N_{Me}S_4)}]$ shows only six $\mathrm{C_{arom}}$ and two $\mathrm{C_{bridge}}$ signals. Although this complex is not characterized by X-ray structure analysis, it was expected to have the "trans" structure because it is prepared from "trans" $[\mathrm{Fe(CO)(N_HS_4)}]$ by deprotonation and subsequent alkylation (see below).

Thus, it is only possible to state that a $[\mathrm{Fe(CO)(XS_4)}]$ complex showing more than six $\mathrm{C_{arom}}$ and two $\mathrm{C_{bridge}}$ signals cannot have the meso structure.

Mechanism of Formation of Meso and "Trans" $[\mathrm{Fe(CO)(XS_4)}]$ Complexes (X = O, S, NH) from *cis*-$[\mathrm{Fe(CO)_2(S_2C_6H_4)_2}]^{2-}$. The formation of the $[\mathrm{Fe(CO)(XS_4)}]$ complexes raises questions: (a) How does the rearrangement of the $\mathrm{S_2C_6H_4}$ units from their cis-octahedral configuration in $[\mathrm{Fe(CO)_2(S_2C_6H_4)_2}]^{2-}$ to their planar trans position in $[\mathrm{Fe(CO)(XS_4)}]$ occur? (b) Which factors determine the formation of either the meso or the "trans" isomer of $[\mathrm{Fe(CO)(XS_4)}]$? Two points are of interest in this context: (1) In five-coordinate complexes, rearrangement of $\mathrm{S_2C_6H_4}$ units can easily take place, if the coordination number is raised to 6. This was observed for the square-pyramidal $[\mathrm{Ru(NO)(S_2C_6H_4)_2}]^-$, which upon addition of $\mathrm{PMe_3}$ forms the cis-octahedral $[\mathrm{Ru(NO)(PMe_3)(S_2C_6H_4)_2}]^-$.[19a] (2) The alkylation of $[\mathrm{Fe(CO)_2(S_2C_6H_4)_2}]^{2-}$ by $\mathrm{X(C_2H_4Br)_2}$ is accompanied by the rapid loss of one CO ligand, suggesting a coordinatively unsaturated five-coordinate intermediate. Taking into account the well-known interconversion of trigonal-bipyramidal (tbpy) and square-pyramidal (sq) structures of five-coordinate species,[20] we propose the mechanism outlined in Scheme I for the formation of $[\mathrm{Fe(CO)(XS_4)}]$.

Independent of the question whether the loss of CO is caused by lowering of the negative charge of the anion or by single electron transfer, the first step of alkylation leads to the coordinatively unsaturated species a, which rearranges to give species b. The b ⇄ c equilibrium yields the square-pyramidal species c, in which the $\mathrm{S_2C_6H_4}$ units are in plane, allowing the coordination of the donor X trans to the remaining CO ligand and generating the coordinatively saturated species d. As can be seen, the second step of alkylation should finally lead with equal probability to either the meso or the "trans" isomer. Subtle effects, e.g. the size of the X donor, tendency to crystallize, and the anti and gauche effects of $\mathrm{C_2H_4{-}X{-}CH_2}$ groups, which have been discussed for the structure of crown ethers,[20b] might determine which of the two isomers forms or is isolated.

Reactions of $[\mathrm{Fe(CO)(XS_4)}]$ (X = O, NH, S). The $[\mathrm{Fe(CO)(XS_4)}]$ complexes with S, O, or NH donors trans to the CO ligand show different thermal stabilities with respect to decarbonylation (eq 3). No decarbonylation is observed for X = S,

$$[\mathrm{Fe(CO)(XS_4)}] \xrightarrow[\text{reflux}]{\mathrm{CH_2Cl_2}/1.5\ \mathrm{h}} [\mathrm{Fe(XS_4)}]_n + \mathrm{CO} \tag{3}$$

NH, even after 15 h, but for X = O, a rapid reaction takes place. After 1.5 h, the originally purple solution decolorizes and a yellow powder precipitates, which is analyzed as $[\mathrm{Fe(OS_4)}]_n$ and is practically insoluble in all common solvents: *n* might be two; i.e., two $[\mathrm{Fe(OS_4)}]$ fragments are bridged by thiolato S atoms of the $\mathrm{OS_4}^{2-}$ ligand. When CO is substituted by $\mathrm{PMe_3}$, again the complex with X = O proves to be much more reactive:

$$[\mathrm{Fe(CO)(XS_4)}] + \mathrm{PMe_3} \xrightarrow[\text{reflux}]{\text{THF}} [\mathrm{Fe(PMe_3)(XS_4)}] + \mathrm{CO} \tag{4}$$

The reaction is complete after 15 min for X = O; it does, however, take 5 h for X = NH. Obviously, the O donor labilizes the Fe–CO bond. The labilizing effect is also seen with $[\mathrm{Fe(PMe_3)(OS_4)}]$: When it is dissolved in THF without additional $\mathrm{PMe_3}$, a precipitate of $[\mathrm{Fe(OS_4)}]_n$ forms slowly, while $[\mathrm{Fe(PMe_3)(N_HS_4)}]$ is stable under the same conditions. $[\mathrm{Fe(PMe_3)(OS_4)}]$ and $[\mathrm{Fe(PMe_3)(N_HS_4)}]$ were isolated as green microcrystals, which are soluble in THF, $\mathrm{CH_2Cl_2}$, $\mathrm{CHCl_3}$, and $\mathrm{CS_2}$. In the KBr IR spectra, the $\mathrm{PMe_3}$ ligands may be identified by their intense $\rho_{\mathrm{CH_3}}$ bands at 950 cm^{-1}.

The same effect may be responsible for the different products obtained in the reaction with $\mathrm{N_2H_4}$ (eq 5a and 5b). Adding $\mathrm{N_2H_4}$

$$[\mathrm{Fe(CO)(OS_4)}] \xrightarrow[-\mathrm{CO}/3\ \mathrm{h}]{+\mathrm{N_2H_4}/\mathrm{THF}} [\mathrm{Fe(OS_4)}]_n \tag{5a}$$

$$[\mathrm{Fe(CO)(N_HS_4)}] \xrightarrow[-\mathrm{CO}/24\ \mathrm{h}]{+\mathrm{N_2H_4}/\mathrm{THF}} [\mathrm{Fe(N_2H_4)(N_HS_4)}] \tag{5b}$$

to a violet solution of $[\mathrm{Fe(CO)(OS_4)}]$ yields a yellow precipitate, which is identified as $[\mathrm{Fe(OS_4)}]_n$. When $\mathrm{N_2H_4}$ is added to a solution of $[\mathrm{Fe(CO)(N_HS_4)}]$, however, heating is necessary to

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[20] (a) Holms, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119. (b) Wolf, R. E., Jr.; Hartman, J. A. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328.

Table V. Selected Spectroscopic Data of the Iron Complexes[a]

compd	IR (KBr), cm^{-1}	^1H NMR, ppm[b]	FD-MS, *m/e*
$[Fe(CO)(OS_4)]$	1940 (ν_{CO})	6.7–7.9[c] (C_6H_4) m; 2.6–3.7 (C_2H_4) m	408 (M^+ – CO)
$[Fe(CO)(N_HS_4)$	3180 (ν_{NH}); 1960 (ν_{CO})	6.8–7.8[c] (C_6H_4) m; 4.45 (NH); 2.2–3.9 (C_2H_4) m	435 w (M^+), 407 (M^+ – CO)
$[Fe(CO)(N_{Me}S_4)]$	1940 (ν_{CO})	6.8–7.8[d] (C_6H_4) m; 2.4–3.1 (C_2H_4) m; 3.0 (CH_3)	421 (M^+ – CO)
$[Fe(PMe_3)(OS_4)]$	950 (δ_{CH_3})	6.7–7.9[e] (C_6H_4) m; 2.6–3.7 (C_2H_4) m; 0.75 (CH_3) s	484 (M^+)
$[Fe(PMe_3)(N_HS_4)]$	3180 (ν_{NH}); 950 (δ_{CH_3})	6.7–8.0[c] (C_6H_4) m; 3.8 (NH) s; 1.8–3.3 (C_2H_4) m; 1.0 (CH_3) s	483 (M^+)
$[Fe(N_2H_4)N_HS_4)]$	3260, 3240, 3210, 3140 (ν_{NH})	440 (M^+)	

[a] Abbreviations: FD, field desorption; s, singlet; m, multiplet; w, weak. [b] Relative to TMS. [c] In $CDCl_3$. [d] In CD_2Cl_2. [e] In CS_2.

Table VI. Selected Spectroscopic Data of the Free Ligands and of the Molybdenum and Ruthenium Complexes[a]

compd	IR, cm^{-1}	^1H NMR, ppm[b]	MS, *m/e*
OS_4-H_2	2480 (ν_{SH})[c]	6.8–7.3 m[d] (C_6H_4); 4.2 s (SH); 3.4 t (C_2H_4); 2.9 t (C_2H_4)	354 (M^+) [EI]
N_HS_4-H_2	2380 (ν_{SH})[c]	6.8–7.5 m[f] (C_6H_4); 3.3 s (NH); 2.9–3.2 m (C_2H_4, SH)	353 (M^+) [EI]
$[Mo(Cl)(NO)(OS_4)]$	1670 (ν_{NO})[e]	6.7–7.6[g] (C_6H_4) m; 2.7–3.9 (C_2H_4) m	515 (M^+) [FD]
$[Mo(Cl)(NO)(N_HS_4)]$	3140 (ν_{NH});[e] 1665 (ν_{NO})		514 (M^+) [FD]
$[Mo(CO)_2(OS_4)]$	1930,[e] 1870 (ν_{CO})	6.8–8.0[g] (C_6H_4) m; 2.6–4.3 (C_2H_4) m	568 ($[MoO(OS_4)]$) [FD]
$[Ru(PPh_3)(OS_4)]$		7.0–7.9[f] (C_6H_4) m; 7.3 (C_6H_5) s; 2.6–4.1 (C_2H_4) m	716 (M^+) [FD]

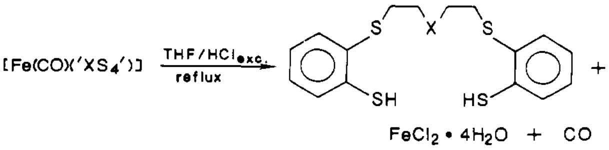
[a] Abbreviations: EI, electron impact ionization; FD, field desorption; s, singlet; t, triplet; m, multiplet. [b] Relative to TMS. [c] Between NaCl disks. [d] In CCl_4. [e] In KBr. [f] In $CDCl_3$. [g] In DMSO-d_6.

achieve a reaction. From reaction 5b the hydrazine complex $[Fe(N_2H_4)(N_HS_4)]$ is obtained as brown microcrystals. They are identified by the ν_{NH} band of the N_HS_4 ligand at 3140 cm^{-1} and three ν_{NH} bands of the N_2H_4 ligand at 3260, 3240, and 3200 cm^{-1} as well as the two δ_{NH} bands at 1610 and 1590 cm^{-1}. $[Fe(N_2H_4)(N_HS_4)]$ is only soluble in DMSO. The red solution, however, changes color almost instantaneously, indicating a reaction. The insolubility in other solvents prevented further investigations and even the recording of a ^1H NMR spectrum.

The NH group of $[Fe(CO)(N_HS_4)]$ rendered possible the convenient synthesis of derivatives of the N_HS_4 ligand. Adding $LiN(SiMe_3)_2$ to a THF solution of $[Fe(CO)(N_HS_4)]$ leads to a color change from red to green and a ν_{CO} band shift from 1960 to 1940 cm^{-1}. Subsequent addition of MeI regenerates a red solution and shifts the ν_{CO} band to 1955 cm^{-1}, and $[Fe(CO)(N_{Me}S_4)]$ can be isolated in the form of copper-colored needles. These observations are compatible with the reaction scheme suggested in eq 6. $[Fe(CO)(N_{Me}S_4)]$ is soluble in THF, CH_2Cl_2, $CHCl_3$, and DMSO. It shows a characteristic ν_{CO} band at 1940 cm^{-1} in the KBr and IR spectrum but no ν_{NH} band. Also, the singlet in the ^1H NMR spectrum at 3.0 ppm and the absence of any NH signals prove that the alkylation takes place only at the N atom and not at a thiolato S atom, which might be attacked as well.[21] Table V summarizes selected spectroscopic data of the synthesized iron complexes.

$$[Fe(CO)(N_HS_4)] \xrightarrow[-HN(SiMe_3)_2]{+LiN(SiMe_3)_2/THF} Li[Fe(CO)(NS_4)] \xrightarrow[-LiI]{+MeI/THF} [Fe(CO)(N_{Me}S_4)] \quad (6)$$

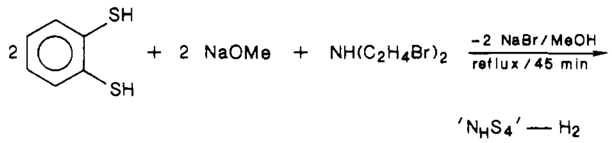
Synthesis of the Free Ligands OS_4-H_2 and N_HS_4-H_2 and Their Molybdenum and Ruthenium Complexes. In order to investigate the ligating properties of XS_4-H_2 toward other metals, e.g. molybdenum and ruthenium, free ligands were needed. They were obtained by decoordination from their iron complexes in analogy to the synthesis of dttd-H_2[22] or S_5-H_2:[23]



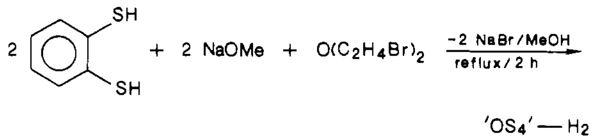
(7)

In the presence of an excess of concentrated aqueous hydrochloric acid the purple or red THF solutions of the carbonyl complexes changed color to yellow upon heating. OS_4-H_2 is easily separated from the reaction mixture as a colorless oil. The isolation of N_HS_4-H_2 caused serious problems, however. In acidic media, N_HS_4-H_2 is protonated and gives $[N_HS_4$-$H_2]\cdot HCl$; in neutral to basic media, it reacts with the Fe(II) ions that are still present in the reaction mixture, and thus it could only be isolated in trace amounts.

Therefore, we tried to obtain the free N_HS_4-H_2 by direct synthesis from *o*-benzenedithiol and $NH(C_2H_4Br)_2$ despite previous discouraging results with S_5-H_2 in this type of synthesis. Indeed, with the stoichiometry of eq 8, good yields of N_HS_4-H_2 were obtained. Subsequent experiments showed OS_4-H_2 to be accessible by this method as well (eq 9). The ^1H NMR spectra of OS_4-H_2 and N_HS_4-H_2 respectively show characteristic multiplet patterns in the region of aromatic protons; the multiplet originating from the C_2H_4 protons is superimposed by the singlet of the SH protons in the case of N_HS_4-H_2.



(8)



(9)

Orienting experiments resulted in a number of new molybdenum and ruthenium complexes. Molybdenum nitrosyl complexes were obtained by reaction of OS_4-H_2 and N_HS_4-H_2, respectively, with $[MoCl_3(NO)(CH_3CN)_2]$ (eq 10 and 11). The addition of OS_4-H_2 to the green THF solution of $[MoCl_3(NO)(CH_3CN)_2]$ causes a color change to red and shift of the ν_{NO} band from 1710 to 1680 cm^{-1}. A brown powder is separated from the reaction mixture, being soluble in THF, CH_2Cl_2, and DMSO; it is analyzed as $[Mo(Cl)(NO)(OS_4)]$ and shows a molecular ion at *m/e* = 516 (^{98}Mo) in the FD mass spectrum, suggesting a seven-coordinate

$$[MoCl_3(NO)(CH_3CN)_2] + OS_4\text{-}H_2 \xrightarrow[3\ h]{THF} [Mo(Cl)(NO)(OS_4)] + 2HCl + 2CH_3CN \quad (10)$$

$$[MoCl_3(NO)(CH_3CN)_2] + N_HS_4\text{-}H_2 \xrightarrow[reflux/5\ h]{CH_2Cl_2} [Mo(Cl)(NO)(N_HS_4)] + 2HCl + 2CH_3CN \quad (11)$$

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(21) Sellmann, D.; Waeber, M.; Huttner, G.; Zsolnai, L. *Inorg. Chim. Acta* **1986**, *118*, 49.

(22) Sellmann, D.; Böhlen, E. *Z. Naturforsch.* **1982**, *37B*, 102.

(23) Sellmann, D.; Kleine-Kleffmann, U. *J. Organomet. Chem.* **1983**, *258*, 315.

and 18e-configurated Mo(III) complex.

The analogous $[Mo(Cl)(NO)(N_HS_4)]$ is obtained in methylene chloride (eq 11). It forms red crystals and shows spectroscopic properties similar to those of $[Mo(Cl)(NO)(OS_4)]$ (cf. Table VI).

The reaction according to eq 12 yields $[Mo(CO)_2(OS_4)]$, which forms orange crystals and is soluble in CH_2Cl_2 and DMSO; it

$$[MoCl_2(CO)_3(PPh_3)_2] + OS_4\text{-}Li_2 \xrightarrow[15\ h]{CH_2Cl_2} [Mo(CO)_2(OS_4)] + 2LiCl + 2PPh_3 + CO \quad (12)$$

shows two equally intense ν_{CO} bands at 1930 and 1870 cm^{-1}, indicating a cis geometry of the CO ligands.

A ruthenium complex was obtained according to eq 13.

$$[RuCl_2(PPh_3)_3] + OS_4\text{-}Li_2 \xrightarrow[reflux/2.5\ h]{THF} [Ru(PPh_3)(OS_4)] + 2LiCl + 2PPh_3 \quad (13)$$

$[Ru(PPh_3)(OS_4)]$ is easily soluble in THF, CH_2Cl_2, $CHCl_3$, and DMSO in contrast to the case for $[Ru(PPh_3)(S_5)]$, and it was characterized by spectroscopy and by elemental analysis. Table VI summarizes selected spectroscopic data of the free ligands as well as of their Mo and Ru complexes.

Conclusion

$[Fe(CO)(XS_4)]$ complexes with the novel pentadentate ligands OS_4^{2-} and $N_HS_4^{2-}$ respectively were synthesized and characterized, including X-ray structure analyses. The X donor atoms occupy positions trans to the CO ligand, resulting in different reactivities of the Fe–CO bonds. This shows that O or N donors in a coordination sphere dominated by sulfur can not only determine the reaction site of a complex but also influence markedly the degree of its reactivity. In contrast to the short Fe–CO bond of $[Fe(CO)(OS_4)]$, however, this species is the most reactive, with respect to CO substitution. The free ligands $XS_4\text{-}H_2$ or their lithium salts (X = O, NH) show good ligating properties and yield the new complexes $[Mo(Cl)(NO)(XS_4)]$, $[Mo(CO)_2(OS_4)]$, and $[Ru(PPh_3)(OS_4)]$. The NH function in $[Fe(CO)(N_HS_4)]$ renders possible the synthesis of the alkyl derivative $[Fe(CO)(N_{Me}S_4)]$ and potentially of a whole series of N_RS_4 complexes.

Acknowledgment. These investigations were supported by the Deutsche Forschungsgemeinschaft, by the Fonds der Chemischen Industrie, by the Dr. Otto Röhm Gedächtnisstiftung, and by the donation of $RuCl_3\cdot xH_2O$ by Degussa AG, Hanau, West Germany. We gratefully acknowledge this support.

Registry No. $[MoCl_3(NO)(CH_3CN)_2]$, 65060-56-2; $[Fe(CO)(OS_4)]$, 116888-20-1; $[Fe(CO)(N_HS_4)]$, 116888-21-2; $[Fe(CO)_2(S_2C_6H_4)_2]^{2-}$, 66350-60-5; $Fe(OS_4)$, 116888-22-3; $[Fe(PMe_3)(OS_4)]$, 116888-23-4; $[Fe(PMe_3)(N_HS_4)]$, 116888-24-5; $[Fe(N_2H_4)(N_HS_4)]$, 116888-25-6; $[Fe(CO)(N_{Me}S_4)]$, 116888-26-7; $OS_4\text{-}H_2$, 116888-31-4; $N_HS_4\text{-}H_2$, 116888-30-3; $[Mo(NO)(Cl)(OS_4)]$, 116888-27-8; $[Mo(NO)(Cl)(N_HS_4)]$, 116888-28-9; $[Mo(CO)_2(OS_4)]$, 116926-19-3; $[MoCl_2(CO)_3(PPh_3)_2]$, 17250-39-4; $[Ru(PPh_3)(OS_4)]$, 116888-29-0; $[RuCl_2(PPh_3)_3]$, 15529-49-4; bis(2-bromoethyl) ether, 5414-19-7; bis(2-bromoethyl) amine, 3890-99-1; *o*-benzenedithiol, 17534-15-5.

Supplementary Material Available: Listings of crystallographic data and data collection parameters, anisotropic thermal parameters, all bond distances and bond angles, and fractional coordinates of hydrogen atoms (9 pages); listings of F_o and F_c values (34 pages). Ordering information is given on any current masthead page. Further details of the X-ray crystal structure analyses have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, West Germany, and can be obtained by quoting Deposition No. CSD-52957, the authors' names, and the reference.

Contribution from the Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7,
and Chemistry Division, National Research Council, Ottawa, Canada K1A 0R6

Binuclear Nickel(II) and Cobalt(II) Complexes of Sexadentate (N_6) Phthalazine Ligands. Crystal and Molecular Structures of [μ-1,4-Bis((6-methylpyridine-2-carboxaldimino)amino)phthalazine-N^4,N^3,μ-N^1,μ-N^{1A},N^{3A},N^{4A}](μ-chloro)tetraaquodicobalt(II) Trichloride-4.3-Water, $Co_2C_{22}H_{28}Cl_4N_8O_4\cdot 4.3H_2O$, and [$\mu$-1,4-Bis((6-methylpyridine-2-carboxaldimino)amino)phthalazine-N^4,N^3,μ-N^1,μ-N^{1A},N^{3A},N^{4A}](μ-chloro)tetraaquodinickel(II) Trichloride-4.6-Water, $Ni_2C_{22}H_{28}Cl_4N_8O_4\cdot 4.6H_2O$[†]

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The ligand 1,4-bis((6-methylpyridine-2-carboxaldimino)amino)phthalazine (PHP6Me) forms binuclear cobalt(II) and nickel(II) complexes, $[M_2(PHP6Me)X(H_2O)_4]X_3\cdot$solvent (M = Co, Ni; X = Cl, Br), involving six-coordinate metal centers bridged by the phthalazine diazine (N_2) group and a halogen. Other binuclear (1:1) derivatives $[Ni_2(APHP)_2]X_4\cdot 4H_2O$ (X = NO_3, BF_4) (APHP = 1,4-bis((pyrid-2-ylacetaldimino)amino)phthalazine) involve two six-coordinate metal centers sandwiched between adjacent sexadentate ligands. All the complexes exhibit antiferromagnetic exchange between the metal centers with the 1:1 nickel derivatives being very weakly coupled. The crystal and molecular structures of $[Co_2(PHP6Me)Cl(H_2O)_4]Cl_3\cdot 4.3H_2O$ (I) and $[Ni_2(PHP6Me)Cl(H_2O)_4]Cl_3\cdot 4.6H_2O$ (III) are reported. I crystallized in the trigonal system, space group $P3_121$, with $a = 17.1624$ (14) Å, $c = 10.2358$ (7) Å, and three formula units per unit cell. III crystallized in the trigonal system, space group $P3_221$, with $a = 17.1237$ (4) Å, $c = 10.21360$ (20) Å, and three formula units per unit cell. Refinement by full-matrix least squares gave final residuals of $R = 0.040$ and $R_w = 0.043$ for I and $R = 0.049$ and $R_w = 0.054$ for III. Very large metal–metal separations are observed in these systems with Co–Co = 3.712 Å (I) and Ni–Ni = 3.678 Å (III). All the complexes exhibit very intense metal-to-ligand charge-transfer absorptions ($\epsilon > 10000$ L mol^{-1} cm^{-1}) in the visible region (19000–20200 cm^{-1}).

Introduction

The study of the coordination chemistry of the ligand 1,4-dihydrazinophthalazine (DHPH) and its derivatives has been somewhat limited and includes binuclear nickel(II)[2,3] cobalt(II),[4] and molybdenum(IV)[5] complexes of DHPH, a binuclear nickel(II)

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