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ANTIFERROMAGNETIC COMPLEXES WITH METAL—METAL BONDS

VII *. SYNTHESIS AND MOLECULAR STRUCTURE OF $(CpCrSCMe_3)_2S \cdot Mn(CO)_2Cp$ AND FORMATION OF THE TETRANUCLEAR CLUSTERS $Cp_4Cr_3MS_4$ (M = Cr, V, Nb)

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Summary

Photochemical reaction of $(CpCrCSMe_3)_2S$ (I) with $CpMn(CO)_3$ gave the complex $(CpCrSCMe_3)_2S \cdot Mn(CO)_2Cp$ (II). According to X-ray analysis its fragments are joined by an Mn—S (sulfide) bond (2.334 Å) with almost no change in geometry of complex I upon coordination (Cr—Cr 2.704, Cr—S (sulfide) 2.29, Cr—S (thiolate) 2.35, Cr—C(Cp) 2.256 Å, CrS(sulfide)Cr 72.2°, CrS(thiolate)Cr 70.0°). However, the reaction of I with $CpM(CO)_4$ (M = V, Nb) under the same conditions yielded the corresponding paramagnetic heteronuclear complexes $[Cp_3Cr_3(\mu^3\text{-}S)_4]MCp$ (III and IV, respectively) probably containing a tetrahedral metallic skeleton. The reason for the rearrangement of I in the latter reactions may be a greater steric hindrance in the intermediate complexes $(CpCrSCMe_3)_2S \cdot M(CO)_3Cp$ with respect to II. The known diamagnetic tetrahedral analog of III and IV, $Cp_4Cr_4S_4$, was obtained by pyrolysis of I.

Introduction

Recently, we have studied the possibility of employing the binuclear complex $(CpCrSCMe_3)_2S$ (I), which contains a Cr—Cr bond (2.689 Å) [1—4], as an unusual antiferromagnetic ligand in mono- and binuclear metal carbonyl derivatives.

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* For part VI see ref. 12.

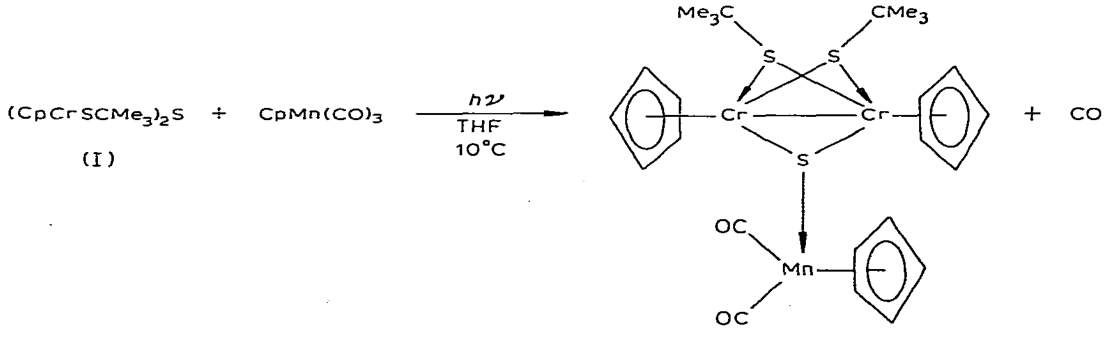
The reaction has been shown to depend upon the metal coordination number (CN) in the respective carbonyl. When CN = 6, for $M(CO)_6$ (M = Cr, Mo, W) [5,6] or $Mn_2(CO)_{10}$ [7], the reactions take place only by the substitution of one CO group, giving rise to the complexes $I \cdot M(CO)_5$ or $I \cdot Mn_2(CO)_9$ in which unchanged I is coordinated to M or Mn through the sulfide bridge lone electron pair. When CN = 5, for $Fe(CO)_5$ [8] or unbridged $Co_2(CO)_8$ in solutions [7], an elimination of one tert-butyl group is observed with formation of the binuclear chelate fragment $(Cp_2Cr_2SCMe_3)(S)_2$ which is coordinated through the two sulfide bridges to $Fe(CO)_3$ (with additional formation of an Cr—Fe bond) [8] or to $Co(CO)_2$ (with additional formation of two Cr—Co bonds) [7].

The next logical step was to study the reactions of I with cyclopentadienylcarbonyl complexes which would enable comparison of CN = 6 (for $CpMn(CO)_3$) and CN = 7 (in $CpV(CO)_4$ and $CpNb(CO)_4$).

Results

a) Synthesis and properties of the complexes

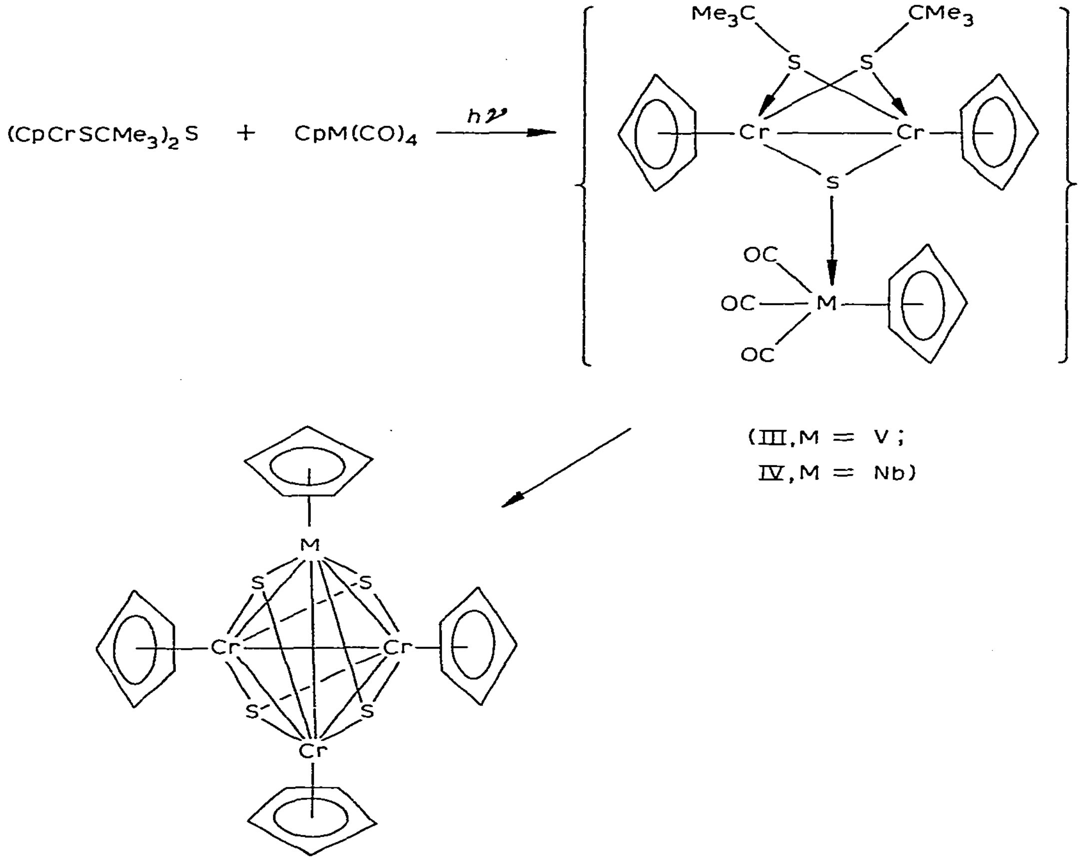
The photochemical reaction of I with hexacoordinated cyclopentadienylmanganese tricarbonyl involves the substitution of one carbonyl group. Complex II was isolated in the form of brown prism which were soluble in all organic solvents. Its IR spectrum contains two stretching bands of the terminal carbonyl groups at 1912 and 1845 cm^{-1} as well as characteristic bands of the cyclopentadienyl (810, 1020, 1440, 1460 and 3075 cm^{-1}).



(I)

(II)

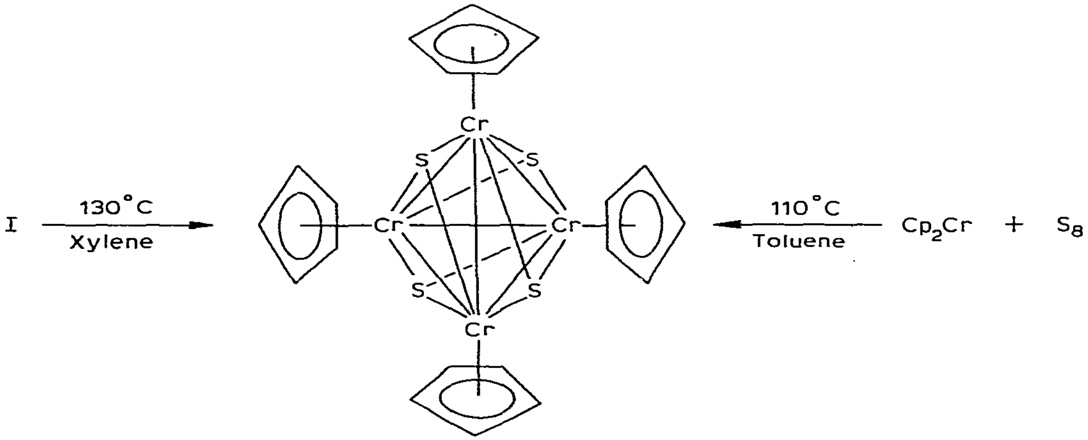
Analogously, the photochemical reactions of I with heptacoordinated cyclopentadienylvanadium tetracarbonyls (in hexane) or those of niobium (in toluene) result in complete loss of the carbonyl and tert-butyl ligands affording the heteronuclear tetrahedral clusters $Cp_4Cr_3MS_4$. Complexes III and IV were isolated in the form of dark-brown finely crystalline products insoluble in organic solvents. Their IR spectra are similar and show the bands characteristic of the C_5H_5 ring vibrations (805, 1018, 1440 and 3080 cm^{-1}). The mass spectrum of III and IV contains peaks of the molecular ions (*m/e* 595 and 637, respectively). Complexes III and IV are paramagnetic with the temperature behaviour of their magnetic succeptibility obeying the Curie-Weiss law; the effective magnetic moment corresponding to the presence of one unpaired electron per



(III, M = V;
IV, M = Nb)

molecule. For III the magnetic moment is close (1.61 BM) to the spin only value 1.73 BM. For IV μ_{eff} is 2.2 BM, which could be due to a small contribution from the ferromagnetic intercluster exchange.

The analogous diamagnetic cluster $Cp_4Cr_4S_4$ (V), prepared earlier from Cp_2Cr and elemental sulfur [9], was synthesized by pyrolysis of I in xylene at 130°C.



(V)

The IR spectrum of the brown crystals of V coincides with the spectra of the product prepared by a literature method [9] in boiling toluene and with the spectra of III and IV. The mass spectrum of V contains the molecular ion peak (*m/e* 596) and the peaks of products with successive elimination of C_5H_5 ligands down to the Cr_4S_4 ion (*m/e* 336); i.e. the cluster V skeleton is reasonably stable.

The structure of the complex $(CpCrSCMe_3)_2S \cdot Mn(CO)_2Cp$ (II)

To elucidate the structure of II we performed an X-ray study of the complex which showed that the molecule includes a mononuclear $CpMn(CO)_2$ fragment and a binuclear $(CpCrSCMe_3)_2S$ fragment joined by a short Mn—S bond (2.334(2) Å) (Fig. 1). The structure of the binuclear fragment is almost unchanged with respect to that of I [3]: the two Cr atoms are joined directly by Cr—Cr (2.704(1) Å) bond, by two bridged $SCMe_3$ groups (Cr—S 2.355(2)

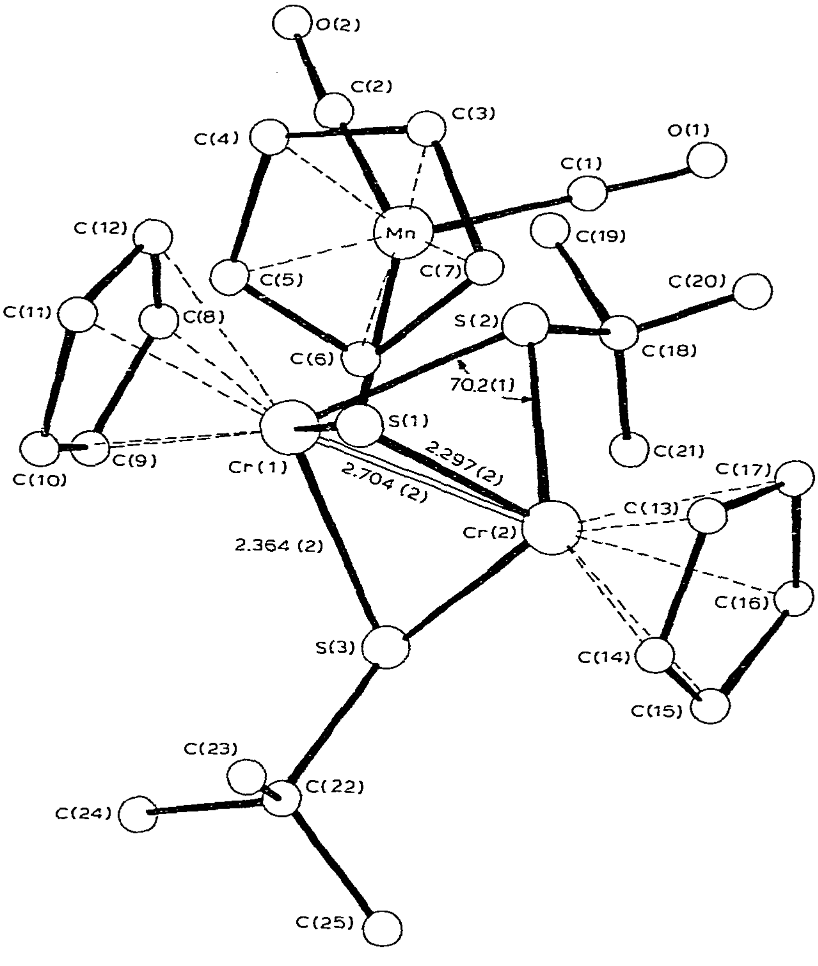


Fig. 1. Structure of $(CpCrSCMe_3)_2S \cdot CpMn(CO)_2$.

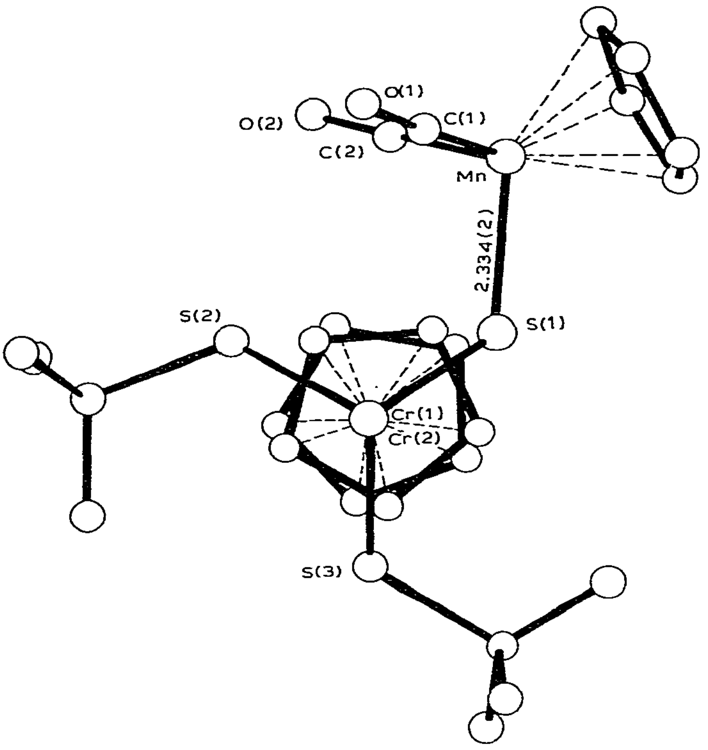


Fig. 2. Projection of the molecule II to the plane S(1)S(2)S(3).

Å) and by one sulfide bridge (Cr—S 2.295(2) Å); the CrSCr angles being 70.0 and 72.2°, respectively. Each Cr atom is also bonded to a π-cyclopentadienyl ligand (mean Cr—C 2.25(1), mean C—C 1.43(1) Å), the ring centers being in the Cr—Cr bond axis, and the ring conformation being close to staggered (Fig. 2). The dihedral angles between the CrS(1)Cr, CrS(2)Cr and CrS(3)Cr planes are 114, 119.5 and 126.5°, respectively. The Mn and tertiary C atoms of the two CMe_3 groups bonded to S(1), S(2) and S(3), respectively, are in the S(1)S(2)S(3) plane, almost perpendicular to the Cr—Cr bond, and on a 3-fold pseudoaxis. The geometry of the $CpMn(CO)_2$ fragment is similar to that of other complexes of the type $CpMn(CO)_2L$ [10]. The π-cyclopentadienyl ligand (mean Mn—C(Cp) 2.17(1), mean C—C 1.43(1) Å), the two carbonyl groups (mean Mn—C 1.76(1), C—O 1.17(1) Å) and the S atom are bonded to the Mn atom in a piano stool structure (C(CO)MnC(CO) 97.3(2)°, mean C(CO)MnS(1) 98.3(2)°). No short contacts (<3.4 Å) are observed between the CO or C_5H_5 ligands at the Mn atom and between the $SCMe_3$ bridges.

Discussion

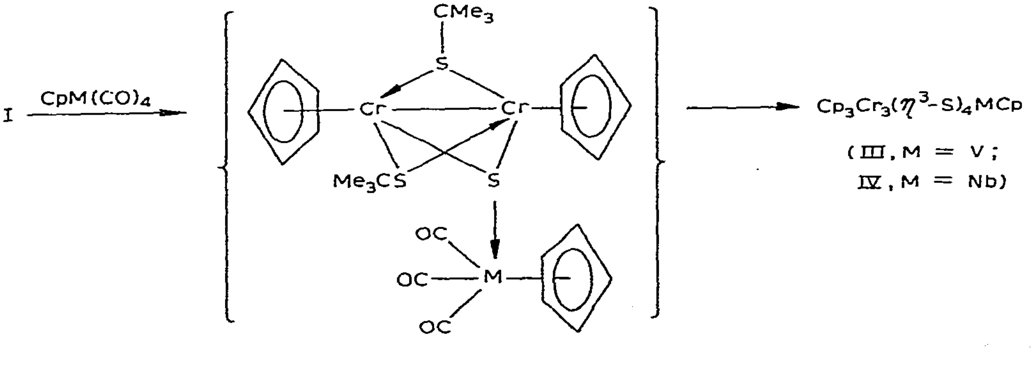
The photochemical reaction of $(CpCrSCMe_3)_2S$ (I) with hexacoordinated $CpMn(CO)_3$ gives the product of simple substitution of one CO group by the sulfide-bridge lone pair of complex I, $(CpCrSCMe_3)_2S \cdot Mn(CO)_2Cp$ (II). This is similar to the reaction of I with other hexacoordinated complexes ($M(CO)_6$

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) IN THE STRUCTURE $(CpCrSCMe_3)_2S \cdot CpMn(CO)_2$

Atom	*X*	*Y*	*Z*
Mn	3510(1)	3682(1)	6233(6)
Cr(1)	1325(1)	5561(1)	7098(1)
Cr(2)	1724(1)	4386(1)	8306(1)
S(1)	1694(2)	4118(1)	6920(1)
S(2)	3142(2)	5508(1)	7997(1)
S(3)	−50(2)	5336(1)	8200(1)
O(1)	4834(5)	5344(3)	6095(3)
O(2)	5267(5)	3312(4)	7629(3)
C(1)	4269(7)	4695(5)	6154(4)
C(2)	4511(7)	3463(4)	7098(4)
C(3)	4367(7)	3116(4)	5192(3)
C(4)	3222(6)	3564(4)	4908(4)
C(5)	2151(7)	3177(4)	5294(4)
C(6)	2632(6)	2491(4)	5808(4)
C(7)	3999(5)	2447(5)	5748(4)
C(8)	9(7)	6518(5)	6439(4)
C(9)	267(8)	5821(5)	5899(4)
C(10)	1609(8)	5819(5)	5763(4)
C(11)	2192(8)	6509(5)	6224(4)
C(12)	1184(7)	6942(5)	6642(4)
C(13)	2243(7)	3002(4)	8549(4)
C(14)	1019(7)	3158(4)	8875(4)
C(15)	1187(7)	3785(5)	9517(4)
C(16)	2502(7)	4024(5)	9579(4)
C(17)	3169(7)	3540(4)	8970(4)
C(18)	3383(7)	6424(4)	8729(4)
C(19)	3912(8)	7169(5)	8228(5)
C(20)	4400(8)	6129(5)	9379(5)
C(21)	2148(7)	6692(5)	9142(5)
C(22)	−1658(7)	4828(5)	7937(5)
C(23)	−2040(7)	4341(5)	8720(5)
C(24)	−2599(7)	5588(6)	7752(6)
C(25)	−1619(7)	4206(6)	7212(5)

where M = Cr, Mo, W, and $Mn_2(CO)_{10}$) discussed in the Introduction. In this case the same factors hinder coordination of both thiolate and sulfide sulfur atoms: a) electronic and coordinational unsaturation of the Mn atom in II, b)



(A)

TABLE 2

ANISOTROPIC TEMPERATURE FACTORS $\times 10^2$ ($\times 10$ FOR Mn, Cr AND S) [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	9.8(4)	11.9(4)	11.9(4)	0.2(3)	1.5(3)	0.5(3)
Cr(1)	13.6(5)	10.3(5)	11.4(5)	1.5(3)	0.1(4)	1.3(4)
Cr(2)	12.9(5)	9.7(5)	10.8(5)	−0.1(3)	1.6(4)	0.6(3)
S(1)	13.9(7)	12.6(7)	12.9(7)	1.4(6)	2.1(5)	−0.3(6)
S(2)	13.8(8)	12.3(7)	15.0(7)	−1.2(6)	−0.5(6)	1.5(6)
S(3)	13.3(8)	12.3(7)	15.4(7)	−0.9(6)	1.8(5)	−3.2(6)
O(1)	31(4)	23(3)	34(3)	−12(2)	9(2)	1(2)
O(2)	18(2)	37(3)	23(2)	3(2)	−2(2)	4(2)
C(1)	17(3)	23(4)	18(3)	0(2)	2(3)	1(3)
C(2)	20(3)	18(3)	18(3)	−1(3)	5(3)	3(3)
C(3)	20(3)	18(3)	14(3)	0(3)	2(3)	−1(2)
C(4)	15(3)	20(3)	15(3)	−1(2)	2(2)	−1(3)
C(5)	25(3)	18(3)	11(3)	0(3)	2(2)	−4(2)
C(6)	20(3)	15(3)	16(3)	−1(3)	0(2)	−5(2)
C(7)	21(3)	16(3)	16(3)	0(3)	4(3)	−3(2)
C(8)	27(4)	22(3)	18(3)	8(3)	−6(3)	6(3)
C(9)	34(4)	23(4)	17(3)	8(3)	−10(3)	7(3)
C(10)	35(4)	22(3)	13(3)	9(3)	0(3)	12(3)
C(11)	41(4)	18(3)	16(3)	4(3)	6(3)	10(3)
C(12)	29(4)	19(3)	20(3)	6(3)	2(3)	7(3)
C(13)	28(4)	11(3)	18(3)	4(3)	−4(3)	7(3)
C(14)	30(4)	15(3)	18(3)	−3(3)	2(3)	7(3)
C(15)	29(4)	21(3)	15(3)	4(3)	3(3)	8(3)
C(16)	30(4)	16(3)	13(3)	7(3)	−1(3)	7(3)
C(17)	28(4)	16(3)	16(3)	8(3)	−3(3)	2(3)
C(18)	20(3)	13(3)	17(3)	−4(2)	−6(2)	0(2)
C(19)	38(4)	17(3)	39(4)	−14(3)	−5(3)	6(3)
C(20)	26(4)	27(4)	27(4)	1(3)	−13(3)	−4(3)
C(21)	23(4)	25(4)	33(4)	4(3)	1(3)	−10(3)
C(22)	12(3)	22(3)	28(4)	−3(3)	2(3)	−11(3)
C(23)	23(4)	29(4)	27(4)	−10(3)	11(3)	−7(3)
C(24)	12(4)	34(4)	59(5)	2(3)	−8(3)	1(4)
C(25)	19(4)	45(4)	27(4)	−11(3)	4(3)	−20(3)

[a] In the form $T = \exp[-1/4(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*)$.

TABLE 3

BOND LENGTHS IN THE STRUCTURE $(CpCrSCMe_3)_2S \cdot Mn(CO)_2Cp$

Bond	d (Å)	Bond	d (Å)	Bond	d (Å)	Bond	d (Å)
Mn—S(1)	2.334(2)						
Mn—C(1)	1.765(7)	Cr—C(Cp)	2.256(7)	C(9)—C(10)	1.42(1)	C(22)—C(23)	1.55(1)
Mn—C(2)	1.754(7)	S(2)—C(18)	1.868(7)	C(10)—C(11)	1.34(1)	C(22)—C(24)	1.56(1)
Mn—C(Cp)	2.163(7)	S(3)—C(22)	1.885(7)	C(11)—C(12)	1.44(1)	C(22)—C(25)	1.53(1)
Cr(1)—S(1)	2.292(2)			C(12)—C(8)	1.42(1)	Cp(1)—Mn	1.785
Cr(2)—S(1)	2.297(2)	C(1)—O(1)	1.172(9)	C(13)—C(14)	1.42(1)	Cp(2)—Cr(1)	1.902
Cr(1)—Cr(2)	2.704(1)	C(2)—O(2)	1.172(9)	C(14)—C(15)	1.44(1)	Cp(3)—Cr(2)	1.902
Cr(1)—S(2)	2.352(2)	C(3)—C(4)	1.44(1)	C(15)—C(16)	1.42(1)		
Cr(1)—S(3)	2.364(2)	C(4)—C(5)	1.43(1)	C(16)—C(17)	1.44(1)		
Cr(2)—S(2)	2.350(2)	C(5)—C(6)	1.43(1)	C(17)—C(13)	1.42(1)		
Cr(2)—S(3)	2.364(2)	C(6)—C(7)	1.43(1)	C(18)—C(19)	1.53(1)		
		C(7)—C(4)	1.44(1)	C(18)—C(20)	1.54(1)		
		C(8)—C(9)	1.43(1)	C(20)—C(21)	1.53(1)		

TABLE 4

BOND ANGLES IN THE STRUCTURE $(CpCrSCMe_3)_2S \cdot CpMn(CO)_2$

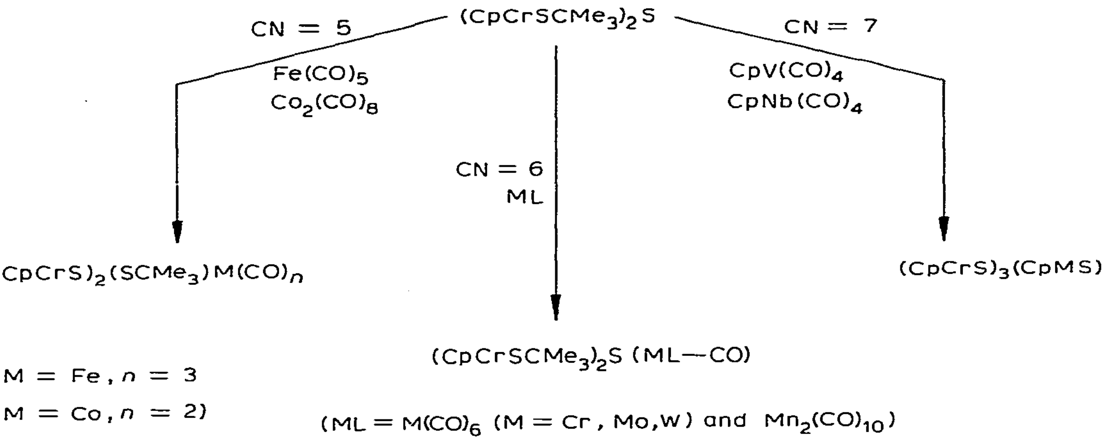
Angle	ω (°)	Angle	ω (°)
Cp(1)MnS(1)	117.5	C(15)C(16)C(17)	107.6(6)
S(1)MnC(1)	98.7(2)	C(16)C(17)C(13)	107.5(6)
S(1)MnC(2)	98.0(2)	S(2)C(18)C(19)	106.0(5)
MnS(1)Cr(1)	119.1(1)	S(2)C(18)C(20)	106.6(5)
MnS(1)Cr(2)	122.9(1)	S(2)C(18)C921)	113.1(5)
Cr(1)S(1)Cr(2)	72.2(1)	C(19)C(18)C(20)	109.6(6)
S(1)Cr(1)Cr(2)	54.0(5)	C(19)C(18)C(21)	110.9(6)
Cp(2)Cr(1)Cr(2)	176.8	C(20)C(18)C921)	110.2(6)
Cp(3)Cr(2)Cr(1)	175.9	S(3)C(22)C(23)	105.7(5)
S(2)Cr(1)Cr(2)	54.8(5)	S(3)C(22)C(24)	106.0(5)
S(3)Cr(1)Cr(2)	55.1(5)	S(3)C(22)C(25)	113.0(5)
S(1)Cr(2)Cr(1)	53.8(5)	C(23)C(22)C(24)	110.5(6)
S(2)Cr(2)Cr(1)	54.9(5)	C(23)C(22)C(25)	110.1(6)
S(3)Cr(2)Cr(1)	55.1(5)	C(24)C(22)C(25)	111.3(6)
Cr(1)S(2)Cr(2)	70.2(1)	S(2)Cr(1)S(1)	84.8(1)
Cr(1)S(3)Cr(2)	69.8(1)	S(2)Cr(1)S(3)	91.0(1)
Cr(1)S(2)C(18)	117.2(2)	S(3)Cr(1)S(1)	93.5(1)
Cr(2)S(2)C(18)	119.8(2)	S(2)Cr(2)S(1)	84.7(1)
Cr(1)S(3)C(22)	116.5(2)	S(2)Cr(2)S(3)	91.1(1)
Cr(2)S(3)C922)	116.1(2)	S(3)Cr(2)S(1)	93.4(1)
MnC(1)O(1)	176.4(6)		
MnC(2)O(2)	174.1(6)		
C(4)C(3)C(7)	108.2(6)		
C(3)C(4)C(5)	107.8(6)		
C(4)C(5)C(6)	107.9(6)		
C(5)C(6)C(7)	108.7(6)		
C(6)C(7)C(3)	107.4(6)		
C(12)C(8)C(9)	108.3(6)		
C(8)C(9)C(10)	107.9(6)		
C(9)C(10)C(11)	108.4(6)		
C(10)C(11)C(12)	107.2(6)		
C(11)C(12)C(8)	108.2(6)		
C(17)C(13)C(14)	108.7(6)		
C(13)C(14)C(15)	107.6(6)		
C(14)C(15)C(16)	108.6(6)		

hindrance to the approach of the thiolate sulfur atom towards Mn by the presence of two carbonyls (Fig. 2). The $CpMn(CO)_2$ fragment causes practically no change in the geometry of I.

On other hand, the heptacoordinated complexes $CpM(CO)_4$ (M = V, Nb) react with I to give rearrangement in both reacting molecules, finally producing $Cp_3Cr_3(\mu^3\text{-}S)_4MCp$ with a tetrahedral Cr_3M skeleton. One cannot describe the sequence of steps giving such a clusters exactly; however, the first step of the photochemical reaction may be similar to that of I with $CpMn(CO)_3$, i.e. one CO group is replaced by the sulfide-bridge lone electron pair, yielding an intermediate A.

The structure of intermediate A should be different from that of the stable complex II: it has an extra carbonyl group which must be oriented towards the coordinated binuclear skeleton of I. This may result in its immediate decomposition or rearrangement to III or IV or in the elimination of another CO from M giving a vacant coordination site, followed by coordination the thiolate sulfur, loss of CMe_3 and further skeletal rearrangement to give III or IV.

In general, in reactions of I with the carbonyl-containing organometallic Lewis acids the following dependence of the product composition on coordination number of M is observed:



The tetrahedral structure of the Cr_3M skeleton in III and IV was assumed on the basis of the similarity of their IR and mass spectra with the spectra of the $Cp_4Cr_4S_4$ cluster [9]. This cluster was obtained by a published method [9] and by pyrolysis of I, and may be similar to the tetrahedral $Cp_4Mo_4S_4$ investigated by X-ray diffraction [11]. A similar, but somewhat distorted, tetrahedral structure may be assigned to the cluster $Cp_3Cr_3(\mu^3\text{-}S)_4Co(CO)$ (VI) recently prepared by the authors. In V and VI each metal atom has an 18-electron valence shell (including a μ^3-bridged four-electron-donor sulfur atom as ligand), which is in agreement with the diamagnetism of these complexes. Substitution of the CpCr group in V or the Co(CO) group in VI by CpM (M = V, Nb) gives a 17-electron valence shell in M. This explains the paramagnetic character of III and IV, corresponding to one unpaired electron per cluster molecule.

Experimental

All operations were carried out under pure argon. $(CpCrSCMe_3)_2S$ and $CpM(CO)_4$ (M = V, Nb) were obtained by literature methods [3,13,14]. Commercial $CpMn(CO)_3$ was purified by sublimation under vacuum. The hydrocarbons were distilled over Na suspension under an argon counterflow The IR spectra were taken an on UR-20 instrument. The mass spectra were recorded on a DS-50 instrument. Magnetic succeptibilities were measured by Faraday's method at 295—277 K [15].

X-ray data were recorded on a Syntex $P2_1$ autodiffractometer (λ(Mo-K_α), $2\theta \leqslant 48°$, $T = -120°C$). 1820 reflections with $F^2 \geqslant 2$ were included in full matrix iteration. The structure was decoded by direct methods. The crystals are monoclinic: a 10.414(7), b 13.513(3), c 16.302(9) Å, β 92.16(5)°, $Z = 4$, space group $P2_1/a$, $R_1 = 0.056$, $R_w = 0.051$.

$(CpCrSCMe_3)_2S \cdot Mn(CO)_2Cp$ (II)

A hot filtered violet solution of 0.15 g (0.34 mmol) of $(CpCrSCMe_3)_2S$ in hexane was added to a hot, filtered yellow solution of 0.07 g (0.34 mmol) of $CpMn(CO)_3$ in the same solvent. After 5—7 h of UV irradiation at 70°C the violet reaction mixture became green. The solution was cooled to —5°C, the precipitated black crystals were separated, washed with pentane and dried under vacuo. Yield 15%. Found: S, 15.64. $C_{23}H_{32}Cr_2MnO_2S_3$ calcd.: S, 15.48%. IR spectrum, ν (cm^{-1}): 440w, 485w, 520w, 810s, 1020m, 1070w, 1162m, 1370w, 1440w, 1460w, 1475w, 1845m, 1912m, 2930w, 3075w.

$Cp_4Cr_3VS_4$ (III)

A mixture of 0.38 g (0.8 mmol) of $CpCrSCMe_3)_2S$ and 0.2 g (0.8 mmol) $CpV(CO)_4$ in 15 ml of heptane was UV-irradiated in a quartz Schlenk vessel for 7 h under reflux. Then the reaction mixture was cooled to —5°C. The black finely crystalline solid precipitated was separated from solution, washed with cold hexane and dried under vacuo. Yield 55%. Found: C, 40.92; H, 4.10. $C_{20}H_{20}Cr_3S_4V$ calcd.: C, 40.34; H, 3.36%. IR spectrum, ν (cm^{-1}): 427w, 805s, 1018m, 1080w, 1440w, 3080w.

$Cp_4Cr_3NbS_4$ (IV)

A mixture of 0.95 g (2.14 mmol) of $(CpCrSCMe_3)_2S$ and 0.37 g (1.28 mmol) $CpNb(CO)_4$ in 50 ml of toluene was UV-irradiated in a quartz Schlenk vessel for 6 h at 80°C. After cooling the reaction mixture to room temperature, the precipitated crystals were separated from solution, washed with toluene and dried under vacuum. Yield 65%. Found: C, 37.22; H, 3.30; Cr, 24.36; Nb, 14.51. $C_{20}H_{20}Cr_3NbS_4$ calcd.: C, 37.71; H, 3.15; Cr, 24.51; Nb, 14.62%. IR spectrum, ν (cm^{-1}): 807s, 1030m, 1070w, 1445w, 3083w.

$Cp_4Cr_4S_4$ (V)

A solution of 0.1 g of $(CpCrSCMe_3)_2S$ (0.28 mmol) in 3 ml of xylene was sealed in an ampoule and heated to 130°C for 24 h. The solution decolourized; the black crystals precipitated were separated from the solution, washed with heptane and dried under vacuo. Yield 85%. Found: C, 40.83; H, 3.61. $C_{20}H_{20}Cr_4S_4$ calcd.: C, 40.27; H, 3.55%. IR spectrum, ν (cm^{-1}): 510w, 810s, 1010w, 1020m, 1140m, 1450m, 3120w.

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