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Formation of Antiferromagnetic Heteronuclear Thiolate and Sulfide Bridged Complexes. 1. Synthesis, Magnetic Properties, and Molecular Structures of Chromium and Rhenium Containing Clusters

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The formation of heteronuclear antiferromagnetic complexes and clusters containing CpCr and Re(CO)(NO) fragments was studied. The antiferromagnetic adducts $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re(CO)_2(NO)$ with cis and trans (μ_3-S)Re(NO) units (**3a** and **3b**, respectively) (**3a** Cr–Cr 2.777(6) Å, $-2J$ = 328 cm^{-1}; **3b** Cr–Cr 2.788(3) Å, $-2J$ = 328 cm^{-1}) were prepared by reaction of the binuclear antiferromagnetic complex $Cp_2Cr_2(SCMe_3)_2S$ (**1**) and $(CO)_4(NO)_2Re_2Cl_4$ (**2**) (ratio 2:1) at 40 °C in benzene or toluene. It was shown that **3a** reacts with **1** (ratio 2:1) at 80 °C in benzene to give the antiferromagnetic cluster $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2Re(CO)(NO)$ (**6**, Re–Cr 2 × 2.940(5) Å, Cr–Cr 3.014(6) Å; $-2J$ = 231 cm^{-1}) as the major reaction product and the paramagnetic tetranuclear compound $[CpCr(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re(CO)(NO)]_2$ (**4**, μ_{eff}/Cr atom = 4.04 μ_B (291–79 K); Cr–Re 3.129(1) Å, Re···Re 3.6681(5) Å) in low yield. **4** can also be prepared by direct thermolysis of **3a** at 60–70 °C in toluene and **6** was formed by the conversion of either **2** with **1** (ratio 3:1) at 80 °C in MeCN or of **4** with **1** (ratio 2:1). Refluxing of **3a** with $P(OiPr)_3$ (ratio 1:1) and subsequent chromatographic separation yields **4**, **6**, and a new paramagnetic trinuclear complex $CpCr(\mu\text{-}OSCMe_3)_2(\mu_3\text{-}S)Re_2(\mu\text{-}Cl)(\mu\text{-}SCMe_3)(CO)_2(NO)_2$ (**8**, μ_{eff}/Cr atom = 3.98 μ_B (291–79 K)) containing no M–M bonds (Re···Re 3.270(1) Å, Re···Cr 3.900 (3) and 3.906(3) Å). It is proposed that formation of **4** and **6** proceeds via the unstable binuclear remetalation product $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)Re(CO)_2(NO)$ (**5**). Compounds **3a**, **3b**, **4**, **6**, and **8** were characterized by X-ray analyses. Crystal data: **3a**, triclinic, space group $P\bar{1}$, a = 10.201(6) Å, b = 11.546(6) Å, c = 11.776(7) Å, α = 97.19(4)°, β = 91.45(5)°, γ = 91.94(5)°, V = 1375(2) Å^3, Z = 2; **3b**·$0.5C_6H_6$, monoclinic, space group $C2/c$, a = 18.526(8) Å, b = 10.184(4) Å, c = 16.693(5) Å, β = 97.28(2)°, V = 3124(2) Å^3, Z = 4; **4**, monoclinic, space group $P2_1/n$, a = 11.163(3) Å, b = 11.977(3) Å, c = 14.521(3) Å, β = 91.32°, V = 1941.0(8) Å^3, Z = 2; **6**, monoclinic, space group $C2$, a = 14.163(3) Å, b = 9.934(2) Å, c = 8.449(2) Å, β = 93.63(2)°, V = 1240.1(5) Å^3, Z = 2; **8**, monoclinic, space group $P2_1/n$, a = 11.946(4) Å, b = 12.185(6) Å, c = 20.890(8) Å, β = 102.62(2)°, V = 2967(2) Å^3, Z = 4.

Introduction

Earlier it was shown that a valuable synthetic route to diamagnetic mixed metal sulfide bridged compounds usually involves the reaction of binuclear sulfur containing species with mono- or binuclear complexes bearing replaceable ligands like CO, diene, or PR_3. For example, $Fe_2S_2(CO)_6$ or $(RC_5H_4)_2V_2S_4$ can be applied in the preparation of heteronuclear iron and vanadium sulfide bridged clusters.[1,2] We have developed synthetic access to antiferromagnetic heteronuclear thiolate and sulfide bridged clusters by using the binuclear antiferromagnetic chromium complexes $(\eta^5\text{-}RC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**1**, R = H; **1a**, R = Me) as sources for appropriate "building blocks".[3] According to X-ray data, magnetic measurements,[4] and theoretical studies[5] compound **1** should have a Cr–Cr single bond (2.689 Å) and two half-occupied orbitals on each Cr(III) atom. Lone pairs on the sulfur atoms of the thiolate and sulfide bridges of **1** (or **1a**) provide valency for further interactions with various unsaturated metal fragments generated from mono- or binuclear low

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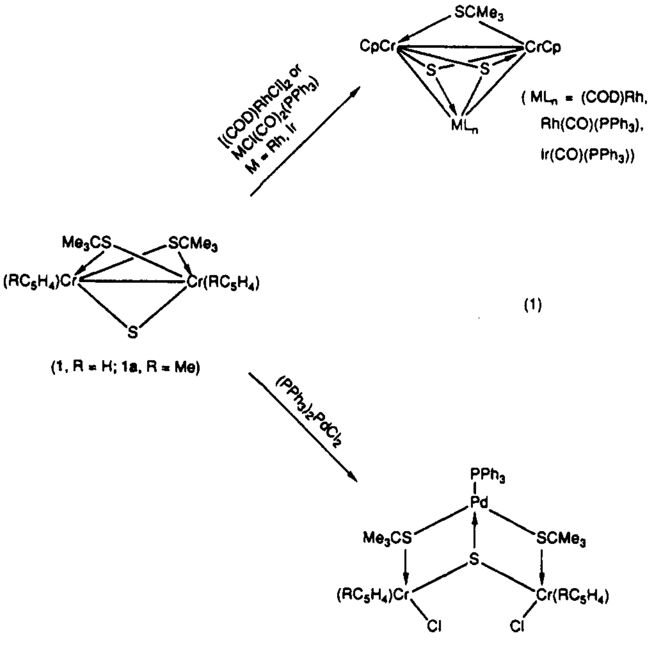
valent transition metal carbonyls or cyclopentadienyl carbonyls $ML(CO)_n$ (L = Cp or CO) upon UV irradiation or heating. In this way a stepwise assembly of heteronuclear clusters was achieved with formation of adducts of the type $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)ML(CO)_{n-1}$. A subsequent rearrangement into the triangular heteronuclear compounds $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)ML(CO)_m$ occurred accompanied by loss of CO groups and by the transformation of one S-CMe$_3$ into a S–M bond. Thus the triangular antiferromagnetic clusters $(RC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2ML(CO)_m$ (R = H, $ML(CO)_m$ = $Fe(CO)_3$, $Mn(CO)_3$, $Co(CO)_2$, $Fe(C_5H_5)$; R = Me, $ML(CO)_m$ = $Co(CO)_2$) were obtained.[3] A similar behavior has been observed in the reaction of the thiophenolate bridged complex $Cp_2Cr_2(SPh)_2S$ (Cr–Cr 2.676 Å)[6] which leads to a $Cp_2Cr_2(SPh)_2SCr(CO)_5$ adduct in the presence of $Cr(CO)_5$-THF.[7]

If 1 is reacted with halogen containing transition metal complexes, one can obtain various products which are not of a uniform type concerning composition and structure. For example, the interaction of 1 with $[(COD)RhCl]_2$ or $MCl(CO)_2(PPh_3)$ (M = Rh, Ir) affords the antiferromagnetic triangular clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2ML_n$ (ML_n = CODRh,[8] $Rh(CO)(PPh_3)$, $Ir(CO)(PPh_3)$[9]) and in contrast to this the reaction of 1 (or 1a) with $(Ph_3P)_2PdCl_2$ leads to the formation of the trinuclear ferromagnetic complexes $(RC_5H_4)_2Cr_2Cl_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Pd(PPh_3)$[10] (eq 1).



(1)

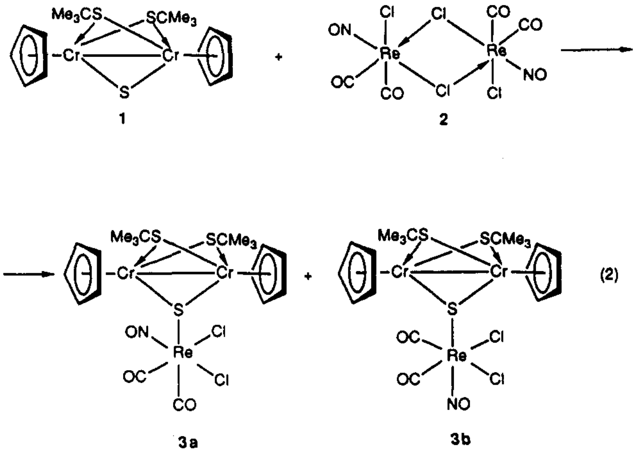
From the reaction of 1 (or 1a) with $Re(CO)_5X$ (X = Cl, Br) heteronuclear clusters could not be obtained; instead the tetranuclear chromium compounds $(RC_5H_4)_4Cr_4S_4^{\,n}$ (n = 0 or +1)[11] were isolated.

In this paper we report on investigations aiming at Cr–Re cluster formation via the reaction of 1 with $(CO)_4(NO)_2Re_2Cl_2(\mu\text{-}Cl)_2$ (2). The idea behind the choice of 2 containing nitrosyl groups was that these might stabilize the bonding of different acido ligands at the Re(I) centers and which in turn could assist cluster formation via their bridging capabilities.

Results and Discussion

It has previously been shown that the binuclear complex $(CO)_4(NO)_2Re_2Cl_2(\mu\text{-}Cl)_2$ (2) can be cleaved with N or P donor ligands (L) to produce the mononuclear species $ReCl_2(CO)_2(NO)L$[12] or $ReCl_2(CO)(NO)L_2$.[13] Taking these findings into account, the preparation of antiferromagnetic heteronuclear clusters could be avisaged by fission of the binuclear complex 2 applying $Cp_2Cr_2(SCMe_3)S$ (1) as the ligand L.

Formation of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)ReCl_2(CO)_2(NO)$ Adducts with Cis and Trans (μ_3-S)Re(NO) Fragments. The reaction of 1 with 2 in the ratio 2:1 proceeds smoothly in benzene or toluene at 40 °C to afford the two antiferromagnetic isomeric adducts $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)ReCl_2(CO)_2(NO)$ (**3a** and **3b**, respectively) containing cis and trans (μ_3-S)Re(NO) fragments (eq 2).



(2)

3a and **3b** were separated by column chromatography and were isolated in analytically pure form. IR spectra of the black prisms of **3a** and **3b** exhibit terminal CO and NO stretching vibration bands (**3a**, ν(CO) 2088 and 2018 cm^{-1}, ν(NO) 1748 cm^{-1}; **3b**, ν(CO) 2063 and 1998 cm^{-1}, ν(NO) 1745 cm^{-1}). According to the results of the X-ray diffraction studies of **3a** and **3b** (Figures 1 and 2, Tables 1 and 2) the binuclear Cr_2S_3 unit of 1 is coordinated to the Re(I) atom via the lone pair of the bridging sulfide atom (**3a**, Re(1)–S(1) 2.502(9) Å; **3b**, Re(1)–S(1) 2.461(3) Å). Isomers **3a** and **3b** are distinguished by the geometrical arrangement of the (μ_3-S)Re(NO) fragments showing cis configuration in **3a** (Re(1)–N(1) 1.77(3) Å, S(1)–Re(1)–N(1) 97.2(12)°) and trans configuration in **3b** (Re(1)–N(1) 1.780(12) Å, S(1)–Re(1)–N(1) 180.0(3)°). The main features of the bonding of 1 to the $ReCl_2(CO)_2(NO)$ moiety

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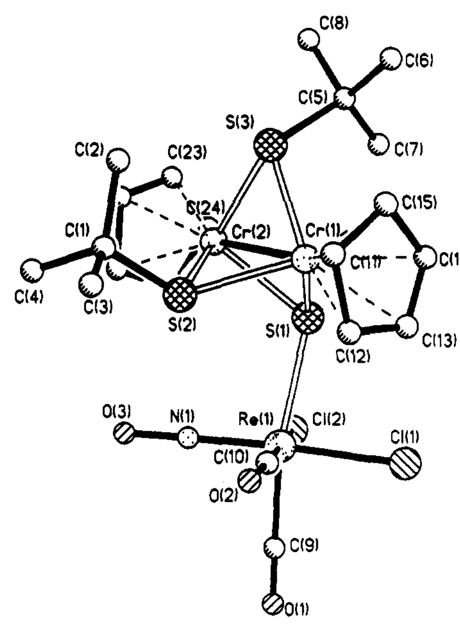

Figure 1. Perspective view of the molecular structure of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)ReCl_2(CO)_2(NO)$ with a cis configuration of the SRe(NO) fragment (**3a**).

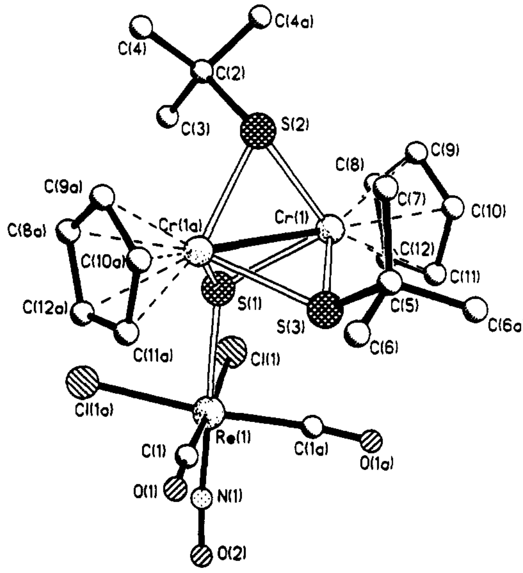

Figure 2. Perspective view of the molecular structure of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)ReCl_2(CO)_2(NO)$ with a trans configuration of the SRe(NO) fragment (**3b**).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of 3a

Re(1)–S(1)	2.502(9)	Re(1)–Cl(1)	2.383(12)
Re(1)–Cl(2)	2.455(11)	Re(1)–N(1)	1.77(3)
Re(1)–C(9)	1.98(5)	Re(1)–C(10)	1.81(3)
Cr(1)–Cr(2)	2.777(6)	Cr(1)–S(1)	2.338(9)
Cr(1)–S(2)	2.343(9)	Cr(1)–S(3)	2.384(9)
Cr(2)–S(1)	2.313(9)	Cr(2)–S(2)	2.370(9)
Cr(2)–S(3)	2.375(9)	O(1)–C(9)	1.09(6)
O(2)–C(10)	1.20(5)	O(3)–N(1)	1.25(4)
S(1)–Re(1)–Cl(1)	85.2(4)	S(1)–Re(1)–Cl(2)	84.7(3)
Cl(1)–Re(1)–Cl(2)	90.4(4)	S(1)–Re(1)–N(1)	97.2(12)
Cl(1)–Re(1)–N(1)	177.3(12)	Cl(2)–Re(1)–N(1)	91.0(10)
S(1)–Re(1)–C(9)	168.1(12)	Cl(1)–Re(1)–C(9)	86.8(14)
Cl(2)–Re(1)–C(9)	86.5(13)	N(1)–Re(1)–C(9)	90.9(18)
S(1)–Re(1)–C(10)	97.4(12)	Cl(1)–Re(1)–C(10)	90.6(10)
Cl(2)–Re(1)–C(10)	177.7(10)	N(1)–Re(1)–C(10)	88.0(14)
C(9)–Re(1)–C(10)	91.4(18)	Cr(2)–Cr(1)–S(1)	52.9(2)
Cr(2)–Cr(1)–S(2)	54.3(2)	S(1)–Cr(1)–S(2)	82.7(3)
Cr(2)–Cr(1)–S(3)	54.1(2)	S(1)–Cr(1)–S(3)	94.1(3)
S(2)–Cr(1)–S(3)	88.6(3)	Cr(1)–Cr(2)–S(1)	53.8(2)
Cr(1)–Cr(2)–S(2)	53.5(2)	S(1)–Cr(2)–S(2)	82.6(3)
Cr(1)–Cr(2)–S(3)	54.4(2)	S(1)–Cr(2)–S(3)	95.0(3)
S(2)–Cr(2)–S(3)	88.2(3)	Re(1)–S(1)–Cr(1)	115.5(3)
Re(1)–S(1)–Cr(2)	117.0(3)	Cr(1)–S(1)–Cr(2)	73.3(3)
Cr(1)–S(2)–Cr(2)	72.2(3)	Cr(1)–S(3)–Cr(2)	71.4(3)
Re(1)–N(1)–O(3)	177.6(31)	Re(1)–C(9)–O(1)	176.7(31)
Re(1)–C(10)–O(2)	170.6(27)		

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of 3b

Re(1)–S(1)	2.461(3)	Re(1)–Cl(1)	2.435(3)
Re(1)–N(1)	1.780(2)	Re(1)–C(1)	1.923(14)
Cr(1)–Cr(1A)	2.788(3)	Cr(1)–S(1)	2.332(2)
Cr(1)–S(2)	2.358(3)	Cr(1)–S(3)	2.361(3)
S(2)–C(2)	1.897(13)	S(3)–C(5)	1.884(14)
C(1)–O(1)	1.11(2)	N(1)–O(2)	1.16(2)
S(1)–Re(1)–Cl(1)	84.8(1)	S(1)–Re(1)–N(1)	180.0(2)
Cl(1)–Re(1)–N(1)	95.2(3)	S(1)–Re(1)–C(1)	90.1(4)
Cl(1)–Re(1)–C(1)	174.6(4)	N(1)–Re(1)–C(1)	90.0(4)
S(1)–Cr(1)–S(2)	89.4(1)	S(1)–Cr(1)–S(3)	84.8(1)
S(2)–Cr(1)–S(3)	90.9(1)	Re(1)–S(1)–Cr(1)	125.8(1)
Cr(1)–S(1)–Cr(1A)	73.4(1)	Cr(1)–S(2)–Cr(1A)	72.5(1)
Cr(1)–S(3)–Cr(1A)	72.4(1)	Re(1)–N(1)–O(2)	174.2(10)
Re(1)–C(1)–O(1)	174.6(12)		

in **3a** and **3b** are comparable to those of the known adduct $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re_2(CO)_9$ (**3c**) (Cr–Cr 2.732(2) Å, Cp(centroid)CrCr 176.7(1)°)[12] containing a binuclear dirhenium carbonyl fragment (Re–Re 3.0691(8) Å).[14] However **3c** exhibits a Re–S bond (2.555(2) Å) which is significantly longer than that in **3a** and **3b**. This effect is obviously due to the presence of the NO group causing enhanced transfer of electron density from the sulfide bridge to the rhenium(I) atom. This redistribution of electron density in the Cr_2S_3 fragment may be also responsible for the elongation of the Cr–Cr bonds in **3a** (2.777(6) Å, Cp(centroid)CrCr 177.0(5)°) and in **3b** (2.788(3) Å, Cp(centroid)CrCr 179.3(1)°) showing approximately the same extent in both cases. In comparison with **3c** the difference in Cr–Cr bond lengths of **3a** and **3b** gives rise to changes in the magnetic properties (Table 6). The energy of the spin–spin exchange interactions for **3a** and **3b** ($-2J = 328$ cm^{-1} for both compounds) is found to be lower than that for **3c** ($-2J = 426$ cm^{-1}) or for the transition metal carbonyl adducts $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)ML_n$ ($ML_n = Cr(CO)_5$, $-2J = 410$ cm^{-1}; $ML_n = Mo(CO)_5, W(CO)_5$, $-2J = 440$ cm^{-1}; $ML_n = Mn_2(CO)_9$, $-2J = 430$ cm^{-1}; $ML_n = CpMn(CO)_2$, $-2J = 440$ cm^{-1})[3] and for **1** ($-2J = 430$ cm^{-1}).[4]

Formation of the Tetranuclear Compound $[CpCr(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re(CO)(NO)]_2$ (4) and the Triangular Cluster $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2Re(CO)(NO)$ (6). The next step to take in our investigation was the attempt to transform **3a** into clusters with Cr–Re bonds. This process can be initiated by heating **3a** in toluene at 60–70 °C. A new tetranuclear compound $[CpCr(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re(CO)(NO)]_2$ (**4**) resulted as the major reaction product. In addition the triangular cluster $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2Re(CO)(NO)$ (**6**) was isolated in low yield. It can be obtained in much better yield by the reaction of **3a** and **1** (ratio 2:1) in boiling benzene or by the direct reaction of **1** and **2** (ratio 3:1) in MeCN at 80 °C. In these latter two cases a small amount of **4** was also formed (eq 3).

The IR spectrum of the brown crystals of **4** showed characteristic ν(CO) bands (1963 and 1958 cm^{-1}, further splitting in the solid state) and a ν(NO) (1715 cm^{-1}) band.

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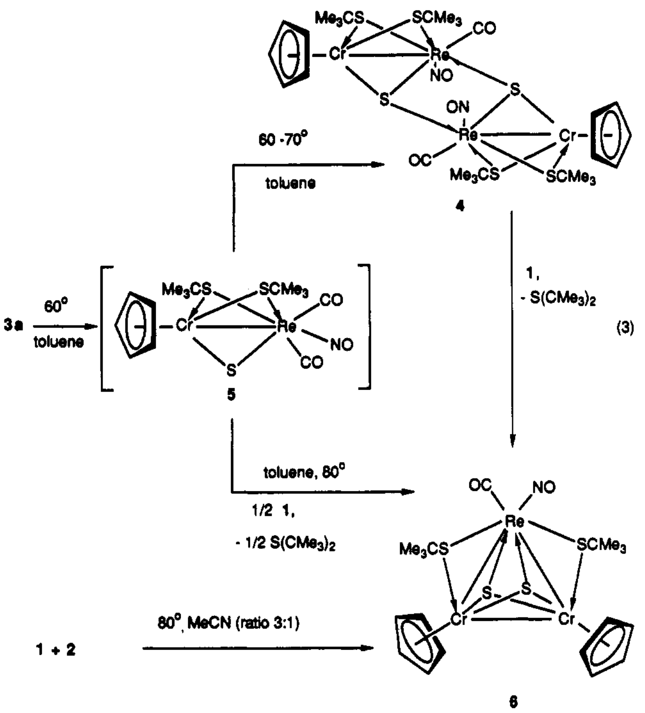


(3)

An X-ray structural study of **4** (Figure 3, Table 3) revealed that it consists of two equivalent binuclear units CpCr(μ-SCMe$_3$)$_2$(μ-S)Re(CO)(NO) held together by Re–S bonds (2.466(2) Å), thus forming a planar Re$_2$S$_2$ moiety (Re···Re 3.6681(5) Å). The ligand environments of the Cr(III) atoms of **4** (Cr–SCMe$_3$ 2.344(2) 2.372(2) Å, Cr–S 2.352(2) Å) are practically the same as in **1**.[4] In addition, one finds a linear Cp(centroid)CrRe arrangement (178.7°) which resembles the linear Cp(centroid)CrCr unit (176.3°) in **1** having a Cr–Cr single bond (2.689(8) Å).[4,5] It can be envisaged to result from the overlap of two semioccupied orbitals at each Cr center. For **4**, however, it has to be assumed that the Re–Cr interaction is established by a semioccupied orbital from the Cr(III) atom (15 electron configuration) and a filled orbital from the Re(I) atom (18 electron configuration).

In this view the Cr–Re distance (3.126(3) Å) should formally correspond to a bond order of 1/2. Magnetic measurements support this bonding model. They are in accord with three unpaired electrons at each Cr(III) atom, which do not take part in super or direct exchange via the ligand bridges. The effective magnetic moment of 4.04 μ_B per Cr atom is close to the spin only value (3.96 μ_B). It is temperature independent in the range 292–80 K.

Mechanistically, it seems reasonable to propose that **4** is a dimerization product of the unstable remetalation intermediate CpCr(μ-SCMe$_3$)$_2$(μ-S)Re(CO)$_2$(NO) (**5**), the assembly of which can be rationalized by chlorine ligand redistribution in **3a** or **3b** initiating extrusion of CpCrCl$_2$ and of CO groups. In the presence of an excess of **1** a thermally generated[4] CpCrS fragment could add to **4** or **5** and induce formation of the Cp$_2$Cr$_2$(μ_3-S)$_2$(μ-SCMe$_3$)$_2$-Re(CO)(NO) cluster (**6**). Its IR spectrum exhibits bands of stretching vibrations at 1951 and 1683 cm^{-1} for the terminal CO and NO groups. The structure of **6** was determined by an X-ray diffraction study. **6** possesses a triangular Cr$_2$Re core (Figure 4, Table 4) with two sulfide bridges placed above and below the plane of the metal atoms (Re–S 2.453(7) Å, Cr–S 2.344(8) and 2.354(6) Å). The Re–Cr edges in **6** are bridged by thiolate groups (Re–SCMe$_3$ 2.384(6) Å, Cr–SCMe$_3$ 2.759(9) Å). The Cr–SR distances are significantly longer than that in **4**, probably due to a strong competition of electron pair donation at the Cr(III) atom between the SR groups and the diamagnetic 18 electron Re(I) center. The Re–Cr interaction amounts to a single bond (2.940(5) Å). The Cr–Cr distance (3.010(6) Å) of **6** is also longer than those of **1**, **3a**, **3b**, and **3c** (Table 6). In these adducts or in **1** the CpCrCrCp moieties are arranged linearly and therefore have better overlapping conditions for appropriate σ type orbitals of the Cr(III) atoms.[5] In **6** the CpCrCrCp moiety has a bent geometry (Cp(centroid)CrCr 124.6°) which causes a reduced σ interaction of the Cr centers. A similar situation has been observed earlier for the tetranuclear cluster Cp$_2$-

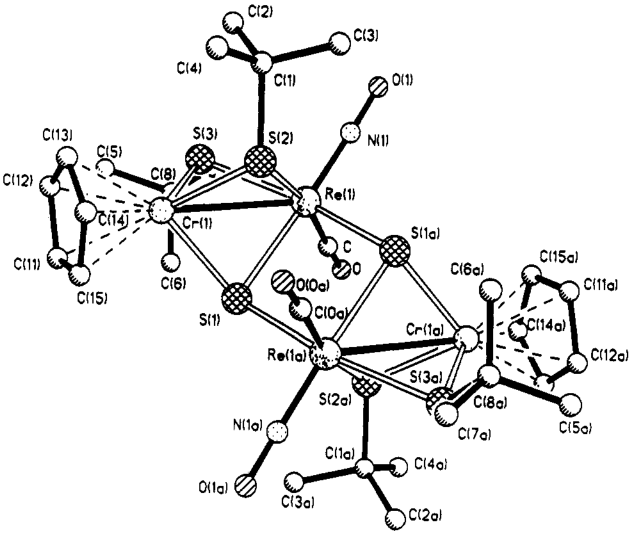
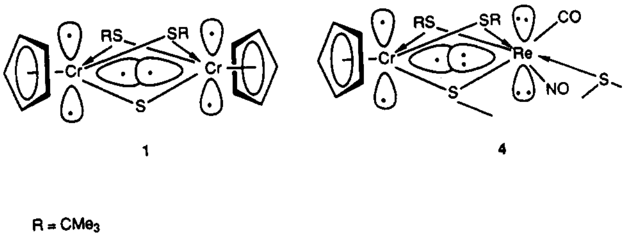


Figure 3. Perspective view of the molecular structure of [CpCr(μ-SCMe$_3$)$_2$(μ_3-S)Re(CO)(NO)]$_2$ (**4**).

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of 4

Re(1)–Cr(1)	3.129(1)	Re(1)–S(1)	2.494(1)
Re(1)–S(2)	2.508(2)	Re(1)–S(3)	2.451(2)
Re(1)–N(1)	1.789(5)	Re(1)–C	1.925(6)
Re(1)–S(1A)	2.466(2)	Cr(1)–S(1)	2.352(2)
Cr(1)–S(2)	2.344(2)	Cr(1)–S(3)	2.371(2)
S(2)–C(1)	1.850(6)	S(3)–C(8)	1.860(6)
C–O	1.152(7)	N(1)–O(1)	1.176(7)
S(1)–Re(1)–S(2)	77.1(1)	S(1)–Re(1)–S(3)	82.6(1)
S(2)–Re(1)–S(3)	80.2(1)	S(1)–Re(1)–N(1)	177.4(2)
S(2)–Re(1)–N(1)	102.0(2)	S(3)–Re(1)–N(1)	94.8(2)
S(1)–Re(1)–C	90.2(2)	S(2)–Re(1)–C	167.4(2)
S(3)–Re(1)–C	99.2(2)	N(1)–Re(1)–C	90.6(2)
S(1)–Re(1)–S(1A)	84.6(1)	S(2)–Re(1)–S(1A)	80.8(1)
S(3)–Re(1)–S(1A)	159.0(1)	N(1)–Re(1)–S(1A)	97.7(2)
C–Re(1)–S(1A)	97.3(2)	S(1)–Cr(1)–S(2)	83.3(1)
S(1)–Cr(1)–S(3)	87.5(1)	S(2)–Cr(1)–S(3)	85.3(1)
Re(1)–S(1)–Cr(1)	80.4(1)	Re(1)–S(1)–Re(1A)	95.4(1)
Cr(1)–S(1)–Re(1A)	125.5(1)	Re(1)–S(2)–Cr(1)	80.2(1)
Re(1)–S(2)–C(1)	117.9(2)	Cr(1)–S(2)–C(1)	119.1(2)
Re(1)–S(3)–Cr(1)	80.9(1)	Re(1)–S(3)–C(8)	116.5(2)
Cr(1)–S(3)–C(8)	117.5(2)	Re(1)–N(1)–O(1)	178.6(5)
Re(1)–C–O	177.6(5)		

Chart 1



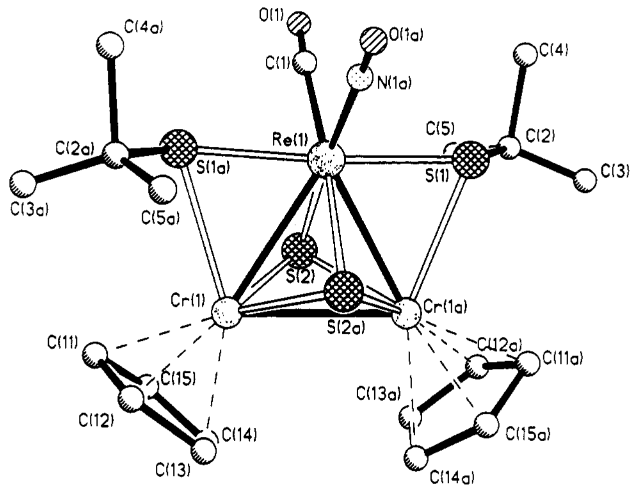
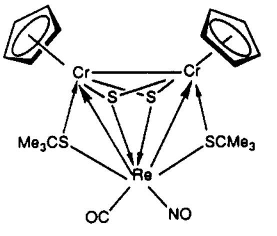


Figure 4. Perspective view of the molecular structure of $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2Re(CO)(NO)$ (6).

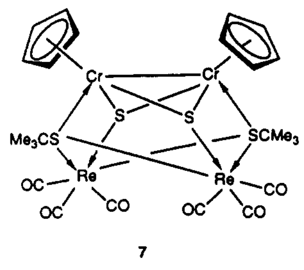
Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of 6

Re(1)–Cr(1)	2.940(5)	Re(1)–S(1)	2.384(6)
Re(1)–S(2)	2.453(7)	Re(1)–C(1)	1.94(3)
Re(1)–Cr(1A)	2.940(5)	Cr(1)–Cr(1A)	3.010(6)
Cr(1)–S(2)	2.344(8)	Cr(1)–S(2A)	2.354(7)
S(1)–C(2)	1.79(3)	S(1)–Cr(1A)	2.759(9)
O(1)–C(1)	1.11(4)		
Cr(1)–Re(1)–S(1)	122.7(5)	Cr(1)–Re(1)–S(2)	50.6(2)
S(1)–Re(1)–S(2)	95.3(4)	Cr(1)–Re(1)–C(1)	130.4(8)
S(1)–Re(1)–C(1)	91.7(9)	S(2)–Re(1)–C(1)	96.3(8)
Cr(1)–Re(1)–Cr(1A)	61.6(2)	S(1)–Re(1)–Cr(1A)	61.4(5)
S(2)–Re(1)–Cr(1A)	50.8(2)	C(1)–Re(1)–Cr(1A)	130.0(8)
Cr(1)–Re(1)–S(1A)	61.4(5)	S(1)–Re(1)–S(1A)	175.9(10)
S(2)–Re(1)–S(1A)	87.7(4)	C(1)–Re(1)–S(1A)	85.2(9)
S(2)–Re(1)–S(2A)	84.9(3)	C(1)–Re(1)–S(2A)	178.7(9)
Cr(1A)–Re(1)–S(2A)	50.6(2)	S(1A)–Re(1)–S(2A)	95.3(4)
Cr(1)–Re(1)–C(1A)	130.0(8)	C(1)–Re(1)–C(1A)	82.5(12)
S(1A)–Re(1)–C(1A)	91.7(9)	S(2A)–Re(1)–C(1A)	96.3(9)
Re(1)–Cr(1)–S(2)	53.9(2)	Re(1)–Cr(1)–S(1A)	49.3(2)
S(2)–Cr(1)–S(1A)	81.6(3)	Re(1)–Cr(1)–S(2A)	53.8(2)
S(2)–Cr(1)–S(2A)	89.6(3)	S(1A)–Cr(1)–S(2A)	88.4(3)
Re(1)–S(1)–Cr(1A)	69.3(4)	Re(1)–S(2)–Cr(1)	75.6(2)
Re(1)–S(2)–Cr(1A)	75.4(2)	Cr(1)–S(2)–Cr(1A)	79.7(3)
Re(1)–C(1)–O(1)	163.5(12)		

Chart 2



6



7

$Cr_2(\mu_3\text{-}S)_2(\mu_3\text{-}SCMe_3)_2Re_2(CO)_6$ (7) in which the binuclear $Cp_2Cr_2S_2$ fragment (Cr–Cr 2.96(1) Å, Cp(centriod)CrCr 137.5°) is associated with a dimeric $Re_2(\mu\text{-}SCMe_3)_2(CO)_6$ unit (Re⋯Re 3.938(1) Å).[14]

In 7 contacts of significant Re–Cr bond character are not found (Re⋯Cr 3.645(1) and 3.646(1) Å). Nevertheless the Cr–$SCMe_3$ distances (Cr–$SCMe_3$ 2.39(2) and 2.45(2) Å) appear to be normal.[12] The weakening of the Cr–Cr bonds in 6 and 7 is reflected in the magnetic properties of both compounds (Table 6). The exchange parameters $-2J$ for 7 (302 cm^{-1}) and especially for 6 are lower than the values for 1, **3a**, **3b**, and **3c**.

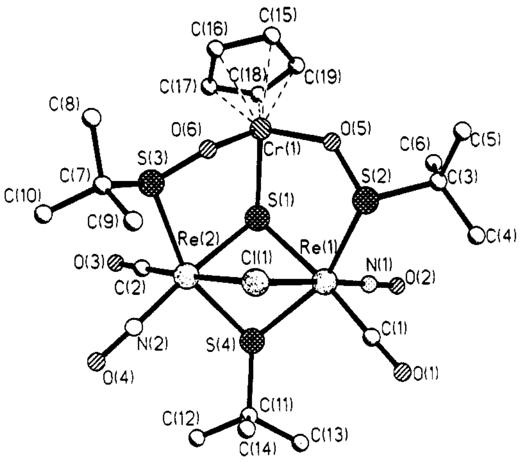
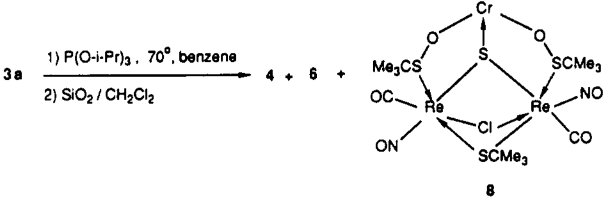


Figure 5. Perspective view of the molecular structure of $CpCr(\mu\text{-}OSCMe_3)_2(\mu_3\text{-}S)Re_2(\mu\text{-}Cl)(\mu\text{-}SCMe_3)(CO)_2(NO)_2$ (8).

Formation of the Trinuclear Cluster $CpCr(\mu\text{-}OSCMe_3)_2(\mu_3S)Re_2(\mu\text{-}Cl)(\mu\text{-}SCMe_3)(CO)_2(NO)_2$ (8). In order to trap the unstable electron deficient intermediate **5** which is produced from the thermal transformation of **3a**, we attempted the reaction of **3a** in the presence of $P(OiPr)_3$. This reaction in benzene at 70 °C took however another course, leading to the formation of **4**, **6**, and a new cluster $CpCr(\mu\text{-}OSCMe_3)_2(\mu_3\text{-}S)Re_2(\mu\text{-}Cl)(\mu\text{-}SCMe_3)(CO)_2(NO)_2$ (**8**) (eq 4).



(4)

8

Upon column chromatography compound **8** was isolated as green prisms. The IR spectrum of **8** shows characteristic ν(CO) (1982 cm^{-1}) and ν(NO) (1709 cm^{-1}) bands. According to its X-ray data (Figure 5, Table 5) there are no bonding contacts between the metals (Cr⋯Re 3.900(3) and 3.906(3) Å, Re⋯Re 3.270(1) Å). The metal atoms are held together by a triply bridging sulfur atom (Re–S 2.459(4) Å and Cr–S 2.351(4) Å) and by oxothiolate ligands (Cr–O 1.937(10) and 1.983(10) Å, Re–S 2.448(3) and 2.456(3) Å). Moreover, the binding of the two Re(CO)(NO) fragments is further enhanced by the bridges of a chlorine atom (Re–Cl 2.500(4) and 2.511(4) Å) and of a thiolate group (Re–S 2.468(4) and 2.469(3) Å). The paramagnetism of **8** is caused by the presence of a Cr(III) atom containing three unpaired electrons with an effective magnetic moment of 3.98 μ_B, which is close to the pure spin only value and which is not dependent on temperature. The formation of **8** containing oxothiolate ligands is surprising, but may be explained by the contact of the thiolate bridged precursor of **8** with silica gel used at the stage of the chromatographic separation or by oxidation through contact with air during the isolation process. Related transformations to form S- or O-sulfenato groups from thiolate ligands were observed in dimolybdenum and cobalt complexes upon column chromatography[15] or by oxidation.[16]

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[15] Vasjutinskaja, E. A.; Eremenko, I. L.; Pasynskii, A. A.; Nefedov, S. E.; Yanovsky, A. I.; Struchkov, Yu. T. *Zh. Neorg. Khim.* **1991**, *36*, 1707 (in Russian).

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) of 8

Re(1)–S(1)	2.459(4)	Re(1)–S(2)	2.448(3)
Re(1)–S(4)	2.468(4)	Re(1)–Cl(1)	2.500(4)
Re(1)–N(1)	1.785(12)	Re(1)–C(1)	1.895(15)
Re(2)–S(1)	2.475(4)	Re(2)–S(3)	2.456(3)
Re(2)–S(4)	2.469(3)	Re(2)–Cl(1)	2.511(4)
Re(2)–N(1)	1.823(14)	Re(2)–C(2)	1.858(14)
Cr(1)–S(1)	2.351(4)	Cr(1)–O(5)	1.937(10)
Cr(1)–O(6)	1.983(10)	S(2)–O(5)	1.585(9)
S(3)–O(6)	1.592(10)	N(1)–O(2)	1.19(2)
N(2)–O(4)	1.19(2)	C(1)–O(1)	1.16(2)
C(2)–O(3)	1.16(2)	Re(1)···Re(2)	3.270(1)
Re(1)···Cr(1)	3.906(3)	Re(2)···Cr(1)	3.900(3)

S(1)–Re(1)–S(2)	89.9(1)	S(1)–Re(1)–S(4)	74.8(1)
S(2)–Re(1)–S(4)	157.4(1)	S(1)–Re(1)–Cl(1)	86.0(1)
S(2)–Re(1)–Cl(1)	79.3(1)	S(4)–Re(1)–Cl(1)	83.0(1)
S(1)–Re(1)–N(1)	95.5(4)	S(2)–Re(1)–N(1)	102.2(4)
S(4)–Re(1)–N(1)	95.9(4)	Cl(1)–Re(1)–N(1)	177.9(4)
S(4)–Re(1)–C(1)	101.6(4)	Cl(1)–Re(1)–C(1)	87.7(5)
N(1)–Re(1)–C(1)	90.7(6)	S(1)–Re(2)–S(3)	84.2(1)
S(1)–Re(2)–S(4)	74.5(1)	S(3)–Re(2)–S(4)	157.1(1)
S(1)–Re(2)–Cl(1)	85.4(1)	S(3)–Re(2)–Cl(1)	87.4(1)
S(4)–Re(2)–Cl(1)	82.8(1)	S(1)–Re(2)–N(2)	174.6(4)
S(3)–Re(2)–N(2)	101.1(4)	S(4)–Re(2)–N(2)	100.1(4)
Cl(1)–Re(2)–N(2)	94.0(5)	S(1)–Re(2)–C(2)	91.6(4)
S(3)–Re(2)–C(2)	91.2(4)	S(4)–Re(2)–C(2)	97.5(4)
Cl(1)–Re(2)–C(2)	176.8(4)	N(2)–Re(2)–C(2)	89.1(6)
S(1)–Cr(1)–O(5)	94.8(3)	S(1)–Cr(1)–O(6)	93.2(3)
O(5)–Cr(1)–O(6)	94.3(4)	Re(1)–S(1)–Re(2)	83.0(1)
Re(1)–S(1)–Cr(1)	108.6(1)	Re(2)–S(1)–Cr(1)	107.8(1)
Re(1)–S(2)–O(5)	111.1(4)	Re(2)–S(3)–O(6)	105.0(3)
Re(1)–S(4)–Re(2)	83.0(1)	Re(1)–Cl(1)–Re(2)	81.5(1)
Cr(1)–O(5)–S(2)	133.0(5)	Cr(1)–O(6)–S(3)	115.5(5)

Conclusion

The formation of the Cr_2Re cluster **6** starting from **1** and **2** can be achieved via the adducts **3a** or **3b** containing the mononuclear $ReCl_2(CO)_2(NO)$ fragment. Then at elevated temperatures the process of remetalation is completed with extrusion of a $CpCrCl_2$ moiety to generate the binuclear unit $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)Re(CO)_2(NO)$ (**5**). **5** is unstable under the reaction conditions and dimerizes to a tetranuclear cluster **4** with loss of a CO group. In the presence of an excess of **1** an unsaturated CpCrS fragment is presumably produced which leads to the build up of cluster **6**.

The type of remetalation process observed in these investigations was up to now unknown for paramagnetic organometallic polynuclear compounds, but is a well established reaction step for electron saturated or electron excess clusters.[17] The obviously straightforward assembly of **4** or **5** (in situ) by "cluster block building" may be taken as a strong hint that this synthetic strategy could be more generally applicable to the preparation of a whole series of magnetically active cluster systems with quite different sets of metals.

Experimental Section

General Comments. All operations including the synthesis of the initial and the final compounds were carried out in an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Benzene, toluene, and tetrahydrofuran (THF) were purified by distillation from sodium/benzophenone ketyl under nitrogen atmosphere. Pentane, hexane, and heptane were dried by reflux over sodium and distilled under nitrogen. Acetonitrile (MeCN) was purified by double distillation from P_2O_5 under N_2. Thin layer chromatography (TLC) (Merck, 5 × 7.5 cm, Kieselgel 60 F_{254}) was used whenever possible to monitor the progress of the reactions being studied. Column chromatography was applied to separate the reaction mixtures (Kieselgel 60, Merck, 70–230 mesh ASTM). The starting materials, $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (1) and $(CO)_4(NO)_2ReCl_2(\mu\text{-}Cl)_2$ (2) were prepared as described elsewhere.[4,13] Infrared spectra were obtained on a Bio-Rad FTS-45 spectrometer in KBr pellets. MS spectra (EI and FAB) were measured on a Finnigan MAT 8320 instrument (70 eV).

Reaction of $(\eta^5\text{-}C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (1) with $(CO)_4(NO)_2Re_2Cl_2(\mu\text{-}Cl)_2$ (2) (Ratio 2:1) at 40 °C. A deep violet solution of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2S$ (1) (880 mg, 2 mmol) and $(CO)_4(NO)_2Re_2Cl_2(\mu\text{-}Cl)_2$ (2) (680 mg, 1 mmol) in benzene or toluene (40 mL) was stirred at 40 °C. After 30 min a black solution was obtained. TLC (CH_2Cl_2) showed the presence of two black bands and the absence of the starting materials. Both new products were separated by use of column chromatography (5 × 30 cm, silica gel, CH_2Cl_2/heptane 2:1) with formation of two fractions:

(I) A black solution (50 mL) in CH_2Cl_2/heptane which afforded black plates of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)ReCl_2(CO)_2(NO)$ (**3a**) (1000 mg, 1.27 mmol, 63.5%) upon concentration to 10 mL and cooling (−5 °C). **3a** was recrystallized from a benzene/heptane mixture with the formation of black prisms suitable for X-ray investigation. Anal. Calcd for $Cp_2Cr_2(SCMe_3)_2SReCl_2(CO)_2(NO)$: C, 30.47; H, 3.55; N, 1.78. Found: C, 30.60; H, 3.60; N, 1.77. MS (FAB), *m/z*: 789, $Cp_2Cr_2(SCMe_3)_2ReCl_2(CO)_2(NO)$. IR, ν, cm^{-1}: 3094 (w), 2976 (m), 2960 (m), 2918 (m), 2855 (w), 2088 (vs), 2018 (vs), 1748 (vs), 1460 (w), 1453 (sh, m), 1438 (m), 1392 (w), 1360 (m), 1351 (m), 1152 (m), 1070 (w), 1015 (m), 829 (m), 806 (s), 625 (w), 610 (w), 563 (m), 485 (w), 469 (w). μ_{eff}/Cr atom (291–79 K), μ_B: 1.36–0.60.

(II) A black solution (30 mL) in CH_2Cl_2/heptane which after concentration to 10 mL gave a microcrystalline precipitate of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)ReCl_2(CO)_2(NO)$ (**3b**) (340 mg, 0.43 mmol, 21.6%). Anal. Calcd for $Cp_2Cr_2(SCMe_3)_2SReCl_2(CO)_2(NO)$: C, 30.47; H, 3.55; N, 1.78, Cl, 9.01. Found: C, 30.50; H, 3.49; N, 1.85; Cl, 8.92. Recrystallization of **3b** from a benzene/heptane mixture yielded black prisms of **3b**·$0.5C_6H_6$ which are used in the X-ray crystallographic study. MS (FAB), *m/z*: 789, $Cp_2Cr_2(SCMe_3)_2$-

Table 6. Comparison of Cr–Cr Distances, Magnetic Properties, and IR Data for the Antiferromagnetic Thiolate and Sulfide Bridged Compounds 1–7

compd	Cr–Cr dist (Å)	μ_{eff}/Cratom (μB) (temp/range (K))	exchange param $-2J$ (cm^{-1})	least sq err (%)	ν(CO) (cm^{-1})	ν(NO) (cm^{-1})	ref
1	2.689(8)	0.98–0.02 (296–79)	430	3.2			2
3c	2.732(2)	1.29–0.32 (296–77)	424	3.8	1895 1922 1940 1970 2020 2080		12
3a	2.777(6)	1.36–0.60 (291–79)	328	4.7	2088 2018	1748	this work
3b	2.788(3)	1.39–0.62 (291–79)	328	2.2	2063 1998	1745	this work
7	2.96(1)	1.50–0.75 (292–79)	302	3.0	1885 1992		12
6	3.010(6)	1.67–0.55 (288–79)	231	2.4	1951	1683	this work

Table 7. Data Collection and Processing Parameters

compd	**3a**	**3b**	**4**	**6**	**8**
formula	$C_{20}H_{28}Cl_2NO_3S_3Cr_2Re$	$C_{20}H_{28}Cl_2NO_3Cr_2Re\cdot 0.5C_6H_6$	$C_{28}H_{46}N_2O_4S_6Cr_2Re_2$	$C_{19}H_{28}NO_2S_4Cr_2Re$	$C_{19}H_{32}ClN_2O_6S_4CrRe_2$
mol wt	787.7	825.7	1143.4	720.6	972.6
color and habit	black prism	black prism	brown prism	green plate	green prism
space group	$P\bar{1}$ (No. 2)	$C2/m$ (No. 12)	$P2_1/n$ (No. 14)	$C2$ (No. 5)	$P2_1/n$ (No. 14)
a, Å	10.201(6)	18.526(8)	11.163(3)	14.163(3)	11.946(4)
b, Å	11.546(6)	10.184(4)	11.977(3)	9.934(2)	12.185(6)
c, Å	11.776(7)	16.693(5)	14.521(3)	8.449(2)	20.890(8)
α, deg	97.19(4)				
β, deg	91.45(5)	97.28(2)	91.32(2)	93.63(2)	102.62(2)
γ, deg	91.94(5)				
V, Å^3	1375(2)	3124(2)	1941.0(8)	1240.1(5)	2967(2)
Z	2	4	2	2	4
ρ_{calcd}, g cm^{-1}	1.903	1.732	1.956	1.882	2.127
radiation; λ, Å	graphite monochromator, Mo Kα; 0.710 73	graphite monochromator, Mo Kα; 0.710 73	graphite monochromator, Mo Kα; 0.710 73	graphite monochromator, Mo Kα; 0.710 73	graphite monochromator, Mo Kα; 0.710 73
temp, °C	22	22	−60	22	22
abs coeff, cm^{-1}	59.49	49.43	71.79	61.11	89.05
transm factors	0.321–0.155	0.679–0.375	0.411–0.196	0.357–0.107	0.365–0.127
cryst size, mm	0.3 × 0.35 × 0.2	0.3 × 0.25 × 0.18	0.4 × 0.25 × 0.25	0.30 × 0.30 × 0.05	0.30 × 0.25 × 0.25
scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
scan speed, deg min^{-1}	variable; 2.49–14.65	variable; 2.02–14.65	variable; 2.49–14.65	variable; 1.50–14.65	variable; 2.02–14.65
scan width	1.90	2.00	1.20	1.60	1.90
collcn range	$h\pm k\pm l$	$h,k\pm l$	$h,k\pm l$	$h,k\pm l$	$h,k\pm l$
2θ range	5–48	3–56	5–52	4–55	4–56
no. of unique data	4314	3994	3684	1516	6625
no. of refl obsd	2985 ($F \geq 6\sigma(F)$)	2163 ($F \geq 4\sigma(F)$)	3457 ($F \geq 4\sigma(F)$)	1446 ($F \geq 4\sigma(F)$)	3364 ($F \geq 4\sigma(F)$)
no. of variables	289	189	199	70	316
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0032F^2$	$w^{-1} = \sigma^2(F) + 0.0100F^2$	$w^{-1} = \sigma^2(F) + 0.0000F^2$	unit weight	$w^{-1} = \sigma^2(F) + 0.0050F^2$
R	0.070	0.041	0.029	0.086	0.035
R_W	0.078	0.064	0.033	0.098	0.056
residual extrema in final diff map, e Å^{-3}	+1.24 to −1.19	+0.80 to −0.98	+0.95 to −0.85	1.62 to −1.34	+0.88 to −0.70

$SReCl_2(CO)_2(NO)$. IR, ν, cm^{-1}: 3109 (w), 3088 (w), 2982 (m), 2957 (m), 2918 (m), 2891 (w), 2854 (w), 2063 (vs), 1998 (vs), 1745 (vs), 1470 (w), 1450 (m), 1433 (w), 1391 (w), 1361 (m), 1153 (m), 1066 (w), 1018 (w), 839 (w), 817 (s), 701 (w), 680 (w), 607 (w), 579 (w), 482 (w). μ_{eff}/Cr atom (291–79 K), μ_B: 1.39–0.62.

Reaction of 1 and 2 (Ratio 3:1) in Boiling MeCN. A deep violet solution of 1 (1320 mg, 3 mmol) and of 2 (680 mg, 1 mmol) was refluxed in MeCN (50 mL). After a few minutes the reaction mixture became black, and after 2 h it had changed to a dark green color. TLC assured the absence of the initial compounds. The newly formed products were separated by column chromatography (5 × 30 cm, silica gel, CH_2Cl_2) with the evolution of two bands:

(I) A brown solution in CH_2Cl_2 (30 mL) which after addition of heptane (5 mL) and concentration to 8–10 mL gave brown prisms of $[CpCr(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re(CO)(NO)]_2$ (4) (160 mg, 0.140 mmol, 14%) Anal. Calcd for $[CpCr(SCMe_3)_2SRe(CO)(NO)]_2$: C, 29.39, H, 4.02; N, 2.45. Found: C, 29.41; H, 3.99; N, 2.22. IR, ν, cm^{-1}: 3115 (w), 2977 (m), 2959 (m), 2921 (m), 2893 (w), 2853 (w), 1963 (sh, vs), 1958 (vs), 1715 (vs), 1454 (m), 1388 (w), 1362 (m), 1154 (m), 1061 (w), 1016 (m), 819 (m), 813 (sh, m), 668 (w), 635 (w), 616 (w), 523 (w), 515 (w). μ_{eff}/Cr atom (292–80 K), μ_B: 4.04.

(II) A green solution in CH_2Cl_2 (50 mL) which after addition of heptane (10 mL), concentration to 15 mL, and cooling (−5 °C) gave deep green plates of $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2Re(CO)(NO)$ (6) (910 mg, 1.26 mmol, 63.1%). Anal. Calcd for $Cp_2Cr_2(SCMe_3)_2S_2Re(CO)(NO)$: C, 31.66; H, 3.89; N, 1.94. Found: C, 31.86; H, 3.94; N, 1.87. MS (EI, FAB), m/z: 721, $Cp_2Cr_2(S)_2(SCMe_3)_2Re(CO)(NO)$; 693, $Cp_2Cr_2(S)_2(SCMe_3)_2Re(NO)$; 636, $Cp_2Cr_2(S)_3(SCMe_3)Re(NO)$; 579, $Cp_2Cr_2(S)_4Re(NO)$; 549, $Cp_2Cr_2(S)_4Re$; 484, $CpCr_2(S)_4Re$; 419, $Cr_2(S)_4Re$. IR, ν, cm^{-1}: 3085 (w), 2974 (w), 2957 (m), 2936 (w), 2889 (w), 2855 (w), 1951 (vs), 1683 (vs), 1452 (m), 1436 (m), 1390 (w), 1365 (m), 1359 (m), 1159 (m), 1065 (w), 1019 (w), 1012 (w), 811 (s), 796 (m), 607 (w), 597 (w), 573 (w), 538 (w), 483 (w). μ_{eff}/Cr atom (288–79 K), μ_B: 1.67–0.55.

Reaction of 3a with 1 (Ratio 2:1) at 80 °C. A black-violet solution of **3a** (200 mg, 0.25 mmol) and 1 (60 mg, 0.135 mmol) was refluxed in benzene (30 mL) for 1 h until the formation of a green solution was observed. At this stage the TLC indicated the absence of **3a** and 1, but the presence of 6 (as a main product) and traces of 4. The separation by column chromatography gave $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2Re(CO)(NO)$ (6) (95 mg, 0.132 mmol, 52.8%) as a major product and a small amount of $[CpCr(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re(CO)(NO)]_2$ (4).

Thermolysis of 3a in Toluene at 60–70 °C. A black solution of **3a** (410 mg, 0.520 mmol) in toluene (50 mL) was stirred at 60–70 °C. After 3.5 h a brown-green solution was obtained. TLC indicated the presence of 4 and 6 and the absence of the starting material **3a**. The products were separated by column chromatography. Yield of 4: 230 mg, 0.201 mmol, 77.3%. Yield of 6: 60 mg, 0.083 mmol, 16%.

Reaction of 4 with 1 at 80 °C. A brown-violet solution of 4 (80 mg, 0.07 mmol) and 1 (20 mg, 0.045 mmol) was refluxed in benzene (15 mL) for 30 min. A green solution developed. TLC indicated the presence of 6 and traces of 1. After filtration of the solution, concentration to 5 mL, and cooling to +10 °C the green prismatic crystals of 6 were obtained. These crystals were separated by decanting the supervescent solvent, washed with pentane, and dried in vacuo. Yield of 6: 60 mg, 0.084 mmol, 59.4%.

Thermolysis of 6 in Boiling *o*-Xylene. A deep green solution of 5 (120 mg, 0.17 mmol) was refluxed in *o*-xylene (30 mL) for 12 h. No changes of the reaction mixture were observed by TLC (CH_2Cl_2) and IR monitoring. The yield of recovered 6: 110 mg, 0.15 mmol, 88.2%.

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(17) See for example: (a) Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Engl. Ed.* **1978**, *17*, 864. (b) Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Engl. Ed.* **1979**, *18*, 531. (c) Richter, F.; Vahrenkamp, H. *Organometallics* **1982**, *1*, 756. (d) Roland, E.; Vahrenkamp, H. *Chem. Ber.* **1984**, *117*, 1039. (e) Pasynskii, A. A.; Kolobkov, B. I.; Eremenko, I. L.; Nefedov, S. E.; Katser, C. B.; Porai-Koshits, M. A. *Zh. Neorg. Khim.* **1992**, *37*, 563 (in Russian).

Table 8. Atom Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) of 3a

	x	*y*	*z*	*U*(eq)[a]
Re(1)	2540(1)	1306(1)	4485(1)	35(1)
Cr(1)	1124(4)	3416(4)	2224(4)	32(2)
Cr(2)	3847(4)	3609(4)	2338(4)	30(2)
S(1)	2495(7)	3280(7)	3820(7)	33(2)
S(2)	2544(8)	2054(7)	1333(7)	34(2)
S(3)	2438(8)	4928(6)	1565(7)	32(2)
Cl(1)	832(11)	1984(11)	5713(11)	77(5)
Cl(2)	4196(11)	2220(9)	5896(9)	69(4)
O(1)	2545(24)	−824(28)	5808(28)	74(12)
O(2)	673(35)	−37(22)	2759(32)	92(14)
O(3)	4679(31)	322(21)	2973(28)	71(12)
N(1)	3778(27)	736(30)	3578(31)	58(12)
C(1)	2542(31)	1768(28)	−318(32)	48(12)
C(2)	2545(37)	2949(29)	−786(30)	52(13)
C(3)	1683(64)	918(28)	−745(40)	121(28)
C(4)	3860(32)	1150(49)	−488(38)	78(20)
C(5)	2366(37)	6451(20)	2435(23)	39(10)
C(6)	1040(63)	6860(39)	1979(56)	150(32)
C(7)	2566(45)	6455(41)	3646(37)	73(17)
C(8)	3304(49)	7179(36)	1909(33)	75(17)
C(9)	2582(50)	−72(41)	5332(36)	78(18)
C(10)	1343(23)	574(28)	3453(36)	46(13)
C(11)	−833(30)	2950(54)	1198(49)	97(24)
C(12)	−759(30)	2289(40)	2160(46)	63(17)
C(13)	−711(47)	3047(39)	3194(44)	71(18)
C(14)	−719(28)	4075(57)	2941(43)	83(23)
C(15)	−825(25)	4139(37)	1699(39)	54(15)
C(21)	5815(31)	2744(52)	2095(57)	110(25)
C(22)	5768(32)	3740(44)	1482(40)	59(16)
C(23)	5720(35)	4647(45)	2208(48)	71(19)
C(24)	5632(34)	4423(32)	3310(37)	54(14)
C(25)	5696(29)	3157(41)	3232(46)	68(18)

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

Table 9. Atom Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) of 3b

atom	*x*	*y*	*z*	*U*[a]
Re(1)	387(1)	0	1841(1)	59(1)
Cr(1)	−1610(1)	−1369(1)	2564(1)	46(1)
S(1)	−592(1)	0	2710(2)	48(1)
S(2)	−2160(2)	0	3452(2)	53(1)
S(3)	−2029(2)	0	1461(2)	54(1)
Cl(1)	942(1)	−1663(3)	2771(2)	94(1)
O(1)	−379(6)	2088(15)	751(7)	184(7)
O(2)	1513(6)	0	749(8)	104(5)
N(1)	1096(6)	0	1215(7)	75(4)
C(1)	−112(6)	1350(16)	1182(7)	100(5)
C(2)	−1723(8)	0	4543(8)	68(5)
C(3)	−901(12)	0	4636(14)	47(7)
C(3)a	−2341(33)	0	5047(27)	211(44)
C(4)	−2026(11)	1239(23)	4899(13)	73(8)
C(4)a	−1384(43)	1328(57)	4757(18)	352(44)
C(5)	−3028(8)	0	1069(9)	74(5)
C(6)	−3169(7)	1192(15)	555(8)	132(7)
C(7)	−3489(7)	0	1762(10)	89(6)
C(8)	−1280(8)	−3232(10)	3211(8)	94(5)
C(9)	−2037(6)	−3240(11)	3030(8)	87(5)
C(10)	−2203(6)	−3232(10)	2220(8)	88(5)
C(11)	−1571(6)	−3218(10)	1868(7)	80(4)
C(12)	−987(6)	−3223(10)	2483(9)	88(5)
C(1)b	5000	1133(67)	5000	275(43)
C(2)b	5366(21)	778(46)	4474(17)	284(28)

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

Table 10. Atom Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) of 4

	x	*y*	*z*	*U*(eq)[a]
Re(1)	999(1)	1215(1)	71(1)	18(1)
Cr(1)	590(1)	939(1)	−2056(1)	23(1)
S(1)	708(1)	−465(1)	−925(1)	21(1)
S(2)	−679(1)	1796(1)	−1003(1)	25(1)
S(3)	2160(1)	1866(1)	−1237(1)	23(1)
O	3003(4)	38(4)	1189(3)	39(2)
O(1)	1415(4)	3267(4)	1174(3)	47(2)
N(1)	1236(4)	2451(4)	742(3)	29(2)
C	2250(5)	458(5)	758(4)	25(2)
C(1)	−998(6)	3305(5)	−1121(4)	37(2)
C(2)	104(7)	4003(5)	−1290(6)	62(3)
C(3)	−1619(7)	3640(6)	−243(5)	55(3)
C(4)	−1913(8)	3400(7)	−1915(6)	70(3)
C(5)	4170(6)	1660(6)	−2265(4)	46(2)
C(6)	3731(6)	18(5)	−1292(5)	36(2)
C(7)	4450(6)	1798(6)	−552(4)	43(2)
C(8)	3698(5)	1288(5)	−1334(4)	32(2)
C(11)	1153(6)	73(7)	−3344(4)	47(3)
C(12)	1255(7)	1240(8)	−3476(4)	62(3)
C(13)	125(8)	1701(7)	−3422(4)	53(3)
C(14)	−683(7)	844(6)	−3270(4)	44(2)
C(15)	−51(6)	−148(6)	−3217(4)	43(2)

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

Table 11. Atom Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) of 6

	x	*y*	*z*	*U*(eq)[a]
Re(1)	0	0	0	53(1)
Cr(1)	−382(3)	2542(5)	1609(5)	52(1)
S(1)	463(4)	−85(20)	−2650(7)	92(2)
S(2)	1037(4)	1821(8)	859(7)	50(2)
O(1)	1350(4)	−2085(8)	1249(7)	70(5)
C(1)	806(4)	−1471(8)	648(7)	39(4)
C(2)	1621(19)	−141(35)	−3137(30)	80(5)
C(3)	1823(20)	382(31)	−4692(30)	86(5)
C(4)	1545(28)	−1771(35)	−3345(39)	122(5)
C(5)	2333(15)	166(35)	−1849(25)	63(4)
C(11)	−716(25)	3325(34)	3991(37)	98(5)
C(12)	−1375(26)	3703(34)	2854(36)	97(5)
C(13)	−1026(26)	4583(34)	1623(38)	111(5)
C(14)	−104(21)	4868(40)	2052(32)	93(5)
C(15)	91(22)	4103(30)	3420(33)	77(5)

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

Preparation of (η^5-C_5H_5)Cr(μ-OSCMe$_3$)$_2$(μ_3-S)Re$_2$(μ-Cl)(μ-SCMe$_3$)(CO)$_2$(NO)$_2$(8). A black solution of **3a** (220 mg, 0.279 mmol) with 0.06 mL of P(OiPr)$_3$ in benzene (50 mL) was stirred at 70 °C for 4 h until the formation of a green solution was observed. TLC indicated the presence of **4**, **6**, and a new green-blue product **8**. After separation of the reaction mixture by column chromatography three fractions were obtained:

(I) A brown solution in CH_2Cl_2/benzene, which gave brown crystals of **4** upon evaporation (40 mg, 0.034 mmol, 25%).

(II) A green solution in CH_2Cl_2, which gave deep green crystals of **6** by the same procedure as for **4** (35 mg, 0.048 mmol, 17.4%).

(III) A green-blue solution which gave green prisms of CpCr(μ-OSCMe$_3$)$_2$(μ_3-S)Re$_2$(μ-Cl)(μ-SCMe$_3$)(CO)$_2$(NO)$_2$ (**8**) (80 mg, 0.082 mmol, 58.6%). Anal. Calcd for CpCr(OSCMe$_3$)$_2$SRe$_2$Cl(SCMe$_3$)(CO)$_2$(NO)$_2$: C, 23.44; H, 3.29; N, 2.88. Found: C, 23.67; H, 3.35; N, 2.65. IR, ν, cm^{-1}: 3088 (w), 2963 (m), 2924 (m), 2900 (w), 2859 (m), 1982 (vs), 1709 (vs), 1468 (w), 1456 (m), 1442 (m), 1388 (w), 1359 (m), 1159 (m), 1060 (w), 1018 (w), 1007 (w), 858 (m), 842 (m), 825 (m), 816 (s), 678 (w), 625 (w), 613 (w), 595 (w), 582 (w), 535 (m), 501 (w), 483 (w), 470 (w). μ_{eff}/Cr atom (291–79 K), μ_B: 3.98.

Magnetic Measurements and Calculations. The temperature dependence of the magnetic susceptibilities (χ_m) of the investigated compounds was determined by the Faraday technique between 77 and 296 K using the original device of the Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.[18] The effective magnetic moments were

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(18) Novotortsev, V. M. Ph.D. Thesis. Institute of General and Inorg. Chem. Moscow 1974.

Table 12. Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) of 8

atom	*x*	*y*	*z*	U^a
Re(1)	4531(1)	829(1)	1534(1)	48(1)
Re(2)	3450(1)	3261(1)	1125(1)	49(1)
Cr(1)	1186(2)	923(2)	1017(1)	46(1)
S(1)	2783(3)	1723(3)	1720(2)	48(1)
S(2)	3353(3)	−547(3)	843(2)	48(1)
S(3)	1552(3)	3097(3)	388(2)	49(1)
S(4)	5147(3)	2675(3)	1956(2)	54(1)
Cl(1)	4121(3)	1795(3)	452(2)	63(1)
O(1)	6709(10)	−75(10)	1185(7)	92(5)
O(2)	5122(11)	−304(10)	2827(6)	88(5)
O(3)	2541(11)	4920(10)	1958(6)	85(5)
O(4)	4468(10)	5145(9)	514(6)	82(5)
O(5)	2029(7)	−322(7)	789(5)	56(3)
O(6)	1376(8)	1815(8)	253(4)	56(3)
N(1)	4877(9)	156(10)	2311(6)	57(4)
N(2)	4074(11)	4376(11)	737(7)	72(5)
C(1)	5888(12)	282(13)	1320(7)	60(5)
C(2)	2899(12)	4288(10)	1637(7)	52(5)
C(3)	3483(11)	−1926(9)	1207(7)	53(5)
C(4)	4748(12)	−2235(12)	1350(8)	65(5)
C(5)	2794(13)	−2682(13)	703(8)	72(6)
C(6)	3022(15)	−1945(11)	1834(8)	70(6)
C(7)	1455(14)	3621(12)	−455(7)	64(6)
C(8)	285(14)	3292(14)	−828(9)	82(7)
C(9)	2376(16)	3150(16)	−764(8)	89(8)
C(10)	1540(14)	4860(12)	−395(7)	69(6)
C(11)	6553(12)	3159(12)	1839(6)	58(5)
C(12)	6621(15)	4381(13)	2010(9)	81(7)
C(13)	7467(14)	2509(16)	2314(9)	89(7)
C(14)	6705(12)	3027(13)	1133(8)	70(6)
C(15)	−537(13)	89(17)	890(8)	77(7)
C(16)	−691(13)	1207(21)	786(9)	91(9)
C(17)	−197(15)	1731(16)	1382(12)	90(9)
C(18)	242(13)	918(17)	1818(8)	74(7)
C(19)	47(13)	−57(15)	1515(9)	75(7)

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

calculated by the formula

$$\mu_{\text{eff}} = \sqrt{8\chi_m T} \tag{5}$$

The Heisenberg–Dirac–van Vleck (HDVV) model was used for the calculation of the exchange parameters ($-2J$) between paramagnetic chromium atoms.[19] In this case the spin Hamiltonian took the form

$$H = -2JS_1S_2 + g\beta H(\hat{S}_{1Z} + \hat{S}_{2Z}) \tag{6}$$

where J is the isotropic exchange parameter, g is the isotropic g factor, and S are the spins of the exchange coupled Cr(III) atoms (for all compounds, **1**, **3a** **3b**, **4**, **6** and **8**, $S_1 = S_2 = {}^3/_2$). The calculation of the theoretical χ_m values and a least squares treatment of the data were carried out using a program package described elsewhere.[20]

Crystal Structure Determinations. The crystals of **3a**, **3b**, **4**, **6**, and **8** were mounted in air on glass fibers using 5-min epoxy resin. The unit cells were determined and refined from 25–30 equivalent reflections with $2\theta \geq 22–28°$ obtained by a Siemens R3/m (for **3a**, **4**, and **6**) or a Nicolet R3 (for **3b** and **8**) four-circle diffractometer. Intensity data were collected and corrected for Lorentz and polarization effects. An empirical absorption correction[21] was performed for **3b**, **4**, and **6**. Backgrounds were scanned for 25% (for **3a**, **4**, and **6**) and 12.5% (for **3b** and **8**) of the peak widths on each end of the scans. Three reflections were monitored periodically for each compound as a check for crystal decomposition or movement. No significant variation in these standards was observed; therefore no correction was applied. Details of crystal parameters, data collection, and structure refinement are given in Table 7.

All structures were solved by direct methods, to locate the Re, Cr, and S atoms. The other atoms were found in subsequent difference Fourier maps. Anisotropic refinement was applied to all non-hydrogen atoms in the case of **3a**, **3b**, **4**, and **8**. For compound **6** the O, N, and C atoms were refined isotropically. For this compound a disordering of the CO and NO groups of the Re(CO)(NO) fragment located on a crystallographic 2-fold axis was observed. The positions of these groups were not resolved accurately and therefore refined as $Re(CO)_2$ fragment. In Figure 5 one of these groups was labeled as NO and the other one as CO. The DIFABS method[22] was used for all structures, leading to a better correction at the stage of the isotropic refinement. The H atoms in structures **3a**, **3b**, **4**, and **8** were generated geometrically (C–H bonds fixed at 0.96 Å), and all H atoms were assigned the same isotropic temperature factor of $U = 0.08$ Å^2. Computations were performed using the SHELXTL PLUS program package[23] on a VAXstation 3100 (for **3a**, **4**, and **6**) or on a 486 IBM PC (for **3b** and **8**) computer. Selected bond lengths and angles are given in Tables 1–5, and positional parameters and equivalent isotropic terminal parameters are listed in Tables 8–12. Additional information is available as supplementary material.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, crystal data, non-hydrogen atomic parameters, and bond distances and angles for **3a**, **3b**, **4**, **6**, and **8** (35 pages). Ordering information is given on any current masthead page.

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