Formation of Antiferromagnetic Heteronuclear Thiolate- and Sulfide-Bridged Complexes. 3. Preparation, Magnetic Properties, and Structures of Cr_2W Clusters and Nitrosylchromium Complexes

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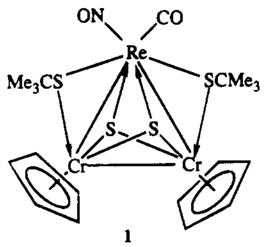
The reaction of the polymeric $[W(NO)_2Cl_2]_n$ (**8**) with the antiferromagnetic complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**3**) (benzene, 40 °C) leads to formation of the adduct $[Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)]_2W(NO)_2Cl_2$ (**9**). Thermolysis of **9** initiates both cluster formation and nitrosylation of the binuclear dichromium unit yielding the antiferromagnetic triangular clusters $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)_2$ (**11**, $-2J = 272\ cm^{-1}$, W–Cr = 2 × 3.088(3) Å, Cr–Cr = 3.025(4) Å), $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)Cl$ (**12**, $-2J = 270\ cm^{-1}$, W–Cr = 2.843(3)–2.889(3) Å, Cr–Cr = 3.036(4) and 3.068(4) Å), and the known species $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)(SCMe_3)$ (**2**) and furthermore the diamagnetic nitrosyl-containing chromium complexes $Cp_2Cr_2(NO)_2(\mu\text{-}SCMe_3)(\mu\text{-}Cl)$ (**16**, Cr–Cr = 2.959(2) Å), $Cp_4Cr_4(NO)_3Cl(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S_2)$ (**17**, Cr–Cr = 2.968(2) Å, S–S = 2.107(3) Å), and $Cp_2Cr_2(NO)_2(\mu\text{-}SCMe_3)(\mu\text{-}SSCMe_3)$ (**15**). Compounds **15**, **16**, and $Cp_2Cr_2(NO)(Cl)(\mu\text{-}SCMe_3)_2$ (**18**, Cr–Cr = 3.071(8)–3.116(8) Å) were also prepared by the reaction of **3** with NOCl. In the presence of moisture the intended conversions to **3** and **8** led to insoluble powders containing no NO groups. Upon addition of PPr^i_3 to this mixture a small amount of the paramagnetic ionic complex $[WCl(H)_2(H_2O)(PPr^i_3)_2][CpCrCl_3]$ (**10**, W–Cl = 2.296(2) Å, W–P = 2.357(2) Å, W–H = 1.50(3) and 1.63(3) Å) is produced. **10**–**12** and **16**–**18** were characterized by X-ray studies: **10**·MeCN, space group $P2_1/m$, $a = 10.679(5)$ Å, $b = 12.967(5)$ Å, $c = 13.678(5)$ Å, $\beta = 111.97(2)°$, $Z = 2$, $V = 1756.6(12)$ Å^3; **11**, space group $C2/c$, $a = 21.741(13)$ Å, $b = 9.932(4)$ Å, $c = 14.868(10)$ Å, $\beta = 129.01(2)°$, $Z = 4$, $V = 2495(2)$ Å^3; **12**·$0.25CH_2Cl_2$, space group $P2_1/n$, $a = 9.495(5)$ Å, $b = 32.89(2)$, $c = 17.451(8)$ Å, $\beta = 90.76(2)°$, $Z = 8$ (two independent molecules), $V = 5449(5)$ Å^3; **16**, space group $P2_12_12_1$, $a = 6.533(3)$ Å, $b = 9.390(3)$ Å, $c = 29.206(13)$ Å, $Z = 4$, $V = 1791.7(13)$ Å^3; **17**·C_6H_6, space group $P1$, $a = 9.619(5)$ Å, $b = 10.320(5)$ Å, $c = 11.799(6)$ Å, $\alpha = 106.32(2)°$, $\beta = 108.45(2)°$, $\gamma = 102.75(2)°$, $Z = 1$, $V = 1002.8(9)$ Å^3; **18**, space group $P2_1/n$, $a = 16.311(11)$ Å, $b = 16.644(11)$ Å, $c = 28.869(17)$ Å, $\beta = 95.85(2)°$, $Z = 12$ (three independent molecules), $V = 6859(5)$ Å^3.

Introduction

Recently we have shown that the triangular antiferromagnetic clusters $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2M(NO)X$ (**1**, M = Re, X = CO; **2**, M = W, X = $SCMe_3$) (Chart 1) can be built up in a two-stage process from the antiferromagnetic binuclear complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**3**) and the carbonyl nitrosyl containing rhenium or tungsten complexes, $Re_2(CO)_4(NO)_2Cl_4$ or $WI(CO)_4(NO)$. In a first step the adducts $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)ML_n$ (**4**, $ML_n = Re(CO)_2(NO)Cl_2$; **5**, $ML_n = W_2(\mu\text{-}I)_2(CO)_4(NO)_2$) bearing two halogen atoms are formed. Subsequently, a remetalation process with the extrusion of a $CpCrHal_2$ unit occurs leading to **1** or **2** supposedly via reactive intermediates of the type $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)M(CO)_2(NO)$ (**6**, M = Re; **7**, M = W).[1,2]

The presence of NO ligands is obviously essential to the course of these transformations presumably through stabilization by a push/pull synergism of the sulfur π donors with the π acceptor NO. Therefore, we anticipated that the formation of new sulfur ligand containing heteronuclear clusters can be accomplished, if one of the starting compounds would bear two nitrosyl groups. We therefore employ in our synthetic efforts the polymeric $[W(NO)_2Cl_2]_n$ (**8**) complex, which was known to react with two electron donors to give stable 18-electron adducts.[3,4]

Chart 1



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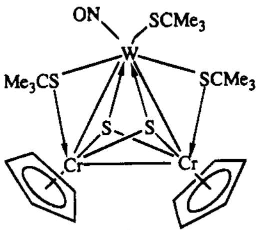

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Results and Discussion

It was reported earlier that phosphine ligands can cleave the chloride bridges in **8** to yield monomeric $W(NO)_2Cl_2L_2$

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1995.

(1) Eremenko, I. L.; Berke, H.; Kolobkov, B. I.; Novotortsev, V. M. *Organometallics* **1994**, *13*, 244.

(2) Eremenko, I. L.; Berke, H.; Van der Zeijden, A. A. H.; Kolobkov, B. I.; Novotortsev, V. M. *J. Organomet. Chem.* **1994**, *471*, 123.

(3) (a) Cotton, F. A.; Johnson, B. F. G. *Inorg. Chem.* **1964**, *3*, 1609. (b) Johnson, B. F. G.; Al-Obadi, K. H. *Inorg. Synth.* **1970**, *12*, 264.

(4) (a) Hunter, A. D.; Legzdins, P. *Inorg. Chem.* **1984**, *23*, 4198. (b) Anker, M. W.; Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1968**, *21*, 1149.

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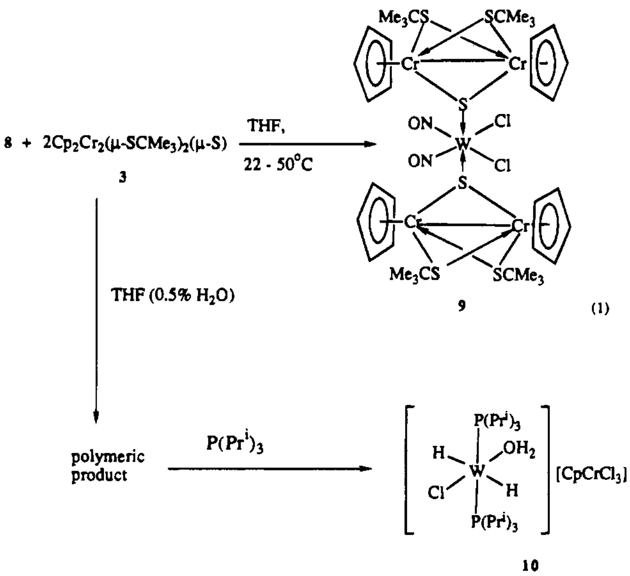
complexes containing trans L−W−L units. We made use of this property for the preparation of new adducts with the binuclear complex **3**.

Formation of Adduct $[Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)]_2W(NO)_2Cl_2$ (9). The reaction of **3** with **8** (THF, 22 −50 °C, ratio 2:1) yields black crystals of the antiferromagnetic adduct $[Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)]_2W(NO)_2Cl_2$ (**9**) (eq 1).



9 is stable in the solid state but slowly decomposes in solution. The IR spectrum of **9** shows two strong ν(NO) bands at 1609 and 1729 cm^{-1}, respectively, and characteristic absorptions for the π C_5H_5 ligands (812, 1014, and 3106 cm^{-1}) and the CMe_3 groups (1153 and 2857−2952 cm^{-1}). The MS(FAB) spectrum displays a weak peak of the parent ion (*m/e* 1203) and strong one for $[M]^+ - Cl$ (*m/e* 1168 and 1166). The two antiferromagnetically coupled dichromium units are responsible for the temperature dependent magnetic behavior of **9**. The effective magnetic moment (μ_{eff}/Cr atom) changes from 1.69 to 0.58 μ_B in the temperature range between 290 and 79 K.

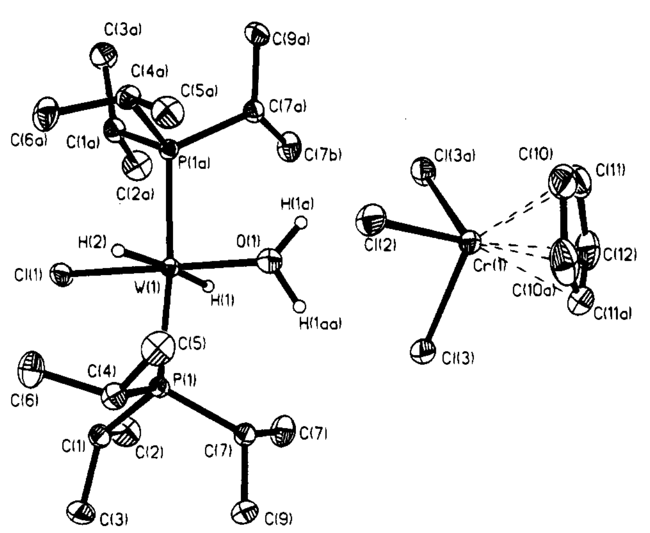


Figure 1. Perspective view of the molecular structure of $[WCl(H)_2(H_2O)(P(Pr^i)_3)_2][CpCrCl_3]$ (**10**).

Table 1. Selected Bond Distances and Angles for **10**

	Distances (Å)		
W(1)−P(1)	2.357(2)	Cr(1)−Cl(2)	2.316(3)
W(1)−Cl(1)	2.296(2)	Cr(1)−Cl(3)	2.322(2)
W(1)−O(1)	2.067(4)	O(1)−H(1A)	1.03(4)
W(1)−H(1)	1.63(3)	H(1A)···Cl(3)	2.51(3)
W(1)−H(2)	1.50(3)		
	Angles (deg)		
P(1)−W(1)−Cl(1)	88.5(1)	Cl(1)−W(1)−H(2)	74.0(13)
P(1)−W(1)−O(1)	91.5(1)	O(1)−W(1)−H(1)	84.9(13)
Cl(1)−W(1)−O(1)	179.7(2)	O(1)−W(1)−H(2)	105.6(13)
P(1)−W(1)−H(1)	94.3(13)	H(1A)−O(1)−H(2A)	106.7(30)
P(1)−W(1)−H(2)	86.2(14)	O(1)−H(1A)···Cl(3)	140.2(30)
Cl(1)−W(1)−H(1)	95.4(13)		

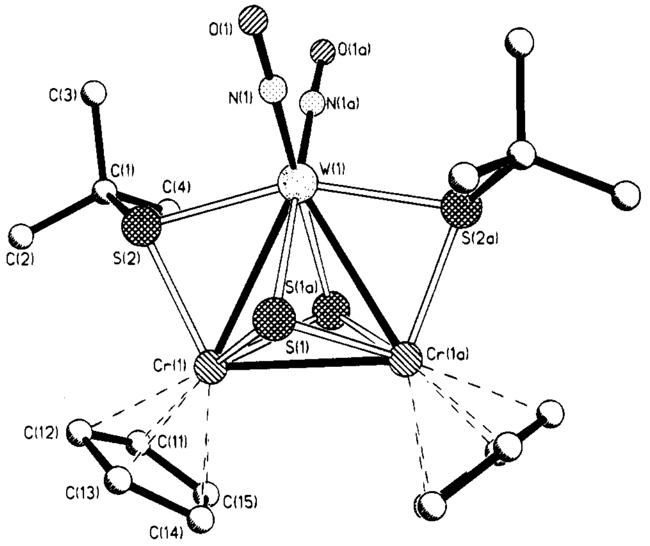


Figure 2. Molecular structure of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2W(NO)_2$ (**11**).

The formation of **9** is suppressed in the presence of moisture. For example, when the THF used was not specially purified, a green-blue precipitate was obtained, which was insoluble in organic solvents. In the IR spectrum this compound exhibited no ν(NO) bands, however, indicating the presence of the absorptions of a π-C_5H_5 ligand (820, 1009, and 3105 cm^{-1}). It is therefore assigned a polymeric mixed Cr,W chloride sulfide structure. It was assumed that the addition of $P(Pr^i)_3$ would lead to a breakage of this polymer into mononuclear units. Indeed such a process is observed to just a small extent (2.4%) producing the ionic paramagnetic complex $[WCl(H)_2(H_2O)(P(Pr^i)_3)_2][CpCrCl_3]$ (**10**). **10** was cheracterized by an X-ray analysis as a solvate with one molecule of MeCN (Figure 1, Table 1). The cation, anion, and the solvate molecule are located on a crystallographic mirror plane. The phosphine ligands of the cationic part form a practically linear P−W−P fragment (W−P = 2.357(2) Å, P−W−P = 171.6(1)°). Perpendicular to this axis there is an equatorial plane which contains the W atom, the two trans-positioned H atoms (W−H = 1.50(3) and 1.63(3) Å, H−W−H = 169(1)°), one chlorine atom (W−Cl = 2.296(2) Å , Cl−W−H = 95(1) and 74(1)°), and a water molecule (W−O = 2.067(4) Å, O−H = 1.03(4) Å). The W−P and the W−Cl bond lengths are in this 14-electron species significantly shorter than the respective values of the 18-electron seven-coordinated neutral $WCl(H)(CO)_2(PMe_3)_3$ complex (W−P = 2.472(4)−2.520(4) Å, W−Cl = 2.510(3) Å, W−H = 1.78 Å).[5] This is presumably due to a different steric situation and the open shell electron configuration in **10**. The anion $CpCrCl_3$ has an usual geometry (Cr−Cl = 2.322(2) and 2.316(3) Å, Cl−Cr−Cl = 95.2(1)−97.3(1)°) which was also found in other ionic complexes.[6] The specific orientation of the $CpCrCl_3^-$ anion in the unit cell can be explained by weak intermolecular hydrogen bonding between the protons of the coordinated H_2O molecule

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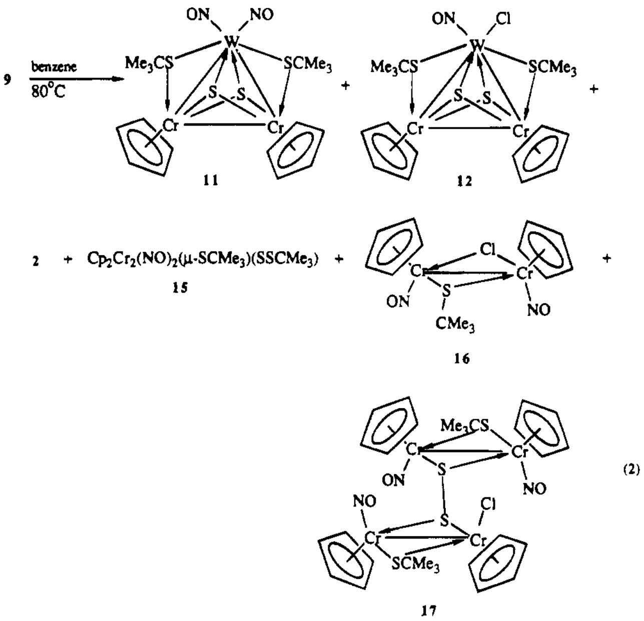
(5) Contreras, L.; Monge, A.; Pizzano, A.; Ruiz, C.; Sànchez, L.; Carmona, E. *Organometallics* **1993**, *12*, 4228.

(6) Muller, B.; Krausse, J. *J. Organomet. Chem.* **1972**, *44*, 144.

and the chlorine atoms of the anion (H••Cl = 2.51(3) Å, O−H••Cl = 140(2)°), thus leading to [Cat]••[An] pairing.

Thermolysis of 9. As noted above, **9** decomposes slowly in benzene even at room temperature. This process can be accelerated by heating **9** to 80 °C. A green solution results containing two types of products: three triangular Cr_2W clusters and a nitrosylation product of **3** (eq 2). All these compounds were separated chromatographically and isolated in crystals suitable for X-ray analysis.



(2)

Triangular Cr_2W Clusters. The triangular clusters $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)_2$ (**11**), $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)Cl$ (**12**), and the known $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)(SCMe_3)$ complex (**2**) display strong ν(NO) bands in their IR spectra (**11**, 1614 and 1713 cm^{-1}; **12**, 1598 cm^{-1}; **2**, 1588 cm^{-1}). The green crystals of **11** and the brown crystals of **12** were characterized by X-ray studies (Figures 2 and 3, Tables 2 and 3). The molecule **11** shows a symmetrical Cr_2W arrangement with long M−M distances (W−Cr = 2 × 3.088(3) Å, Cr−Cr = 3.025(4) Å). The tungsten atom carries two NO groups (W−N = 1.834(13) Å, N−O = 1.165(22) Å, N−W−N = 89.8(8)°) and two $SCMe_3$ ligands (W−S = 2 × 2.488(3) Å). The two CpCr units adopt a bent Cp_2Cr_2 geometry (Cp(cen)−Cr−Cr = 124.2(4)°, torsion ω angle CpCrCrCp is 3.3°) bridged by two sulfide atoms (Cr−S = 2.343(4) Å). The $Cp_2Cr_2S_2$ moiety is connected to the W atom by means of both W−S (2 × 2.557(3) Å) and Cr−$SCMe_3$ (2 × 2.374(3) Å) bonds. The essential geometries of the cluster cores of **12** and **11** are similar. In **12** the tungsten atom bears two different terminal ligands: the NO group (W−N = 1.786(15) and 1.773(14) Å in two independent molecules) and the Cl atom (W−Cl = 2.434(5) and 2.429(5) Å). The $SCMe_3$ residues which are bridging the W and Cr centers (W−S = 2.418(5)−2.439(4) Å, Cr−S = 2.375(5)−2.380(5) Å) are in anti conformation with respect to the M_3 plane in both independent molecules of **12** and are in syn arrangement in **11**. The bent $Cp_2Cr_2S_2$ moiety in **12** (Cr−Cr = 3.036(4) and 3.068(4) Å, Cp(cen)−Cr−Cr = 124.2(5)−127.9(5)°, torsion ω angle CpCrCrCp = 3.6 and 1.6°) reveals some shortening of the Cr−S distances (2.288(5)−2.317(5) Å) in comparison to the corresponding fragment in **11**. An unsymmetrical W−μ_3-S binding is observed in both independent molecules (W−S = 2.559(5) and 2.447(5) Å; 2.542(5) and 2.468(5) Å), and the distances of the W−Cr bonds in **12** (2.877(3) and 2.889(3) Å in molecule A and 2.863(3) and 2.843(3) Å in molecule B) correspond to single bond values.

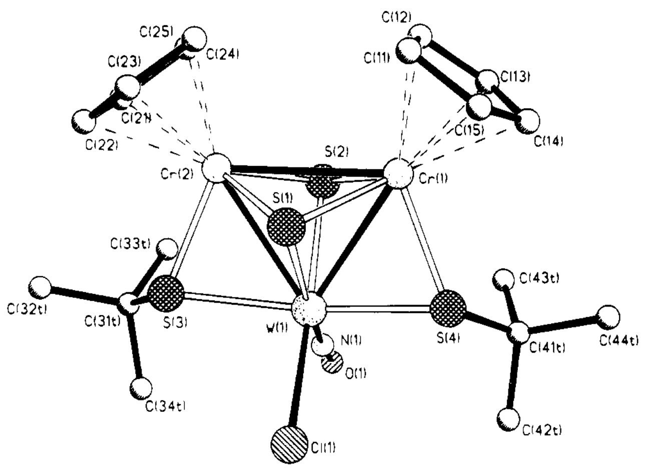


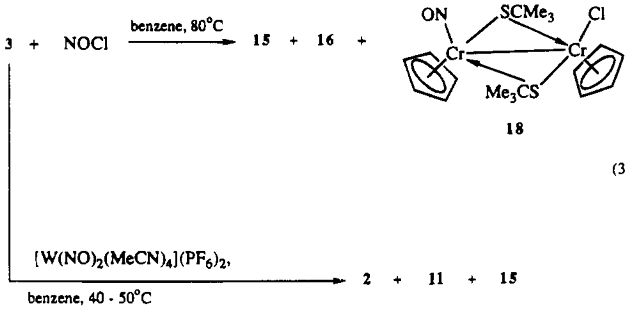
Figure 3. Molecular structure of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2W(NO)Cl$ (**12**).

Table 2. Selected Bond Distances and Angles for **11**

	Distances (Å)		
W(1)−Cr(1)	3.088(3)	Cr(1)−Cr(1A)	3.025(3)
W(1)−S(1)	2.557(3)	Cr(1)−S(1)	2.343(4)
W(1)−S(2)	2.488(3)	Cr(1)−S(2)	2.374(3)
W(1)−N(1)	1.834(13)	N(1)−O(1)	1.165(22)
	Angles (deg)		
S(1)−W(1)−S(2)	77.0(1)	S(1)−Cr(1)−S(2)	83.6(1)
S(1)−W(1)−N(1)	95.3(4)	W(1)−S(1)−Cr(1)	78.0(1)
S(1)−W(1)−N(1A)	174.7(4)	W(1)−S(2)−Cr(1)	78.8(1)
S(2)−W(1)−N(1)	95.7(3)	Cr(1)−S(1)−Cr(2)	80.3(1)
N(1)−W(1)−N(1A)	89.8(8)	W(1)−N(1)−O(1)	176.7(11)

The planar fragments $W(NO)_2Cl_2$ and $Re(CO)(NO)Cl_2$ of the adducts **9** and **4** are isoelectronic. For this reason the thermal transformations of both molecules might take a similar course including the remetalation step. In the tungsten case the intermediacy of a $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)W(NO)_2L$ complex (**13**, L = $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$) can be envisaged which is the isoelectronic analog of the $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)Re(CO)_2(NO)$ (**6**) compound isolated as a dimer.[1] **13** however breaks down further with extrusion of CpCrS to yield the cluster **11** (Scheme 1).

The $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ unit can also act as a source of a SR group, which eventually replaces one NO ligand in **13** to produce the cluster **2**. Judging from the composition of **12** containig a Cl atom, it seems reasonable to assume that its formation is induced by an elemination of NOCl from **9** additionally generating the intermediate $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)W(NO)(Cl)L$ (**14**). **14** may be transformed into **12** by the same manner as **13**. With the appearence of NO and NOCl (Scheme 1) it can be explained why the coordinated chromium fragments of **3** become nitrosylated (eq 3).

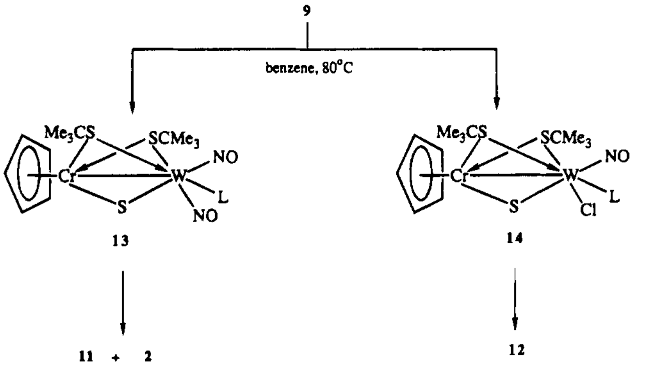


(3)

Table 3. Selected Bond Distances and Angles for **12**

molecule A				molecule B			
			Distances (Å)				
W(1)−Cr(1)	2.873(3)	Cr(1)−Cr(2)	3.036(4)	W(2)−Cr(3)	2.863(3)	Cr(3)−Cr(4)	3.068(4)
W(1)−Cr(2)	2.889(3)	Cr(1)−S(1)	2.317(5)	W(2)−Cr(4)	2.843(3)	Cr(3)−S(5)	2.305(6)
W(1)−S(1)	2.559(5)	Cr(1)−S(2)	2.289(5)	W(2)−S(5)	2.542(5)	Cr(3)−S(6)	2.288(5)
W(1)−S(2)	2.447(5)	Cr(1)−S(4)	2.380(5)	W(2)−S(6)	2.468(5)	Cr(3)−S(7)	2.379(5)
W(1)−S(3)	2.439(4)	Cr(2)−S(1)	2.303(5)	W(2)−S(7)	2.418(5)	Cr(4)−S(5)	2.305(5)
W(1)−S(4)	2.436(4)	Cr(2)−S(2)	2.292(6)	W(2)−S(8)	2.413(5)	Cr(4)−S(6)	2.298(6)
W(1)−Cl(1)	2.434(5)	Cr(2)−S(3)	2.375(5)	W(2)−Cl(2)	2.429(5)	Cr(4)−S(8)	2.385(5)
W(1)−N(1)	1.786(15)	N(1)−O(1)	1.205(20)	W(2)−N(2)	1.773(14)	N(2)−O(2)	1.205(20)
			Angles (deg)				
S(1)−W(1)−S(2)	81.61(1)	S(2)−Cr(1)−S(4)	97.5(2)	S(5)−W(2)−S(6)	81.5(1)	S(6)−Cr(3)−S(7)	98.8(2)
S(1)−W(1)−S(3)	79.6(1)	W(1)−S(1)−Cr(1)	72.0(1)	S(5)−W(2)−S(7)	78.1(2)	W(2)−S(5)−Cr(3)	72.2(1)
S(1)−W(1)−S(4)	79.0(1)	W(1)−S(1)−Cr(2)	72.7(1)	S(5)−W(2)−S(8)	80.8(2)	W(2)−S(5)−Cr(4)	72.4(1)
S(2)−W(2)−S(3)	90.2(1)	W(1)−S(2)−Cr(1)	74.6(1)	S(6)−W(2)−S(7)	93.0(2)	W(2)−S(6)−Cr(3)	73.9(1)
S(2)−W(2)−S(4)	91.9(1)	W(1)−S(2)−Cr(2)	75.0(2)	S(6)−W(2)−S(8)	92.4(1)	W(2)−S(6)−Cr(4)	73.1(1)
S(3)−W(1)−S(4)	158.0(1)	W(1)−S(3)−Cr(2)	73.7(1)	S(7)−W(2)−S(8)	157.2(2)	W(2)−S(7)−Cr(3)	73.3(1)
S(1)−W(1)−N(1)	171.4(5)	W(1)−S(4)−Cr(1)	73.2(1)	S(5)−W(2)−N(2)	169.8(5)	W(2)−S(8)−Cr(4)	72.4(1)
S(2)−W(1)−Cl(1)	173.4(2)	Cr(1)−S(1)−Cr(2)	82.2(2)	S(6)−W(2)−Cl(2)	175.2(2)	Cr(3)−S(5)−Cr(4)	83.5(2)
Cl(1)−W(1)−N(1)	96.8(5)	Cr(1)−S(2)−Cr(2)	83.0(2)	Cl(2)−W(2)−N(2)	96.4(5)	Cr(3)−S(6)−Cr(4)	84.0(2)
S(1)−Cr(1)−S(2)	90.6(2)	W(1)−N(1)−O(1)	174.3(14)	S(5)−Cr(3)−S(6)	90.8(2)	W(2)−N(2)−O(2)	172.0(14)
S(1)−Cr(1)−S(4)	85.2(2)			S(5)−Cr(3)−S(7)	83.7(2)		

Scheme 1



Nitrosyl-Containing Chromium Complexes. Among the nitrosyl-containing compounds of the reaction according to Scheme 1, a binuclear $Cp_2Cr_2(NO)_2(\mu\text{-}SCMe_3)(\mu\text{-}SSCMe_3)$ (**15**) complex is the major thermolysis product of **9**. **15** was also prepared earlier by the direct reaction between **3** and NO(gas).[7] In addition, small amounts of the diamagnetic binuclear $Cp_2Cr_2(NO)_2(\mu\text{-}SCMe_3)(\mu\text{-}Cl)$ (**16**) and of the tetranuclear $Cp_4Cr_4(NO)_3(Cl)(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S_2)$ (**17**) were found. The IR spectra of **16** and **17** show strong ν(NO) bands (**16**, 1670 and 1653 cm^{-1} (split in solid state); **17**, 1659 and 1639 cm^{-1}). Their structures were determined by X-ray diffraction studies (Figures 4 and 5, Tables 4 and 5). Two CpCr(NO) fragments (Cr−N = 1.695(7) and 1.688(7) Å, N−O = 1.177(10) and 1.181(19) Å, Cr−N−O = 170.4(6) and 170.1(6)°) in **16** are held together by means of a Cr−Cr bond (2.959(2) Å) and by two bridges of the $SCMe_3$ group (Cr−S = 2.316(2) and 2.318(2) Å, Cr−S−Cr = 79.4(1)°) and of the Cl atom (Cr−Cl = 2.341(3) and 2.349(3) Å, Cr−Cl−Cr = 78.2(3)°). The Cr_2SCl core is planar in analogy to the Cr_2S_2 system observed in **15**[7] and in $Cp_2Cr_2(NO)_2(SPh)_2$.[8] The molecule of **17** has two planar Cr_2S_2 units (Cr−Cr = 2.968(2) Å, Cr−$SCMe_3$ = 2.320(3) and 2.317(3) Å, Cr−S = 2.321(2) and 2.325(2) Å) which are in addition connected by a S−S bond (2.107(3) Å). Three chromium atoms of **17** carry terminal NO ligands (Cr−NO = 1.729(5) and 1.597(14) Å), and one bears a Cl atom (Cr−Cl = 2.294(6) Å).

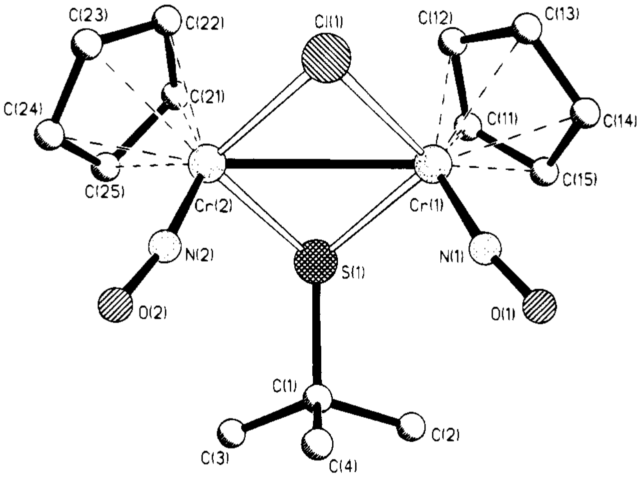


Figure 4. Perspective view of the molecular structure of $Cp_2Cr_2(NO)_2(\mu\text{-}SCMe_3)(\mu\text{-}Cl)$ (**16**).

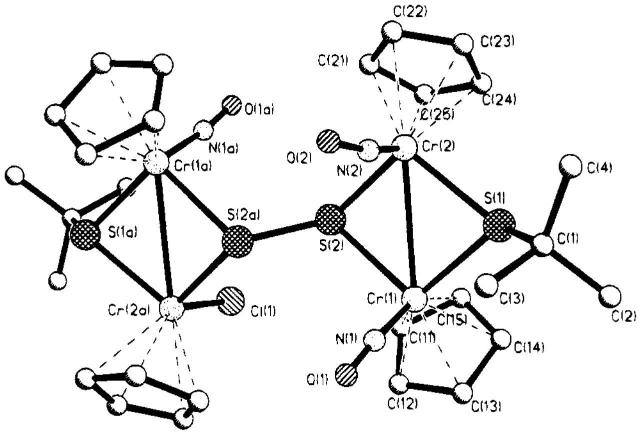


Figure 5. Perspective view of the molecular structure of $Cp_4Cr_4(NO)_3(Cl)(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S_2)$ (**17**).

The formation of **15** and **16** and $Cp_2Cr_2(NO)(Cl)(\mu\text{-}SCMe_3)_2$ (**18**) was observed upon the reaction of **3** with NOCl (benzene, 80 °C). Under these circumstances **15** was isolated as the main product.

The IR spectrum of **18** displays a strong ν(NO) band at 1638 cm^{-1}. According to an X-ray investigation (Figure 6, Table 6) the two chromium atoms and the two sulfide atoms of this molecule form a planar Cr_2S_2 unit (Cr−S = 2.335(9)−2.373-

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[7] Eremenko, I. L.; Pasynskii, A. A.; Kalinnikov, V. T.; Struchkov, Yu. T.; Aleksandrov, G. G. *Inorg. Chim. Acta* **1981**, *52*, 107.

[8] Satchell, D. P. N. *Chem. Soc. Rev.* **1977**, *6*, 345.

Table 4. Selected Bond Distances and Angles for **16**

	Distances (Å)		
Cr(1)–Cr(2)	2.959(2)	Cr(2)–Cl(1)	2.349(3)
Cr(1)–S(1)	2.318(2)	Cr(2)–N(2)	1.688(7)
Cr(1)–Cl(1)	2.341(3)	N(1)–O(1)	1.177(10)
Cr(1)–N(1)	1.695(7)	N(2)–O(2)	1.181(1)
Cr(2)–S(1)	2.316(2)		
	Angles (deg)		
Cl(1)–Cr(1)–S(1)	101.2(1)	S(1)–Cr(2)–N(2)	102.0(2)
Cl(1)–Cr(1)–N(1)	97.6(2)	Cr(1)–Cl(1)–Cr(2)	78.2(1)
S(1)–Cr(1)–N(1)	101.6(2)	Cr(1)–S(1)–Cr(2)	79.4(1)
Cl(1)–Cr(2)–S(1)	101.0(1)	Cr(1)–N(1)–O(1)	170.4(7)
Cl(1)–Cr(2)–N(2)	96.1(2)	Cr(2)–N(2)–O(2)	170.1(6)

Table 5. Selected Bond Distances and Angles for **17**

	Distances (Å)		
Cr(1)–Cr(2)	2.968(2)	Cr(2)–Cl(1)	2.294(6)
Cr(1)–S(1)	2.320(3)	Cr(2)–N(2)	1.597(14)
Cr(1)–S(2)	2.321(2)	S(1)–S(2A)	2.107(3)
Cr(1)–N(1)	1.729(5)	N(1)–O(1)	1.096(7)
Cr(2)–S(1)	2.317(2)	N(2)–O(2)	1.330(21)
Cr(2)–S(2)	2.325(2)		
	Angles (deg)		
S(1)–Cr(1)–S(2)	100.0(1)	S(1)–Cr(2)–Cl(1)	101.3(2)
S(1)–Cr(1)–N(1)	102.0(2)	S(2)–Cr(2)–Cl(1)	101.9(2)
S(2)–Cr(1)–N(1)	100.1(2)	Cr(1)–S(1)–Cr(2)	79.6(1)
S(1)–Cr(2)–S(2)	100.0(1)	Cr(1)–S(2)–Cr(2)	79.4(1)
S(1)–Cr(2)–N(2)	99.1(9)	Cr(1)–S(2)–S(2A)	109.0(1)
S(2)–Cr(2)–N(2)	100.6(8)	Cr(2)–S(2)–S(2A)	110.0(1)

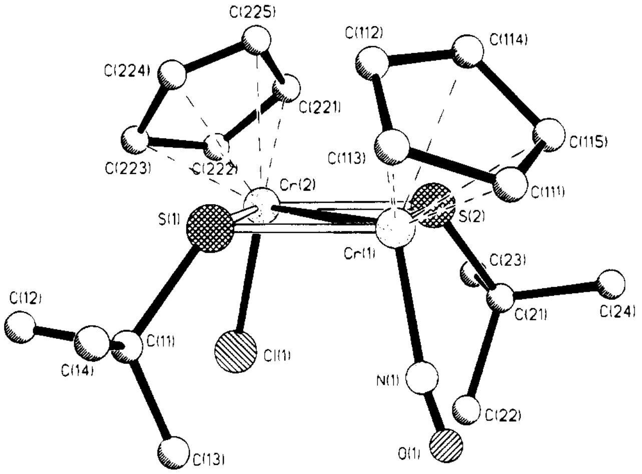

Figure 6. Molecular structure of $Cp_2Cr_2((NO)(Cl)(\mu\text{-}SCMe_3)_2$ (**18**).

Table 6. Selected Bond Distances and Angles for **18**

	Distances (Å)		
Cr(1)–Cr (2)	3.071(8)	Cr–Cl	2.281(12)–2.297(13)
Cr(3)–Cr(4)	3.116(8)		
Cr(5)–Cr(6)	3.083(8)	$Cr-N_{av}$	1.73(3)
Cr–S	2.335(9)–2.373(10)	$N-O_{av}$	1.10(4)
	Angles (deg)		
Cr–S–Cr	82.0(3)–82.9(4)	S–Cr–N	99.4(10)–105.1(9)
S–Cr–Cl	102.4(4)–104.0(4)	Cr–N–O	158.1(32)–176.3(28)

(10) Å, Cr–S–Cr = 82.0(3)–82.9(3)°, three independent molecules in the unit cell) as in other similar compounds. The *tert*-butyl residues are in syn position which is similar to the situation of **15** and **17** in which cases the S–C and S–S bonds are syn. The π-C_5H_5 rings occupy trans positions with respect to the Cr_2S_2 plane (Cr–Cr = 3.071(8)–3.116(8) Å). The metal–metal separation in **18** is significantly longer than that of the binuclear compounds **15**, **16**, and $Cp_2Cr_2(NO)_2(SPh)_2$.[7,8] Probably this is due to different electron counts for these Cr atoms in **18** ($Cr-N_{av}$ = 1.73(3), Cr–Cl = 2.281(12)–2.297(13) Å). Furthermore the Cr–Cr distance is also longer than the respective value the tetranuclear compound **17** with similar nonsymmetrical binuclear fragments (2.968(2) Å). Nitrosylation of **3** was also observed when $[W(NO)_2(MeCN)_4](PF_6)_2$ was used as a starting material instead of $[W(NO)_2Cl_2]_n$ (benzene, 40–50 °C) . In this case **2**, **11**, and **15** were obtained as products.

Magnetic Behavior and Metal–Metal Bonding in the Cr_2W Triangular Clusters. The $Cp_2Cr_2(\mu\text{-}S)_2$ units forming the core of the triangular clusters **1**, **2**, **11**, and **12** have similar geometrical features. They display a bent arrangement of the CpCrCrCp moiety and a "butterfly" Cr_2S_2 core (Table 7). This geometry does not allow effective σ orbital overlap of the Cr centers, and therefore the Cr–Cr bonds are supposedly very weak in all clusters. Thus the energy of the spin–spin interaction between the coupling chromium centers ($S_{Cr(1)} = S_{Cr(2)} = {}^3/_2$) of these triangular clusters are significantly different from the values of the starting material **3** or any ML_n adduct of **3**,[1,2,9] containing linear CpCrCr units. Like **1** and **2**, the clusters **11** and **12** are antiferromagnetic. The effective magnetic moments of **11** and **12** decrease from 1.61 to 0.74 μ_B (for **11**) and from 1.49 to 0.40 μ_B (for **12**) on lowering of the temperature from 290 to 79 K. This behavior may be rationalized within the concept of the Heisenberg–Dirac–Van Vleck (HDVV) model[10] for two coupled chromium ions ($S_1 = S_2 = {}^3/_2$) with the exchange parameters of $-2J = 272\ \mathrm{cm}^{-1}$ (for **11**) and $-2J = 270\ \mathrm{cm}^{-1}$ (for **12**). There are certainly many ways how to envisage the binding situation in these clusters on a qualitative base. We have chosen here one kind of view, which seems to cope with the experimental facts. It should be noted that it is still a matter of discussion how the magnetic M/M interactions in bridged complexes may be established, whether it is the bridges or the M–M bonds which are responsible for the mediation of the effects. In our cases of trinuclear complexes we have chosen for the sake of a proper electron counting descriptions emphasizing the existence of M–M bonding, even though the experimental observations especially the magnetic measurements would also be in accord with an exclusive antiferromagnetic coupling mechanism. In agreement with their magnetic properties each chromium center of the triangular cluster of **11** and **12** contains three half-occupied orbitals, one of which takes part in a weak Cr–Cr bonding. In the cases of the attached fragments $M(NO)(SCMe_3)_2X$ (**1**, M = Re, X = CO; **2**, M = W, X = $SCMe_3$; **11**, M = W, X = NO; **12**, M = W, X = Cl) the Cr atom has three orbitals still available (the other six orbitals are used for the formation of the Cr–Cr bond (one orbital), the CpCr unit (three orbitals), and the two Cr–S bonds (two orbitals)). Completing the bonding picture of the $Cp_2Cr_2S_2$ fragment, it is noteworthy that the sulfide bridges donate two lone pairs to the M center leading to an 18-electron configuration of the Re and W atoms in **1** and **11** and to a 16-electron configuration of the W atoms in **2** and **12**. The 18-electron centers are connected to each chromium atom of the $Cp_2Cr_2S_2$ unit by the use of 4 electrons in two orbitals (one lone pair of the $SCMe_3$ bridge and one occupied metal orbital). These interact with one half-occupied and one empty orbital or with two half-occupied orbitals of the Cr atom. The analysis of the torsion ω angles of the Cp(centroid)CrCrCp(centroid) unit shows that they are close to zero for all moieties of the $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2M(NO)X$ clusters. This suggests that

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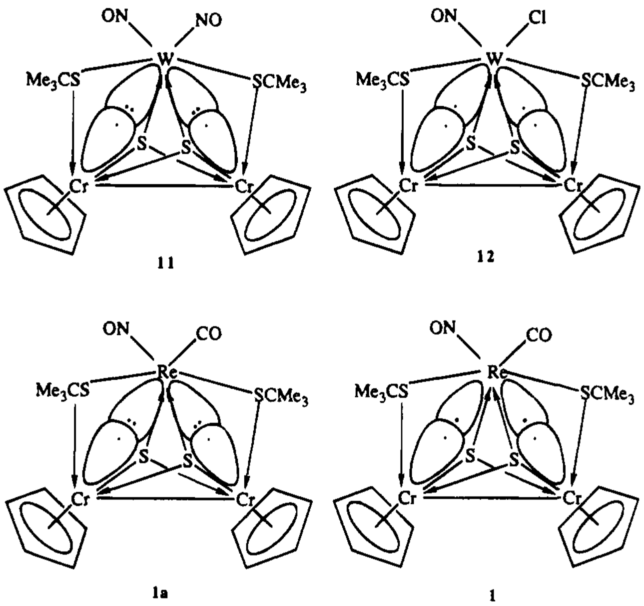
(9) Eremenko, I. L.; Pasynskii, A. A.; Orazsakhatov, B.; Shestakov, A. F.; Gasanonv, G. Sh.; Katugin, A. S.; Struchkov, Yu. T.; Shklover, V. E. *J. Organomet. Chem.* **1988**, *338*, 369.

(10) Van Vleck, J. H. *The Theory of Electronic and Magnetic Susceptibilities*; Oxford Univ. Press: London, 1932.

Table 7. Geometrical Parameters and Magnetic Properties for $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2M(NO)X$ Clusters

		geometry of $Cp_2Cr_2S_2$ moiety							
no.	M and X	Cr–Cr (Å)	Cr–S (Å)	CpCrCr (deg)	tors angle (ω) CpCrCrCp (deg)	M–Cr (Å)	μ_{eff}/Cr atom (μB) (temp range (K))	exchange param $-2J$ (cm^{-1})	ref
1	M = Re, X = CO	3.010(6)	2.344(6)	126.5(6)	3.6	2.940(5)	1.65–0.55 (288–79)	231	1
1a	M = Re, X = CO	3.002(4)	2.335(5)	127.0(5)	3.1	3.080(2)	1.67–0.58 (296–82)	228	this work
2	M = W, X = SR	3.027(1)	2.338(2)	126.9(1)	0.0	3.090(1)	1.52–0.59 (291–79)	246	2
11	M = W, X = NO	3.025(4)	2.343(4)	124.2(4)	3.3	3.088(3)	1.61–0.74 (290–79)	272	this work
12	M = W, X = Cl	3.036(4), 3.068(4)	2.288(5)–2.317(5)	124.2(5)–127.9(5)	3.6, 1.6	2.843(3)–2.889(3)	1.49–0.40 (290–79)	270	this work

Chart 2



11 **12**

1a **1**

all the fragments have practically planar geometry (Table 7) and in all cases the same orbitals are used for further bonding of the $Cp_2Cr_2S_2$ fragments. Similar structures for the syn SR-bridged cores in **1** and **11** suggest the participation of similar sulfur orbitals for the bonding with the Cr centers. This allows us to view the $Cr-SCMe_3$ bonds in **11** as normal two electron donor/acceptor interactions. In contrast, the long W–Cr bonds (3.088(3) Å) should result from the overlap of a fully occupied tungsten and a half-occupied chromium orbital resulting in a bond order of $^1/_2$ (Chart 2). In **1**, containing an asymmetric Re(CO)(NO) unit, the bonding situation is more complicated. In this case a strong loosening of the Cr–SR bonds (2.759(5) Å) is observed concomitantly with a shortening of the Re–Cr bonds (2.940(5) Å) with respect to the two electron Cr–Re interaction of 3.05 Å in $(OC)_5Re-Cr(CO)_4{\equiv}C\text{-}p\text{-}tolyl$[11] and the Re–Cr distance (3.123(2) Å, bond order $^1/_2$) in $[CpCr(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re(CO)(NO)]_2$.[1] This would implicate a bond order of $^1/_2$ for the Cr–SR unit and a normal, two electron interaction between the Cr and Re atoms (Chart 2). This represents a possible, but quite rare, type of distribution of the binding electrons. The crystals of the second Cr_2Re isomer, **1a**, were obtained by slow cooling of a MeCN solution of **1**. The X-ray study of **1a** (Figure 7, Table 8) shows that this isomer is practically isostructural to the isoelectronic W-containing cluster **11**. It has a short Cr–SR (2.367(5) Å) and a long Cr–Re (3.080(2) Å) distance. The remaining geometrical parameters of **1a** are similar to those in **1** (Cr–Cr = 3.002(4) Å in **1a** and 3.010(5) Å in **1**; Cr–μ_3-S = 2.335(5) Å in **1a** and 2.344(6) Å in **1**; Cp(centroid)CrCr = 127.0(4)° in **1a** and 126.5(6)° in **1**). The IR spectrum of **1a** differs in the region of CO and NO absorptions only slightly from that of **1** (ν(CO) 1950 cm^{-1} and ν(NO) 1685 cm^{-1} for **1a** and ν(CO) 1951 cm^{-1} and ν(NO) 1683 cm^{-1}). The magnetic properties are also quite close (Table 7) ($-2J$ = 228 cm^{-1} for **1a** and 231 cm^{-1} for **1**). The similarity of the magnetic and spectroscopic characteristics demonstrates that, despite the strong difference of the bonding between $Cp_2Cr_2S_2$ and $Re(CO)(NO)(SCMe_3)_2$ units in **1** and **1a** (Chart 2), the spin–spin interactions in bent magnetic Cp_2Cr_2 fragment are merely dependent on their intrinsic electronic and geometric parameters and are not influenced by the presence of a peripheral metallo fragment. This situation differs from that found for the triangular $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2ML_n$ clusters with a linear Cp_2Cr_2 unit where the addition of diamagnetic ML_n fragments leads to an increase of the spin–spin interaction energy.[12]

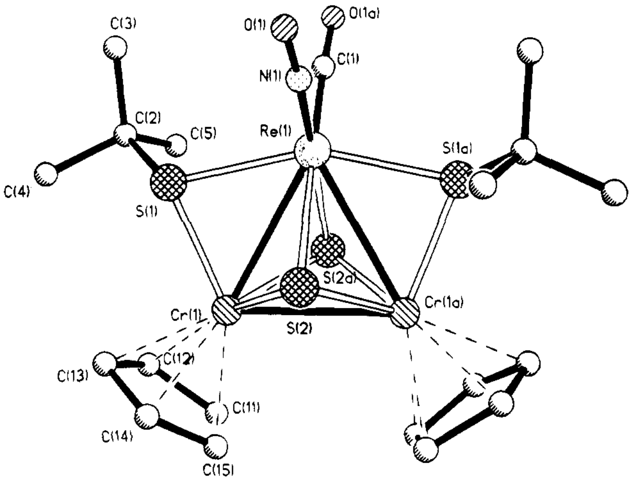


Figure 7. Perspective view of the molecular structure of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2Re(CO)(NO)$ (isomer **1a**).

Table 8. Selected Bond Distances and Angles for **1a**

	Distances (Å)		
Re(1)–Cr(1)	3.080(2)	Re(1)–S(1)	2.445(3)
Re(1)–S(2)	2.543(4)	Re(1)–N,C	1.807(28)
Cr(1)–Cr(1A)	3.002(4)	Cr(1)–S(1)	2.367(5)
Cr(1)–S(2)	2.335(5)	N,C–O	1.165(41)
	Angles (deg)		
S(1)–Re(1)–S(2)	77.3(1)	S(1)–Re(1)–N,C	94.8(9)
S(1)–Re(1)–S(1A)	156.2(2)	S(2)–Re(1)–S(1A)	84.5(1)
N,C–Re(1)–S(1A)	102.7(6)	S(2)–Re(1)–S(2A)	79.7(2)
N,C–Re(1)–S(2A)	174.4(9)	S(1)–Cr(1)–S(2)	83.0(2)
S(1)–Cr(1)–S(2A)	88.5(2)	S(1)–Cr(1)–S(2A)	91.0(2)
Re(1)–S(1)–Cr(1)	79.6(1)	Re(1)–S(2)–Cr(1)	78.2(2)
Cr(1)–S(2)–Cr(1A)	80.0(2)	Re(1)–N,C–O	176.7(13)

In contrast to **1**, **1a**, and **11** cluster **12** contains a 16 electron W atom. The removal of two electrons from the metal core leads to a strengthening of the W–Cr bonds (2.843(3)–2.889-

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(11) Abad, J. A.; Delgado, E.; Garcia, M. E.; Grosse-Ophoff, M. J.; Hart, I. J.; Jeffery, J. C.; Simmons, M. S.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 41.

(12) (a) Pasynskii, A. A.; Eremenko, I. L. *Sov. Sci. Rev., Sect. B* **1987**, *10*, 443 and references cited therein. (b) Pasynskii, A. A.; Eremenko, I. L. *Usp. Khim.* **1989**, *58*, no. 2, 303 (in Russian) and references cited therein.

(3) Å), which can be envisaged by the interaction of two half-occupied orbitals of the W and Cr centers (Chart 2). However, in **12** a small elongation of the Cr−Cr distance is recognized (3.036(4) and 3.068(4) Å), which indicates redistribution of the electronic density over the M_3 core. The great stretching of the W−Cr bonds in **2**, which occurs with conservation of the other geometrical parameters (Table 7), can only be explained in terms of the steric demand of the bulky terminal $SCMe_3$ ligand.

Conclusion

The formation of the $[Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)]_2W(NO)_2Cl_2$ (**9**) adduct from two molecules of **3** and from the $W(NO)_2Cl_2$ fragment and its further transformation to the triangular clusters with the Cr_2W core demonstrate the successful application of the building block route for the preparation of antiferromagnetic heteronuclear sulfide clusters. Thermolysis of **9** leads to a remetalation process with participation of a bound dichromium unit **3** with the formation of the heterobinuclear Cr,W moiety. The second molecule of **3** provides a CpCrS (and SR) fragment. These different functions of **3** in **9** allow the formation of the $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2W(NO)X$ clusters. Presumably due to the presence of two NO groups in **9**, a side reaction of nitrosylation of the dichromium unit is initiated yielding nitrosylchromium complexes.

The Cr−Cr bonds in these triangular clusters are very weak because of the bent geometry of their Cp_2Cr_2 units. In **11** and **1a** (M = W and Re), containing 18-electron metal centers, the metal−metal bonds result in a bond order of $^1/_2$. In the case of a 16-electron configuration of the metal (like the W(II) center in **12**) a two-electron bond between the Cr and W centers can be formulated. The close energies for the spin−spin exchange of both types of clusters demonstrate that there is only minor influence of the diamagnetic metallo bridge between the coupled chromium atoms. In such a situation the magnetic behavior of the clusters is apparently determined only by the geometrical and electronic features of the $Cp_2Cr_2S_2$ system.

Experimental Section

General Comments. All manipulations including the syntheses of the starting materials were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. THF, Et_2O, benzene, and toluene were purified by distillation from sodium/benzophenone ketyl. Pentane, hexane, and heptane were dried by boiling over sodium. Dichloromethane (CH_2Cl_2) and MeCN were distilled twice from P_2O_5. Thin layer chromotography (TLC) (Merck, 5 × 7.5 cm, Kieselgel 60 F_{254}) was used when possible to monitor the progress of the reactions being studied. Column chromatography was applied using Kieselgel 60 (Merck, 70−230 mesh ASTM). The starting materials $[W(NO)_2Cl_2]_n$ (**8**), $[W(NO)_2(MeCN)_4](PF_6)_2$, and $Cp_2Cr_2(SCMe_3)_2S$ (**3**) were prepared as described elsewhere.[3,13,14] Infrared spectra were obtained from a Bio-Rad FTS-45 spectrometer in KBr pellets or in solution. MS (EI or FAB) were measured on a Finnigan MAT 8320 (70 eV). The temperature dependence of the magnetic susceptibilities (χ_m) were determined by the Faraday technique in the temperature range 296−77 K. Details of the calculation of the effective magnetic moment (μ_{eff}) and of the exchange parameters ($-2J$) by means of the HDVV model[10] were described earlier.[1,15] NMR measurements were performed on a Varian Gemini 300 instrument.

Formation of $[Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)]_2W(NO)_2Cl_2$ (9). A violet solution of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**3**) (2100 mg, 4.73 mmol) and **8** (750 mg, 2.38 mmol) in 50 mL of THF (or THF/Et_2O, 1:1) was stirred at 40−50 °C for 20−30 min (or at room temperature for 4−5 h) during which time the color changed to black. TLC (benzene−Et_2O) indicated the absence of the starting matrials. Then the solvent was evaporated under vacuo to dryness at −15 °C. The resulting black powder was extracted with a mixture of benzene/heptane (1:1, 150 mL), and a black solution formed, which was concentrated to 50 mL at 20 °C/0.1 Torr. Cooling of it to 5 °C gave 2300 mg (1.912 mmol, 80.3%) of fine black needle-shaped crystals of **9**. Further recrystallizations of this product from benzene/hexane (1:1), benzene/Et_2O (2:1), Et_2O, CH_2Cl_2/heptane (1:1), or CH_2Cl_2 yielded large black needles. Crystals of similar shape were obtained by slow diffusion of hexane into a solution of **9** in benzene or Et_2O. In all cases the obtained crystals were not suitable for an X-ray study, because of their poor reflection capability. Anal. Calcd for $C_{36}H_{56}Cl_2Cr_4N_2O_2S_6W$: C, 35.91; H, 4.66; N, 2.33; Cl, 5.90. Found: C, 35.19; H, 4.66; N, 2.43; Cl, 6.04. MS(FAB) (*m/e*): 1203 $[M]^+$; $[M]^+ - Cl$. IR (ν, cm^{-1}) (KBr pellet): 3088 (w), 2915 (m), 2883 (m), 2857 (m), 1729 (vs), 1609 (vs), 1469 (w), 1446 (m), 1431 (m), 1389 (w), 1356 (m), 1153 (m), 1118 (w), 1063 (w), 1016 (m), 839 (m), 812 (s), 676 (m), 569 (m).

Reaction of 3 and 8 in THF in the Presence of PPr^i_3. A violet solution of **3** (670 mg, 1.51 mmol) and **8** (250 mg, 0,79 mmol) in 50 mL of commerical THF (Fluka, 0.5% H_2O) was stirred at room temperature for 3 h. A deep blue-green precipitate, which displayed no ν(NO) bands in the IR spectrum, was formed. The addition of PPr^i_3 (0.4 mL) and further heating of the reaction mixture to 60 °C leads to formation of a slightly blue violet solution, which was filtered and evaporated to dryness. The blue violet powder was extracted by a mixture CH_2Cl_2/hexane (1:1) (20 mL). This extract gave air sensitive violet crystals of $[WCl(H)_2(H_2O)(P(Pr^i)_3)_2][CpCrCl_3]$ (**10**) (15 mg, 0.019 mmol, 2.4%) after concentration to 15 mL and cooling (−30 °C). The violet prisms of **10**·MeCN which were suitable for an X-ray study were obtained by slow cooling of a hot solution (60 °C) of a mixture of CH_2Cl_2/MeCN (1:1). Anal. Calcd for $C_{23}H_{51}Cl_4CrOP_2W$: C, 35.29; H, 6.52. Found: C, 35.11; H, 6.43. IR (ν, cm^{-1}) (KBr pellet): 3416 (m), 3098 (w), 2962 (m), 2921 (m), 2868 (m), 2029 (w), 1627 (m), 1452 (w), 1428 (m), 1377 (w), 1362 (w), 1345 (w), 1248 (w), 1089 (w), 1013 (m), 822 (s), 674 (m), 660 (w), 527 (m).

Thermolysis of 9. A black solution of **9** (900 mg, 0.748 mmol) in 50 mL of benzene was refluxed for 1 h during which time the color changed to deep green. TLC (benzene/Et_2O) showed the presence of six new bands and a green blue spot at the starting position. All products were separated by column chromatography (5 × 40 cm, silica gel):

(i) A red solution in benzene/hexane (1:1) was isolated which gave red needles of the known $Cp_2Cr_2(NO)_2(SCMe_3)(SSCMe_3)$ (**15**) (75 mg, 0.149 mmol, 9.9%).

(ii) A brown yellow solution in benzene/hexane (1:1) was isolated which gave brown prisms of the complex $Cp_2Cr_2(NO)_2(SCMe_3)(Cl)$ (**16**) (20 mg, 0.048 mmol, 3.2%). Anal. Calcd for $C_{14}H_{19}ClCr_2N_2O_2S$: C, 40.09; H, 4.53; N, 6.68. Found: C, 40.00; H, 4.49; N, 6.45. MS(EI) (*m/e*): 419, $[M]^+$; $[M]^+ - NO$; $[M]^+ - 2NO$; $[M]^+ - 2NO - CMe_3$; $[M]^+ - 2NO - CMe_3 - Cp$; $[M]^+ - 2NO - CMe_3 - 2Cp$; 182, Cp_2Cr^+. IR (ν, cm^{-1}) (KBr pellet): 3117 (w), 2972 (m), 2925 (m), 2895 (m), 2860 (m), 1670 (vs), 1653 (vs), 1474 (m), 1437 (w), 1426 (m), 1358 (m), 1258 (w), 1157 (m), 1118 (w), 1061 (w), 1015 (m), 1005 (m), 839 (m), 824 (m), 817 (s), 637 (w), 628 (m). ^1H NMR (C_6D_6) δ 4.80 (s, 10H, C_5H_5), 1.59 (s, 9H, CMe_3).

(iii) A green solution in benzene was isolated which gave green prismatic crystals of $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)_2$ (**11**) (150 mg, 0.208 mmol, 27.8%). Anal. Calcd for $C_{18}H_{28}Cr_2N_2O_2S_4W$: C, 29.96; H, 3.88; N, 3.74. Found: C, 30.15; H, 3.91; N, 3.65. MS (FAB or EI) (*m/e*): 721, $[M]^+$; $[M]^+ - NO$; $[M]^+ - NO - CMe_3$; $[M]^+ - 2NO - 2CMe_3$; 182, Cp_2Cr^+; 117, $CpCr^+$. IR (ν, cm^{-1}) (KBr pellet): 3084 (w), 2977 (w), 2960 (m), 2933 (w), 2913 (m), 2893 (m), 2856 (m), 1713 (vs), 1614 (vs), 1452 (m), 1435 (m), 1391 (w), 1359 (m), 1158 (m), 1065 (w), 1017 (w), 1011 (m), 833 (w), 823 (m), 812 (s), 798 (s), 571 (w), 552 (w), 470 (w).

(iv) A green solution in benzene was isolated which gave green

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Table 9. Data Collection and Processing Parameters

	compound						
	1a	**10**	**11**	**12**	**16**	**17**	**18**
formula	$C_{19}H_{28}Cr_2NO_2ReS_4$	$C_{23}H_{51}Cl_4CrOP_2$-W·MeCN	$C_{18}H_{28}Cr_2N_2O_2S_2W$	$C_{18}H_{28}ClCr_2NOS_4$-W·0.25CH_2Cl_2	$C_{14}H_{19}ClCr_2N_2O_2S$	$C_{28}H_{38}ClCr_4N_3O_3$-S_4·C_6H_6	$C_{18}H_{28}ClCr_2NOS_2$
mol wt	720.9	824.3	720.5	747.2	418.8	908.4	478.0
color and habit	green prism	violet prism	green prism	brown prism	brown prism	brown prism	brown prism
space group	$C2/c$	$P2_1/m$	$C2/c$	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$
a, Å	21.614(8)	10.679(5)	21.741(13)	9.495(5)	6.533(3)	9.619(5)	16.311(11)
b, Å	9.899(3)	12.967(5)	9.932(4)	32.89(2)	9.390(3)	10.320(5)	14.644(11)
c, Å	14.661(5)	13.678(5)	14.868(10)	17.451(8)	29.206(13)	11.799(6)	28.87(2)
α, deg						106.32(2)	
β, deg	128.86(2)	111.97(2)	129.01(2)	90.76(2)		108.45(2)	95.85(2)
γ, deg						102.75(2)	
V, Å^3	2442.4(13)	1756.6(12)	2495(2)	5449(5)	1791.7(12)	1002.8(9)	6860(8)
Z	4	2	4	8[a]	4	1	12[b]
ϱ_{calcd}, g/cm^{-1}	1.966	1.553	1.918	1.820	1.553	1.504	1.388
abs coeff, cm^{-1}	62.13	47.72	58.07	54.60	14.84	13.66	12.56
cryst size, mm	0.35 × 0.35 × 0.20	0.25 × 0.25 × 0.25	0.35 × 0.15 × 0.15	0.30 × 0.15 × 0.08	0.43 × 0.21 × 0.15	0.30 × 0.30 × 0.20	0.35 × 0.35 × 0.22
scan speen	variable; 2.00−14.65	variable; 2.55−14.65	variable; 1.50−14.65	variable; 1.50−14.65	variable; 2.02−14.65	variable; 2.02−14.65	variable; 1.50−14.65
scan width	2.00	1.60	2.40	1.70	2.40	2.00	1.60
collcn range	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
2θ range	4−52	4−56	3−56	3−54	3−52	3−56	3−46
unique data	2293	4445	3027	9643	3528	4874	8856
refl obsd ($F \geq 4\sigma(F)$)	2208	3991	1455	3890	2340	1913	1889
no. of variabl	131	178	132	517	199	235	406
weighing scheme	unit weights	$w^{-1} = \sigma^2(F) + 0.0050F^2$	$w^{-1} = \sigma^2(F) + 0.0100F^2$	$w^{-1} = \sigma^2(F) + 0.0100F^2$	$w^{-1} = \sigma^2(F) + 0.0100F^2$	$w^{-1} = \sigma^2(F) + 0.0100F^2$	$w^{-1} = \sigma^2(F) + 0.0050F^2$
R[c]	0.087	0.038	0.036	0.041	0.050	0.040	0.084
R_w[d]	0.090	0.058	0.049	0.058	0.077	0.057	0.094
residual extrema in final diff map, e Å^{-3}	+2.47 to −1.19	+1.46 to −2.58	+1.02 to −1.04	+1.44 to −0.60	+1.05 to −0.90	+0.53 to −0.48	+0.78 to −0.54

[a] Two independent molecules in unit cell. [b] Three independent molecules in unit cell. [c] $\sum|F_o - F_c|/F_o$. [d] $[\sum w(|F_o - F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 10. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for $[WCl(H)_2(H_2O)(P(iPr)_3)_2][CpCrCl_3]$·MeCN (**10**)

atom	x	y	z	U(eq)[a]
W(1)	1633(1)	2500	2887(1)	33(1)
P(1)	1741(1)	687(1)	2819(1)	37(1)
Cl(1)	3844(2)	2500	4038(2)	60(1)
O(1)	−354(4)	2500	1844(4)	64(1)
H(1)a	−931(12)	3134(11)	1836(12)	51(4)
C(1)	2974(4)	95(3)	4035(3)	53(1)
C(2)	2672(5)	320(4)	4999(4)	78(1)
C(3)	3233(5)	−1057(4)	3939(4)	73(1)
C(4)	2347(4)	335(3)	1762(3)	49(1)
C(5)	1447(4)	829(4)	712(4)	71(1)
C(6)	3823(4)	655(4)	2026(4)	74(1)
C(7)	85(3)	40(3)	2450(3)	44(1)
C(7)	−589(4)	258(4)	3245(4)	68(1)
C(9)	44(4)	−1120(3)	2204(4)	64(1)
H(1)	992(8)	2500	3799(8)	83(3)
H(2)	2467(8)	2500	2218(8)	57(3)
Cr(1)	−4039(1)	2500	−336(1)	45(1)
Cl(2)	−2210(2)	2500	−858(2)	70(1)
Cl(3)	−3248(1)	1155(1)	859(1)	66(1)
C(10)	−5554(5)	3047(5)	−1850(5)	104(1)
C(11)	−6004(5)	3328(4)	−1076(5)	92(1)
C(12)	−6220(5)	2500	−585(6)	85(1)
N(1)s	760(6)	7500	5059(6)	121(1)
C(1)s	1766(6)	7500	5708(5)	80(1)
C(2)s	3066(6)	7500	6560(6)	110(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized **U**(i,j) tensor.

Table 11. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for $CpCr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2W(NO)_2$ (**11**)

atom	x	y	z	U(eq)[a]
W(1)	5000	2683(1)	2500	37(1)
Cr(1)	4198(1)	−29(1)	1310(1)	39(1)
S(1)	4567(1)	704(2)	3087(2)	36(1)
S(2)	3650(2)	2165(3)	684(2)	49(2)
O(1)	4461(9)	4850(10)	3266(12)	131(14)
N(1)	4683(6)	3991(9)	3001(9)	60(7)
C(1)	3428(7)	2803(12)	−681(10)	61(7)
C(2)	2655(9)	2167(17)	−1691(11)	95(10)
C(3)	3352(12)	4345(14)	−652(14)	116(16)
C(4)	4085(9)	2475(12)	−744(11)	71(10)
C(11)	3622(10)	−1273(15)	−280(12)	87(11)
C(12)	3034(8)	−940(14)	−160(11)	72(9)
C(13)	3284(7)	−1538(13)	869(11)	66(9)
C(14)	3986(9)	−2239(11)	1371(12)	67(9)
C(15)	4176(10)	−2064(13)	627(14)	77(11)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized **U**(i,j) tensor.

prisms of known $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)(SCMe_3)$ (**2**) (180 mg, 0.231 mmol, 30.9%).

(v) A brown solution in benzene/Et_2O (1:1) was isolated which gave a brown microcrystalline precipitate of $Cp_4Cr_4(NO)_3(Cl)(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S_2)$ (**17**) (25 mg, 0.030 mmol, 4.0%). Anal. Calcd for $C_{28}H_{38}ClCr_4N_3O_3S_4$: C, 40.19; H, 4.54; N, 5.02. Found: C, 39.85; H, 4.49; N, 4.94. MS (FAB) (*m/e*): 836, $[M]^+$. IR (ν, cm^{-1}) (KBr pellet): 3100 (w), 3063 (w), 2953 (m), 2917 (m), 2885 (m), 2852 (m), 1659 (vs), 1639 (vs), 1452 (w), 1438 (m), 1387 (w), 1358 (m), 1215 (w), 1151 (m), 1064 (w), 1017 (w) 1006 (m), 839 (m), 813 (s), 806 (m), 667 (w), 573 (w), 550 (w). The brown prisms of **17**·C_6H_6 which were suitable for an X-ray study were obtained by slow evaparation of benzene/CH_2Cl_2 solution from a NMR ampule.

(vi) A brown solution in benzene/CH_2Cl_2 (1:1) was isolated which gave brown plates of $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)Cl$ (**12**) (90 mg, 0.124 mmol, 16.6%). Anal. Calcd for $C_{18}H_{28}ClCr_2NOS_4W$: C, 29.75; H, 3.86; N, 1.93; Cl, 4.89. Found: C, 29.15; H, 3.70; N, 1.88; Cl, 5.01. MS (EI) (*m/e*): 726, $[M]^+$; $[M]^+ - Cl$; $[M]^+ - Cl - CMe_3$; $[M]^+ - Cl - 2CMe_3$; $[M]^+ - Cl - 2CMe_3 - NO$. IR (ν, cm^{-1}) (KBr pellet): 3099 (w), 2958 (m), 2917 (m), 2889 (m), 2854 (m), 1598 (vs), 1454 (m), 1431 (m), 1388 (w), 1358 (m), 1149 (m), 1062 (w), 1012 (m), 849 (w), 815 (s), 666 (w). Brown prismatic crystals of **12**·0.25CH_2-

Cl_2 obtained by slow cooling of a hot solution in CH_2Cl_2 (55 °C) were suitable for an X-ray investigation.

Reaction of 3 with $[W(NO)_2(MeCN)_4](PF_6)_2$. A violet solution of **3** (630 mg, 1.419 mmol) and suspended $[W(NO)_2(MeCN)_4](PF_6)_2$ (480 mg, 0.688 mmol) in 50 mL of benzene were stirred at 50 °C for 3 h. A black precipitate, which display no ν(NO) bands in the IR spectrum, was filtered off from the green solution. TLC (benzene) of the filtrate showed the absence of **3**. This solution was concentrated to 25 mL and chromatographed on silica gel (5 × 30 cm, benzene/CH_2Cl_2) affording three bands: (i) a red band in benzene which gave red needles of **15** (75 mg, 0.149 mmol, 10.8%); (ii) a green solution in benzene/CH_2Cl_2 (1:1) which gave after concentration and cooling (5 °C) green crystals of **11** (75 mg, 0.104 mmol, 15.0%); (iii) a green solution in CH_2Cl_2 which yielded green prisms of **2** (250 mg, 0.321 mmol, 46.76%).

Reaction of 3 with NOCl. A violet solution of **3** (440 mg, 1 mmol) and NOCl (0.3 mL) in 30 mL of benzene was stirred at room temperature for 15 min, during which time the color changed to green. The solvent was removed to dryness. A green precipitate was extracted by heptane (100 mL) yielding a brown red solution. It was chromatographed (5 × 30 , silica gel, benzene/hexane (1:1)) with the formation of three major fractions containing **15**, **16**, and $Cp_2Cr_2(NO)(Cl)(\mu\text{-}SCMe_3)_2$ (**18**): 250 mg (0.556 mmol, 55.6%) of **15**; 65 mg (0.155 mmol, 15.5%) of **16**; 60 mg (0.136 mml, 13.6%) of **18**. Anal. Calcd for $C_{18}H_{28}ClCr_2NOS_2$ (**18**): C, 45.28; H, 5.87; N, 2.94; Cl, 7.34. Found: C, 45.13; H, 5.65; N, 2.75; Cl, 7.30. MS (EI) (*m/e*): 477 and 479, $[M]^+$; $[M]^+ - NO$; $[M]^+ - NO - CMe_3$; $[M]^+ - NO - 2CMe_3$; 182, Cp_2Cr^+; 117, $CpCr^+$. IR (ν, cm^{-1}): 3098 (w), 2957 (m), 2922 (m), 2892 (w), 2852 (m), 1638 (vs), 1472 (w), 1456 (m), 1435 (w), 1386 (w), 1359 (m), 1156 (m), 1013 (w), 840 (w), 811 (s), 806 (m), 667 (w), 566 (w), 531 (w). Single crystals suitable for X-ray investigation were obtained by slow cooling of a hot (60 °C) CH_2Cl_2/benzene solution to room temeperature.

Crystal Structure Determinations. Single crystals of **10**−**12** and **16**−**18** for X-ray studies were obtained as described above. The crystals of **1a** were prepared by slow cooling of a hot acetonitrile solution (60 °C) to room temperature. The samples were all mounted in air on glass fibers using 5 min epoxy resin (for the oxygen sensitive complex **10** this operation was performed under nitrogen). The unit cells were determined and refined from 24 equivalent reflections with $2\theta \le 22-30°$ and obtained from a Siemens R3/m (for **1a**, $T = -80$ °C) or a Nicolet R3 (for other compounds, $T = 22$ °C) four-circle diffractometer (graphite monochromator, Mo Kα, $\lambda = 0.710\,73$ Å). The intensity data set was corrected for Lorentz and polarization effects. A semiempirical absorption correction (min/max transmission 0.0286/0.0802) was employed for **10** to give good agreement with 12 intense reflections as observed at different values of ϕ.[16] The DIFABS method[17] was used for absorption correction of all other compounds at the stage of an isotropic approximation. Backgrounds were scanned for 25% of the peak widths on each end of a scan. 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 9.

All structures were solved using direct methods to locate the transition metals and the P, S, or Cl atoms. Standard Fourier methods were used to locate the remaining non-hydrogen atoms in the molecules. An anisotropic refinement was applied to all non-hydrogen atoms. The H atoms of the C_5H_5 or Ph rings, PPr^i_3 ligands, and $SCMe_3$ groups were generated geometrically (C−H bonds fixed at 0.96 Å) and assigned the same isotropic temperature factor of $U = 0.08$ Å^2. Computations were performed using the SHELXTL PLUS program package[18] on a VAXstation 3100 (for **1a**) or on an 486 IBM PC (for other compounds). The function minimized in the least-squares calculations was $\sum w(F_o - F_c)^2$. Atomic coordinates are listed in Tables 10−16. Selected bond lengths and angles for the investigated compounds are given in Tables 1−6 and 8. Additional information is avaliable as supplementary material.

Table 12. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2W(NO)Cl{\cdot}0.25\ CH_2Cl_2$ (**12**)

atom	*x*	*y*	*z*	*U*(eq)[a]
W(1)	8491(1)	1895(1)	2121(1)	35(1)
Cr(1)	5998(3)	2188(1)	2854(2)	42(1)
Cr(2)	5872(3)	1508(1)	1677(2)	44(1)
S(1)	6686(4)	1513(1)	2926(2)	42(1)
S(2)	6348(5)	2189(1)	1559(3)	46(2)
S(3)	8163(4)	1284(1)	1345(2)	40(1)
S(4)	8357(4)	2335(1)	3240(2)	42(1)
Cl(1)	10446(5)	1555(2)	2772(3)	60(2)
O(1)	10123(19)	2406(5)	1028(9)	108(8)
N(1)	9529(15)	2194(5)	1488(9)	58(6)
C(11)	3756(21)	2391(10)	2761(14)	84(11)
C(12)	3858(21)	2092(7)	3312(14)	72(9)
C(13)	4727(22)	2241(8)	3920(13)	72(9)
C(14)	5146(24)	2643(11)	3677(20)	120(15)
C(15)	4544(32)	2702(7)	2963(20)	93(13)
C(21)	4664(32)	1204(16)	782(18)	109(15)
C(22)	4901(38)	919(9)	1244(33)	135(21)
C(23)	4264(39)	1047(18)	1869(21)	138(22)
C(24)	3589(28)	1405(18)	1758(30)	157(23)
C(25)	3906(34)	1515(10)	963(25)	101(14)
C(41)t	9025(20)	2866(5)	3094(10)	53(7)
C(42)t	10642(16)	2819(7)	3040(12)	73(9)
C(43)t	8389(23)	3071(6)	2401(12)	75(9)
C(44)t	8714(24)	3115(6)	3828(11)	77(9)
C(31)t	8694(19)	1334(6)	325(10)	55(7)
C(32)t	8260(22)	926(6)	−54(10)	67(8)
C(33)t	7974(22)	1685(6)	−86(9)	69(8)
C(34)t	10283(18)	1397(6)	316(10)	56(7)
W(2)	−194(1)	841(1)	6756(1)	38(1)
Cr(3)	1911(3)	237(1)	6486(2)	48(1)
Cr(4)	1846(3)	1057(1)	5649(1)	46(1)
S(5)	2471(5)	885(1)	6889(2)	48(2)
S(6)	434(5)	491(1)	5557(2)	48(2)
S(7)	339(5)	252(1)	7536(3)	49(2)
S(8)	166(5)	1509(1)	6192(2)	44(2)
Cl(2)	−603(7)	1197(2)	7953(3)	80(2)
O(2)	−3156(15)	669(5)	6293(9)	85(6)
N(2)	−1992(15)	761(5)	6515(9)	57(6)
C(31)	3919(27)	−46(10)	6805(20)	100(13)
C(32)	2876(38)	−324(10)	6932(20)	109(14)
C(33)	2267(33)	−417(9)	6215(25)	111(16)
C(34)	2911(31)	−204(10)	5705(18)	96(13)
C(35)	3934(24)	32(7)	6020(18)	77(10)
C(41)	2363(28)	1516(8)	4759(16)	92(12)
C(42)	2315(24)	1141(10)	4412(12)	79(10)
C(43)	3324(27)	913(8)	4700(12)	81(10)
C(44)	4102(22)	1111(10)	5279(12)	86(11)
C(45)	3540(26)	1477(9)	5310(13)	79(11)
C(71)t	−1107(21)	−124(6)	7619(12)	63(8)
C(72)t	−1646(22)	−267(6)	6835(12)	79(9)
C(73)t	−2295(22)	83(7)	8056(13)	85(10)
C(74)t	−511(26)	−484(6)	8076(13)	98(11)
C(81)t	−1349(20)	1698(5)	5591(10)	49(7)
C(82)t	−946(23)	2106(6)	5286(12)	81(9)
C(83)t	−1750(21)	1400(6)	4959(11)	71(8)
C(84)t	−2554(20)	1736(6)	6136(11)	66(8)
Cl(1)s	4444(15)	619(5)	8807(8)	102(4)
Cl(2)s	2256(20)	277(6)	9632(11)	153(7)
C(1)s	2691(35)	647(11)	9080(18)	45(9)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized **U**(*i,j*) tensor.

Specific Comments on the Solutions and Refinements of 1a, 10, 12, 17, and 18. $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2Re(CO)(NO)$ (1a). Inspection of the indices showed that reflections having *hkl*, $h + k = 2n + 1$, 0*k*0, $k = 2n + 1$, and *h*0*l*, $l = 2n + 1$, were systematically absent in agreement with the space group *C*2/*c*. Further solution and refinemet led to the location of the molecule of **1a** on a crystallographic 2-fold axis (the Re atom), which therefore displayed a disorder of the NO and CO groups. Hence the fragment Re(CO)(NO) was refined as Re-

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(17) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(18) Sheldrick, G. M. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*; Clarendon Press: New York, 1985; p 175.

Table 13. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $Cp_2Cr_2(NO)_2(\mu\text{-}SCMe_3)(\mu\text{-}Cl)$ (**16**)

atom	*x*	*y*	*z*	*U*(eq)[a]
Cr(1)	1140(2)	265(1)	798(1)	37(1)
Cr(2)	813(2)	−2603(1)	1212(1)	38(1)
Cl(1)	−1005(4)	−1628(2)	593(1)	59(1)
S(1)	2777(3)	−671(2)	1435(1)	39(1)
O(1)	−1860(11)	2172(8)	1165(3)	82(3)
O(2)	−2468(11)	−2708(8)	1859(3)	77(3)
N(1)	−666(10)	1311(7)	1044(2)	51(2)
N(2)	−1141(10)	−2539(7)	1590(2)	47(2)
C(1)	2220(13)	172(9)	2004(3)	48(3)
C(2)	3207(24)	1642(11)	1969(4)	97(5)
C(3)	3236(25)	−766(14)	2357(4)	109(6)
C(4)	−5(18)	376(16)	2118(4)	106(6)
C(11)	4317(13)	596(11)	538(3)	64(3)
C(12)	3320(17)	−161(10)	216(3)	70(4)
C(13)	1595(16)	695(10)	64(3)	65(3)
C(14)	1806(15)	1953(10)	295(3)	62(3)
C(15)	3414(15)	1882(9)	597(3)	57(3)
C(21)	3761(17)	−3657(9)	994(4)	71(4)
C(22)	2305(14)	−4089(9)	695(3)	57(3)
C(23)	725(18)	−4788(9)	950(4)	71(4)
C(24)	1297(21)	−4825(10)	1390(4)	80(4)
C(25)	3202(19)	−4113(11)	1441(4)	84(5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized **U**(*i*,*j*) tensor.

Table 14. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $Cp_4Cr_4(NO)_3(Cl)(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S_2)\cdot C_6H_6$ (**17**)

atom	*x*	*y*	*z*	*U*(eq)[a]
Cr(1)	1004(1)	3498(1)	1609(1)	44(1)
Cr(2)	−1377(1)	4850(1)	1803(1)	42(1)
S(1)	−654(2)	3212(2)	2651(1)	46(1)
S(2)	520(2)	5369(2)	1015(1)	41(1)
Cl(1)	−3522(9)	3365(8)	−55(7)	77(7)
O(1)	−559(7)	1225(6)	−828(5)	76(3)
O(2)	−4094(24)	3066(29)	−596(15)	79(9)
N(1)	−53(6)	2111(6)	116(5)	52(3)
N(2)	−2827(21)	3760(24)	500(15)	51(9)
C(1)	−2137(8)	1411(7)	2137(7)	58(3)
C(2)	−1338(9)	652(7)	2921(7)	78(4)
C(3)	−2725(9)	513(7)	711(7)	81(4)
C(4)	−3471(10)	1695(8)	2491(10)	89(5)
C(11)	3479(8)	4856(10)	2353(10)	89(5)
C(12)	3279(8)	3480(10)	1621(8)	76(4)
C(13)	2828(9)	2575(9)	2225(8)	76(4)
C(14)	2807(8)	3439(10)	3346(7)	76(4)
C(15)	3155(9)	4849(10)	3416(8)	86(4)
C(21)	−1223(15)	7108(9)	2335(10)	95(7)
C(22)	−2668(12)	6321(10)	2164(8)	86(5)
C(23)	−2513(10)	5721(8)	3070(7)	70(4)
C(24)	−947(10)	6156(8)	3840(6)	69(4)
C(25)	−136(10)	7021(8)	3398(9)	83(4)
C(1s)a	4377(25)	10956(14)	5599(25)	145(11)
C(2s)a	3571(14)	10082(18)	4271(20)	131(8)
C(3s)a	4229(24)	9186(15)	3715(12)	133(9)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized **U**(*i*,*j*) tensor.

$(NO)_2$; however, in Figure 7 we denoted one ligand as CO and the other one as NO.

$[WCl(H)_2(H_2O)(P(Pr^i)_3)_2][CpCrCl_3]\cdot MeCN$ (10). Inspection of the data set showed that reflections having 0*k*0, $k = 2n + 1$, were systematically absent, consistent with the space group $P2_1$ or $P2_1/m$. The solution of the structure and further refinement in $P2_1/m$ resulted in the position of the W, Cl, and $O(H_2O)$ atoms of the cation and the Cr and one Cl atoms of the anion on a crystallographic mirror plane. After anisotropic refinement of all non-hydrogen atoms with fixed H atoms of the Pr^i residues and of the Cp ring, the hydride ligands and the H atoms of the coordinated H_2O molecule were taken from a difference Fourier map and refined isotropically.

Table 15. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $Cp_2Cr_2(NO)(Cl)(\mu\text{-}SCMe_3)_2$ (**18**)

atom	*x*	*y*	*z*	*U*(eq)[a]
Cr(1)	3170(3)	7671(3)	1513(2)	54(2)
Cr(2)	2411(3)	8642(4)	2310(2)	71(2)
S(1)	2154(5)	8800(6)	1501(3)	71(3)
S(2)	3421(5)	7499(6)	2319(3)	62(3)
Cl(1)	3180(8)	9912(9)	2523(4)	156(4)
N(1)	4071(16)	8313(18)	1339(10)	68(5)
O(1)	4483(14)	8571(17)	1252(7)	84(5)
C(11)	2298(22)	9877(24)	1244(13)	89(7)
C(12)	1729(21)	10556(25)	1419(12)	134(8)
C(13)	3096(20)	10328(24)	1332(12)	121(8)
C(14)	2098(22)	9757(25)	713(12)	142(8)
C(21)	4464(18)	7734(21)	2642(11)	66(7)
C(22)	4905(21)	8572(22)	2419(12)	130(8)
C(23)	4377(18)	7870(20)	3132(10)	84(7)
C(24)	4977(21)	6897(23)	2565(13)	135(8)
C(111)	3342(20)	6704(20)	942(11)	75(7)
C(112)	2122(23)	6764(22)	1203(12)	99(7)
C(113)	2581(21)	7043(23)	848(12)	92(7)
C(114)	2655(20)	6236(22)	1521(12)	83(7)
C(115)	3443(21)	6210(22)	1401(11)	86(7)
C(221)	1821(22)	7862(27)	2831(14)	110(7)
C(222)	1804(21)	8832(26)	2964(14)	112(7)
C(223)	1250(21)	9146(26)	2573(12)	103(7)
C(224)	1061(22)	8350(26)	2303(13)	108(7)
C(225)	1387(22)	7608(29)	2433(13)	112(8)
Cr(3)	2182(3)	3662(4)	−29(2)	69(2)
Cr(4)	975(3)	3906(3)	−929(2)	59(2)
S(3)	746(5)	3508(6)	−156(3)	57(3)
S(4)	2432(5)	3815(6)	−809(3)	68(3)
Cl(2)	584(8)	2607(9)	−1339(4)	155(4)
N(2)	2448(18)	2530(25)	60(11)	113(5)
O(2)	2738(16)	1977(18)	215(10)	130(5)
C(31)	339(20)	2377(22)	−8(12)	75(7)
C(32)	479(18)	2277(21)	498(10)	88(7)
C(33)	666(19)	1560(21)	−246(11)	100(7)
C(34)	−549(20)	2448(24)	−138(12)	127(8)
C(41)	2987(25)	2797(27)	−1066(14)	116(7)
C(42)	2696(25)	1986(29)	−980(16)	200(8)
C(43)	3114(25)	2980(29)	−1544(15)	202(8)
C(44)	3872(19)	2878(23)	−821(12)	114(7)
C(331)	1929(22)	5044(23)	294(11)	90(7)
C(332)	2671(21)	5103(23)	77(12)	86(7)
C(333)	3251(24)	4509(25)	248(13)	111(7)
C(334)	2952(21)	4079(23)	621(12)	90(7)
C(335)	2123(20)	4375(22)	643(12)	82(7)
C(441)	−134(20)	4749(20)	−1120(11)	70(7)
C(442)	302(19)	4683(21)	−1522(11)	74(7)
C(443)	1057(22)	5081(21)	−1409(12)	82(7)
C(444)	1093(17)	5439(18)	−965(10)	47(6)
C(445)	321(18)	5264(20)	−781(11)	68(7)
Cr(5)	8769(3)	6594(4)	4264(2)	73(2)
Cr(6)	8466(3)	6558(4)	3193(2)	75(2)
S(5)	9310(6)	7472(7)	3684(3)	87(3)
S(6)	7848(5)	5740(6)	3759(3)	70(3)
Cl(3)	7943(7)	7596(8)	4604(4)	120(4)
N(3)	7745(19)	7233(22)	2990(9)	94(5)
O(3)	7249(15)	7695(19)	2778(9)	119(5)
C(51)	9111(26)	8785(27)	3670(15)	124(8)
C(52)	8226(19)	8990(33)	3605(12)	107(7)
C(53)	9606(27)	9098(32)	4059(16)	237(8)
C(54)	9399(27)	9040(31)	3231(16)	233(8)
C(61)	6675(21)	5866(24)	3782(13)	87(7)
C(62)	6340(24)	5273(27)	3416(14)	171(8)
C(63)	6553(21)	5441(25)	4256(12)	134(8)
C(64)	6440(18)	6850(20)	3775(10)	83(7)
C(551)	9513(19)	5346(23)	4387(11)	81(7)
C(552)	9294(23)	6240(27)	4961(14)	125(8)
C(553)	10055(24)	6042(27)	4426(14)	123(8)
C(554)	9890(25)	6597(29)	4750(14)	136(8)
C(555)	8989(24)	5459(27)	4772(14)	122(8)
C(661)	8662(22)	5151(25)	2866(12)	96(7)
C(662)	9376(22)	5539(24)	3035(12)	89(7)
C(663)	9603(28)	6286(29)	2837(15)	149(8)
C(664)	8958(21)	6435(25)	2515(12)	102(7)
C(665)	8359(23)	5748(25)	2519(13)	111(7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized **U**(*i*,*j*) tensor.

Table 16. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for Cp$_2$Cr$_2$(μ-SCMe$_3$)$_2$(μ_3-S)Re(NO)(CO) **(1a)**

atom	*x*	*y*	*z*	*U*(eq)[a]
Re(1)	5000	2689	2500	26(1)
Cr(1)	4194(1)	−28(2)	1316(2)	27(1)
S(1)	3662(2)	2179(5)	712(3)	38(2)
S(2)	4585(2)	716(4)	3120(3)	25(2)
O(1)	4414(13)	4790(20)	3239(18)	109(17)
N(1)	4666(14)	3971(15)	2980(20)	77(17)
C(2)	3441(10)	2827(21)	−661(14)	48(10)
C(3)	3343(20)	4321(26)	−679(24)	105(26)
C(4)	2639(11)	2146(29)	−1692(17)	76(13)
C(5)	4087(11)	2489(19)	−756(16)	48(11)
C(11)	4190(13)	−2071(21)	647(20)	60(14)
C(12)	3566(12)	−1256(26)	−325(17)	68(13)
C(13)	3025(10)	−941(22)	−144(16)	58(10)
C(14)	3287(9)	−1541(19)	904(14)	44(8)
C(15)	3986(11)	−2251(20)	1373(18)	52(11)

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

Cp$_2$Cr$_2$(μ_3-S)$_2$(μ-SCMe$_3$)$_2$W(NO)Cl·0.25CH$_2$Cl$_2$ (12). Inspection of the indices showed that reflections having $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, were systematically absent consistent with the space group $P2_1/n$. Solution and refinement led to the location of two independent molecules of **12** and to the electron density for the solvate molecule. This molecule was determined as CH$_2$Cl$_2$ with the population factor 0.5 (refinement gave values for C of 0.46 and for both Cl atoms of 0.44).

Cp$_4$Cr$_4$(NO)$_3$(Cl)(μ-SCMe$_3$)$_2$(μ_4-S$_2$)·C$_6$H$_6$ (17). **17** was located in a crystallographic center (in the middle of the S−S bond), which therefore showed disordering of the Cl atom and one NO group. They are bonded symmetrically (crystallographically dependent) to the Cr atoms (Cr(2)). The positions of these ligands were solved, and refinement of the population parameter resulted in a value close to 0.5.

Cp$_2$Cr$_2$(NO)(Cl)(μ-SCMe$_3$)$_2$ (18). Inspection of the data set showed that reflections with $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, were systematically absent in agreement with the space group $P2_1/n$. Further solution and refinement led to the position of three independent molecules in the unit cell. For this compound the Cr, S, Cl, N, and O atoms were refined in an anisotropic approximation; however, isotropic refinement was applied to the carbon atoms due to the limited number of observed reflections with $I \geq 3\sigma$ (the single crystal of **18** had a poor reflection capability).

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Supplementary Material Available: Full tables of data collection parameters, bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and *U* values for **1a**, **10**−**12**, and **17**−**19** (43 pages). Ordering information is given on any current masthead page.

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