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Heterocyclic Thionates as a New Class of Bridging Ligands in Oxo-Centered Triangular Cyclopentadienylchromium(III) Complexes

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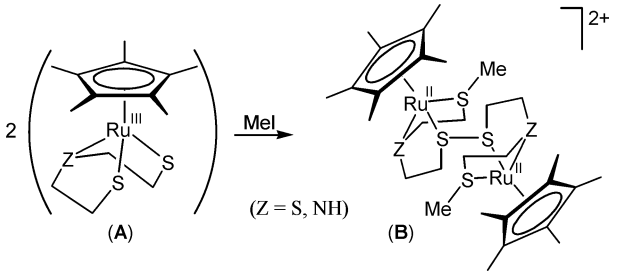
The interactions of the benzothiazolate complex, $CpCr(CO)_2(SCSN(C_6H_4))$ (**2**), and the tetrazole thiolate complex, $CpCr(CO)_3(\eta^1\text{-}SCN_4Ph)$ (**3**), with controlled amounts of Me_3OBF_4 and $(MeO)_2SO_2$, respectively, produced the corresponding μ_3-oxo trinuclear thionate-bridged complexes, $[Cp_3Cr_3(\mu_2\text{-}OH)(\mu_3\text{-}O)(\mu_2\text{-}\eta^2\text{-}SCSN(C_6H_4))_2](\mathbf{5})BF_4$ (45%) and $[Cp_3Cr_3(\mu_2\text{–}OH)(\mu_3\text{–}O)(\mu_2\text{-}\eta^2\text{-}SCN_4Ph)_2](\mathbf{9})(MeOSO_3)$ (53%), together with their respective free dimethylated thiolate ligands, $[MeSCSNMe(C_6H_4)](\mathbf{4})BF_4$ and $(Me_2SCN_4Ph)(\mathbf{8})MeOSO_3$. The reaction of **3** with Me_3OBF_4 resulted in the isolation of a binuclear complex, $[Cp_2Cr_2(\mu\text{-}OH)(\mu\text{-}\eta^2\text{-}SCN_4Ph)_2](\mathbf{7})BF_4$ (43%), and $(\mathbf{8})BF_4$ (27%). The reaction of the thiopyridine complex, $CpCr(CO)_2(SPy)$ (**4**), with I_2 also produced a similar μ_3-oxo complex **10** (31%), together with $CpCrI_2(THF)$ (**11**) and the disulfide $(SPy)_2$. Similar reactions with **2** and **3** and I_2 yielded species **5** and **7**, together with **11** and disulfides derived from their respective ligands. Cyclic voltammograms recorded in solutions of **5** and **9** indicated that the compounds could be reduced and oxidized at very similar potentials. An EPR spectrum characteristic of a compound with axial symmetry was obtained for **9** at 7 K. Single-crystal X-ray diffraction analyses confirmed that species **7** is dinuclear, whereas **5** and **9** are structural trinuclear analogues, each containing a μ_3-oxo central core.

Introduction

In recent work, we have encountered unanticipated outcomes from the electrophilic attack of alkylating agents on the ligated thiolate sulfur atoms at both Ru and Cr centers (Schemes 1 and 2). In the case of **A**, alkylation at the thiolate S had initiated an internal electron transfer which resulted in the formation of a thiyl radical with consequent dimerization to **B**.[1] In the Cr(III) complex, **C**, methylation of the thiolate S donor atoms led to the dissociation of the resulting weakened Cr−thioether bonds, thus generating an oxophilic unsaturated Cr(III) species.[2] These findings prompted us to carry out similar reactions on some of the numerous thiolate-containing CpCr complexes which we have previously obtained from the interactions of $[CpCr(CO)_3]_2$ ($Cp = \eta^5\text{-}C_5H_5$) (**1**) with S−S bonded organic substrates.[3−8] Such investigations will also fit in with our endeavors on reactivity studies, which have largely been focused on homolytic bond

Scheme 1



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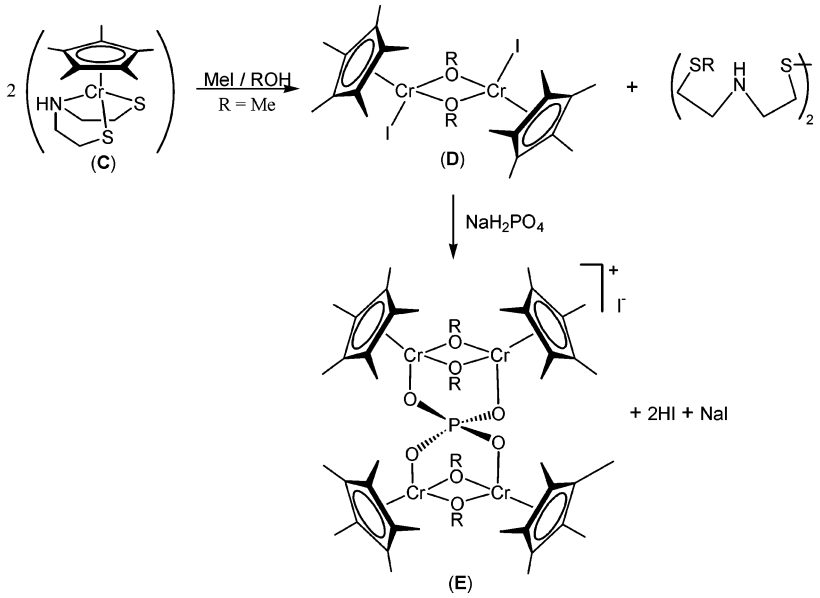
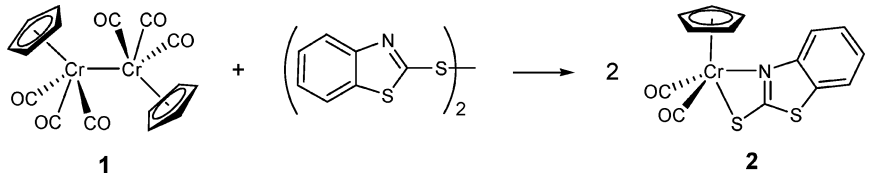
Scheme 2

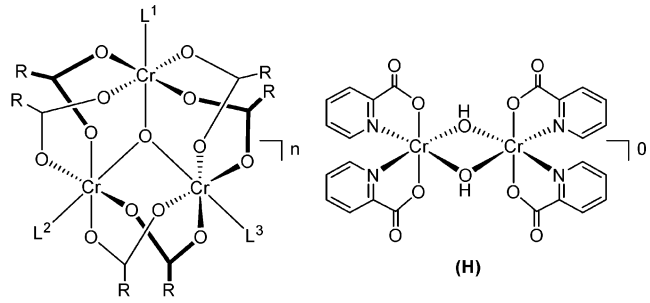


Scheme 3



cleavage reactions by $CpCr(CO)_3$•(**1A**), the incumbent 17-electron mononuclear derivative of **1**,[3] and lately, include some protonation reactions.[9] We selected complex **2** for the present study because the organic ligand therein, interestingly, contains three potential alkylation sites: one N and two S donor atoms. Complex **2** was obtained from dibenzothiazolyl disulfide $[(C_6H_4)NSCS]_2$[8] (Scheme 3). Alkylation at the N site requires the availability of a lone electron pair and hence can only occur concurrently with or following Cr−N bond cleavage; it would be interesting to compare the subsequent reactivity of the derived complex versus the aggregation of radical fragments formed from homolytic cleavage by **1A**.[8,10] Moreover, any derivatives containing Cr and a thiazole ring, a component in many bioactive molecules,[11] are likely to be of biochemical interest. The reaction was extended to complexes $CpCr(CO)_3(\eta^1\text{-}SCN_4Ph)$ (**3**)[10] and $CpCr(CO)_2(SPy)$ (**4**)[9] because these also contain both N and S alkylation sites, and for complex **4**, a protonation study is already available for comparison.

Chart 1



(F) R = Me, Et; $L^1 = L^2 = L^3 = H_2O$; n = +1

(G) R = NEt_2; L^1 = Cl, $L^2 = L^3 = NHEt_2$; n = 0

Unexpectedly, we obtained μ-oxo-bridged di- and tri-chromium cationic complexes, resembling species **F**−**H**[12−14] (see Chart 1), which contain bridging carboxylate, dithiocarbamate, and picolinate ligands, respectively. Such compounds, especially those of the **F** category, have been well studied.[15−18] Interest has been stimulated by the occurrence of the μ_3-O moiety in the active sites of numerous non-heme iron and manganese metalloproteins.[19] In recent years, these multinuclear carboxylate assemblies of Cr(III) have been increasingly used as functional biomimetic models for studies of the insulin-related function of the unique low-molecular-weight chromium-binding oligopeptide (LMWCr) (chromodulin).[20−26]

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Scheme 4

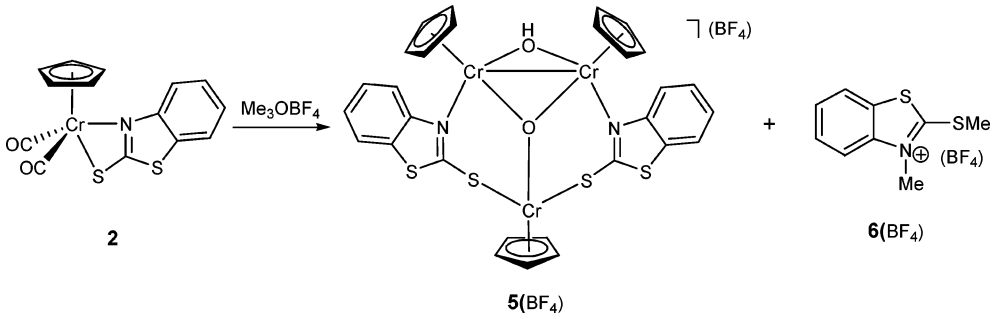

Table 1. Products from Reactions with Methylating Reagents[a]

substrate complex	reagents	products[e] (μ_3-oxo)Cr_3	(μ_2-OH)Cr_2	Me_2L [f]	noncharacterizable CpCr-containing compounds
2	Me_3OBF_4	**5**, 45%	N	+	N
	excess Me_3OBF_4[b]	N	N	+	+
	$(MeO)_2SO_2$	+	N	+	N
3	Me_3OBF_4	N	**7**, 43%	27%	26%
	excess Me_3OBF_4[b]	N	+	+	+
	$(MeO)_2SO_2$[c]	**9**, 53%	N	+	N
4	Me_3OBF_4	N	N	+	+
	$(MeO)_2SO_2$[d]	−	−	−	−

[a] Using 2 mol equiv of the methylating agent unless otherwise stated. [b] Using 3−4 mol equiv of the methylating agent. [c] Using 10 mol equiv of the methylating agent. [d] No reaction. [e] N = not observed. + = present but yields not quantified. [f] Free dimethylated ligand.

This paper will describe the isolation and characterization of the new μ-oxo complexes together with its cyclic voltammetric and EPR measurements.

Results and Discussion

Reactions with Methylating Reagents. Complexes $CpCr(CO)_2(SCSN(C_6H_4)$ (**2**), $CpCr(CO)_3(\eta^1\text{-}SCN_4Ph)$ (**3**), and $CpCr(CO)_2(SPy)$ (**4**) were treated with Me_3OBF_4 and $(MeO)_2SO_2$ in toluene at ambient temperature. The reaction of **2** with 2 mol equiv of Me_3OBF_4 for 18 h led to the isolation of air-sensitive navy blue crystals of $[Cp_3Cr_3(\mu_2\text{-OH})(\mu_3\text{-O})(\mu_2\text{-}\eta^2\text{-SCSN}(C_6H_4))_2](\mathbf{5})BF_4$ (45% yield) (Scheme 4). The supernatant mother liquor was found to contain $(\mathbf{5})BF_4$ and the free dimethylated ligand, identified as $[MeSCSNMe(C_6H_4)](\mathbf{6})BF_4$ from a mass spectral analysis (*m*/*z* 196.0 and HR-MS *m*/*z* 196.0248 (found), 196.0255 (calcd)) and a comparison of its ^1H NMR spectrum with that reported in the literature for the iodide analogue.[27] A similar product composition was obtained with $(MeO)_2SO_2$. It is noticeable that no dimeric species analogous to **7** (described below) was detected. When excess Me_3OBF_4 was used, species **5** was no longer detected. However, **6** and a yet to be characterized Cp−Cr species were observed (Table 1).

The reaction between complex **3** and 2 or more mol equiv of Me_3OBF_4 in toluene for 18 h led to the isolation of $Cp_2Cr_2(\mu\text{-OH})(\mu\text{-}\eta^2\text{-SCN}_4Ph)_2(\mathbf{7})BF_4$, $(Me_2SCN_4Ph)(\mathbf{8})BF_4$, and a noncharacterized CpCr-containing compound, which with the use of 2 mol equiv of the methylating reagent, were isolated as deep blue crystals (43%), colorless crystals (27%), and magenta needlelike crystals (26% by mass), respectively (Scheme 5). The dimethylated species $(\mathbf{8})BF_4$ was synthesized previously by Quast and co-workers via methylation of $MeSCN_4Ph$ with Me_3OBF_4.[28] The negligibly low incidence of S in the magenta crystals is suggestive of a degradation

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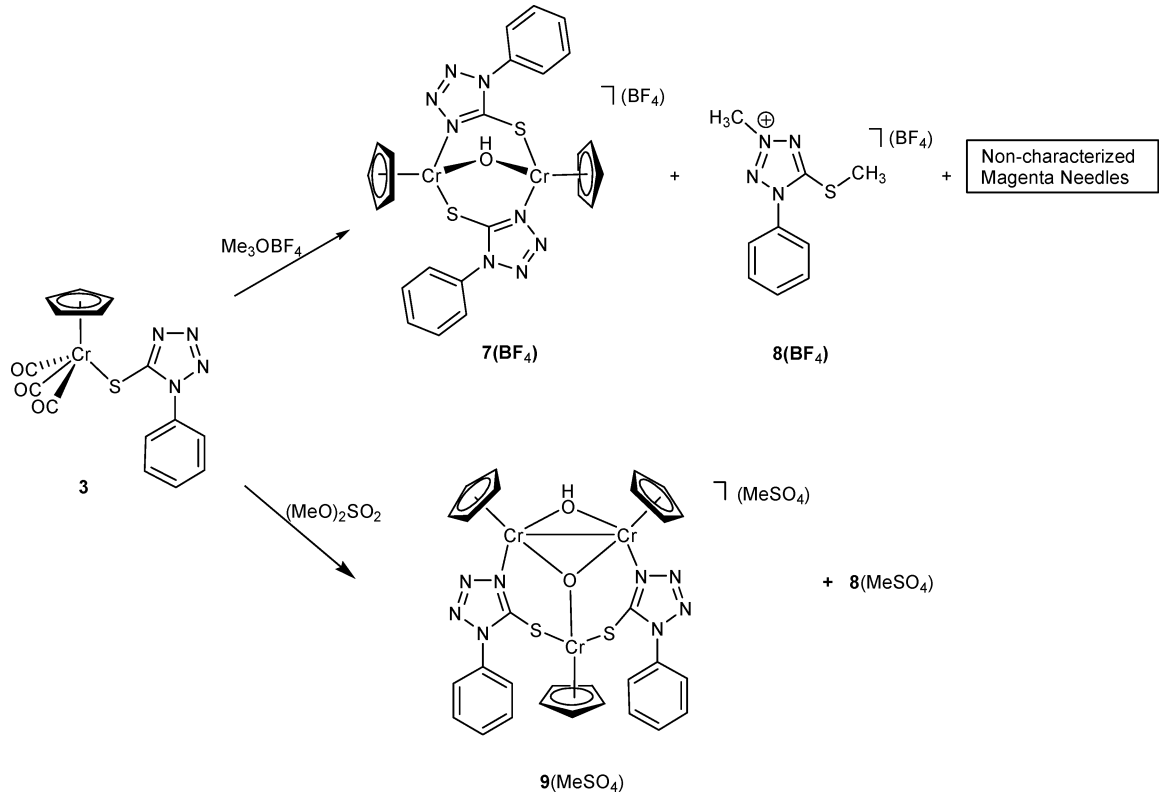
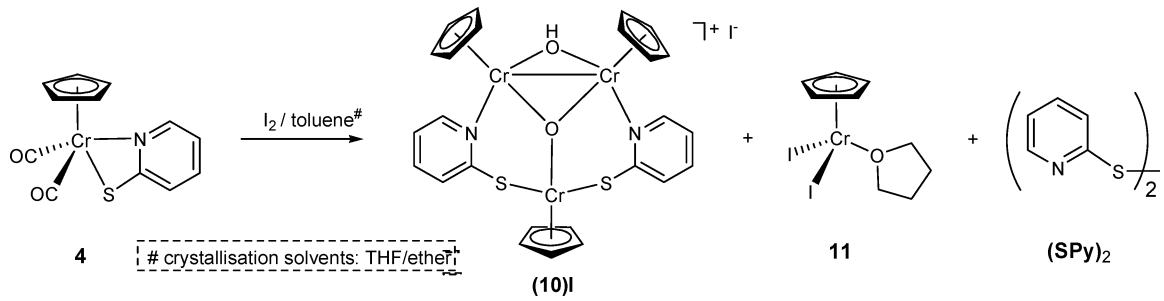
Scheme 5



Scheme 6



product resulting from the extensive cleavage of S from the thiotetrazolyl ligand. The analogous reaction between **3** and excess $(MeO)_2SO_2$ produced the trinuclear cation $Cp_3Cr_3(\mu_2\text{-}OH)(\mu_3\text{-}O)(\mu_2\text{-}\eta^2\text{-}SCN_4Ph)_2^+$ (**9**), isolated as the $MeOSO_3^-$ salt in a 53% yield, and **8**$(MeOSO_3)$. (Scheme 5 and Table 1).

Unlike complexes **2** and **3**, $CpCr(CO)_2(SPy)$ (**4**) was rather unreactive toward methylating agents. It did not react with $(MeO)_2SO_2$ at ambient temperature and reacted slowly with Me_3OBF_4 (75% consumed after 48 h) to give a product mixture possessing positive mass fragments for a dimethylated ligand species, $(SC_5H_4N_2Me_2)$, and $Cp_2Cr_2(SC_5H_4N_2Me)_2$. Notably, cationic $(\mu_2\text{-}OH)Cr_2$ and $(\mu_3\text{-}O)Cr_3$ complexes similar to **5**, **7**, and **9** were not observed.

Reactions with Iodine. Because all of these compounds contain Cr(III) centers, it was of interest to us to see if they could be obtained via oxidation of **4**, for instance with I_2. It was found that treatment of **4** with a stoichiometric amount of I_2 in toluene at ambient temperature for 18 h led to isolation of air-sensitive deep green crystals of $Cp_3Cr_3(\mu_2\text{-}OH)(\mu_3\text{-}O)(\mu_2\text{-}\eta^2\text{-}SC_5H_4N))_2I$ (**10**)I (31% yield) and a dark green microcrystalline solid, $CpCrI_2(THF)$ (**11**) (49% yield), after recrystallization of the viscous product mixture from THF/ether solution. It was observed that part of the ligated ligand was oxidized to the organic disulfide compound, $(SPy)_2$. (Scheme 6 and Table 2) Compound **11** had previously been isolated by Bräunlein and co-workers from the reaction of $[CpCrI_2]_2$ with THF donor solvent or Cp_2Cr with HI.[29] The isolation of **11** indicated that cleavage of the ligands in **4** had generated a CpCr fragment, which, as we have recently

Table 2. Products from Reactions with 1 mol equiv of I_2

substrate complex	products[a]			
	$(\mu_3\text{-oxo})Cr_3$	$(\mu_2\text{-OH})Cr_2$	$CpCrI_2(THF)$ (**11**)	$(-S-S-)$[b]
4	**10**, 31%	N	49%	+
3	N	+	+	+
2	+	N	+	+

[a] N = not observed. + = present but yields not quantified. [b] Disulfide from coupling of released ligand.

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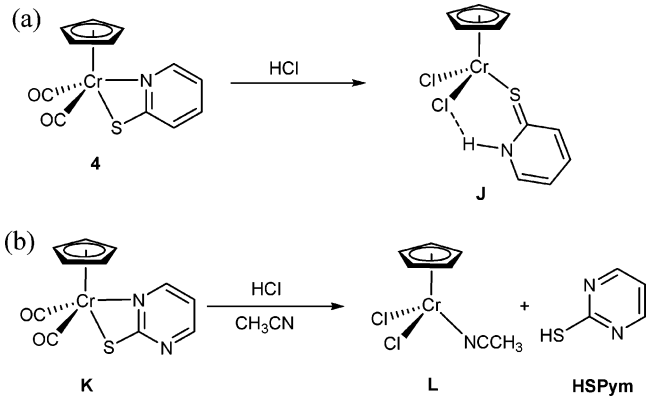
Scheme 7



observed, is very halophilic, readily forming $CpCrCl_2(X)$ [X = ligand or solvent]. (Scheme 7)[9]

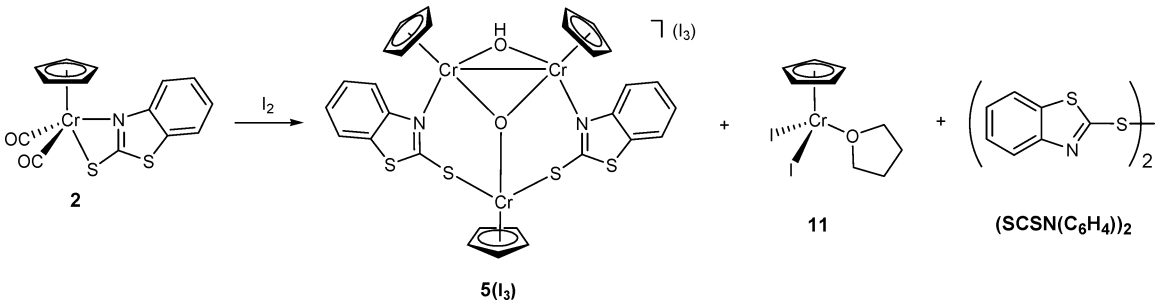
A similar reaction between **2** and I_2 resulted in products analogous to those from **4**. A qualitative analysis of a small-scale reaction gave a product mixture which contained trinuclear species (**5**)I_3, complex **11**, and organic disulfide compound $(SCSN(C_6H_4))_2$ (Scheme 8 and Table 2). When I_2 was used in large excess, species **5** was not detected.

Similar qualitative analysis of the small-scale reaction of **3** with I_2 gave evidence of the formation of dinuclear species (**7**)I_3, complex **11**, and organic disulfide $(SCN_4Ph)_2$ (Scheme 9 and Table 2). As in the reaction with Me_3OBF_4, it is noticeable that the $(\mu_2\text{-OH})Cr_2$ species, complex **7**, was formed instead of the $(\mu_3\text{-O})Cr_3$ species, complex **9**.

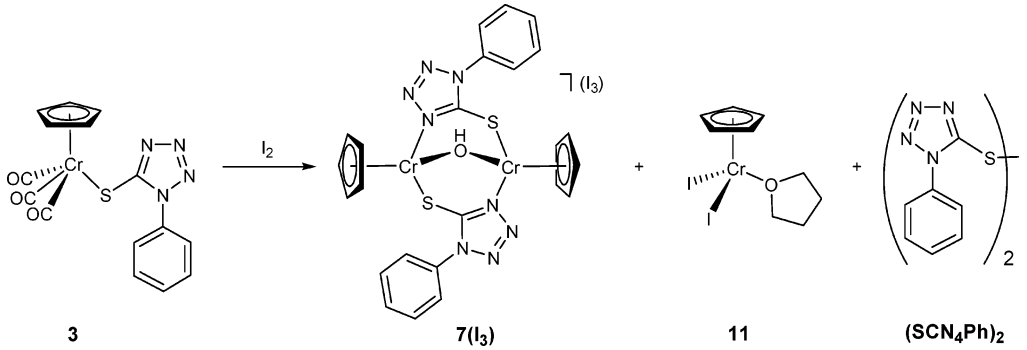
X-ray diffraction analyses (see below) showed a dinuclear structure for species **7** and trinuclear structures for species **5**, **9**, and **10**. In essence, the trinuclear structures of the latter compounds could be viewed as being formed by an aggregation of a "bare" $\{CpCr(III)^{2+}\}$ intermediate, **M**, with two units of η^1-N bonded Cr(III) analogues of **2**, **3,** and **4** held together by a M−M bond and μ_2-OH and (μ_3-O) bridges. A proposed pathway via **M** is consistent with the isolation or observation of dimethylated ligand species **6** and **8** released upon the methylation of **2** and **3**, respectively, and of the disulfide derivatives formed upon oxidation of the thiolate ligand by iodine (e. g., $(SPy)_2$ from the reaction of **2**). The latter reaction with iodine also produced $CpCrI_2$(solvent) (**11**), in agreement with the presence of halophilic **M** in the presence of iodide ions. The subsequent assembly of **M** to form the $(\mu_3\text{-O})Cr_3$ complexes requires a source of O and OH, presumably insidious water from methylating agents or solvent, or both, as hydrolytic processes are the most commonly encountered pathway to μ_n-O (n = 3, 4) metal complexes.[13] It was demonstrated for complex **2** that this aggregation required controlled methylation and controlled oxidation with iodine. Treatment with excess $MeOBF_4$ or with a large excess of I_2, to provide conditions for the excessive cleavage of the thiolate ligand, resulting from exhaustive methylation or oxidation, completely hindered the formation of **5**.

Structural analysis showed that the molecular structure of **7** is merely an aggregation of two units of a Cr(III) analogue of **3** with the aid of a bridging OH group. However, it was demonstrated that added water in the presence of air and $NaBF_4$ could not effect a transformation of **3** to **7**, or to the trinuclear **9** cation, but instead resulted in the total degradation of **3**. Although the bonding mode of the thiolate ligand in **3** differs from that in both **2** and **4** (monodentate vs (N,S)-chelate), it is not immediately clear why it will only form a $(\mu_2\text{-OH})Cr_2$ complex, **7**, with both Me_3OBF_4 and I_2, but will form a $(\mu_3\text{-oxo})Cr_3$ complex, **9**, with $(MeO)_2SO_2$. It is also noticeable that, in contrast to the reaction of **2**, excess Me_3OBF_4 could not completely cleave the ligand and, hence, had little or no effect on the product composition.

Scheme 8



Scheme 9



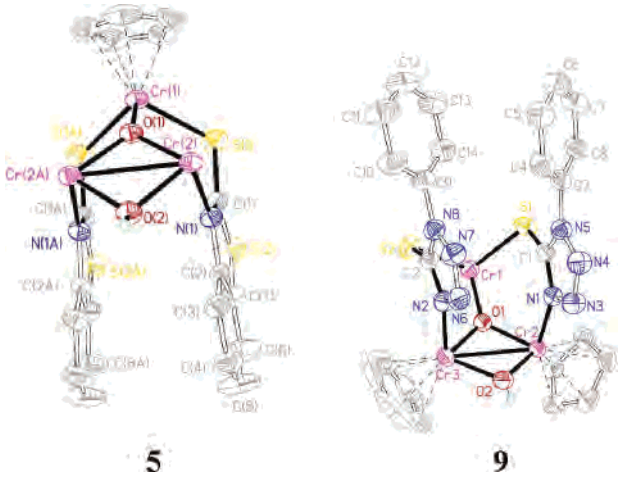


Figure 1. ORTEP plots for the molecular structures of **5** and **9**. The Cp rings at Cr(2) and Cr(2A) in **5** and at Cr(1) in **9** are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

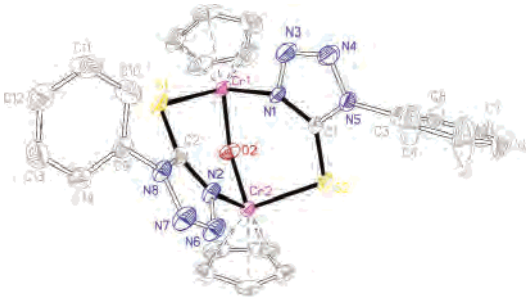


Figure 2. ORTEP plot for the molecular structure of **7**. Thermal ellipsoids are drawn to 50% probability level.

Crystallographic Studies. The molecular structures of **5**, **7,** and **9** have been determined by X-ray diffraction analyses and are shown in Figures 1 and 2. An X-ray diffraction analysis of **10** was also attempted, but its intensity data were very poor because of the poor crystal quality. However, the main features showing the connectivity of the atoms (see Scheme 6) could be determined. The molecular structures of **5**, **9**, and **10** are strikingly similar, belonging to the category of triangular (μ_3-O)M_3 compounds, in which the metal atoms are linked by heterocyclic thionate moieties, which constitute a new class of bridging ligands for such trinuclear complexes.

The Cr atoms of the μ_3-O-$(CrCp)_3$ core are linked by two −N═C−S− moieties, which are components of mercaptotetrazole, benzothiazole, and 2-thiopyridine, respectively; two of the Cr centers are additionally bridged by a OH group. Thus, there exists, in each of them, a ten-membered puckered metallacycle (namely Cr(1), S(1), C(1), N(1), Cr(2), O(2), Cr(3), N(2), C(2), and S(2)). Two six-membered CrSCNCrO subrings and a four-membered CrOCrO subring are located within the periphery of this macrocycle and annelated at O. Each of the Cr(1) centers possesses a three-legged piano-stool configuration, coordinated to the exocyclic thiolate S atoms of two bridging 5-mercaptotetrazole/benzothiazole/thiopyridine ligands, and a μ_3-bridging oxygen atom, O(1). Each of the other two Cr centers possesses an asymmetric three-legged piano-stool configuration, with coordination to the endocyclic N-atom of a bridging mercaptotetrazole/benzothiazole/thiopyridine ligand, a μ-OH ligand, and a μ_3-O oxygen atom. The structure of **5** contains a mirror plane, cutting through the CpCr(1) moiety, μ_3-O, and μ_2-OH. In both **5** and **9**, the Ph rings of the two hetero bridging ligands face each other; the dihedral angles between the planes of the rings are 11.0° and 13.1°, respectively.

Their bond parameters are given in Table 3, and the metric data of the (μ_3-O)Cr_3 cores of **5** and **9** are listed in Table 4 with those of a CpCr analogue (**J**) and inorganic carboxylato analogues (**F** and **K**), for comparison. One can see that the Cr−Cr distances in **5** and **9** fall within the range of 2.676−3.343 Å, observed for such single bonds,[4a] and incidentally are very close to the M−M distances in **J**.[30] As expected, these distances are substantially shorter than the Cr···Cr nonbond distances (3.407−3.467 Å), which are 0.081−0.204 Å longer than similar distances in complexes **F**[15c,31] and **K**[17,32]. The (μ_3-O)−Cr distances fall in the range of 1.877(3)−1.916(2)Å and closely resemble values previously reported for **J** and the inorganic complexes **F** and **K**. Of the three angles subtended at the μ_3-O center by the Cr atoms in **5** and **9**, two are much more obtuse (128.19(9)−131.31(11)°) than the third, in accordance with the greater expanse of the N−C−S hetero bridging ligands compared with those of μ-OH and a Cr−Cr bond. In contrast, the corresponding angles fall in the narrow range, 120.0 ± 0.9°, in the complexes **F** and **K**, in which the three Cr atoms are symmetrically bridged by identical ligands. The corresponding Cr−S, Cr−N, and S−C distances of the bridging linkages are very similar to those in **5** and **9** and resemble values of such bond lengths found in chromium complexes from our earlier studies.[5,7]

In the molecular structure of cationic **7** (Figure 2), each chromium center possesses a three-legged piano-stool configuration, coordinated to a bridging OH ligand and different donor atoms (N and S) of the two bridging 5-mercaptotetrazole ligands. The Cr−μ-OH distances (1.949(3)−1.950(3) Å) are marginally longer than those found in **5** and **9** (1.936(2)−1.945(2) Å). We note that these are all longer than the four μ-OH bonds (1.909(5)−1.926(5) Å) in the $[Cr_3(\mu\text{-OH})_2(\mu\text{-OAc})_4(OAc)_2(bpy)_2]^+$ cation.[26b] The bridging OH ligand in **7** shows a secondary hydrogen bonding to F(3) of the BF_4^- anion with an O···F interatomic distance of 2.755 Å. In addition, the two bridging mercaptotetrazole ligands and the two chromium centers form an eight-membered puckered metallacycle (namely Cr(1)N(1)C(1)S(2), Cr(2)N(2)C(2)S(1)), wherein a μ-hydroxo bridge between the two Cr centers creates two six-membered subcycles (viz. from Cr(1), N(1), C(1), S(2), Cr(2) and O(2) and from Cr(2), N(2), C(2), S(1), Cr(1) and O(2)). This is the first example of an anionic 5-mercaptotetrazole-bridged complex.

The ORTEP diagram and selected metric data of **8** are given in Figure 3. The structure shows that it is an N- and S-methylated derivative of the tetrazole thiolate ligand.

Cyclic Voltammetry Studies. Cyclic voltammograms obtained at a GC electrode in solutions of the BF_4 salt of **5** and the $MeOSO_3$ salt of **9** showed one oxidation and one reduction process, although for species **9** the oxidation process appeared chemically irreversible at a scan rate of 100 mV s^{-1}, indicating that the oxidized state was very unstable (even at 243 K). The nature of the heterocyclic

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **5**, **7**, and **9**

	5[a]	**9**		**7**
Cr(2)−Cr(3)	2.9187(13)	2.8392(7)	−	
Cr(1)−O(1)	1.877(3)	1.891(2)	−	
Cr(2)−O(1)	1.911(2)	1.914(2)	−	
Cr(3)−O(1)	−	1.916(2)	−	
Cr(2)−O(2)	1.945(2)	1.943(2)	[Cr(1)−O(2)]	1.950(3)
Cr(3)−O(2)	−	1.936(2)	[Cr(2)−O(2)]	1.949(3)
Cr(1)−S(1)	2.3811(12)	2.4007(10)	Cr(1)−S(1)	2.3978(12)
Cr(1)−S(2)	−	2.4207(11)	[Cr(2)−S(2)]	2.4032(11)
Cr(2)−N(1)	2.066(3)	2.061(3)	[Cr(1)−N(1)]	2.090(3)
Cr(3)−N(2)	−	2.072(3)	[Cr(2)−N(2)]	2.085(3)
S(1)−C(1)	1.719(4)	1.712(3)	[S(1)−C(2)]	1.739(4)
S(2)−C(2)	−	1.716(3)	[S(2)−C(1)]	1.734(4)
N(1)−C(1)	1.318(5)	1.331(4)	N(1)−C(1)	1.358(4)
N(2)−C(2)	−	1.337(4)	N(2)−C(2)	1.361(5)
S(1)−C(1)−N(1)	128.0(3)	128.6(2)	[S(1)−C(2)−N(2)]	129.9(3)
S(2)−C(2)−N(2)	−	126.1(2)	[S(2)−C(1)−N(1)]	130.7(3)
C(1)−S(1)−Cr(1)	107.73(13)	109.44(10)	[C(2)−S(1)−Cr(1)]	104.66(13)
C(2)−S(2)−Cr(1)	−	100.00(10)	[C(1)−S(2)−Cr(2)]	104.35(12)
C(1)−N(1)−Cr(2)	122.7(2)	130.7(2)	[C(1)−N(1)−Cr(1)]	136.7(2)
C(2)−N(2)−Cr(3)	−	124.6(2)	[C(2)−N(2)−Cr(2)]	138.1(3)
Cr(3)−O(2)−Cr(2)	97.25(15)	94.08(11)	[Cr(2)−O(2)−Cr(1)]	128.94(16)
Cr(2)−O(1)−Cr(3)	99.57(15)	95.70(10)	−	
Cr(1)−O(1)−Cr(2)	128.19(9)	131.31(11)	−	
Cr(1)−O(1)−Cr(3)	−	128.50(11)	−	
N(1)−Cr(1)−S(1)	−	−	N(1)−Cr(1)−S(1)	93.53(9)
N(2)−Cr(2)−S(2)	−	−	N(2)−Cr(2)−S(2)	96.03(9)
O(1)−Cr(1)−S(1)	95.59(8)	97.00(7)	[O(2)−Cr(1)−S(1)]	96.30(10)
O(1)−Cr(1)−S(2)	−	96.96(7)	[O(2)−Cr(2)−S(2)]	96.33(9)
O(2)−Cr(2)−N(1)	91.84(14)	90.58(10)	[O(2)−Cr(1)−N(1)]	93.69(12)
O(2)−Cr(3)−N(2)	−	88.96(10)	[O(2)−Cr(2)−N(2)]	93.81(12)
O(1)−Cr(2)−N(1)	93.17(14)	91.54(9)	−	
O(1)−Cr(3)−N(2)	−	88.96(10)	−	
O(1)−Cr(2)−O(2)	81.44(11)	84.66(10)	−	
O(1)−Cr(3)−O(2)	−	84.81(10)	−	
N(1)−Cr(2)−Cr(3)	95.97(9)	95.84(7)	−	
N(2)−Cr(3)−Cr(2)	−	95.75(7)	−	
S(1)−Cr(1)−S(2)	98.10(7)	96.49(3)	−	

[a] Cr(3), S(2), C(2), and N(2) in column 1 are equivalent to Cr(2A), S(1A), C(1A), and N(1A) in the ORTEP diagram of **5**.

Table 4. Comparison of the Metric Data of the (μ_3-O)Cr Triangular Cores

					$[Cr_3(\mu_3\text{-O})(PhCO_2)_6L_3]^n$		
	5	**9**	$[Cp_3Cr_3(\mu_3\text{-O})(\mu\text{-O}^t\text{Bu})_3]^+$ (**J**)[30]	$Cr_3O(CH_3CO_2)_6(H_2O)_3$ (**F**)[15c,31]	L = MeOH $n = +1$ (**K1**)[17b]	L = py $n = +1$ (**K2**)[32]	$L_3 = (F)_2(H_2O)$ $n = -1$ (**K3**)
Cr−Cr	2.9187(13)	2.8392(7)	2.920(6)−	−	−	−	−
Cr···Cr	3.407(2)	3.467(2)	2.943(6)	3.281(1)	3.266(1)	3.263(8)	3.290(1)
	−	3.429(2)	2.950(6)	3.288(1)	3.277(1)		3.291(1)
	−	−	−	3.279(1)	3.287(1)		3.326(1)
$Cr-O^{2-}$	1.877(3)	1.891(2)	1.91(1)	1.902(4)	1.888(2)	1.883	1.896(4)
	1.911(2)	1.914(2)	1.91(1)	1.855(3)	1.893(2)		1.908(4)
	−	1.916(2)	1.89(2)	1.899(44)	1.895(3)		1.917(4)
$Cr-O^{2-}-Cr$	99.57(15	95.70(10)	93.6(7)	120.05(18)	119.5(1)	120.0	119.4(2)
	128.19(9)	131.31(11)	101.7(7)	119.78(18)	120.1(1)		119.8(2)
	−	128.50(11)	102.0(7)	120.13(18)	120.4(1)		120.9(2)

nitrogen-containing ligands had only a small influence on the reduction and oxidation potentials of species **5** and **9** (Figure 4), indicating that the redox processes most likely occurred within the region of the Cr atoms.

Table 5 lists the reversible reduction potentials ($E^r_{1/2}$) that were calculated from the CV data under conditions where the ratio of the oxidative (i_p^{ox}) to reductive (i_p^{red}) peak currents were equal to unity. In situations where no reverse peak was observed, only the peak potential is given. The anodic to cathodic peak-to-peak separations (ΔE_{pp}) for each chemically reversible process were between 60 and 80 mV, which are close to the values expected for a one-electron electrochemically reversible transfer. The i_p^{ox} and i_p^{red} values obtained for equivalent concentrations of **5** and **9** were very similar (albeit with small differences resulting from expected changes in the diffusion coefficients) suggesting that all the electron transfers occur by the same number of electrons (i.e., n = 1).

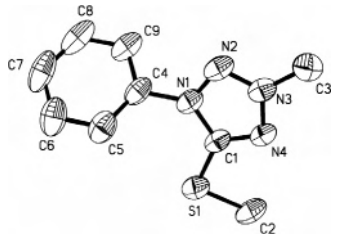


Figure 3. ORTEP plot for the molecular structure of **8**. Thermal ellipsoids are drawn at the 50% probability level. Selected metric data are as follows: N(1)−N(2), 1.338(3); N(2)−N(3), 1.284(4); N(3)−N(4), 1.338(3); C(1)−N(4), 1.318(4); and C(1)−N(1), 1.363(3) Å. Planar at C(1) and N(3).

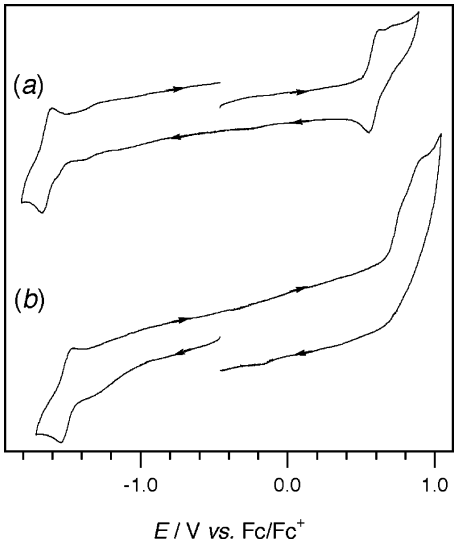


Figure 4. Cyclic voltammograms recorded with a GC electrode at 0.1 V s^{-1} in CH_3CN containing 0.25 M Bu_4NPF_6 at 243 K of 0.5 mM: (a) **5** and (b) **9**.

Table 5. Cyclic Voltammetric Data[a]

	reduction processes[b]				oxidation processes[b]			
compound	E_p^{red} (V)[c]	E_p^{ox} (V)[c]	$E^r_{1/2}$ (V)[e]	ΔE (mV)[f]	E_p^{ox} (V)[d]	E_p^{red} (V)[c]	$E^r_{1/2}$ (V)[e]	ΔE (mV)[f]
5	−1.67	−1.61	−1.64	60	+0.62	+0.55	+0.59	70
9	−1.54	−1.46	−1.50	80	+0.78			

[a] Obtained at a scan rate of 0.1 V s^{-1} with a 1 mm diameter GC electrode at 243 K in CH_3CN with 0.25 M Bu_4NPF_6 as the supporting electrolyte. [b] All potentials are relative to the ferrocene/ferrocenium redox couple. [c] E_p^{red} = reductive peak potential. [d] E_p^{ox} = oxidative peak potential. [e] $E^r_{1/2} = (E_p^{red} + E_p^{ox})/2$. [f] $\Delta E = |E_p^{ox} - E_p^{red}|$.

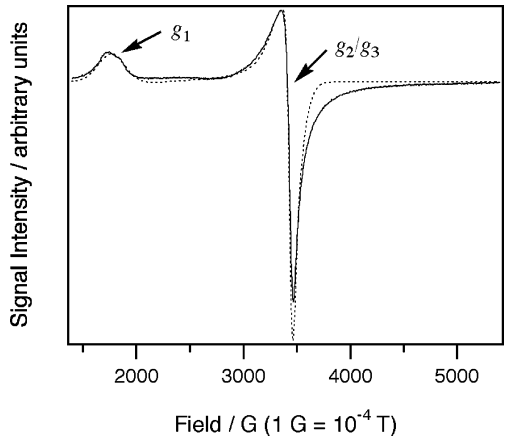


Figure 5. First derivative X-band EPR spectrum of species **9** in CH_3CN at 7 K. The EPR modulation amplitude = 0.5 mT, time constant = 0.16 s, sweep time = 160 s, microwave frequency = 9.437563 GHz, and microwave power = 0.2 μW. The dashed line is the simulated spectra with 100% Lorentzian line shape: $g_1 = 3.93$ ($\Delta H_{pp} = 25$ mT), $g_2 = 1.99$ ($\Delta H_{pp} = 22.5$ mT), and $g_3 = 1.99$ ($\Delta H_{pp} = 5.0$ mT).

EPR Studies. The EPR studies were carried out on compounds **5** and **9**. An EPR spectrum that was characteristic of a compound with axial symmetry was obtained for a frozen solution of **9** at 7 K (Figure 5), although no spectrum was detected at room temperature. Surprisingly, no EPR spectrum was detected for **5** at room or low (7 K) temperatures even though it contains three Cr(III) ions and was also expected to be paramagnetic. We recently observed that the tetranuclear μ_4-PO_4 complex, $[\{((\eta^5\text{-}C_5Me_5)\ Cr)_2(\mu\text{-}OMe)_2\}_2(\mu_4\text{-}PO_4)]^+$, also did not yield an EPR spectrum, and it was reasoned that the unpaired electron on each of the four Cr(III) ions paired to produce a diamagnetic compound.[2] In the case of **5**, the lack of an EPR spectrum is not easily rationalized by an electron pairing (i.e., delocalization) mechanism but, instead, may be the result of a relaxation problem.

Conclusion. The treatment of η^1-S-tetrazole and η^2-N,S-thiazole complexes of CpCr with methylating agents or iodine and the oxidation of a η^2-N,S-thiopyridine complex resulted in decarbonylation with formation of μ_2-hydroxo dichromium and μ_3-oxo trichromium cationic complexes (Chart 2); the heterocyclic thionates linking the metal centers in the latter compounds form a new class of bridging ligands, among which carboxylates predominate in such trinuclear complexes. The formation of the μ_3-oxo complexes demonstrates the oxo-philicity of coordinatively unsaturated CpCr(III) moieties, as found in two previous instances.[2,33]

Experimental Section

General Procedures. All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or under argon in an M. Braun Labmaster 130 Inert Gas System. NMR spectra were measured on a Bruker 300 MHz FT NMR spectrometer; ^1H and ^{13}C chemical shifts were referenced to residual C_6H_6 in C_6D_6 or to CH_2DCN in CD_3CN. IR spectra in KBr disks were measured in the range of 4000−600 cm^{-1} using a BioRad FTS-165 FTIR instrument. Mass spectra were run on a Finnigan Mat 95XL-T, MatLCQ, or TSQ 7000 spectrometer. Elemental analyses were carried out by the microanalytical laboratory, in-house. Voltammetric experiments were conducted with a computer-controlled Eco Chemie μAutolab III potentiostat. The electrochemical cell was jacketed in a glass sleeve and cooled to 243 K using a Lauda RL6 variable-temperature methanol-circulating bath. EPR spectra were recorded on a Bruker ESP 300e spectrometer in a TE_{102} cavity at 7 K using liquid He cooling. $[CpCr(CO)_3]_2$ (Cp = η^5-C_5H_5) (**1**) was synthesized as described by Manning[34] from chromium hexacarbonyl (98% purity from Fluka). 5,5′-Dithiobis(1-phenyl-1H-tetrazole), dibenzothiazolyl disulfide, and 2,2′-dithiodipyridine were obtained from Sigma-Aldrich and used as supplied. These disulfides were used to react with **1** to produce $CpCr(CO)_2(\eta^2\text{-}SCSN(C_6H_4)$ (**2**),[8] $CpCr(CO)_3(\eta^1\text{-}SCN_4Ph)$ (**3**),[10] and $CpCr(CO)_2(\eta^2\text{-}SNC_5H_4)$ (**9**),[9] as described in our prior reports. All solvents were dried over sodium benzophenone and distilled before use. Celite (Fluka AG) and silica gel (Merck Kieselgel 60, 230−400 mesh) were dried at 140 °C overnight before chromatographic use.

Reactions with Methylating Agents. Reaction of $CpCr(CO)_2(SCSN(C_6H_4)$ (2) with *2* mol equiv of Me_3OBF_4. Trimethyloxonium tetrafluoroborate, Me_3OBF_4 (30 mg, 0.20 mmol), was added to a deep red solution of **2** (34 mg, 0.10 mmol) in toluene (5 mL), and the suspension was stirred at room temperature for 18 h. This

(30) Nefedov, S. E.; Pasynskii, A. A.; Eremenko, I. L.; Orazsakhatov. B.; Ellert, O. G.; Novotortsev, V. M.; Struchkov, Yu.; Yanovsky, A. I. *J. Organomet. Chem.* **1990**, *385*, 277.
(31) Anson, C. E.; Bourke, J. P.; Cannon, R. D.; Jayasooriya, U. A.; Molinier, M.; Powell, A. K.; *Inorg. Chem.* **1997**, *36*, 1265.
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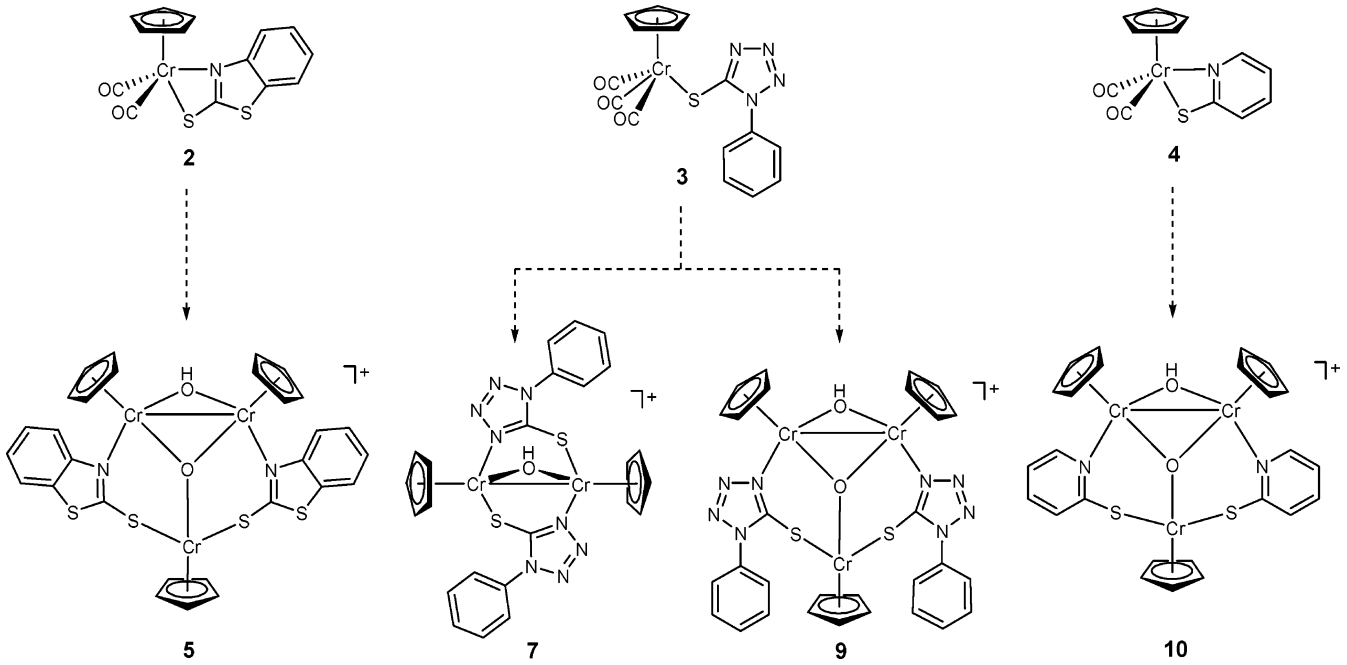
(33) Weng, Z.; Leong, W. K.; Vittal, J. J.; Goh, L. Y. *Organometallics* **2003**, *22*, 1645.
(34) Manning, A. R.; Hackett, P.; Birdwhistell, R.; Soye, P. *Inorg. Synth.* **1990**, *28*, 148.

Chart 2



resulted in the precipitation of green solids suspended in a light red supernatant, the ^{1}H NMR spectrum of which indicated the presence of some unreacted **2**, of which ca. 3 mg was recovered. The green solid was separated by filtration, washed with toluene, and recrystallized in acetonitrile/ether at −30 °C. Air-sensitive navy blue crystals of $[Cp_3Cr_3(\mu_2\text{-OH})(\mu_3\text{-O})(\mu_2\text{-}\eta^2\text{-SCSN}(C_6H_4))_2]$(**5**)$BF_4$ (12 mg, 0.02 mmol, 45% yield) were obtained after 2 days. Anal. Calcd for $C_{29}H_{24}Cr_3N_2O_2S_4BF_4$: C, 43.3; H, 3.0; N, 3.5; S, 15.9. Found: C, 43.0; H, 2.7; N, 3.7; S, 16.0. IR (KBr, cm^{-1}): ν 3107 w; 1634 w, 1496 w, 1454 wsh, 1429 m, 1378 m, 1244 w, 1083 s, 1036 s, 823 m, 752 w. FAB$^+$-MS: *m*/*z* 716 [M, $Cp_3Cr_3(OH)(O)(SCSN(C_6H_4))_2]^+$, 652 [MH − Cp, $Cp_2Cr_3(OH)(O)(SCSN(C_6H_4))_2]^+$, 416 $[Cp_2Cr_2SCSN(C_6H_4)O]^+$, 283 $[CpCrSCSN(C_6H_4)]^+$. FAB$^-$-MS: *m*/*z* 87 $[BF_4]^-$. HR FAB$^+$-MS: *m*/*z* for [M$^+$] 715.8911 (found), 715.8936 (calcd). The ^{1}H NMR spectrum in CD_3CN showed no peaks in the normal region, in agreement with paramagnetic Cr(III) centers. An aliquot of the mother liquor of species **5** was evacuated to dryness, and samples were taken for measurement of its proton NMR and mass spectra. These spectra indicated the presence of $[S(CH_3)CSN(CH_3)(C_6H_4)]$(**6**)$BF_4$. ^{1}H NMR ($CD_3CN$): δ 2.96 (s, 3H, S−CH_3), 3.97 (s, 3H, N−CH_3), 7.31−8.08 (m, 5H, C_6H_5). Literature values[25] (CF_3COOD): δ 2.67 (s, 3H, S−CH_3), 3.78 (s, 3H, N−CH_3), 7.2−7.9 (m, 4H, C_6H_4)]. FAB$^+$-MS: *m*/*z* 196 $[S(CH_3)CSN(CH_3)(C_6H_4)]^+$ and 149 $[S(CH_3)CSN(C_6H_4)]^+$, HR FAB$^+$-MS: *m*/*z* for [M$^+$] 196.0248 (found), 196.0255 (calcd). FAB$^-$-MS: *m*/*z* 87 $[BF_4]^-$. Mass fragments of **5** were also seen in the spectrum.

Reaction of $CpCr(CO)_2(SCSN(C_6H_4)$ (2) with 3 mol equiv of Me_3OBF_4. Me_3OBF_4 (20 mg, 0.15 mmol) was added to a deep red solution of **2** (17 mg, 0.05 mmol) in toluene (5 mL), and the suspension was stirred at room temperature for 18 h. This resulted in the precipitation of green solids (ca. 22 mg) suspended in a light red supernatant, the ^{1}H NMR spectrum of which indicated the presence of unreacted **2**, ca. 1 mg (recovered). The green solids were separated by filtration and washed with toluene (5 × 2 mL) and THF (3 × 2 mL). They possessed a FAB$^+$ mass spectrum showing fragments at *m*/*z* 196 $[S(CH_3)CSN(CH_3)(C_6H_4)]^+$ (species **6**) and 283 $[CpCrSCSN(C_6H_4)]^+$ and unassignable Cr-containing fragments at *m*/*z* 268, 402, 658, 686, and 793. FAB$^-$-MS: *m*/*z* 87 $[BF_4]^-$, 240, 393, 554, 619 (unassignable Cr-containing fragments). The significant absence of *m*/*z* 716 in the FAB$^+$-MS indicated that the trinuclear species was not formed.

Reaction of $CpCr(CO)_2(SCSN(C_6H_4)$ (2) with $(MeO)_2SO_2$. $(MeO)_2SO_2$, (5 μL, 0.05 mmol) was added to a reddish brown solution of **2** (7 mg, 0.02 mmol) in toluene (3 mL), and the mixture was stirred at room temperature for 18 h. This resulted in the precipitation of green solids suspended in a light red supernatant, the ^{1}H NMR spectrum of which indicated the presence of unreacted **2** and the methylated species **6**. The green solids were subjected to mass spectral analysis, which indicated the presence of the trinuclear species, $[Cp_3Cr_3(OH)(O)(SCSN(C_6H_4))_2]$(**5**)$(MeOSO_3)$. ESI$^+$/FAB$^+$-MS: *m*/*z* 716 [M, $Cp_3Cr_3(OH)(O)(SCSN(C_6H_4))_2]^+$. ESI$^-$/FAB$^-$-MS: *m*/*z* 111 $[MeOSO_3]^-$.

Reaction of $CpCr(CO)_3(\eta^1\text{-}SCN_4Ph)$ (3) with Me_3OBF_4. Me_3OBF_4 (30 mg, 0.20 mmol) was added to a deep magenta solution of **3** (38 mg, 0.10 mmol) in toluene (7 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, followed by 18 h at room temperature. The resulting deep purple solution was evacuated to dryness, and the residue was redissolved in CH_3CN and filtered through a glass frit. The filtrate was concentrated to ca. 2 mL, and diethyl ether (ca. 2 mL) was added. Subsequent cooling at −30 °C overnight produced noncharacterizable thermal- and air-sensitive magenta needlelike crystals (10 mg, 26% yield by weight. Anal. Found: C, 20.1; H, 4.2; N, 4.0; S, negligible). The ^{1}H NMR spectrum of this crystalline product showed no peaks in the normal region, indicative of paramagnetism, while the ^{19}F NMR spectrum showed a peak at δ −71.9, pertaining to the BF_4^- anion. The FAB$^+$-MS spectrum showed only 3 prominent peaks at *m*/*z* 391, 231, and 207, which may be assigned to mass fragments $[CpCr(O)(CH_3CN)_2(SCN_4Ph)]^+$, $[CpCr(O)_2(CH_3CN)_2]^+$, and the dimethylated ligand $[Me_2SCN_4Ph]^+$, respectively. The FAB$^-$-MS spectrum showed a peak at *m*/*z* 87 $[BF_4]^-$. Cooling of the supernatant of these magenta crystals at −30 °C for 2 days yielded a mixture of deep blue crystals of $[Cp_2Cr_2(\mu\text{-OH})(\mu\text{-}\eta^2\text{-SCN}_4Ph)_2]$(**7**)$BF_4$ (ca. 15 mg, 0.02 mmol, 43% yield) and colorless crystals of $[Me_2SCN_4Ph]$(**8**)BF_4 (ca. 8 mg, 0.03 mmol, 27% yield). This mixture of crystals was physically separated using a microscope for characterization.

Thereaction was repeated using *4 mol equiv* of Me_3OBF_4, and it was found to progress in a manner similar to that described above, yielding a similar product composition.

Data for compound **7**(BF_4). Anal. Calcd for $C_{24}H_{21}Cr_2N_8OS_2$-BF_4: C, 41.6; H, 3.0; N, 16.2; S, 9.3. Found: C, 41.4; H, 3.1; N, 16.2; S, 9.4. IR (KBr, cm^{-1}): ν(O−H) 3413 sbr, ν(C−H) 3114 m, ν(others) 1630 w, 1596 m, 1498 s, 1460 w, 1431 m, 1380 s, 1331 s, 1237 m, 1123 s, 1084 vs, 1050 s, 1017 s, 824 s, 762 s, 686 s, 617 m, 588 m, 565 m. FAB^+-MS: *m*/*z* 605 [M, $Cp_2Cr_2(OH)(SCN_4$-$Ph)_2]^+$, 588 [M − OH, $Cp_2Cr_2(SCN_4Ph)_2]^+$. FAB^--MS: *m*/*z* 87 $[BF_4]^-$. HR FAB^+-MS: *m*/*z* for $[M^+]$ 605.0102 (found), 605.0090 (calcd). The ^1H NMR spectrum showed no peaks in the normal region, in agreement with paramagnetic Cr(III) centers.

Data for compound **8**(BF_4). ^1H NMR (CD_3CN): δ 2.84 (s, 3H, S−CH_3), 4.62 (s, 3H, N−CH_3), 7.68−7.82 (m, 5H, C_6H_5). ^{19}F NMR (CD_3CN): δ −75.7 (s, BF_4). ESI^+-MS: *m*/*z* 207 [M, $Me_2SCN_4Ph]^+$. ESI^--MS: *m*/*z* 87 $[BF_4]^-$. Since this is a known compound,[28] elemental analyses were not performed. The ^1H NMR spectrum in CD_3CN is submitted in the Supporting Information as proof of purity.

Reaction of $CpCr(CO)_3(\eta^1$-$SCN_4Ph)$ (3) with $(MeO)_2SO_2$. Excess dimethyl sulfate, $(MeO)_2SO_2$ (100 μL, 1.06 mmol), was added to a deep magenta solution of **3** (38 mg, 0.10 mmol) in toluene (7 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, followed by 18 h at room temperature, resulting in a deep blue solution. The solvent and unreacted dimethyl sulfate were then removed under a vacuum. The residue was dissolved in CH_3-CN, and the mixture was filtered through a frit. The filtrate was concentrated to ca. 2 mL, and diethyl ether (ca. 2 mL) was added. The subsequent cooling to −30 °C overnight resulted in air-sensitive deep purple crystals of $[Cp_3Cr_3(\mu_2$−OH)$(\mu_3$−O)$(\mu_2$-η^2-$SCN_4Ph)_2]$-(**9**)$(MeOSO_3)$ (15 mg, 0.02 mmol, 53% yield). Anal. Calcd for $C_{30}H_{29}Cr_3N_8O_6S_3$: C, 42.4; H, 3.4; N, 13.2; S, 11.3. Found: C, 42.3; H, 3.7; N, 12.7; S, 11.2. IR (KBr, cm^{-1}): ν(O−H) 3254 sbr, ν(C−H) 3104 m, ν(others) 1633 wbr, 1595 m, 1498 s, 1461 w, 1426 w, 1380 s, 1321 s, 1262 s, 1246 s, 1208 s, 1090 m, 1056 s, 1007 s, 825 s, 763 s, 747 s, 695 s, 606 m, 563 s, 430 w. FAB^+-MS: *m*/*z* 738 [M, $Cp_3Cr_3(OH)(O)(SCN_4Ph)_2]^+$, 605 [M − CpCrO, $Cp_2Cr_2(OH)(SCN_4Ph)_2]^+$, 588 [M − CpCrOOH, $Cp_2Cr_2(SCN_4$-$Ph)_2]^+$. FAB^--MS: *m*/*z* 111 $[MeOSO_3]^-$. The ^1H NMR spectrum showed no peaks in the normal region, in agreement with paramagnetic Cr(III) centers. The resonances of species **8** (listed above) were seen in the proton NMR spectrum of the mother liquor.

Effect of H_2O and Air on 3. One mole equivalent of water (0.4 μL, 0.02 mmol) was added to a stirred suspension of $NaBF_4$ (3 mg, 0.03 mmol) in a deep magenta solution of **3** (8 mg, 0.02 mmol) in toluene (3 mL), and 2.4 mL of air was injected to give 1 mol equiv (0.02 mmol) of O_2. The reaction resulted in a deep Prussian blue solution after 4 h. The solution was evacuated to dryness, and an extract of the residue in CH_3CN was examined by mass spectrometry. The ESI^+-MS did not show any fragments above 215; the peaks at *m*/*z* 605 and 738, pertaining to species **7** and **9**, respectively, were significantly absent. The anion BF_4^- was observed at *m*/*z* 87 in the ESI^--MS.

A similar reaction in the absence of air was carried out in the presence of added water (0.04 μL initially). When the color did not to change to deep purple, indicative of the formation of species **7**, an additional 5 μL of water was added at 4 h, and the mixture was allowed to react for a further 20 h. This resulted in the precipitation of an amorphous purple powder, which is the decomposition product of **3**.[10]

Reaction of $CpCr(CO)_2(SPy)$ (4) with Me_3OBF_4. Me_3OBF_4 (35 mg, 0.23 mmol) was added to a reddish brown solution of **4** (28 mg, 0.10 mmol) in toluene, and the mixture was stirred at room temperature for 48 h, resulting in a purple oil in a reddish brown supernatant. The oil was separated using a cannula and washed with toluene (5 × 1 mL) and diethyl ether (5 × 1 mL). The ^1H NMR spectrum of the supernatant indicated the presence of **4**, of which ca. 7 mg (25%) was recovered. Recrystallization of the purple oil in MeOH/Et_2O produced (i) a white solid (ca. 12 mg), which possessed a ^1H NMR spectrum in CD_3OD indicative of a mixture of unreacted Me_3OBF_4 [δ 3.34 (s, OMe)] and the dimethylated ligand species ($SC_5H_4NMe_2$) [δ 2.88 (s, 3H, S−CH_3), 4.21 (s, 3H, N−CH_3), 7.68, 7.96, 8.34, 8.75 (each m, 1H, SPy)], (ii) a purple supernatant, the ESI^+-MS of which showed *m*/*z* 610 [$Cp_2Cr_2(SC_5H_4$-$NMe)_3$ + H]$^+$, 529 [$Cp_2Cr_2(SC_5H_4NMe)_2$ + 3Me]$^+$, and 484 [Cp_2-$Cr_2(SC_5H_4NMe)_2]^+$, and (iii) nonassignable Cr-containing mass fragments at *m*/*z* 1042, 904, 694, 658, and 487. The absence of fragments at *m*/*z* = 471 and 604 corresponding to di- and tri-nuclear complexes of the nature of **7** and **5** (or **9**), respectively, was significant.

Reaction of $CpCr(CO)_2(SPy)$ (4) with $(MeO)_2SO_2$. The reaction did not proceed at all, as indicated by ^1H NMR spectral scans of aliquots of the reaction mixture at intervals up to 48 h.

Reactions with Iodine. Reaction of $CpCr(CO)_2(SPy)$ (4). One mole equivalent of I_2 (51 mg, 0.20 mmol) was added to a reddish brown solution of **4** (56 mg, 0.20 mmol) in toluene (5 mL), and the mixture was stirred at room temperature for 30 min. There was an instantaneous color change to deep green, accompanied by vigorous effervescence. The resultant homogeneous solution was concentrated; upon concentration, a deep greenish oil precipitated out of solution. Trituration of the oil with toluene gave (i) an extract, which possessed FAB^+-MS *m*/*z* 221 $[(SC_5H_4N)_2H{\equiv}(SPy)_2H]^+$ and 112 $[HSC_5H_4NH]^+$ (pertaining to pyridyl disulfide), together with some CpCr fragments at *m*/*z* 466 $[CpCr(SPyH)_2I]^+$, 355 [CpCr-$(SPyH)I]^+$, and 227 $[CpCr(SPy)]^+$ and FAB^--MS *m*/*z* 127 $[I]^-$ and a proton NMR spectrum showing the presence of $CpCrI_2(THF)$ (see below) and (ii) a dark green viscous residue, which upon recrystallization in THF/ether yielded green crystals of $[Cp_3Cr_3(\mu_2$-OH)-$(\mu_3$-O)$(\mu_2$-η^2-$(SC_5H_4N_2))]$(**10**)I (15 mg, 0.02 mmol, 31% yield), after 2 days at −30 °C. Because its extreme air-sensitivity, satisfactory microanalytical data were not obtained. IR (KBr, cm^{-1}): ν 3107 w; 1634 w, 1496 w, 1454 wsh, 1429 m, 1378 m, 1244 w, 1083 s, 1036 s, 823 m, 752 w. FAB^+-MS: *m*/*z* 604 [M, $Cp_3Cr_3(OH)(O)$-$(SC_5H_4N)_2]^+$, 539 [M − Cp, $Cp_2Cr_3(OH)(O)(SC_5H_4N)_2]^+$, 361 [$Cp_2$-$Cr_2(SC_5H_4N)O]^+$, 227 $[CpCrSC_5H_4N]^+$. FAB^--MS: *m*/*z* 127 $[I]^-$. HR FAB^+-MS: *m*/*z* for $[M^+]$ 603.9492 (found), 603.9495 (calcd). The ^1H NMR spectrum showed no peaks in the normal region, indicative of paramagnetism. The mother liquor was evacuated to dryness and recrystallized from THF/ether at −30 °C; this yielded a dark green microcrystalline solid of $CpCrI_2(THF)$ (**11**) (43 mg, 0.01 mmol, 49%) which had been previously reported.[29] Anal. Calcd for $C_9H_{13}CrI_2O$: C, 24.4; H, 3.0. Found: C, 24.0; H, 3.0. The ^1H NMR spectrum in C_6D_6 at 300 K showed broad Cp resonances at δ 283 ($\nu_{1/2}$ ca. 5000 Hz) for $CpCrI_2(THF)$ (**11**) and δ 183 ($\nu_{1/2}$ ca. 6000 Hz) for $[CpCrI_2]_2$ which, as reported, existed in a temperature-dependent equilibrium with mononuclear **11**;[29] it is noted that the chemical shifts lie within the ranges reported (i.e., more than 230 and 149 ppm for $CpCrX_2D$ (X = halogen, D = donor) and $[CpCrCl_2]_2$, respectively, (literature value is δ 270 for **11** in $CDCl_3$ at 305 K)). Diffraction-quality single crystals of $CpCrI_2(MeCN)$ were obtained as deep bluish green rectangular blocks from recrystallization of **11** in acetonitrile/ether after 2 days at −30 °C. (see Supporting Information).

Table 6. Data Collection and Processing Parameters

	5(BF_4)	**7**(BF_4)	**8**(BF_4)	**9**($MeOSO_3$)
formula	$C_{29}H_{24}Cr_3N_2O_2S_4BF_4$·1.5THF	$C_{24}H_{21}Cr_2N_8O_1S_2BF_4$·$CH_3CN$	$C_9H_{11}N_4O_1BF_4$	$C_{30}H_{29}Cr_3N_8O_6S_3$·2.85$CH_3CN$
M_r	911.71	733.47	294.09	966.80
temp (K)	223(2)	223(2)	223(2)	223(2)
cryst color and habit	navy blue rhombus	deep blue rhombus	colorless plate	dark purple rhombus
cryst size (mm)	0.36 × 0.10 × 0.04	0.38 × 0.38 × 0.10	0.40 × 0.30 × 0.10	0.30 × 0.28 × 0.14
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	*C*2/*m*	P$\bar{1}$	$P2_1/c$	P$\bar{1}$
a (Å)	18.3429(9)	9.4536(14)	13.8649(17)	11.634(2)
b (Å)	11.3164(6)	10.9489(17)	6.9857(8)	13.358(2)
c (Å)	18.6615(9)	16.161(3)	13.8649(17)	15.740(3)
α (deg)	90	82.378(3)	90	109.677(3)
β (deg)	102.851(2)	84.912(3)	106.48	109.671(3)
γ (deg)	90	77.518(3)	90	92.603(3)
V ($Å^3$)	3776.6(3)	1615.7(4)	1287.8(3)	2133.7(6)
Z	4	2	4	2
density (Mg m^{-3})	1.602	1.508	1.517	1.505
abs. coeff (mm^{-1})	1.129	0.862	0.290	0.954
F(000)	1856	744	600	991
θ range for data collection	2.13 to 29.43	1.92 to 27.50	3.01 to 25.00	1.48 to 27.50
index ranges	$-25\le h\le 23$ $0\le k\le 14$ $0\le l\le 25$	$-12\le h\le 12$ $-14\le k\le 14$ $-20\le l\le 20$	$-16\le h\le 16$ $-8\le k\le 8$ $-16\le l\le 13$	$-15\le h\le 15$ $-17\le k\le 17$ $-20\le l\le 20$
no. of reflns collected	14493	20040	7197	27766
independent reflns	4989	7288	2280	9757
max and min transmission	0.9562 and 0.6867	0.9188 and 0.7355	0.9716 and 0.8928	0.8780 and 0.7628
no. of data/ restraints/params	4989/3/261	7288/0/411	2280/0/174	9757/4/540
final R indices [$I > 2\sigma(I)$][a,b]	R1 = 0.0741 wR2 = 0.1487	R1 = 0.0701 wR2 = 0.1474	R1 = 0.0615 wR2 = 0.1671	R1 = 0.0543 wR2 = 0.1445
R indices (all data)	R1 = 0.1004 wR2 = 0.1611	R1 = 0.0947 wR2 = 0.1572	R1 = 0.0697 wR2 = 0.1754	R1 = 0.0707 wR2 = 0.1538
GOF on F^2 [c]	1.154	1.133	1.051	1.061
large diff peak and hole (e $Å^{-3}$)	0.719 and −0.363	1.001 and −0.475	0.703 and −0.339	0.723 and −0.540

[a] $R1 = (\sum|F_o| - |F_c|)\sum|F_o|$. [b] $wR2 = [(\sum\omega|F_o| - |F_c|)^2/\sum\omega|F_o|^2]^{1/2}$. [c] $GOF = [(\sum\omega|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

The reaction was repeated in the presence of 2 mol equiv of water and yielded a product mixture of a composition similar to that described above.

Reaction of $CpCr(CO)_3(STz)$ (3). One mole equivalent of I_2 (5 mg, 0. 02 mmol) was added to a deep magenta solution of **3** (8 mg, 0.02 mmol) in toluene (3 mL). The mixture turned deep green, accompanied by vigorous effervescence. After the mixture was stirred for 2 h, the resultant homogeneous solution was evacuated to dryness, leaving a deep bluish green oil. It possessed the following mass fragments. ESI^+-MS: *m*/*z* 605 [M, $Cp_2Cr_2(\mu\text{-OH})(\mu\text{-}\eta^2\text{-}SCN_4Ph)_2]^+$. ESI^--MS: *m*/*z* 381 $[I_3]^-$. FAB^+-MS: *m*/*z* 605 $[M]^+$, 359 $[(SCN_4Ph)_2 + 5H]^+$. FAB^--MS: *m*/*z* 177 $[SCN_4Ph]^-$, 127 $[I]^-$. They are in agreement with the presence of $[Cp_2Cr_2(\mu\text{-OH})(\mu\text{-}\eta^2\text{-}SCN_4Ph)_2]$(**7**), as an I^- or I_3^- salt, and disulfide, $(STz)_2$, the phenyl protons of which were clearly seen in the ^1H NMR spectrum of the *total* products mixture. Notably the absence of peaks at *m*/*z* 738 indicated the absence of the trinuclear species. $CpCrI_2$(THF) (**11**) was also identified, as above, in the proton NMR spectrum.

Reaction of $CpCr(CO)_2(SCSN(C_6H_4))$ (2). I_2 (5 mg, 0.02 mmol) was added to a reddish brown solution of **2** (7 mg, 0.02 mmol) in toluene (3 mL). The mixture turned deep green, accompanied by vigorous effervescence. After the mixture was stirred for 2 h, the resultant homogeneous solution was evacuated to dryness, leaving behind green solids, which possessed the following mass fragments. ESI^+-MS: *m*/*z* 716 [M, $Cp_3Cr_3(OH)(O)(SCSN(C_6H_4))_2]^+$. ESI^--MS: *m*/*z* 381 $[I_3]^-$. FAB^+-MS: *m*/*z* 716 [M, $Cp_3Cr_3(OH)(O)(SCSN(C_6H_4))_2]^+$, 416 $[Cp_2Cr_2SCSN(C_6H_4)O]^+$, 332 $[(SCSN(C_6H_4))_2]^+$, 167 $[SCSN(C_6H_4)+H]^+$. FAB^--MS: *m*/*z* 166 $[SCSN(C_6H_4)]^-$, 127 $[I]^-$. This indicates the presence of the tri-chromium species **5**, as an I^- or I_3^- salt, and disulfide. Indeed, the proton resonances of this disulfide were seen in the NMR spectrum of the products mixture in C_6D_6 and found to match those of an authentic sample (δ 7.84 (d, J = 8 Hz, 1H), a doublet being obscured by residual solvent peak at δ 7.16, 7.02 (ddd, J = 8, 5−6 and 1.7 Hz, 1H), and 6.87 (ddd, J 8, 5−6 and 1.7 Hz, 1H). $CpCrI_2$(THF) (**11**) was again identified in the proton NMR spectrum.

This reaction was repeated with 10 mol equiv of I_2 (viz. **2**, 7 mg with I_2, 50 mg), and a reddish oil was produced after the removal of the solvent. The ESI^+ and FAB^+-mass spectra of the oil showed the absence of the peak at *m*/*z* 716 pertaining to trinuclear species **5**. The I_3^- anion was seen at *m*/*z* 381 in the ESI^--MS. The presence of disulfide was observed as described above in the proton NMR spectrum.

Structure Determinations. Diffraction-quality single crystals were obtained at −30 °C. The BF_4 salts of **7** and **8** and the $MeOSO_3$ salt of **9** were obtained as deep blue, colorless, and dark purple rhombic crystals, respectively, from solutions in acetonitrile/ether, after 1 day. Compounds **5**(BF_4) and **10**(I) were obtained as navy blue and deep green rhombic crystals, respectively, from a solution in THF/ether after 2 days, and $CpCrI_2$(MeCN) was obtained as bluish green crystals from the recrystallization of **11** in acetonitrile/ether after 2 days.

The crystals were mounted on glass fibers. X-ray data were collected on a Bruker SMART APEX diffractometer, equipped with a CCD detector, using Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects with the

SMART suite of programs[35] and for absorption effects with SADABS.[36] Structure solution and refinement were carried out with the SHELXTL suite of programs.[37] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The OH hydrogen atoms in the cations of **5**, **7**, and **9** were located in the electron density difference map. Those in **7** and **9** were refined; for **5**, its thermal parameter was fixed and its O−H distance was fixed at 0.82 Å. There were three acetonitrile solvent molecules in **9**, for one of which the occupancy was fixed at 0.85, and restraints were applied to the C−C and C−N bond lengths so that the refinement could be stabilized. The Cp, Ph, and SPy hydrogens were placed in calculated positions. Data were also collected for complex **10**; however, the intensity data were poor because of the poor crystal quality, and the hydrogen atom of the OH group was not located in the electron difference map. However, its presence is supported by the proximity of the O(2)−I^- atoms, which can be attributed to the hydrogen bonding of the H atom to the I^- anion. The crystal data collection and processing parameters for **5** and **7**−**9** are given in Table 6.

(35) *SMART* & *SAINT*, version 5.0; Bruker AXS Inc.: Madison, WI, 1998.
(36) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 2000.
(37) *SHELXTL*, version 5.1; Bruker AXS Inc.: Madison, WI, 1998.

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Supporting Information Available: A figure showing the ^{1}H NMR spectrum of species **8** in CD_3CN. CIF files of compounds **5**, **7**−**9**, and $CpCrI_2(MeCN)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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