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Antiferromagnetic complexes with metal–metal bonds

XXVII *. Synthesis, molecular structures and magnetic properties of Cr,Re-clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re_2(CO)_9$ and $Cp_2Cr_2(\mu_3\text{-}SCMe_3)_2(\mu_3\text{-}S)_2Re_2(CO)_6$

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Abstract

The antiferromagnetic complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re_2(CO)_9$ (**II**) ($-2J = 424$ cm^{-1}) was obtained by photochemical reaction of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**I**) with $Re_2(CO)_{10}$ in benzene–THF; the dirhenium moiety within complex **II** (Re–Re 3.0691(8) Å) is only bound to the framework of complex **I** through coordination of the rhenium atom by the sulfide bridge (Re–S 2.555(2) Å). It is shown that under more rigorous conditions (*hν*, *m*-xylene, 144°) the reaction proceeds with cleavage of the Re–Re bond and formation of a 66e antiferromagnetic cluster $Cp_2Cr_2(\mu_3\text{-}SCMe_3)_2$ $(\mu_3\text{-}S)_2Re_2(CO)_6$ (**III**) ($-2J = 302$ cm^{-1}) with a distorted cubane core $Cr_2Re_2S_4$ (Cr–S 2.32(1), Cr–SR 2.39(2), Re–S 2.590(8), Re–SR 2.514(8)–2.534(7) Å) which only contains a Cr–Cr bond (Cr–Cr 2.96(1), Cr $\cdots$ Re 3.645(1) and 3.646(1), Re $\cdots$ Re 3.938(1) Å).

1. Introduction

Previously we have shown that the use of the thiolatosulfide complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**I**) as a ligand for different metal carbonyl fragments enables the pre-designed synthesis of heterometallic clusters to be carried out [1]. In the case of decacarbonyldimanganese the reaction under mild conditions in THF (*hν*, 10°C) yields the adduct $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Mn_2(CO)_9$ [2], whereas under more rigorous conditions (*hν*, 64°C) the Mn–Mn and S–CMe_3 bonds are cleaved and the triangular $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$ cluster with pentacoordinated manganese is formed [3]. Further decarbonylation of the manganese ion and the addition of a second $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu\text{-}S)_2$ (Q) group leads to the spirane cluster Q_2Mn, in which the manganese atom is coordinated tetrahedrally by four sulfur atoms and has four weak Cr–Mn links [4]. It seemed interesting to study the similar reaction involving the rhenium carbonyl, $Re_2(CO)_{10}$, which is characterized by a stronger M–M bond and higher metal-atom coordination number in comparison with its manganese analog.

2. Results and discussion

The photochemical reaction between $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**I**) and $Re_2(CO)_{10}$ (ratio of reagents of 2 : 1), even in refluxing benzene–THF (1 : 1) mixture, proceeds without cleavage of the Re–Re bond and leads to high yields of the $Cp_2Cr_2(\mu\text{-}SCMe_3)_2$ $(\mu_3\text{-}S)Re_2(CO)_9$ (**II**) complex, isolated as black rhomboid crystals.

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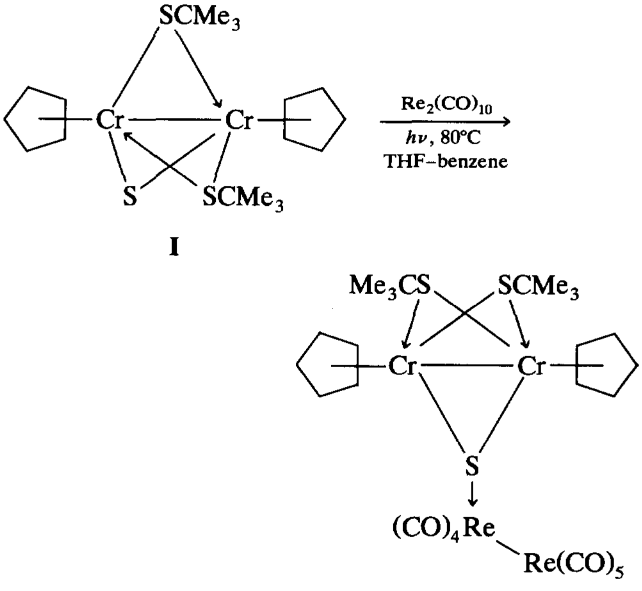


I

II

Its IR spectrum exhibits the terminal CO groups stretching vibration bands (1895, 1922, 1940, 1970, 2020 and 2080 cm^{-1}), as well as the vibrations of Cp rings (805, 1010 and 3100 cm^{-1}) and *t*-butyl moieties (1146, 2850, 2890, 2920 and 2950 cm^{-1}).

According to the X-ray diffraction study (Fig. 1, Table 1) complex **II** represents a product of substitution of one of the equatorial CO groups of the $Re_2(CO)_{10}$ moiety by the lone electron pair of the bridging sulfide atom in **I** (Re–S 2.555(2) Å). This substitution has almost no effect on the geometry of dirhenium and dichromium fragments, both of which retain their respective metal–metal bonds (Cr–Cr 2.732(2), Re–Re 3.0691(8) Å). Accordingly, the magnetic properties of complex **II** ($-2J = 424$ cm^{-1}) do not differ from those of complex **I** ($-2J = 430$ cm^{-1}) [5]. The same situation has been observed for the $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Mn_2(CO)_9$ cluster [2].

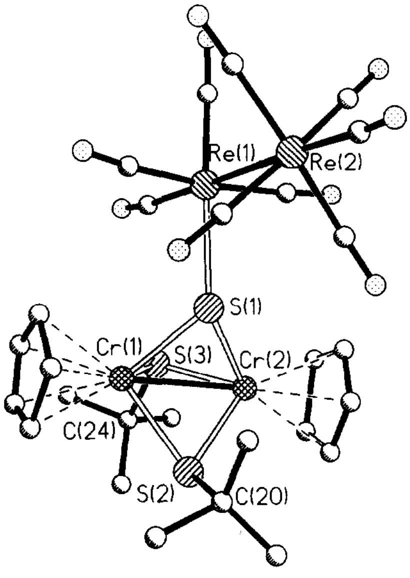


Fig. 1. Molecular structure of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re_2(CO)_9$.

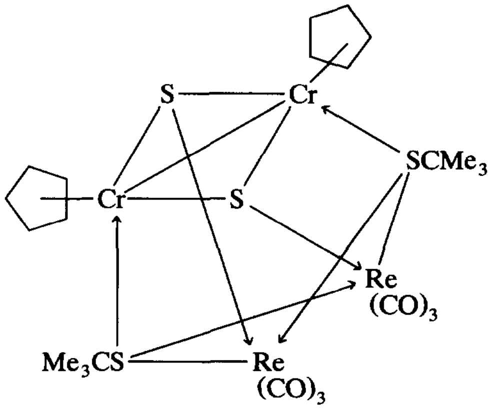
TABLE 1. The main geometric parameters of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re_2(CO)_9$ (**II**)

Bond	Distance (Å)	Angle	Size (°)
Re(1)–Re(1)	3.0691(8)	Re(2)Re(1)S(1)	88.49(3)
Re(1)–S(1)	2.555(2)	ReS(1)Cr(1)	122.99(7)
Cr(1)–Cr(2)	2.732(2)	ReS(1)Cr(2)	126.78(7)
Cr(1)–S(1)	2.318(2)	Cr(1)S(1)Cr(2)	72.01(5)
Cr(2)–S(1)	2.329(2)	Cr(1)S(2)Cr(2)	71.28(6)
Cr–μ-SR	2.330(2)–2.356(2)	Cr(1)S(3)Cr(2)	71.32(6)
		Cp*CrCr [a]	176.7(1)

[a] Cp* is the centroid of the Cp-ring.

Further transformation of the Cr,Re-cluster involving cleavage of the Re–Re bond requires not only much more rigorous conditions (UV irradiation in refluxing *m*-xylene) compared with those necessary for reaction of the manganese complex, but also unexpectedly yields the $Cp_2Cr_2(\mu_3\text{-}SCMe_3)_2(\mu_3\text{-}S)_2Re_2(CO)_6$ (**III**) cluster rather than the triangular cluster with the Cr_2M core, which is formed for M=Mn:

$$Cp_2Cr_2(\mu - SCMe_3)_2(\mu - S) + Re_2(CO)_{10} \xrightarrow[m\text{-xylene}]{h\nu,\ 144°C}$$



III

The IR spectrum of complex **III** exhibits the terminal CO-groups stretching vibration bands at 1885 and 1992 cm^{-1}. According to the X-ray diffraction study (Fig. 2, Table 2), cluster **III** has a cubane core $Cr_2Re_2S_4$ which involves the only direct metal–metal bond, CpCr–CrCp (Cr–Cr 2.96(1) Å, the Cp ligands are in a cisoid orientation, the Cp(centroid)CrCr angle is 137.5°). At the same time the rhenium atoms in the $Re(CO)_3$ moieties of **III** are not bonded directly either to each other (Re ··· Re 3.938(1) Å), or to any of the chromium atoms (Cr ··· Re 3.645(1) and 3.646(1) Å).

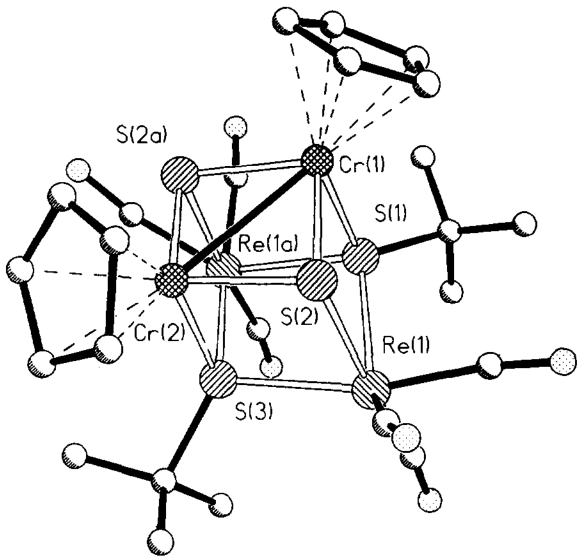


Fig. 2. Molecular structure of $Cp_2Cr_2(\mu_3\text{-}SCMe_3)_2(\mu_3\text{-}S)_2Re_2(CO)_6$.

They are bound to the dichromium moiety via two μ_3-sulfide and two μ_3-thiolate bridges. Thus each rhenium atom acquires its normal 18e configuration and has a typical octahedral environment. However, the ligand environment of each Cr^{III} ion in **III** is similar to that observed earlier in the binuclear complex $Cp_2Cr_2(\mu\text{-}OCMe_3)_2(OCMe_3)_2$ (Cr–Cr 3.004 Å, Cp(centroid)CrCr angle 123.1°) [6], which may become identical with **III** if its terminal OR groups are replaced by the SR groups additionally coordinated by two rhenium atoms, and the OR bridges are replaced by the $SRe(CO)_3$ bridging group. Comparison of **III** and the binuclear *tert*-butylate complex mentioned shows that although in both molecules the Cr^{III} ions have the same electronic configuration, the change of bridging oxygen atoms for sulfur leads to a sharp increase in the antiferromagnetic exchange parameter (from 70 to 302 cm^{-1}) which is analogous to the difference between antiferromagnetic $Cp'_4Cr_4O_4$ and diamagnetic $Cp'_4Cr_4S_4$ ($Cp' = MeC_5H_4$) discussed earlier [7]. The formation of the pseudo-cubane cluster **III** rather than the expected analog of the above-mentioned $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$ [3], triangular $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Re(CO)_3$ complex, is evidently due to the larger size of the rhenium atom which strongly prefers to have a six- rather than a five-coordinate ligand environment. It is quite probable that the same reason causes the formation of cubane clusters $Cp_3Cr_3(\mu_3\text{-}S)_4MCp$ (M = V, Nb) in reactions of complex **I** with $CpM(CO)_4$ [8].

TABLE 2. The main geometric parameters of $Cp_2Cr_2(\mu_3\text{-}SCMe_3)_2(\mu_3\text{-}S)_2Re_2(CO)_6$ (**III**)

Bond	Distance (Å)	Angle	Size (°)
Re–μ_3-S	2.590(8)	S(1)Re(1)S(3)	80.4(3)
Re–μ_3-SCMe$_3$	2.514(8)–2.534(7)	S(2)Re(1)S(3)	76.1(3)
		S(2)Re(1)S(3)	80.3(3)
Cr(1)–Cr(2)	2.96(1)	Cr(1)S(2)Cr(2)	80.1(4)
Cr–μ_3-S	2.28(1)–2.32(1)	Cr(1)S(1)Re(1)	95.2(4)
		Cr(2)S(3)Re(1)	94.6(4)
Cr–μ_3-SCMe$_3$	2.39(2)	Cr(1)S(2)Re(1)	95.4(4)
	2.45(2)	Cr(2)S(2)Re(1)	96.9(3)
Re ··· Re	3.938(1)		
Re ··· Cr(1)	3.646(1)		
Re ··· Cr(2)	3.645(1)		

3. Experimental details

All operations associated with the synthesis and isolation of complexes were carried out in a flow of pure argon. The initial $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**I**) was prepared according to ref. 5. IR spectra were recorded with a Specord 75IR instrument in KBr pellets. The magnetic susceptibility was measured by the Faraday method in the temperature range 296–77 K. X-Ray structural data were obtained with a CAD4 Enraf Nonius automatic diffractometer (λ = Mo Kα, $\theta/2\theta$ scan, t = 20°C) for complex **II** and with a Siemens P3/PC diffractometer (λ = Mo Kα, $\theta/2\theta$ scan, t = −145°C) for complex **III**. Crystal data are listed in Table 3. The structures were solved by the direct method and refined by a full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms. Atomic coordinates are listed in Tables 4 and 5.

3.1. $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re_2(CO)_9$ (II)

A violet solution of 0.98 g (2.21 mmol) $Cp_2Cr_2(SCMe_3)_2S$ (**I**) and 0.73 g (1.11 mmol)

TABLE 3. Crystal data for the $Cp_2Cr_2(SCMe_3)_2(S)Re_2(CO)_9$ (**II**) and $Cp_2Cr_2(SCMe_3)_2(S)_2Re_2(CO)_6$ (**III**) clusters

	II	III
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Cmc2_1$
a (Å)	16.605(2)	11.987(3)
b (Å)	12.048(2)	16.552(4)
c (Å)	18.444(3)	15.422(4)
β (°)	110.46(1)	90
V(Å^3)	3457.1(1)	3059.0(5)
Z	4	4
Number of reflections with $I > 6\sigma$	2508	1652
R_1	0.034	0.058
R_w	0.041	0.060

$Re_2(CO)_{10}$ in 30 ml of benzene–THF (5 : 1) mixture was irradiated by UV light (PRK-4 lamp) and refluxed for 3 h. The dark-brown solution obtained was filtered and concentrated to 5 ml at 50°C, 0.1 Torr. The precipitated dark-brown crystals were isolated by decantation, washed with cool pentane and dried *in vacuo*. The yield was 0.85 g. IR (ν, cm^{-1}): 543m, 585s, 805s, 1010m, 1164m, 1355m, 1382w, 1482w, 1438m, 1465m, 1630w, 1895vs, 1922vs, 1940 vs, 1970sh vs, 2020vs, 2080vs, 2850m, 2890m, 2920m, 2950m, 3100w.

μ_{eff} (μ_B): 1.29 (296 K)–0.32 (77 K).

TABLE 4. Atom coordinates for the cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re_2(CO)_9$ (**II**)

Atom	x	y	z
Re(1)	0.18905(2)	0.45867(3)	0.45401(1)
Re(2)	0.26839(2)	0.47438(3)	0.32697(1)
Cr(1)	0.18067(7)	0.7811(1)	0.54909(5)
Cr(2)	0.34067(9)	0.6970(1)	0.62615(7)
S(1)	0.2516(1)	0.6501(2)	0.50137(9)
S(2)	0.3065(1)	0.8857(2)	0.6023(1)
S(3)	0.2199(2)	0.6683(2)	0.66045(9)
O(1)	0.0961(4)	0.4448(6)	0.5701(3)
O(2)	0.0281(5)	0.5514(7)	0.3226(4)
O(3)	0.1212(5)	0.2283(6)	0.3926(4)
O(4)	0.3563(6)	0.3417(7)	0.5550(4)
O(5)	0.3515(5)	0.4925(7)	0.2025(3)
O(6)	0.1818(5)	0.7084(6)	0.3003(4)
O(7)	0.4291(5)	0.5816(8)	0.4480(4)
O(8)	0.1010(6)	0.3629(9)	0.2181(4)
O(9)	0.3390(5)	0.2378(7)	0.3797(4)
C(1)	0.1279(4)	0.4539(6)	0.5359(4)
C(2)	0.0870(6)	0.5210(7)	0.3720(4)
C(3)	0.1472(6)	0.3150(7)	0.4154(4)
C(4)	0.2955(6)	0.3874(7)	0.5186(4)
C(5)	0.3259(6)	0.4837(7)	0.2511(5)
C(6)	0.2138(6)	0.6230(9)	0.3101(5)
C(7)	0.3687(6)	0.5424(8)	0.4038(4)
C(8)	0.1608(7)	0.401(1)	0.2568(5)
C(9)	0.3128(6)	0.3259(8)	0.3594(4)
C(10)	0.0629(8)	0.868(1)	0.5567(7)
C(11)	0.0402(8)	0.777(1)	0.5288(7)
C(12)	0.0512(7)	0.759(1)	0.4612(6)
C(13)	0.0913(7)	0.858(1)	0.4433(5)
C(14)	0.0946(9)	0.9283(9)	0.512(1)
C(15)	0.4472(9)	0.577(1)	0.6336(9)
C(16)	0.424(1)	0.564(1)	0.698(1)
C(17)	0.450(1)	0.681(1)	0.7368(7)
C(18)	0.4813(8)	0.739(2)	0.6877(7)
C(19)	0.475(1)	0.677(2)	0.625(1)
C(20)	0.3501(6)	0.9590(8)	0.5338(5)
C(21)	0.3473(7)	0.887(1)	0.4645(5)
C(22)	0.286(1)	1.060(1)	0.5016(8)
C(23)	0.439(1)	0.998(1)	0.5820(9)
C(24)	0.2159(7)	0.7326(8)	0.7514(4)
C(25)	0.2389(8)	0.8541(8)	0.7577(5)
C(26)	0.277(1)	0.669(1)	0.8188(5)
C(27)	0.1225(7)	0.717(1)	0.7477(6)

TABLE 5. Atom coordinates ($\times 10^4$) for the cluster $Cp_2Cr_2(SCMe_3)_2(S)_2Re_2(CO)_6$ (**III**)

Atom	x	y	z
Re(1)	1643(1)	1705(1)	2447
Cr(1)	0	1909(7)	474(7)
Cr(2)	0	3375(5)	1578(4)
S(1)	0	1030(7)	1708(6)
S(2)	1466(7)	2624(5)	1094(5)
S(3)	0	2550(7)	2897(7)
O(1)	1837(20)	584(18)	4018(12)
O(2)	3482(21)	762(15)	1485(15)
O(3)	3580(22)	2686(15)	1836(20)
C(1)	1755(29)	978(22)	3397(21)
C(2)	2745(23)	1099(17)	1800(17)
C(3)	2799(30)	2349(18)	2118(21)
C(4)	0	−151(20)	1583(24)
C(5)	0	−428(30)	2400(49)
C(6)	1063(22)	−333(18)	1102(20)
C(7)	0	2981(25)	4056(27)
C(8)	1055(35)	3530(36)	4107(20)
C(9)	0	2140(49)	4586(28)
C(11)	0	946(23)	−547(23)
C(12)	−923(26)	1451(20)	−644(19)
C(13)	−619(32)	2260(23)	−843(18)
C(21)	983(21)	4529(20)	1673(22)
C(22)	0	4643(32)	2260(21)
C(23)	580(32)	4423(17)	744(26)

3.2. *$Cp_2Cr_2(\mu_3\text{-}SCMe_3)_2(\mu_3\text{-}S)_2Re_2(CO)_6$* (**III**)

A violet solution of 0.58 g (1.3 mmol) and $Cp_2Cr_2(SCMe_3)_2S$ (**I**) and 0.85 g (1.3 mmol) $Re_2(CO)_{10}$ in 35 ml of *m*-xylene was irradiated by UV light and refluxed for 1 h. The brown–green solution obtained was chromatographed on an Al_2O_3 column (3 × 15 cm^2), the brown–green zone ($R_f = 0.7$) was eluted by a toluene–heptane–THF (3 : 1 : 1) mixture. The eluate was evaporated to dryness at 80°C, 0.1 Torr, The residue was recrystallized from a benzene–heptane (2 : 1) mixture at −5°C. The precipitated brown–green crystalline product was isolated from the mother liquor by decantation, washed with heptane and dried *in vacuo*. The yield was 0.37 g.

IR (ν, cm^{-1}): 462w, 500m, 598m, 795s, 1000w, 1100m, 1132m, 1345m, 1370w, 1420m, 1670m, 1885vs, 1992vs, 2835w, 2940m, 3055w.

μ_{eff} (μ_B): 1.50 (292 K)–0.72 (79 K).

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