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Antiferromagnetic complexes with a metal–metal bond

XVII *. Synthesis and molecular structures of the antiferromagnetic clusters $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2RhL_2$ ($L_2 = \pi\text{-}C_8H_{12}$ or $(CO)_2$) with long Cr–Rh bonds

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Abstract

The reaction of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (I) with $(\pi\text{-}C_8H_{12}RhCl)_2$ or $(acac)Rh(CO)_2$ in benzene, which leads to the mixed-metal clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2RhL_2$ (II, $L = \frac{1}{2}\pi\text{-}C_8H_{12}$; III, L = CO) have been studied. The structures of the antiferromagnetic clusters II and III were determined by X-ray diffraction study (II: space group $P\bar{1}$, *a* 9.913(8), *b* 13.994(11), *c* 18.242(12) Å; *α* 91.96(3), *β* 95.91(2), *γ* 106.24(2)°, $Z = 4$, two independent molecules; III: space group *Pbca*, *a* 16.966(5), *b* 13.190(5), *c* 17.885(6) Å, $Z = 8$). Long Cr–Rh (3.064(1)–3.009(1) Å in II and 3.134–3.010 Å in III) and short Cr–Cr bonds (2.687(1) Å in II and 2.708(1) Å in III) were observed in both triangular metal clusters. In II and III the two S atoms and the two ligands L are in square planar coordination which is typical of Rh^I atoms.

Introduction

The increase in catalytic activity of the rhodium complexes during hydroformylation upon introduction of the thiolate bridges [1] or in combination with the complexes of early transition metals [2] is well known. In order to elucidate the

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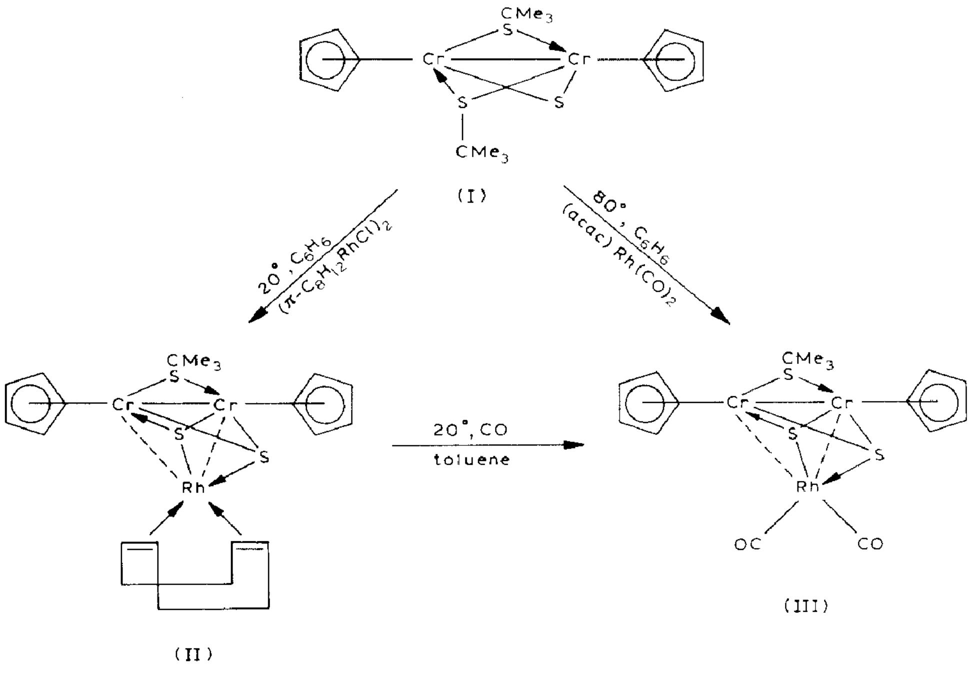
* For Part XVI see Ref. 10.

common features of formation of such mixed systems we used the binuclear antiferromagnetic complex $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (I) ($-2J$ 430 cm^{-1}) with short Cr–Cr bond (2.689 Å) [3] as the metal-thiolate component; it was brought into interaction with rhodium complexes (π-$C_8H_{12}RhCl_2$) and $(acac)Rh(CO)_2$.

Results and discussion

It was found that the clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2RhL_2$ (II, L = $\frac{1}{2}\pi$-C_8H_{12}; III, L = CO) were formed by reaction of $(CpCrSCMe_3)_2S$ (I) with the rhodium complexes (π-$C_8H_{12}RhCl$) or $(acac)Rh(CO)_2$ in benzene at 20 or 80 °C respectively. The products, which were isolated by crystallization from benzene/heptane mixture or by chromatography on Al_2O_3, are evidently the result of the elimination of an acidic Cl or acac ligand from the Rh complex and a t-butyl group from I as Bu^tCl or Bu^tacac. The Rh(π-C_8H_{12}) or $Rh(CO)_2$ species formed in this way contain a Rh in a formal 1 + oxidation state and are bound to the binuclear $Cp_2Cr_2(SCMe_3)(S)_2$ fragment (marked as Q) and so give the QRh(π-C_8H_{12}) (II) or $QRh(CO)_2$ (III) clusters, respectively. II readily converts into III in toluene solution at room temperature under CO (the CO stretching vibration bands are observed in the IR spectrum of III at 1965 and 2000 cm^{-1}).

Greenish-black (II) and violet-blue (III) crystals were isolated. X-ray crystallography (Fig. 1, 2) showed both clusters to contain an Rh^I atom coordinated to the two sulphur atoms of the antiferromagnetic fragment Q; the short Cr–Cr bonds (2.687(1) Å in II and 2.708 Å in II) of III being almost the same as in the starting complex $(CpCrSCMe_3)_2S$ [3]. Of particular interest is the typical square planar coordination of the Rh^I atom coordinated to the two sulphur atoms and to the C=C double bonds of the 1,5-cyclooctadiene (the C=C bonds perpendicular to the RhS_2 plane, mean



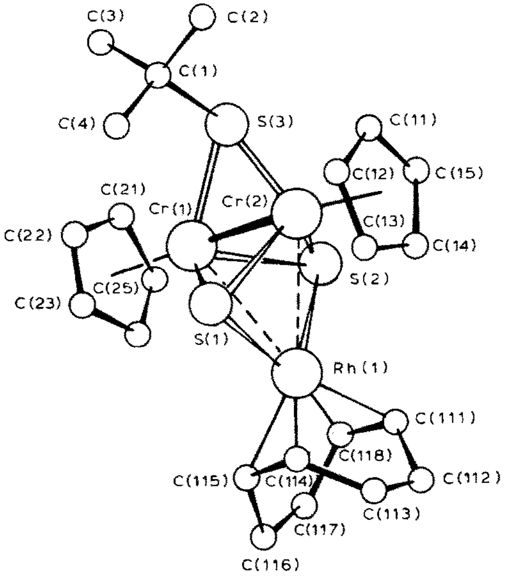


Fig. 1. The molecular structure of $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Rh(\pi\text{-}C_8H_{11})$ (II).

C=C bond length in II is 1.395(9) Å) or to the two CO groups of cluster III. In addition, the Rh–Cr bonds (3.009(1)–3.064(1) Å in II and 3.010(1)–3.134(1) Å in III) which are formed are elongated when compared with the sum of the covalent radii ($r_{Cr} + r_{Rh} = 1.46 + 1.46 = 2.92$ Å [4]) or to the Cr–Rh single bond of 2.757(2) Å in the complex $C_6H_6CrRh(\eta^5\text{-}C_5Me_5)(CO)_2(\mu\text{-}CO)_2$ [5]. It is obvious that such geometry is caused by some peculiarities in the electronic structure of the Rh^I atom. Indeed, in the $QCo(CO)_2$ (IV) cluster, which is analogous to III, the Co^I atom has

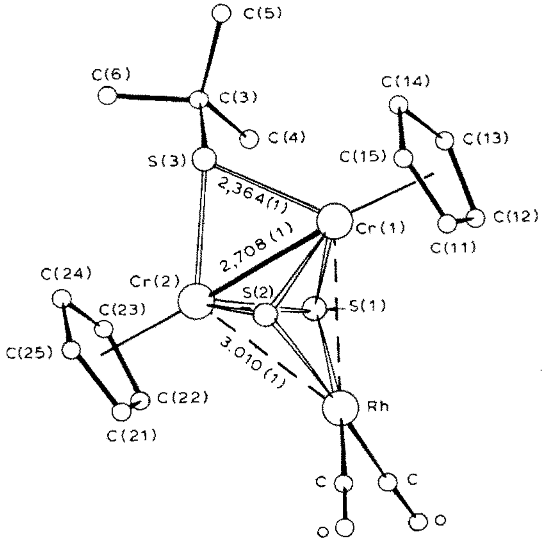


Fig. 2. The molecular structure of $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Rh(CO)_2$ (III).

tetrahedral coordination and forms short Co–Cr bonds (2.579 and 2.592 Å); The Cr–Cr bond in IV also is significantly shortened [3]. It is noteworthy that in spite of the relative weakness of the Cr–Cr and Rh–Cr bonds in III, compared with IV, a noticeable increase in antiferromagnetic exchange interactions in III was observed: the change of μ_{eff} from 0.78 μB at 295 K to 0.58 μB at 90 K can be described by the Heisenberg–Dirak–Van Vleck dimeric model [6] with the exchange parameter $-2J$ 592 cm^{-1} (the monomer admixture 2%, standard deviation 4%) instead of the $-2J$ 530 cm^{-1} value for cluster IV [3]. The antiferromagnetic exchange interaction is also increased in cluster II and in the same temperature range μ_{eff} decreases from 1.17 to 0.89 μB, the corresponding exchange parameter $-2J$ of 568 cm^{-1} (the monomer admixture 5%, standard deviation 5%).

Experimental

All operations were carried out under pure argon in absolute solvents. The starting complexes $(\pi\text{-}C_8H_{12}RhCl)_2$, acacRh$(CO)_2$ and $(CpCrSCMe_3)_2S$ were prepared by published procedures [7–9]. IR spectra were measured with a Specord IR-75 spectrometer in KBr pellets. The temperature-dependent magnetic susceptibility measurements were carried out by use of the Faraday method. X-ray data for II and III were collected with a CAD-4 automatic diffractometer (λ Mo-K_α, θ–2θ scan) (Table 1). Both structures were solved by direct methods and refined anisotropically by full-matrix least squares for all non-hydrogen atoms. The atomic coordinates, temperature factors, bond lengths and bond angles are listed in Tables 2–7.

Table 1

Crystal data for the clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2RhL_2$

	II, $L_2 = \pi\text{-}C_8H_{12}$	III, $L_2 = (CO)_2$
System	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pbca*
a (Å)	9.913(8)	16.966(5)
b (Å)	13.994(2)	13.190(5)
c (Å)	18.242(12)	17.885(6)
α (°)	91.96(3)	90
β (°)	95.91(2)	90
γ (°)	106.24(2)	90
Z	4 [a]	8
Wave length, Mo-K_α (Å)	0.71073	0.71073
Diffractometer	CAD-4	CAD-4
Number of observed reflections	6321	3134
$2\theta_{max}$ (°)	54	48
Number of reflections with $I \geq 5\sigma(I)$	5162	2471
R	0.041	0.035
R_w	0.043	0.047

[a] Two independent molecules in the asymmetric unit.

Table 2

Atomic coordinates and isotropic equivalent thermal parameters for the cluster $Cp_2Cr_2(\eta\text{-}SCMe_3)(\mu_3\text{-}S)_2Rh(\pi\text{-}C_8H_{12})$ (II)

Atom	x	y	z	B_{eq} [a]
Rh(1)	0.15377(4)	0.32583(3)	0.07992(2)	2.839(9)
Rh(2)	−0.22898(4)	0.65577(3)	0.40789(2)	2.424(8)
Cr(1)	0.09965(9)	0.21122(6)	−0.07137(5)	3.05(2)
Cr(2)	0.36171(9)	0.25306(6)	0.00084(5)	3.13(2)
Cr(3)	−0.42815(8)	0.76057(6)	0.46587(5)	2.62(2)
Cr(4)	−0.16615(8)	0.80774(6)	0.53896(5)	2.62(2)
S(1)	0.1575(1)	0.16305(9)	0.04422(8)	3.15(3)
S(2)	0.2438(2)	0.3682(1)	−0.03293(8)	3.63(3)
S(3)	0.3010(2)	0.1977(1)	−0.12515(8)	3.63(3)
S(4)	−0.2213(1)	0.82545(9)	0.41494(7)	2.98(3)
S(5)	−0.3234(1)	0.65082(9)	0.52224(7)	2.71(3)
S(6)	−0.3328(1)	0.89787(9)	0.55270(8)	3.14(3)
C(1)	0.3089(7)	0.0697(5)	−0.1484(3)	4.5(1)
C(2)	0.2602(8)	−0.0007(4)	−0.0866(4)	5.5(2)
C(3)	0.4637(8)	0.0774(6)	−0.1600(5)	7.4(2)
C(4)	0.211(1)	0.0318(6)	−0.2213(4)	7.7(2)
C(5)	−0.4110(6)	0.8880(4)	0.6418(3)	4.0(1)
C(6)	−0.4370(8)	0.7820(5)	0.6691(3)	5.1(2)
C(7)	−0.5506(7)	0.9174(5)	0.6272(4)	5.8(2)
C(8)	−0.3029(8)	0.9673(6)	0.6963(4)	6.3(2)
C(11)	−0.0523(7)	0.2566(5)	−0.1583(4)	5.6(2)
C(12)	−0.0469(7)	0.1631(6)	−0.1762(4)	5.9(2)
C(13)	−0.0964(7)	0.0986(5)	−0.1239(5)	6.9(2)
C(14)	−0.1317(7)	0.1572(8)	−0.0639(4)	8.4(3)
C(15)	−0.1023(7)	0.2550(6)	−0.0853(5)	6.5(2)
C(21)	0.5551(7)	0.2054(6)	0.0304(5)	6.4(2)
C(22)	0.5692(7)	0.2944(6)	−0.0014(5)	6.3(2)
C(23)	0.5660(8)	0.3655(6)	0.0450(6)	7.6(2)
C(24)	0.5047(7)	0.3174(7)	0.1050(4)	7.3(2)
C(25)	0.5005(8)	0.2166(6)	0.0959(4)	6.4(2)
C(31)	−0.6347(6)	0.7973(5)	0.4367(4)	4.3(1)
C(32)	−0.5772(6)	0.7839(5)	0.3709(4)	4.7(2)
C(33)	−0.5696(6)	0.6836(5)	0.3651(4)	4.7(2)
C(34)	−0.6239(6)	0.6345(5)	0.4266(4)	4.5(2)
C(35)	−0.6613(6)	0.7043(5)	0.4727(4)	4.4(1)
C(41)	−0.0269(7)	0.8359(5)	0.6463(4)	4.9(2)
C(42)	−0.0064(6)	0.7536(5)	0.6090(4)	5.1(2)
C(43)	0.0471(7)	0.7821(6)	0.5422(5)	6.4(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as: $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

$Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Rh(\pi\text{-}C_8H_{12})$ (II)

The violet-coloured solution of 1.0 g (2.1 mmol) of $(CpCrSCMe_3)_2S$ in 25 ml of benzene was added to the yellow solution of 0.42 g (0.85 mmol) of $(\pi\text{-}C_8H_{12}RhCl)_2$ in 25 ml of benzene. The reaction mixture immediately change colour to blackish green and the solvent was removed in vacuo (100 °C/20 torr) then heptane was added to the black oily residue, which in turn yield the microcrystalline powder. In order to obtain single crystals the product was washed in heptane, dissolved in 10 ml of CH_2Cl_2 in a Schlenk vessel, covered with a pentane layer (15 ml) and left to

Table 3

Bond distances in the cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Rh(\pi\text{-}C_8H_{12})$ (II)

Bond	*d* (Å)	Bond	*d* (Å)	Bond	*d* (Å)
Rh(1)–Cr(1)	3.064(1)	Rh(2)–C(121)	2.142(5)	Cr(3)–S(4)	2.302(2)
Rh(1)–Cr(2)	3.009(1)	Rh(2)–C(122)	2.136(6)	Cr(3)–S(5)	2.297(2)
Rh(1)–S(1)	2.359(1)	Rh(2)–C(125)	2.129(6)	Cr(3)–S(6)	2.358(1)
Rh(1)–S(2)	2.356(1)	Rh(2)–C(126)	2.148(5)	Cr(4)–S(4)	2.310(2)
Rh(1)–C(111)	2.131(6)	Cr(1)–Cr(2)	2.687(1)	Cr(4)–S(5)	2.299(1)
Rh(1)–C(114)	2.139(6)	Cr(1)–S(1)	2.301(2)	Cr(4)–S(6)	2.369(2)
Rh(1)–C(115)	2.135(7)	Cr(1)–S(2)	2.301(1)	S(3)–C(1)	1.852(7)
Rh(1)–C(118)	2.140(6)	Cr(1)–S(3)	2.363(2)	S(6)–C(5)	1.865(6)
Rh(2)–Cr(3)	3.019(1)	Cr(2)–S(1)	2.298(2)	C(111)–C(118)	1.391(9)
Rh(2)–Cr(4)	3.038(1)	Cr(2)–S(2)	2.306(2)	C(114)–C(115)	1.372(10)
Rh(2)–S(4)	2.353(1)	Cr(2)–S(3)	2.362(2)	C(121)–C(122)	1.413(9)
Rh(2)–S(5)	2.368(1)	Cr(3)–Cr(4)	2.688(1)	C(125)–C(126)	1.395(8)

Table 4

Bond angles in the structure of cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Rh(\pi\text{-}C_8H_{12})$ (II)

Angle	ω(°)	Angle	ω(°)
Cr(1)Rh(1)Cr(2)	52.50(2)	Rh(2)Cr(3)S(6)	118.26(5)
Cr(1)Rh(1)S(1)	48.08(4)	Cr(4)Cr(3)S(4)	54.50(4)
Cr(1)Rh(1)S(2)	48.08(4)	Cr(4)Cr(3)S(5)	54.25(4)
Cr(2)Rh(1)S(1)	48.88(4)	Cr(4)Cr(3)S(6)	55.53(4)
Cr(2)Rh(1)S(2)	49.08(5)	S(4)Cr(3)S(5)	87.86(6)
S(1)Rh(1)S(2)	84.79(5)	S(4)Cr(3)S(6)	83.26(5)
Cr(3)Rh(2)Cr(4)	52.69(2)	S(5)Cr(3)S(6)	97.92(5)
Cr(3)Rh(2)S(4)	48.85(4)	Rh(2)Cr(4)Cr(3)	63.28(3)
Cr(3)Rh(2)S(5)	48.65(4)	Rh(2)Cr(4)S(4)	49.95(4)
Cr(4)Rh(2)S(4)	48.74(4)	Rh(2)Cr(4)S(5)	50.38(4)
Cr(4)Rh(2)S(5)	48.41(3)	Rh(2)Cr(4)S(6)	117.16(4)
S(4)Rh(2)S(5)	85.03(5)	Cr(3)Cr(4)S(4)	54.21(1)
Rh(1)Cr(1)Cr(2)	62.69(3)	Cr(3)Cr(4)S(5)	54.16(4)
Rh(1)Cr(1)S(1)	49.71(4)	Cr(3)Cr(4)S(6)	55.16(4)
Rh(1)Cr(1)S(2)	49.65(4)	S(4)Cr(4)S(5)	87.60(5)
Rh(1)Cr(1)S(3)	116.67(4)	S(4)Cr(4)S(6)	82.86(6)
Cr(2)Cr(1)S(1)	54.22(4)	S(5)Cr(4)S(6)	97.55(5)
Cr(2)Cr(1)S(2)	54.41(5)	Rh(1)S(1)Cr(1)	82.21(5)
Cr(2)Cr(1)S(3)	55.33(4)	Rh(1)S(1)Cr(2)	80.47(5)
S(1)Cr(1)S(2)	87.41(5)	Cr(1)S(1)Cr(2)	71.48(5)
S(1)Cr(1)S(3)	98.19(6)	Rh(1)S(2)Cr(1)	82.27(5)
S(2)Cr(1)S(3)	82.86(6)	Rh(1)S(2)Cr(2)	80.37(5)
Rh(1)Cr(2)Cr(1)	64.80(3)	Cr(1)S(2)Cr(2)	69.32(5)
Rh(1)Cr(2)S(2)	50.55(4)	Cr(1)S(3)C(1)	116.5(2)
Rh(1)Cr(2)S(3)	118.76(5)	Cr(2)S(3)C(1)	115.3(2)
Cr(1)Cr(2)S(1)	54.30(4)	Rh(2)S(4)Cr(3)	80.84(4)
Cr(1)Cr(2)S(2)	54.24(4)	Rh(2)S(4)Cr(4)	81.31(5)
Cr(1)Cr(2)S(3)	55.36(5)	Cr(3)S(4)Cr(4)	71.29(5)
S(1)Cr(2)S(2)	87.34(6)	Rh(2)S(5)Cr(3)	80.63(5)
S(1)Cr(2)S(3)	98.29(5)	Rh(2)S(5)Cr(4)	81.21(5)
S(2)Cr(2)S(3)	82.78(6)	Cr(3)S(5)Cr(4)	71.59(5)
Rh(2)Cr(3)Cr(4)	64.03(3)	Cr(3)S(6)Cr(4)	69.32(5)
Rh(2)Cr(3)S(4)	50.32(4)	Cr(3)S(6)C(5)	115.6(2)
Rh(2)Cr(3)S(5)	50.72(4)	Cr(4)S(6)C(5)	116.2(5)

Table 5

Atomic coordinates and isotropic equivalent thermal parameters for the cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Rh(CO)_2$ (III)

Atom	x	y	z	B_{eq}
Rh	0.98368(2)	0.22209(3)	0.10021(2)	2.870(8)
Cr(1)	0.87525(4)	0.40649(5)	0.14070(4)	2.47(1)
Cr(2)	0.94920(4)	0.30687(5)	0.25301(4)	2.28(1)
S(1)	0.86367(7)	0.23524(9)	0.16658(7)	2.85(2)
S(2)	1.01007(7)	0.38503(9)	0.15176(7)	2.70(2)
S(3)	0.87451(7)	0.45542(8)	0.26783(7)	2.77(2)
O(1)	1.1402(3)	0.2174(4)	0.0222(3)	7.2(1)
O(2)	0.9332(3)	0.0133(3)	0.0557(3)	6.6(1)
C(1)	1.0803(4)	0.2189(4)	0.0510(3)	4.3(1)
C(2)	0.9543(4)	0.0933(4)	0.0710(3)	4.1(1)
C(3)	0.7789(3)	0.4386(4)	0.3187(3)	3.8(1)
C(4)	0.7970(4)	0.4305(7)	0.4014(4)	6.7(2)
C(5)	0.7313(5)	0.5337(6)	0.3055(5)	8.4(2)
C(6)	0.7346(3)	0.3425(5)	0.2943(4)	5.8(2)
C(11)	0.8748(4)	0.5383(4)	0.0618(3)	5.1(1)
C(12)	0.8808(4)	0.4514(5)	0.0188(3)	4.5(1)
C(13)	0.8150(4)	0.3945(5)	0.0291(3)	5.1(1)
C(14)	0.7658(3)	0.4459(6)	0.0792(4)	7.2(2)
C(15)	0.8039(4)	0.5383(5)	0.0986(3)	6.3(2)
C(21)	0.9839(3)	0.2986(4)	0.3726(3)	4.4(1)
C(22)	1.0516(3)	0.2988(4)	0.3317(3)	4.2(1)
C(23)	1.0532(3)	0.2133(4)	0.2876(3)	4.2(1)
C(24)	0.9844(4)	0.2576(4)	0.3024(4)	4.8(1)
C(25)	0.9410(4)	0.2109(5)	0.3555(3)	4.7(1)
H(4A)	0.743(7)	0.403(7)	0.436(6)	20(4)* [a]
H(4B)	0.838(4)	0.469(6)	0.407(4)	11(2)*
H(5B)	0.681(4)	0.545(5)	0.336(4)	9(2)*
H(5A)	0.718(3)	0.534(3)	0.257(2)	4(1)*
H(5D)	0.774(5)	0.598(5)	0.313(4)	7(2)*
H(6B)	0.724(4)	0.323(5)	0.234(4)	10(2)*
H(6C)	0.769(3)	0.302(4)	0.304(3)	5(1)*
H(6A)	0.682(3)	0.339(4)	0.313(3)	5(1)*
H(11)	0.908(4)	0.58695)	0.057(3)	9(2)*
H(12)	0.926(3)	0.427(4)	−0.013(3)	3(1)*
H(13)	0.800(3)	0.340(4)	0.006(3)	7(1)*
H(14)	0.732(4)	0.423(4)	0.088(3)	8(2)*
H(15)	0.78593)	0.581(3)	0.134(3)	4(1)*
H(21)	0.971(3)	0.352(4)	0.406(3)	4(1)*
H(22)	1.081(4)	0.356(6)	0.323(4)	10(2)*
H(23)	1.078(2)	0.201(3)	0.262(2)	1.4(8)*
H(24)	0.967(3)	0.098(4)	0.276(3)	7(1)*
H(25)	0.896(3)	0.190(3)	0.375(2)	5(1)*

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given as the isotropic equivalent thermal parameter which is defined thus: $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

stand for 72 h at 20°C under argon. Black prisms were separated by decantation, washed with heptane, and dried in vacuo. The yield is 0.33 g (64%). IR spectrum (ν cm^{-1}): 475w, 555w, 667w, 785v.s., 1000m, 1051m, 1140m, 1315w, 1349m, 1375m,

Table 6

Bond distances in the cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Rh(CO)_2$ (III)

Bond	d(Å)	Bond	d(Å)	Bond	d(Å)
Rh–Cr(1)	3.134(1)	Cr(1)–S(1)	2.314(1)	S(3)–C(3)	1.873(4)
Rh–Cr(2)	3.010(1)	Cr(1)–S(2)	2.313(1)	O(1)–C(1)	1.141(5)
Rh–S(1)	2.363(1)	Cr(1)–S(3)	2.364(1)	O(2)–C(2)	1.148(5)
Rh–S(2)	2.381(1)	Cr(2)–S(1)	2.321(1)	C(3)–C(4)	1.515(7)
Rh–C(1)	1.860(5)	Cr(2)–S(2)	2.326(1)	C(3)–C(5)	1.510(7)
Rh–C(2)	1.845(4)	Cr(2)–S(3)	2.348(1)	C(3)–C(6)	1.537(6)
Cr(1)–Cr(2)	2.708(1)				

1415s, 1615m, 1820m, 2850m, 2900m, 2945w, 3065w (the coordinated cyclooctadiene is presumably lost during pellet preparation).

$Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Rh(CO)_2$ (III)

A solution containing 0.63 g (2.5 mmol) of $Rh(CO)_2(acac)$ and 1.69 g (3.75 mmol) of $(CpCrSCMe_3)_2S$ in 25 ml of benzene changed colour from violet to red after 3 h at reflux. On cooling the mixture was chromatographed on the Al_2O_3 column (3 × 25 cm), elution by benzene separated the light-green and blue zones from the violet zone of unchanged $(CpCrSCMe_3)_2S$. After the blue eluate was concentrated to a volume of 5 ml in vacuo, fine violet-blue crystals separated (0.30 g, 22%). This product was dissolved in 15 ml of CH_2Cl_2 in a Schlenk vessel then covered carefully with a pentane layer (20 ml) and left to stand for three days at 20 °C. The violet-blue crystals were washed with heptane (2 × 5 ml) and dried in vacuo. IR spectrum (ν, cm^{-1}): 475s, 565s, 800v.s., 1005m, 1150m, 1350w, 1420w, 1965v.s., 2030v.s, 2950w, 3060w.

Table 7

Bond angles in the structure of cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Rh(CO)_2$ (III)

Angle	ω(°)	Angle	ω(°)
Cr(1)RhCr(2)	52.25(1)	Cr(1)Cr(2)S(2)	54.07(3)
S(1)RhS(2)	84.34(3)	Cr(1)Cr(2)S(3)	55.18(3)
S(1)RhC(1)	176.4(1)	S(1)Cr(2)S(2)	86.53(4)
S(1)RhC(2)	88.7(1)	S(1)Cr(2)S(3)	94.44(4)
S(2)RhC(1)	92.2(1)	S(2)Cr(2)S(3)	87.57(3)
S(2)RhC(2)	172.3(1)	RhS(1)Cr(1)	89.15(3)
C(1)RhC(2)	94.8(2)	RhS(1)Cr(2)	79.97(3)
RhCr(1)Cr(2)	61.51(1)	Cr(1)S(1)Cr(2)	71.51(3)
Cr(2)Cr(1)S(1)	54.37(3)	RhS(2)Cr(1)	83.77(3)
Cr(2)Cr(1)S(2)	54.50(3)	RhS(2)Cr(2)	79.51(3)
Cr(2)Cr(1)S(3)	54.65(3)	Cr(1)S(2)Cr(2)	71.44(3)
S(1)Cr(1)S(2)	86.99(3)	Cr(1)S(3)Cr(2)	70.17(3)
S(1)Cr(1)S(3)	94.23(3)	Cr(1)S(3)C(3)	116.1(1)
S(2)Cr(1)S(3)	87.51(4)	Cr(2)S(3)C(3)	115.1(1)
RhCr(2)Cr(1)	66.23(1)	RhC(1)O(1)	178.6(4)
Cr(1)Cr(2)S(1)	54.12(3)	RhC(2)O(2)	176.5(4)

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