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Transfer of the t-butyl group from the thiolate bridge to the cyclopentadienyl ring. The effect of electronic structure on the geometry of $(RC_5H_4)_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)M_2L_n$ clusters (M = Co, Ni) with the butterfly Cr_2M_2 metal core

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Abstract

The reaction of $QMn(CO)_3$ or Q_2M ($Q = ((C_5H_5)_2Cr_2SCMe_3)(\mu_3\text{-}S)_2$, M = Mn or Fe) with $Co_2(CO)_8$ leads to the known $62e^-$ cluster $ZCo_2(CO)_4$ (I), in which $Z = Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)$ with a butterfly Cr_2Co_2 metal core. On the other hand the reaction of Q_2Ni with $Co_2(CO)_8$ yields the analogous cluster $(t\text{-}BuC_5H_4)(C_5H_5)Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$ (II) which has a CMe_3 group in one of the rings along with I. The $62e^-$ diamagnetic cluster II studied by X-ray crystallography (space group $P2_1/c$, *a* 10.114(11), *b* 11.263(4), *c* 19.579(5) Å, β 100.24(7)°, *V* 2194.8 Å^3, Z = 4) has a strongly bonded Cr_2Co_2 metal core with a Cr–Cr distance of 2.551(1) and Cr–Co distances of 2.618(1), 2.640(1), 2.615(1) and 2.621(1) Å. The reaction of binuclear $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ with $(C_5H_5)Co(C_5H_6)$ yields the diamagnetic $64e^-$ cluster, $ZCo_2(C_5H_5)_2$ (IV). Two additional electrons cause only slight weakening of the Co–Cr (2.657(1), 2.675(1), 2.651(1), 2.658(1) Å) and Cr–Cr (2.585(1) Å) bonds in III as compared to II. At the same time considerable weakening of the Co–μ_4-S (2.260(2) and 2.252(2) Å) and Co–C(C_5H_5) (2.1157 Å av.) bonds is observed. The comparison of the geometrical parameters of the $62e^-$ butterfly clusters $(RC_5H_4)_2Cr_2S_3Co_2(CO)_4$ (R = H; R = Me, R = t-Bu and R = H) and their 64 and $66e^-$ analogues III and $(C_5H_5)_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Ni_2(C_5H_5)_2$, respectively, leads to the conclusion that the nature of the R substituent in the cyclopentadienyl rings at the Cr atoms has only a slight effect on the geometry of the metal core. Addition of electrons to the cluster causes weakening of those bonds involved with the heteroatom but does not affect the geometry of the central fragment $(RC_5H_4)_2Cr_2S_3$.

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Introduction

Our recent study [1] has revealed that the interaction of binuclear complexes $(RC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ with $Co_2(CO)_8$ in equimolar ratio leads to the formation of $62e^-$ clusters $(RC_5H_4)_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S) \cdot Co_2(CO)_4$ with a butterfly Cr_2Co_2 metal core (I, R = H; Ia, R = Me). Notwithstanding the different conformations of the Cp-rings at the Cr atoms (eclipsed in I and staggered in Ia) (Table 1), the metal core structures in these clusters are in fact identical. The formal substitution of Mo for Cr atoms to give the known cluster $Cp_2Mo_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$ [2] causes no significant changes in the geometry of the metal core (Mo–Mo 2.646 Å, Mo–Co 2.640 Å) either. On the other hand four additional electrons in I, introduced by the formal substitution of a 15-electron CpNi for a 13-electron $Co(CO)_2$ group leads not only to significant distortion of the cluster core and to weakening of the two opposite Ni–Cr bonds up to 2.86 Å (Table 1), but also to the pronounced weakening of the Ni–C(Cp) bonds (up to 2.17 Å) [3]. In light of this the investigation of the intermediate case, the $64e^-$ cluster with the 14-electron CpCo instead of the 15-electron CpNi, groups seems worthwhile.

Results and discussion

High stability of the $Cp_2Cr_2(S)_3Co_2(CO)_4$ butterfly cluster is reflected in the very fact that this cluster is formed in reactions of $Cp_2Cr_2SCMe_3(S)_2Mn(CO)_3$ or $[CpCr_2SCMe_3(S)_2]_2M$ (M = Mn, Fe) with $Co_2(CO)_8$, which were carried out in an attempt to increase the nuclearity of the triangular or heterometallospirane metal core. On the other hand butterfly cluster formation by M = Ni is accompanied by an unexpected transfer of the t-butyl substituent from the S atom to one of the cyclopentadienyl rings (see Scheme 1).

The unusual mechanism of transfer of thiolate t-butyl group to the Cp-ring is not yet clear. However taking into account that neither Mn, nor Fe derivatives exhibit such reactivity one can assume that this process is due to action by the Ni atom. Four bands at 1945, 1965, 1985 and 2005 cm^{-1} corresponding to the stretching vibrations of the CO groups are observed in the IR spectrum of the unusual cluster II with various substituents in the Cp-rings and at the Cr atoms. It is diamagnetic and according to the results of the X-ray diffraction study has a strongly bonded butterfly metal core. The geometry of the binuclear $(Me_3CC_5H_4)CpCr_2S_3$ moiety is in fact that same as in cluster I (Table 1), although some slight distortion of the metal core in II (Co–Cr 2.615(1)–2.640(1) Å) is observed. It should be emphasized that in spite of the presence of a bulky t-butyl substituent, the Cp-rings in II as well as in I are in the eclipsed conformation (Fig. 1).

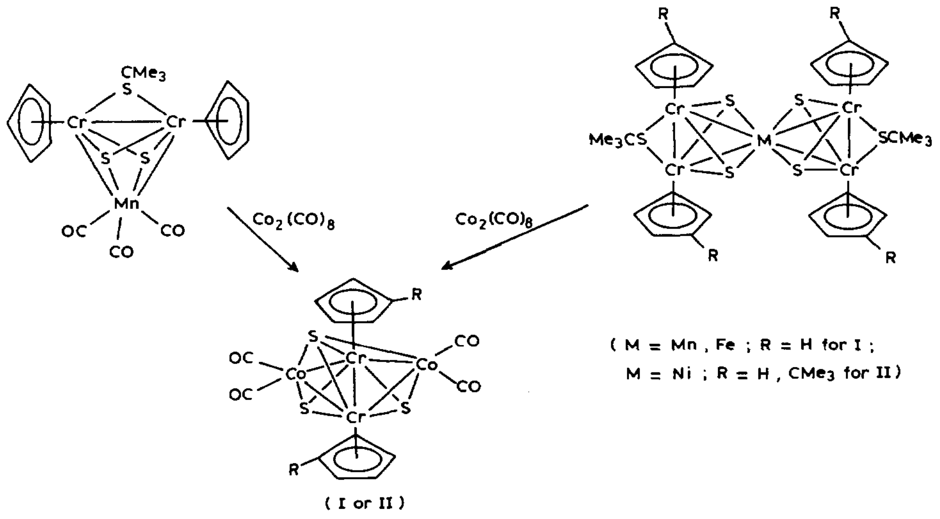
Introduction of additional (in excess of 62) electrons, for example by the formal substitution of two 14-electron fragments CpCo for the 13-electron $Co(CO)_2$ fragments, was expected to change substantially the geometry of the metal core. The $64e^-$ cluster was obtained in the form of green-brown prisms by reaction of $CpCo(C_5H_6)$ with $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu\text{-}S)$ in toluene under reflux (Fig. 2).

However the X-ray diffraction study has shown that significant changes are observed only in those bonds in which the Co atom is involved, the geometry of the binuclear moiety $Cp_2Cr_2S_3$ being in fact the same as in I (Table 1): Cr–Cr 2.551(1), Cr–(μ_3-S) 2.261(2)–2.274(2), Cr–(μ_4-S) 2.276(2) Å. At the same time almost all of

Table 1

Geometric parameters of the Cr-containing butterfly clusters $(RC_5H_4)_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)M_2L_2$

	$(C_5H_5)_2Cr_2S_3Co_2(CO)_4$ (I)	$(MeC_5H_4)_2Cr_2S_3\cdot Co_2(CO)_4$ (Ia)	$(t\text{-}BuC_5H_4)(C_5H_5)Cr_2\cdot S_3Co_2(CO)_4$ (II)	$(C_5H_5)_2Cr_2S_3\cdot Co_2(C_5H_5)_2$ (III)	$(C_5H_5)_2Cr_2S_3\cdot Ni_2(C_5H_5)_2$
Number of electrons in metal core	62	62	62	64	66
Cr–Cr (Å)	2.544(1)	2.544(2)	2.551(1)	2.585(1)	2.62(1)
Cr–M (Å)	2.617(1); 2.622(1)	2.614(2); 2.632(2) 2.615(2); 2.636(2)	2.618(1); 2.640(1) 2.615(1); 2.621(1)	2.657(1); 2.675(1) 2.658(1); 2.651(1)	2.63(1); 2.85(1) 2.65(1); 2.88(1)
Cr–μ_3-S (Å)	2.265(2); 2.253(2)	2.251(3)–2.269(3)	2.251(2)–2.268(2)	2.261(2)–2.274(2)	2.23(1)–2.27(2)
Cr–μ_4-S (Å)	2.326(2)	2.340(3); 2.314(2)	2.323(2); 2.336(2)	2.276(2)	2.24(1); 2.26(2)
M–μ_3-S (Å)	2.178(2)	2.178(3); 2.184(3)	2.169(2); 2.171(2)	2.136(2); 2.139(2)	2.15(1); 2.17(1)
M–μ_4-S (Å)	2.205(1)	2.190(3); 2.197(3)	2.202(2); 2.198(2)	2.262(2); 2.258(2)	2.29(1); 2.30(1)
M–L (av.) (Å)	1.789(7)	1.79(1)	1.743(9)–1.805(9)	2.115(7)	2.17(6)
Cr–μ_3-S–Cr (°)	68.54(6)	68.3(1); 68.6(1)	68.72(6); 68.82(6)	69.50(6); 69.70(6)	71.0(6); 71.3(6)
Cr–μ_4-S–Cr (°)	66.32(5)	66.28(9)	66.39(6)	69.21(5)	71.3(6)
Cr–μ_3-S–M (°)	72.14(6); 72.55(6)	71.9(1)–72.7(1)	72.41(6)–73.31(6)	73.77(6)–74.81(6)	73.9(6); 80.3(6)
Cr–μ_4-S–M (°)	70.51(5); 70.68(5)	70.8(1)–71.0(1)	70.53(6)–71.06(6)	71.57(5)–72.30(5)	71.6(6); 78.9(8)
M–μ_4-S–M (°)	133.23(7)	134.0(1)	133.49(9)	135.42(8)	141.7(8)
Cr_2M/Cr_2M (°)	124.2	124.8	125.0	128.0	127.0



Scheme 1

the equal Co–Cr bonds are elongated by 0.04 Å (2.651(1)–2.675(1) Å) and Co–(μ_4-S) bonds, by 0.06 Å (2.258(2)–2.262(2) Å), though the Co–(μ_3-S) bonds are shortened by 0.03 Å. The antibonding effect of the extra electrons is manifested by the weakening of the Co–C(C_5H_5) bonds (the mean Co–C distance being 2.115(7) Å) compared with the sum of the covalent radii of the Co and C atoms (1.29 + 0.74 = 2.03 Å) or to the Co–Cp distances in the known electron-saturated complex (π-C_5H_5)Co(C_5H_5Ph) (2.06 Å) [6]. Thus the highest occupied orbitals of cluster III are evidently largely made up of the Co atom orbitals. Each of the metal atoms has 19e$^-$ (5-electrons donated by each of the Cp rings and 5 electrons from the S and Cr atoms) and should be paramagnetic (with the spin equal to 1/2). However cluster III is in fact diamagnetic, which indicates that there is strong antiferromagnetic

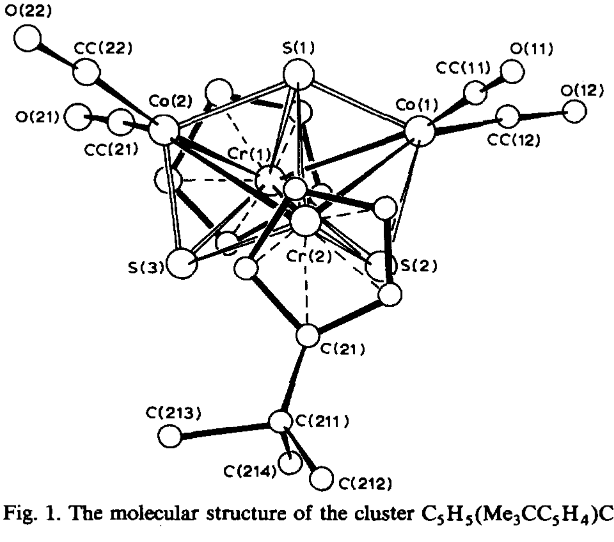
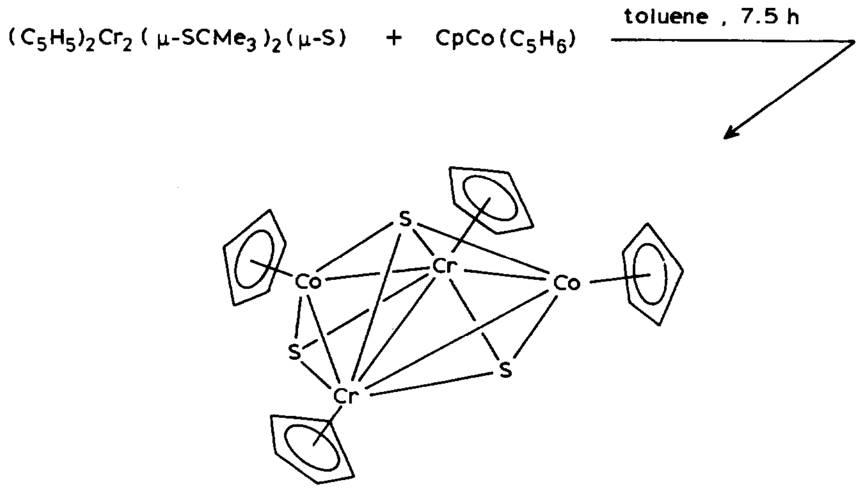


Fig. 1. The molecular structure of the cluster $C_5H_5(Me_3CC_5H_4)Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$ (II).



(III)

interaction between the paramagnetic centers via the Co–Cr–Co and Co–S–Cr–S–Co bridges. It should be mentioned that further increase in the number of electrons in the butterfly cluster, up to 66e$^-$, by substitution of

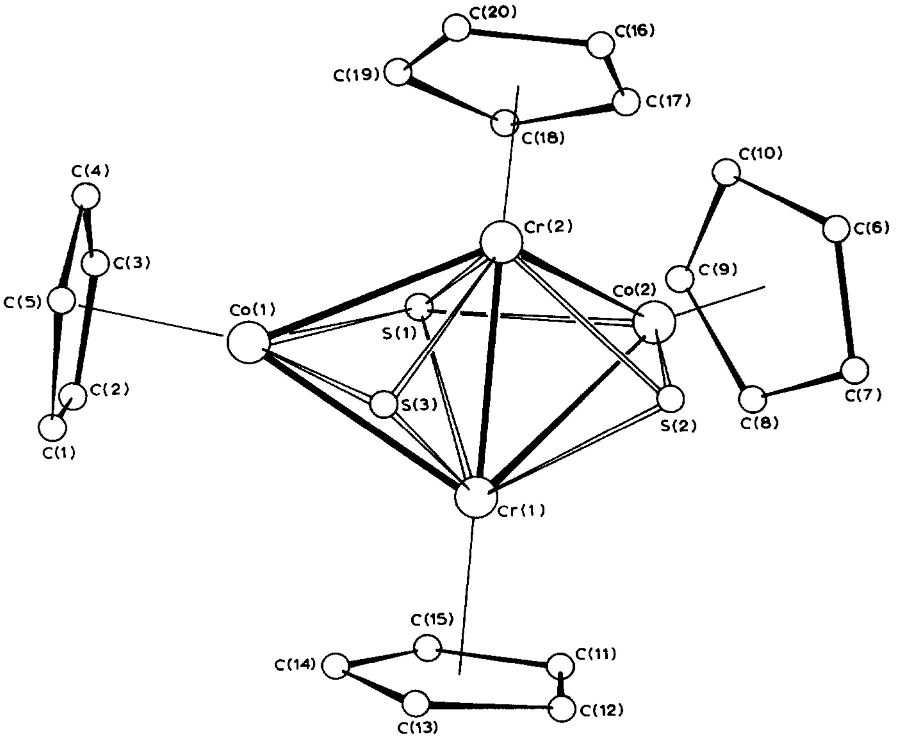


Fig. 2. The molecular structure of the cluster $(C_5H_5)_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(C_5H_5)_2$ (III).

15-electron fragments NiCp for 14-electron CoCp groups for example, causes further weakening of the Ni–Cr, Ni–S and Ni–Cp bonds in the known cluster CpNi($Cp_2Cr_2S_3$)NiCp [3]. One of the Ni–Cr bonds in each pair is elongated up to 2.864(1) Å (mean) in comparison with the shorter bond 2.64(1) Å (mean); average Ni–S and Ni–C bonds being 2.30 and 2.17 Å, respectively. At the same time the $Cp_2Cr_2S_3$ fragments remain almost unchanged (the Cr–Cr bond being only slightly elongated) (Table 1). Each of the two paramagnetic centers (Ni atoms) of the cluster contains 2 unpaired electrons and the interaction of the centers can be characterized by dimeric model with the magnetic exchange parameter being equal to $-2J = 418$ cm^{-1}.

Thus a deliberate change in the number of excess electrons in the metal core allows one to control the geometry and magnetic properties of the butterfly metal clusters.

Experimental

All operations including the synthesis of starting materials and the clusters were carried out under argon in dry solvents. The starting materials $Co_2(CO)_8$ [7], $(C_5H_5)Co(C_5H_6)$ [8] in addition to the complexes $(C_5H_5)_2Cr_2(\mu\text{-SCMe})_3(\mu\text{-S})$, $(C_5H_5)_2Cr_2(\mu\text{-SCMe}_3)$ $(\mu_3\text{-S})_2Mn(CO)_3$ and $[(C_5H_5)_2Cr_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2M$ (M = Mn, Fe, Ni) [5] were prepared by procedures described previously. The IR spectra (KBr pellets) were recorded with a Specord 75-IR instrument. Magnetic susceptibility of clusters II and III was measured by used the Faraday method [9]. X-Ray structural data for clusters II and III were obtained with CAD-4 and Hilger & Watts diffractometers respectively (λ Mo-K_α, $\theta/2\theta$-scan, Table 2); the structures were refined anisotropically by full-matrix, and block-diagonal least-squares techniques for all non-hydrogen atoms of II and III, respectively (see Tables 3–8).

(*Continued on p. 185*)

Table 2

Crystal data for clusters III and IV

	II	III
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pbca*
a (Å)	10.114(12)	12.397(1)
b (Å)	11.263(4)	18.166(1)
c (Å)	19.579(5)	17.562(7)
β (°)	100.24(7)	–
Z	4	8
Radiation Mo-K_α (Å)	0.71073	0.71073
Diffractometer	CAD-4	Hilger and Watts
Number of observed reflections	3054	3096
$2\theta_{max}$	46	52
Number of reflections with $I \geqslant 3\sigma$	1960	2165
R	0.042	0.036
R_w	0.054	0.031

Table 3

Atomic coordinates and thermal parameters[a] for the cluster $(C_5H_5)(Me_3CC_5H_4)Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$ (II)

Atom	x	y	z	$B_{eq.}$
Co(1)	0.2282(1)	0.5534(1)	0.53141(6)	3.00(2)
Co(2)	0.5391(1)	0.7825(1)	0.57702(6)	3.42(3)
Cr(1)	0.3322(1)	0.7384(1)	0.47969(6)	2.46(3)
Cr(2)	0.2990(1)	0.7460(1)	0.60574(6)	2.82(3)
S(1)	0.4387(2)	0.6088(2)	0.5642(1)	3.18(5)
S(2)	0.1305(2)	0.7250(2)	0.5145(1)	2.95(4)
S(3)	0.3689(2)	0.9007(2)	0.5475(1)	3.15(5)
O(11)	0.1416(7)	0.4096(6)	0.4074(3)	5.0(2)
O(12)	0.1172(8)	0.3952(7)	0.6246(3)	6.1(2)
O(21)	0.7543(6)	0.8139(7)	0.4952(4)	6.3(2)
O(22)	0.6944(9)	0.8490(9)	0.7114(4)	9.0(3)
CC(11)	0.1794(8)	0.4655(7)	0.4556(4)	3.5(2)
CC(13)	0.1621(9)	0.4577(8)	0.5896(5)	4.1(2)
CC(21)	0.6709(9)	0.8016(8)	0.5267(5)	4.1(2)
CC(22)	0.631(1)	0.819(1)	0.6582(5)	5.5(3)
C(11)	0.422(1)	0.8292(9)	0.3983(4)	4.1(2)
C(12)	0.2837(9)	0.8393(8)	0.3813(4)	3.7(2)
C(13)	0.2299(8)	0.7234(8)	0.3701(4)	3.5(2)
C(14)	0.3374(9)	0.6416(8)	0.3795(4)	3.6(2)
C(15)	0.4581(9)	0.7055(8)	0.3972(4)	3.7(2)
C(21)	0.2081(8)	0.8588(8)	0.6824(4)	3.4(2)
C(22)	0.3462(9)	0.8415(9)	0.7075(4)	3.7(2)
C(23)	0.373(1)	0.7189(9)	0.7188(4)	4.8(2)
C(24)	0.247(1)	0.6583(9)	0.7001(4)	4.9(2)
C(25)	0.1477(9)	0.7438(9)	0.6769(4)	4.6(2)
C(211)	0.138(1)	0.981(1)	0.6707(5)	5.0(2)
C(212)	0.045(1)	0.991(1)	0.7287(5)	6.2(3)
C(213)	0.045(1)	0.988(1)	0.5976(5)	7.1(3)
C(214)	0.240(1)	1.086(1)	0.6811(7)	6.8(3)

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

Table 4

Bond lengths (Å) in the cluster $(C_5H_5)(Me_3CC_5H_4)Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)\cdot Co_2(CO)_4$ (II)

Co(1)–Cr(1)	2.618(1)	Co(1)–Cr(2)	2.640(1)
Co(1)–S(1)	2.202(2)	Co(1)–S(2)	2.169(2)
Co(1)–CC(11)	1.780(8)	Co(1)–CC(12)	1.782(7)
Co(2)–Cr(1)	2.615(1)	Co(2)–Cr(2)	2.621(1)
Co(2)–S(1)	2.198(2)	Co(2)–S(3)	2.171(2)
Co(2)–CC(21)	1.805(8)	Co(2)–CC(22)	1.743(9)
Cr(1)–Cr(2)	2.551(1)	Cr(1)–S(1)	2.323(2)
Cr(1)–S(2)	2.268(2)	Cr(1)–S(3)	2.250(2)
Cr(2)–S(1)	2.336(2)	Cr(2)–S(2)	2.251(2)
Cr(2)–S(3)	2.263(2)	O(11)–CC(11)	1.143(8)
O(12)–CC(12)	1.133(8)	O(21)–CC(21)	1.139(8)
O(22)–CC(22)	1.170(9)	$C\text{–}C(C_5H_5)_{av.}$	1.412(9)
$C\text{–}C(Me_3CC_5H_4)_{av.}$	1.420(10)	$C\text{–}C(Me_3C)_{av.}$	1.568(11)

Table 5

Bond angles (°) in the cluster $(C_5H_5)(Me_3CC_5H_4)Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)\cdot Co_2(CO)_4$ (II)

Cr(1)Co(1)Cr(2)	58.05(3)	Cr(1)Co(1)S(1)	56.84(5)
Cr(1)Co(1)S(2)	55.61(5)	Cr(2)Co(1)S(1)	56.84(5)
Cr(2)Co(1)S(2)	54.79(5)	S(1)Co(1)S(2)	100.54(7)
Cr(1)Co(2)Cr(2)	58.31(3)	Cr(1)Co(2)S(1)	56.92(5)
Cr(1)Co(2)S(3)	55.14(5)	Cr(2)Co(2)S(1)	57.19(5)
Cr(2)Co(2)S(3)	55.42(5)	S(1)Co(2)S(3)	100.78(7)
Co(1)Cr(1)Co(2)	101.18(4)	Co(1)Cr(1)Cr(2)	61.41(4)
Co(1)Cr(1)S(1)	52.52(5)	Co(1)Cr(1)S(2)	52.10(5)
Co(1)Cr(1)S(3)	116.99(6)	Co(2)Cr(1)Cr(2)	60.95(4)
Co(2)Cr(1)S(1)	52.47(5)	Co(2)Cr(1)S(2)	116.08(6)
Co(2)Cr(1)S(3)	52.36(5)	Co(1)Cr(2)Co(2)	100.46(4)
Co(1)Cr(2)Cr(1)	60.55(4)	Co(1)Cr(2)S(1)	52.10(5)
Co(1)Cr(2)S(2)	51.90(5)	Co(1)Cr(2)S(3)	115.65(6)
Co(2)Cr(2)Cr(1)	60.74(4)	Co(2)Cr(2)S(1)	52.27(5)
Co(2)Cr(2)S(2)	116.47(6)	Co(2)Cr(2)S(3)	52.17(5)
Cr(1)Cr(2)S(1)	56.56(5)	Cr(1)Cr(2)S(2)	55.94(5)
Cr(1)Cr(2)S(3)	55.34(5)	Co(1)S(1)Co(2)	133.49(9)
Co(1)S(1)Cr(1)	70.63(6)	Co(1)S(1)Cr(2)	71.06(6)
Co(2)S(1)Cr(1)	70.61(6)	Co(2)S(1)Cr(2)	70.53(6)
Cr(1)S(1)Cr(2)	66.39(6)	Co(1)S(2)Cr(1)	72.28(6)
Co(1)S(2)Cr(2)	73.31(6)	Cr(1)S(2)Cr(2)	68.72(6)
Co(2)S(3)Cr(1)	72.50(6)	Co(2)S(3)Cr(2)	72.41(6)
Cr(1)S(3)Cr(2)	68.82(6)		

Table 6

Atomic coordinates (for Co, Cr and S×10^5, for C×10^4) for the cluster $(C_5H_5)_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(C_5H_5)_2$ (III)

Atom	*x*	*y*	*z*
Co(1)	13196(7)	49106(4)	18439(5)
Co(2)	10919(7)	70171(4)	8975(5)
Cr(1)	22461(8)	57758(5)	8142(5)
Cr(2)	17615(8)	63146(5)	21333(5)
S(1)	5371(12)	58904(8)	12729(9)
S(2)	27447(13)	69051(9)	12265(9)
S(3)	29052(13)	53622(9)	19358(10)
C(1)	1438(6)	3763(3)	1935(5)
C(2)	487(6)	3964(4)	1467(4)
C(3)	−157(6)	4335(4)	1986(4)
C(4)	391(6)	4365(4)	2684(4)
C(5)	1388(7)	4016(4)	2603(5)
C(6)	723(5)	8140(3)	938(4)
C(7)	1118(6)	7972(4)	207(4)
C(8)	404(6)	7459(4)	−122(4)
C(9)	−423(5)	7313(3)	401(4)
C(10)	236(6)	7723(4)	1060(4)
C(11)	2382(8)	5925(4)	−425(4)
C(12)	3435(6)	5805(4)	−136(4)
C(13)	3436(6)	5095(4)	186(4)
C(14)	2410(7)	4791(4)	81(4)
C(15)	1766(6)	5304(4)	−297(4)
C(16)	1019(7)	7194(4)	2840(4)
C(17)	2122(7)	7178(4)	2983(4)
C(18)	2405(6)	6519(4)	3295(4)
C(19)	1472(8)	6100(4)	3354(4)

Table 7

Bond lengths (Å) in the cluster $(C_5H_5)_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(C_5H_5)$ (III)

Co(1)–Cr(2)	2.658(1)	Co(1)–Cr(1)	2.657(1)
Co(1)–S(1)	2.262(2)	Co(1)–S(3)	2.136(2)
Co(1)–$S_{C_5H_5}$ (av.)	2.110(7)	Co(2)–Cr(1)	2.675(1)
Co(2)–Cr(2)	2.651(1)	Co(2)–S(1)	2.258(2)
Co(2)–S(2)	2.139(2)	Co(2)–$C_{C_5H_5}$ (av.)	2.119(7)
Cr(1)–Cr(2)	2.585(1)	Cr(1)–S(1)	2.276(2)
Cr(1)–S(2)	2.262(2)	Cr(1)–S(3)	2.261(2)
Cr(2)–S(1)	2.276(2)	Cr(2)–S(2)	2.274(2)
Cr(2)–S(3)	2.263(2)		

$(C_5H_5)(C_5H_4CMe_3)Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$ (II)

A solution of 1.26 g (3.68 mmol) of $Co_2(CO)_8$ in 30 ml of benzene was added to 1.54 g (1.84 mmol) of $[(C_5H_5)_2Cr_2(\mu\text{-}CMe_3)S_2]_2Ni$ in 50 ml of benzene, the reaction mixture was kept for 1.5 h at 45 °C. After filtration, to the resulting brown solution was added 10 ml of heptane and the solution was evaporated to 10 ml at 40 °C/torr and kept at −5 °C for 2 h. The fine crystalline precipitate of $(C_5H_5)_2Cr_2S_3Co_2(CO)_4$ (I) was separated from the solution and the filtrate was kept at −18 °C for 3 d. The precipitated large brown prisms of III were separated

Table 8

Bond angles (°) in the cluster $(C_5H_5)_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(C_5H_5)_2$ (III)

Cr(1)Co(1)Cr(2)	58.22(3)	Cr(1)Co(1)S(1)	54.42
Cr(1)Co(1)S(3)	55.00(5)	Cr(2)Co(1)S(1)	54.40(5)
Cr(2)Co(1)S(3)	55.06(5)	S(1)Co(1)S(3)	97.23(7)
Cr(1)Co(2)Cr(2)	58.08(3)	Cr(1)Co(2)S(1)	54.17(5)
Cr(1)Co(2)S(2)	54.69(5)	Cr(2)Co(2)S(1)	54.54(5)
Cr(2)Co(2)S(2)	55.46(5)	S(1)Co(2)S(2)	97.28(7)
Co(1)Cr(1)Co(2)	103.31(4)	Co(1)Cr(1)Cr(2)	60.90(3)
Co(1)Cr(1)S(1)	53.91(5)	Co(1)Cr(1)S(2)	115.90(5)
Co(1)Cr(1)S(3)	50.71(5)	Co(2)Cr(1)Cr(2)	60.50(3)
Co(2)Cr(1)S(1)	53.53(5)	Co(2)Cr(1)S(2)	50.50(5)
Co(2)Cr(1)S(3)	115.21(6)	Cr(2)Cr(1)S(1)	55.39(5)
Cr(2)Cr(1)S(2)	55.48(5)	Cr(2)Cr(1)S(3)	55.20(5)
S(1)Cr(1)S(2)	93.33(7)	S(1)Cr(1)S(3)	93.35(7)
S(2)Cr(1)S(3)	85.63(7)	Co(1)Cr(2)Co(2)	103.94(4)
Co(1)Cr(2)Cr(1)	60.88(3)	Co(1)Cr(2)S(1)	53.90(5)
Co(1)Cr(2)S(2)	115.42(6)	Co(1)Cr(2)S(3)	50.68(5)
Co(2)Cr(2)Cr(1)	61.41(3)	Co(2)Cr(2)S(1)	53.89(5)
Co(2)Cr(2)S(2)	50.77(5)	Co(2)Cr(2)S(3)	116.02(6)
Cr(1)Cr(2)S(1)	55.40(5)	Cr(1)Cr(2)S(2)	55.02(5)
Cr(1)Cr(2)S(3)	55.10(5)	S(1)Cr(2)S(2)	93.00(7)
S(1)Cr(2)S(3)	93.29(7)	S(2)Cr(2)S(3)	85.27(7)
Co(1)S(1)Co(2)	135.42(8)	Co(1)S(1)Cr(1)	71.68(5)
Co(1)S(1)Cr(2)	71.70(5)	Co(2)S(1)Cr(1)	72.30(5)
Co(2)S(1)Cr(2)	71.57(5)	Cr(1)S(1)Cr(2)	69.21(5)
Co(2)S(2)Cr(1)	74.81(6)	Co(2)S(2)Cr(2)	73.77(6)
Cr(1)S92)Cr(2)	69.50(6)	Co(1)S(3)Cr(1)	74.29(6)
Co(1)S(3)Cr(2)	74.26(6)	Cr(1)S(3)Cr(2)	69.70(6)

from the solution by decantation, washed with pentane and dried in vacuo. The yield was 0.20 g (9% relative to Q_2Ni). IR spectrum (ν, cm^{-1}): 470m, 485w, 495w, 535m, 820s, 840vs, 1020vw, 1070w, 1155w, 1270w, 1360w, 1440w, 1945vw, 1965s, 1985vs, 2005s, 2890–2960br w, 3080vw.

$(C_5H_5)_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(C_5H_5)_2$

A solution of 0.58 g (1.31 mmol) of $(C_5H_5)_2Cr(\mu\text{-}SCMe_3)_2$ (μ-S) (I) and 0.50 g (2.62 mmol) of $(C_5H_5)Co(C_5H_6)$ in 40 ml of toluene was refluxed for 8.5 h. The reaction mixture was cooled to room temperature, and the brown-green prisms, which precipitated from the solution, were recrystallized from a CH_2Cl_2/benzene mixture (5/1). The yield was 0.52 g (70%). Single crystals suitable for the X-ray study were obtained by the slow evaporation of the solvent, CH_2Cl_2, from a solution of the cluster. IR spectrum (ν, cm^{-1}): 790m, 810m, 995w, 1005w, 1040vw, 1060vw, 1105w, 1380w, 1410w, 2905vw, 3080vw.

$[(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Ni$

The reaction of $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ with $(COD)_2Ni$. The yellow-brown solution of 0.46 g (1.67 mmol) of $(COD)_2Ni$ (COD = cyclooctadiene) was added to the purple solution of 1.50 g (3.38 mmol) of $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ in 30 ml of benzene. The reaction mixture was refluxed for 1 h. The cherry-brown solution thus formed was chromatographed on a column packed with neutral Al_2O_3 (3 × 15 cm), the cherry-brown zone with $R_f \sim 0.75$ being eluted with benzene. The solution obtained was evaporated at 60 °C/10 torr to a volume of 10–15 ml, 10 ml of heptane was added and the solution was cooled to $-5\,°C$. The fine crystals that precipitated were isolated, washed with heptane and dried in vacuo. The yield was 0.62 g (43.9%). IR spectrum (ν, cm^{-1}): 665w, 802s, 815sh, 1008m, 1050w, 1155m, 1358m, 1390w, 1435m, 1430w, 2850w, 2905m, 2955m, 3080w.

Analysis. Found: C, 40.52; H, 4.29; S, 23.11. $C_{28}H_{38}Cr_4NiS_6$ calc: C, 40.34; H, 4.56; S, 23.05%.

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