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Antiferromagnetic complexes with metal–metal bonds

XXVI *. Synthesis, molecular structure and magnetic properties of mixed-metal triangular clusters, $Cp_2Cr_2(\mu\text{-}SR)(\mu_3\text{-}S)_2FeCp$ ($R = CMe_3$ or Ph), and linear mixed-metal chain $CpCr(\mu\text{-}SPh)_3Fe(\mu\text{-}SPh)_3CrCp$

S.E. Nefedov, A.A. Pasynskii, I.L. Eremenko, G.Sh. Gasanov, O.G. Ellert and V.M. Novotortsev

N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., Moscow 117907 (Russian Federation)

A.I. Yanovsky and Yu.T. Struchkov

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow 117813 (Russian Federation)

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Abstract

The antiferromagnetic triangular cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2FeCp$ (II) ($-2J = 520$ cm^{-1}) with a strongly bonded Cr_2Fe metal core (Cr–Cr 2.650(3), Cr–Fe 2.666(3) and 2.675(2) Å) was obtained by prolonged photochemical reaction of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (I) and $Cp_2Fe_2(CO)_4$ in THF. It was shown that thermal reaction between complex I and $Cp_2Fe_2(CO)_2(\mu\text{-}SPh)_2$ yields two clusters, diamagnetic triangular $Cp_2Cr_2(\mu\text{-}SPh)(\mu_3\text{-}S)_2FeCp$ (III) and antiferromagnetic metal chain $CpCr(\mu\text{-}SPh)_3Fe(\mu\text{-}SPh)_3CrCp$ (IV) (μ_{eff}. 5.29 (296 K) – 3.95 (77 K) μ_B). Complex III as well as II involves the strongly bonded metal core Cr_2Fe (Cr–Cr 2.637(3), Cr–Fe 2.644(3) and 2.672(3) Å), whereas the Fe–Cr bonds in the linear chain of IV are considerably elongated (up to 2.996(3) and 2.969(3) Å), which is in agreement with their reduced bond order (equal to 1/2).

1. Introduction

In previous work on the synthesis of heterometallic clusters we took advantage of the ability of the antiferromagnetic complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (I) to act as a ligand for the carbonyl complexes of Cr, Mo, W, Mn, Fe, Co, Rh, Ir, and Ni, and for the cyclopentadienylcarbonyls of V, Nb, and Mn. In the latter cases the carbonyl groups were substituted, whereas the M–Cp bonds remained intact [1]. In the present work we compare the transformations of I in photochemical reaction with $Cp_2Fe_2(CO)_4$, involving the Fe–Fe bond (2.49 Å [2]) and in thermal reaction with $Cp_2Fe_2(CO)_2(\mu\text{-}SPh)_2$, which has no Fe–Fe bonds, but has easily cleavable thiolate bridges.

2. Results and discussion

In earlier work, we observed how the prolonged photochemical reaction of an excess of the methylcyclopentadienyl analogue of I with $Cp_2Fe_2(CO)_4$ in refluxing toluene led to the rupture of all Fe–CO, Fe–Cp and Fe–Fe bonds with the formation of metallospirane cluster $[(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Fe$ [4]. Here we report the preparation in high yield of the triangular metal cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2FeCp$ (II), by UV-irradiation of a 2:1

Correspondence to: Dr. A.A. Pasynskii.

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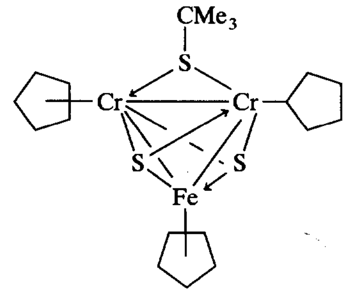
mixture of I and $Cp_2Fe_2(CO)_4$ in refluxing THF and its isolation as black-brown crystals.

$$\underset{\text{(I)}}{Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)} \xrightarrow[h\nu,\text{THF},64^{\circ}\text{C}]{Cp_2Fe_2(CO)_4}$$



(II)

According to the results of X-ray diffraction study (Fig. 1, Table 1) the cluster includes a strongly bonded metal core forming an almost equilateral triangle Cr_2Fe (Cr–Cr 2.650(3), Cr–Fe 2.666(3) and 2.675(3) Å) supported by two μ_3-sulphide bridges (Cr–μ_3-S 2.280(3)–2.285(3), Fe–μ_3-S 2.185(3) Å). The geometric characteristics of the dichromium moiety $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu\text{-}S)_2$ (Q) in II are very similar to those observed in other triangular metal clusters of the QML type [1]. At the same time the equality of both Cr–Fe bonds in the triangle of II reflects the difference between II and the electron rich $QFe(CO)_3$ cluster, where the corresponding bond lengths are 2.72 and 3.11 Å [1]. The Cr–Fe bonds are also non-equivalent in the above-mentioned heterometallospirane $[(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Fe$, which may be attributed to the steric influence of methyl substituents in the Cp-rings.

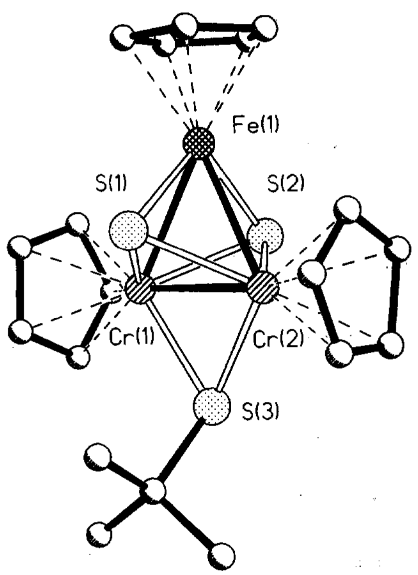


Fig. 1. Molecular structure of $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2FeCp$ (II).

TABLE 1. The main geometric parameters of triangular clusters $Cp_2Cr_2(\mu\text{-}SR)(\mu_3\text{-}S)_2FeCp$(R = CMe_3 (II); R = Ph (III))

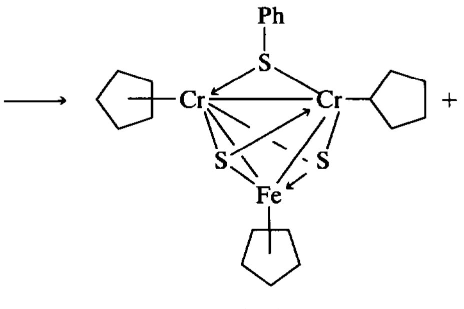
	II	III
Bond lengths (Å)		
Cr–Cr	2.650(3)	2.638(3)
Cr–Fe	2.666(3)	2.644(3)
	2.675(3)	2.671(3)
Cr–μ-SR	2.349(3)	2.344(3)
	2.351(3)	2.336(3)
Cr–μ_3–S	2.280(3)–2.285(3)	2.271(3)–2.293(3)
Fe–μ_3–S	2.185(3)	2.163(4)
	2.186(3)	2.186(4)
S–C(R)	1.875(5)	1.75(2)
Bond angles (°)		
Cr(μ-SR)Cr	68.6(1)	68.6(1)
Cr(μ_3-S)Cr	70.9(1)	70.4(1)
		70.9(1)
Fe(μ_3-S)Cr	73.2(1)–73.6(1)	72.7(1)–73.7(1)
$Cr_2S(R)$/S-C	33.3	27.7

The equality of both Cr–Ce and both Fe–S bond lengths in II results in the parallel disposition of the Cr–Cr bond in respect to the Cp ligand, which is strongly and quite symmetrically coordinated by the Fe atom (Fe–C 2.071(6)–2.115(6) Å). Such disposition is especially interesting in view of the analogy between the Cp- and 5e-donating Q-ligand, suggested in our earlier paper [5]. Within the framework of this analogy complex II represents the analogue of the ferrocene. It is also worth mentioning that complex II and ferrocene have remarkably similar electrochemical characteristics and undergo reversible 1e-oxidation at one and the same potential (0.53 and 0.50 V respectively, Pt-electrode in MeCN solution with $Et_4N^+BF_4^-$ as electrolyte).

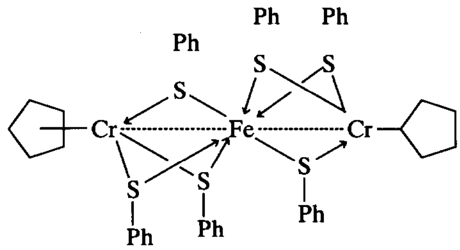
Along with other clusters involving the antiferromagnetic moiety Q, cluster II is antiferromagnetic. Its effective magnetic moment decreases from 1.15 to 0.64 μ_B on decrease of temperature from 295 to 77 K, which may be rationalized within the concept of the dimeric Heisenberg–Dirac–van Vleck (HDVV) model with the exchange parameter $-2J = 520$ cm^{-1}. This parameter is noticeably different from that observed for the starting complex I ($-2J = 430$ cm^{-1}) [6], which indicates significant contribution of exchange interactions *via* Cr–Fe–Cr bridge, which adds to the direct Cr–Cr interaction and indirect exchange *via* sulphide and thiolate bridges.

The reaction between equimolar quantities of I and $Cp_2Fe_2(CO)_2(\mu\text{-}SPh)_2$ proceeds in refluxing toluene even without UV-irradiation. In this case profound rearrangement of both complexes occurs and two trinuclear complexes of different structures result: the diamagnetic triangular cluster $Cp_2Cr_2(\mu\text{-SPh})(\mu_3\text{-S})_2FeCp$ (**III**) and the antiferromagnetic linear metal chain $CpCr(\mu\text{-SPh})_3Fe(\mu\text{-SPh})_3CrCp$ (**IV**):

$$Cp_2Cr_2(\mu\text{-SCMe}_3)_2(\mu\text{-S}) + Cp_2Fe_2(CO)_2(\mu\text{-SPh})_2 \xrightarrow[110°C]{\text{toluene}}$$



(**III**)



(**IV**)

The brown needles of **III** and dark-brown prisms of **IV** were isolated by fractional crystallization. X-Ray diffraction study (Fig. 2, Table 1) has shown that the main geometric features of the $Cr_2Fe(\mu_3\text{-S})_2(\mu\text{-SPh})$ core in **III** are very close to those for the same moiety in the tert-butylthiolate cluster **II**. Thus, strong M–M

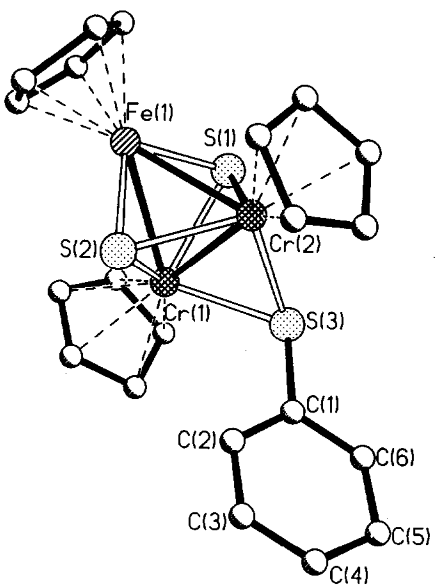


Fig. 2. Molecular structure of $Cp_2Cr_2(\mu\text{-SPh})(\mu_3\text{-S})_2FeCp$ (III).

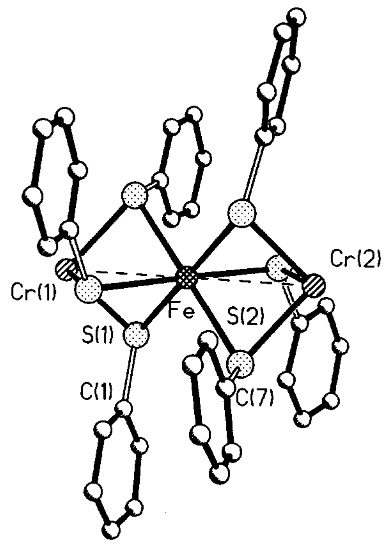


Fig. 3. Molecular structure of $CpCr(\mu\text{-SPh})_3Fe(\mu\text{-SPh})_3CrCp$ (IV). Disordered Cp-ligands are omitted.

and M–μ_3-S bonding is observed in **III** (Cr–Cr 2.637(3); Cr–Fe 2.644(3) and 2.672(3) Å, Cr–S 2.271(4)–2.291(4), Fe–μ_3-S 2.165(4) and 2.184(4) Å)). The only significant difference between the structures **II** and **III** is the elongation of the S–C(CMe$_3$) bond in **II** (1.875(5) Å) as compared to the S–C(Ph) bond in **III** (1.74(2) Å); it is also noteworthy that the latter is less inclined to the Cr_2S plane (by 27.7°) in comparison to the S–C(CMe$_3$) (33.3°) in **II**. By analogy with the data on the hydroxy- and alkoxy-bridged copper complexes [7], a somewhat more planar structure of the Cr_2SC_{Ph} moiety is evidently favourable for the enhancement of the exchange interactions between the paramagnetic centres. One may suppose that it is just this difference in the degree of planarity which is responsible for the different magnetic properties of complexes **II** (antiferromagnetic) and **III** (diamagnetic), whose cluster frameworks have otherwise quite similar structural characteristics.

The second product of the reaction between **I** and $Cp_2Fe_2(CO)_2(\mu\text{-SPh})_2$, cluster **IV**, exhibits the molecular ion peak in the mass-spectrum ($m/z = 944$), corresponding to the Cr_2Fe metal core coordinated by two cyclopentadienyl and six thiophenolate ligands. According to the X-ray diffraction study (Fig. 3, Table 2) the Cp ligands coordinated by the Cr atoms are disordered which makes it quite difficult to locate all of their C atoms (indeed, only two out of five carbon atoms in each Cp-ring were objectively located). The central Fe^{II} atom in the strictly linear group CrFeCr, which occupies a special position on the three-fold axis, is linked with each Cr^{III} atom by means of three SPh bridges, which form an octahedral environment for the Fe atom (Fe–S 2.511(8) and 2.515(8) Å; Cr–S 2.350(7) and 2.383(8) Å; Fe–S–Fe 75.2(2) and 75.4(2)°;

TABLE 2. The main geometric parameters of chain cluster $CpCr(SPh)_3Fe(SPh)_3CrCp$ (**IV**)

Bond lengths (Å)			
Fe–Cr(1)	2.969(3)	Cr(1)–S(1)	2.350(7)
Fe–Cr(2)	2.996(3)	Cr(2)–S(2)	2.383(8)
Fe–S(1)	2.511(8)	S(1)–C(1)	1.77(3)
Fe–S(2)	2.515(8)	S(2)–C(7)	1.81(3)
Bond angles (°)			
Cr(1)FeCr(2)	180.0(2)	S(1)FeS(2)	97.3(2)
Cr(1)FeS(1)	49.9(2)	FeCr(1)S(1)	54.8(2)
Cr(2)FeS(1)	130.1(2)	FeCr(2)S(1)	54.3(3)
Cr(1)FeS(2)	129.7(2)	FeS(1)Cr(2)	75.2(2)
Cr(2)FeS(2)	50.3(2)	FeS(2)Cr(2)	75.4(2)

S–Fe–S 97.3°). The Cr–Fe (2.969(3) and 2.996(3) Å) bonds are considerably elongated as compared to those found in clusters **II** and **III**. This elongation is possibly due to the interaction between the occupied d_{z^2}-orbital of the Fe^{II} atom and two half-occupied d_{z^2}-orbitals of the Cr^{III} ions with the formation of a conventional three-centre linear bond involving bonding, non-bonding and antibonding orbitals. In this system only two out of four electrons occupy the bonding orbital and the other two occupy the non-bonding orbital. It leads to the 0.5 bond order of each of the Fe–Cr bonds. Complex **IV** is antiferromagnetic, its effective magnetic moment decreasing from 5.29 to 3.95 μ_B in the temperature range from 296 to 77 K.

3. Experimental details

All operations including the synthesis of initial and final compounds were carried out in pure argon in absolute solvents. $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**I**) and $Cp_2Fe_2(CO)_2(\mu\text{-}SPh)_2$ were prepared according to refs. 6 and 3, respectively. IR-spectra in KBr pellets were recorded with a Specord 75IR instrument. Magnetic susceptibility was measured by the Faraday method [8].

TABLE 3. Crystal data for the clusters $Cp_2Cp_2(SR)(S)_2FeCp$ (R = CMe_3 (**II**); R = Ph (**III**)) and $CpCr(SPh)_3Fe(SPh)_3CrCp$ (**IV**)

	II	III	IV
Crystal system	Monoclinic	Monoclinic	Cubic
Space group	$P2_1/c$	$P2_1/n$	$Pa3$
a (Å)	13.987(4)	10.251(2)	20.465(2)
b (Å)	9.769(2)	13.661(3)	20.465(2)
c (Å)	14.712(5)	14.834(3)	20.465(2)
β (°)	94,35(2)	95,00(3)	90
V (Å^3)	2006.8(2)	2069.5(7)	8571.1(2)
Z	4	4	8
Number of refl. $I > 4\sigma(I)$	3291	1443	5824
R_1	0.044	0.067	0.088
R_w	0.043	0.063	0.096

TABLE 4. Atom coordinates ($\times 10^4$) for the cluster $Cp_2Cr_2(SCMe_3)(S)_2FeCp$ (**II**)

Atom	x	y	z
Fe(1)	8710(1)	2325(1)	1038(1)
Cr(1)	7653(1)	111(1)	638(1)
Cr(2)	7195(1)	2476(1)	−155(1)
S(1)	8598(1)	1317(1)	−290(1)
S(2)	7219(1)	2057(1)	1371(1)
S(3)	6237(1)	502(1)	−265(1)
C(1)	6126(4)	−378(5)	−1399(3)
C(2)	5862(4)	−1881(6)	−1224(4)
C(3)	5277(4)	306(7)	−1915(4)
C(4)	7021(4)	−272(6)	−1916(4)
C(11)	9969(4)	3421(7)	891(4)
C(12)	9369(4)	4195(6)	1416(4)
C(13)	9203(4)	3416(7)	2215(4)
C(14)	9703(4)	2176(6)	2169(4)
C(15)	10170(4)	2159(6)	1341(4)
C(21)	7440(4)	−1317(5)	1809(3)
C(22)	8444(4)	−1007(5)	1804(4)
C(23)	8772(4)	−1495(5)	967(4)
C(24)	7984(4)	−2088(5)	457(4)
C(25)	7166(4)	−1993(5)	973(4)
C(31)	6053(5)	3940(7)	−628(6)
C(32)	6548(5)	3634(7)	−1351(4)
C(33)	7457(7)	3997(8)	−1264(6)
C(34)	7619(6)	4589(7)	−474(7)
C(35)	6760(7)	4602(6)	27(4)

TABLE 5. Atom coordinates ($\times 10^4$) for cluster $Cp_2Cr_2(SPh)(S)_2FeCp$ (**III**)

Atom	x	y	z
Fe(1)	1482(2)	989(2)	6775(1)
Cr(1)	4065(2)	777(2)	6720(1)
Cr(2)	2719(2)	1889(2)	5518(1)
S(1)	2405(4)	242(3)	5712(2)
S(2)	2937(4)	2147(3)	7042(2)
S(3)	4865(4)	1349(3)	5391(2)
C(24)	1143(19)	2982(15)	5250(11)
C(25)	846(16)	2197(12)	4668(11)
C(35)	−388(20)	384(23)	6541(14)
C(34)	−532(20)	1346(24)	6780(23)
C(14)	6033(17)	484(20)	7392(18)
C(32)	663(20)	563(24)	7945(14)
C(22)	2809(18)	2859(17)	4338(14)
C(15)	5483(29)	−432(23)	6968(13)
C(13)	5209(25)	735(15)	8037(13)
C(33)	153(26)	1435(19)	7706(23)
C(23)	2346(21)	3426(12)	5061(13)
C(21)	1867(19)	2112(13)	4112(10)
C(31)	345(20)	−128(14)	7241(18)
C(12)	4256(23)	64(22)	8071(14)
C(11)	4424(29)	−641(14)	7421(20)
C(6)	6833(15)	2452(11)	4861(11)
C(1)	5946(14)	2338(11)	5523(9)
C(5)	7737(18)	3210(14)	4874(12)
C(4)	7677(17)	3904(13)	5600(15)
C(2)	5990(16)	2991(13)	6230(12)
C(3)	6832(20)	3769(15)	6263(14)

TABLE 6. Atom coordinates ($\times 10^4$) for the cluster $CpCr(SPh)_3Fe(SPh)_3CrCp$ (IV)

Atom	x	y	z
Fe	−1906(2)	3094(2)	1906(2)
Cr(1)	−2743(2)	2256(2)	2743(2)
Cr(2)	−1061(2)	3939(2)	1061(2)
S(1)	−1805(4)	1904(4)	2184(3)
S(2)	−718(3)	3385(4)	2026(4)
C(1)	−1124(14)	1693(14)	2677(13)
C(2)	−944(15)	2030(15)	3194(16)
C(3)	−395(21)	1899(20)	3588(17)
C(4)	11(17)	1399(19)	3397(17)
C(5)	−151(16)	1018(16)	2833(15)
C(6)	−739(13)	1189(13)	2477(15)
C(7)	−454(14)	3954(12)	2648(11)
C(8)	−878(13)	4454(14)	2841(15)
C(9)	−637(14)	4877(14)	3364(14)
C(10)	−6(14)	4797(14)	3621(14)
C(11)	348(13)	4281(13)	3371(12)
C(12)	155(13)	3844(13)	2896(13)
C(1)p	−3659(24)	2262(23)	3415(27)
C(2)p	−2940(23)	1268(20)	3162(27)
C(3)p	−805(32)	4953(22)	743(33)
C(4)p	−1014(22)	4706(32)	266(31)

X-Ray structural data were obtained with automatic Siemens P3/PC diffractometer (λ(Mo Kα)), $\lambda = 0.71069$ Å, $\theta/2\theta$ scan, $\theta \leq 56°$) at −100°C for **II** and at room temperature for **III** and **IV**. Crystal data are listed in Table 3. The structures were solved by the direct method and refined in full-matrix least-squares in the anisotropic approximation for all non-hydrogen atoms (the C atoms of the Cp ligand in complex **IV** were refined isotropically). All calculations were carried out with the help of the SHELXTL-PC program package. Atomic coordinates are listed in Tables 4–6.

3.1. $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2FeCp$ (II)

A solution of 0.60 g (1.36 mM) $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (I) and 0.24 g (0.68 mM) of $Cp_2Fe_2(CO)_4$ in 35 ml of refluxing THF was irradiated by UV light (PRK-4 lamp) for 15 h up to the complete vanishing of the CO bands from the IR spectrum. The filtered solution was then concentrated to 10 ml at 35°C/0.1 torr, treated by 10 ml of heptane and cooled to −5°C. After standing for a day the precipitate of large black-brown crystals was removed from the mother liquor, washed in cool heptane and dried *in vacuo*. The yield was 0.38 g (55%). IR-spectrum (ν, cm^{-1}): 550w, 795s, 806s, 985m, 1005m, 1050w, 1100w, 1115w, 1148s, 1350m, 1335w, 1425m, 1440m, 1530w, 1615w, 2850m, 2880m, 2945m, 3055 w.

3.2. $Cp_2Cr_2(\mu\text{-}SPh)(\mu_3\text{-}S)_2FeCp$ (III) and $CpCr(\mu\text{-}SPh)_3Fe(\mu\text{-}SPh)_3CrCp$ (IV)

A violet solution of 0.55 g (1.24 mM) of **I** and 0.64 g (1.24 mM) of $Cp_2Fe_2(CO)_2(\mu\text{-}SPh)_2$ in 25 ml of toluene was refluxed for 2 h until its colour changed to dark-brown. The solution was concentrated to 5 ml at 110°C in argon flow and cooled slowly to room temperature. Large dark-brown prisms of complex **IV** precipitated after standing for 12 h were isolated by decantation, washed with cool benzene and dried *in vacuo*. The yield of complex **IV** was 0.23 g. IR-spectrum (ν, cm^{-1}): 695vs, 750vs, 800s, 815s, 1020m, 1060w, 1080m, 1440m, 1460m, 1575m.

The mother liquor was evaporated to dryness, the brown residue was extracted in 10 ml of warm THF and concentrated to 5 ml at 40°C/0.1 torr, treated by 30 ml of pentane and left to stand at room temperature. On slow evaporation of the solvent after two days brown needle-shaped crystals were formed which were isolated by decantation, washed in cool hexane and dried *in vacuo*. The yield of complex **III** was 0.14 g. IR-spectrum (ν, cm^{-1}): 695vs, 750vs, 800m, 810s, 1090m, 1440s, 1490m, 1560w.

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