

# Variable temperature proton NMR study and reductively-induced isomerisation and degradation of $[\text{CpCr}(\text{CO})_2(\text{SPh})]_2$ . Crystal structure of $\text{Cp}_2\text{Co}[\text{CpCr}(\text{SPh})_3]$

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## Abstract

The presence of two major (1A and 1C) and one minor (1B) geometrical isomers of the complex  $[\text{CpCr}(\text{CO})_2(\text{SPh})]_2$  (1) in  $\text{CH}_2\text{Cl}_2$  has been observed in variable temperature NMR studies. A reversible one-electron reduction at  $-0.56$  V, as well as a quasi-reversible reduction, attributed to 1A and 1C, respectively, have been observed in electrochemical studies. Bulk chemical reduction of 1 by cobaltocene led to the isolation of  $\text{Cp}_2\text{Co}[\text{CpCr}(\text{CO})_3]$  (2) and  $\text{Cp}_2\text{Co}[\text{CpCr}(\text{SPh})_3]$  (3) in ca. 30% yields each. The compound 3 has been studied by X-ray diffraction analysis. Crystal data: black prisms, monoclinic, space group  $\text{P}2_1/n$  (#14),  $a = 16.225(5)$  Å,  $b = 10.576(3)$  Å,  $c = 19.99(1)$  Å,  $\beta = 113.49(4)^\circ$ ,  $Z = 4$ ,  $V = 3147(5)$  Å<sup>3</sup>.

**Keywords:** Cobalt; Chromium; Variable temperature NMR; Isomerisation; Electrochemistry; Crystal structure

## 1. Introduction

The chemistry of transition-metal thiolate compounds, which currently involves an expanding area of research activity, still remains largely unexplored, owing to inherent difficulties associated with the complexity of the structures and properties of the complexes. The keen interest in this area stems from the richness of the structural, bonding and reactivity features of the complexes [1,2], as well as their relevance to solid-state chemistry and materials science on the one hand, and biology on the other [3,4].

In the last two decades, the electrochemistry of di- $\mu$ -thiolato-bridged dinuclear complexes has come increasingly under study [5–18]. Large structural changes, often involving metal–metal bond formation or scission, are often induced by these electrochemical reactions, as demonstrated in studies on  $[\text{CpMo}(\text{CO})_2(\text{SPh})]_2$  [6,7] and its related complexes [6–13] or similar complexes of Mn [14], Ru [16], Fe [17] and Rh [18]. It was

therefore of interest to us to investigate the redox behaviour of the analogous complex  $[\text{CpCr}(\text{CO})_2(\text{SPh})]_2$  (1) and its partially decarbonylated derivative  $[\text{CpCr}(\text{CO})(\text{SPh})]_2$  (1A), that we have previously reported [19], as well as the Te analogue of 1 [20]. Herein are described the results, together with a variable temperature proton NMR study of 1.

## 2. Experimental

All reactions were carried out under an atmosphere of dry nitrogen. Isolation and purification procedures were performed under argon in a Vacuum Atmospheres Dribox equipped with a Model HE493 Dri-Train. IR spectra in Nujol mull were measured by means of a Perkin-Elmer 1330 instrument. Proton NMR spectra were scanned on a Varian VXR 300S spectrometer and referenced to residual non-deutero solvent. Cyclic voltammograms were obtained using a Princeton Applied Research 173 potentiostat. Elemental analyses were performed by the Analytical Unit of the Research School of Chemistry, Australian National University, except for

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Cr, which was analysed as  $\text{CrO}_4^{2-}$  [21] in our own laboratory.

Solvents were distilled from sodium benzophenone ketyl (THF and ether) and calcium hydride ( $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$ ), and  $\text{CH}_2\text{Cl}_2$  was degassed prior to use in electrochemical studies. The chromium complexes were synthesised as described [19,20]. Cobaltocene  $\text{Cp}_2\text{Co}$  was prepared according to published procedures [22].

## 2.1. Reaction of $[\text{CpCr}(\text{CO})_2(\text{SPh})_2]$ (1) with $\text{Cp}_2\text{Co}$

### 2.1.1. Using 1:2 molar equivalent of 1: $\text{Cp}_2\text{Co}$

To an orange–brown solution of 1 (50 mg, 0.09 mmol) in THF (3 ml) was added a brown solution of  $\text{Cp}_2\text{Co}$  (33 mg, 0.18 mmol) in THF (5 ml) and the mixture stirred at ambient temperature. There was a gradual colour change to green within 5 min, accompa-

**Table 1**  
Data collection and processing parameters

<i>Crystal data</i>	
Empirical formula	$\text{CoCrC}_{33}\text{H}_{30}\text{S}_3$
Formula weight	633.71
Crystal color, habit	black, prism
Crystal dimensions ( $\text{mm}^3$ )	$0.26 \times 0.13 \times 0.13$
Crystal system	monoclinic
No. reflections used for unit cell determination ( $2\theta$ range)	25 ( $13.6^\circ$ – $24.7^\circ$ )
$\omega$ -Scan peak width at half-height	0.33
Lattice parameters	$a = 16.225(5) \text{ \AA}$ $b = 10.576(3) \text{ \AA}$ $c = 19.99(1) \text{ \AA}$ $\beta = 113.49(4)^\circ$ $V = 3147(5) \text{ \AA}^3$
Space group	$P2_1/n$ (No. 14)
Z value	4
$D_{\text{calc}}$	$1.34 \text{ g cm}^{-3}$
$F_{000}$	1338
$\mu(\text{Mo K}\alpha)$	$10.74 \text{ cm}^{-1}$
<i>Intensity measurements</i>	
Diffractometer	Rigaku AFC6S
Radiation	Mo K $\alpha$ ( $\lambda = 0.71069 \text{ \AA}$ )
Temperature	$22^\circ\text{C}$
Take-off angle	$6.0^\circ$
Detector aperture	6.0 mm horizontal, 6.0 mm vertical
Crystal to detector distance	40 cm
Scan type	$\omega$ -2 $\theta$
Scan rate	$8^\circ \text{ min}^{-1}$ (in $\omega$ )
Scan width	$(1.73 + 0.30 \tan \theta)^\circ$
$2\theta_{\text{max}}$	$51.4^\circ$
No. of reflections measured	total 6141, unique 5903 ( $R_{\text{int}} = 0.091$ )
Corrections	Lorentz-polarization, absorption (trans. factors 0.85–1.15), decay (–5.8% decline)
<i>Structure solution and refinement</i>	
Structure solution	heavy atom (Patterson)
Refinement	full-matrix least-squares
Function minimized	$\sum w( F_o  -  F_c )^2$
Least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p-Factor	0.01
Anomalous dispersion	all non-hydrogen atoms
No. observations ( $F_o^2 > 3\sigma(F_o^2)$ ) <sup>a</sup>	3166
No. variables	401
Residuals: $R$ , $R_w$	0.047; 0.048
Goodness of fit indicator	2.54
Max. shift/error in final cycle	0.18
Maximum peak in final difference map	$0.28 \text{ e \AA}^{-3}$
Minimum peak in final difference map	$-0.33 \text{ e \AA}^{-3}$

<sup>a</sup> Refs. [23,24].

nied by precipitation. After 30 min, the suspension was filtered to separate a brown precipitate (28 mg) from its green mother-liquor. Recrystallisation of the precipitate from CH<sub>3</sub>CN/ether at -20°C gave after 4 h deep brown needles of Cp<sub>2</sub>Co[CpCr(CO)<sub>3</sub>] (**2**) (24 mg, 0.061 mmol, 34.2% yield). Anal. Found: C, 55.05; H, 3.78; Co, 15.05; Cr, 13.33. C<sub>18</sub>H<sub>15</sub>CoCrO<sub>3</sub>. Calc.: C, 55.40; H, 3.87; Co, 15.11; Cr, 13.32%. IR (Nujol): ν(CO) 1880s, 1885s, 1755vsbr (cm<sup>-1</sup>). Concentration of the green mother-liquor to ca. 2 ml and overnight cooling at -20°C gave green crystals of Cp<sub>2</sub>Co[CpCr(SPh)<sub>3</sub>] (**3**) (35 mg, 0.055 mmol, 30.7% yield). Anal. Found: C, 62.96; H, 5.40; S, 14.26; Co, 8.96; Cr, 9.06, C<sub>33</sub>H<sub>30</sub>CrCoS<sub>3</sub>. Calc.: C, 62.55; H, 4.77; S, 15.18; Co, 9.31; Cr, 8.21%. IR (Nujol): ν 1909w, 1075wsh, 1030w, 1015w, 870w, 805m, 740m, 700m (cm<sup>-1</sup>).

### 2.1.2. Using 1 : 4 molar equivalent of 1 : Cp<sub>2</sub>Co

To an orange-brown solution of **1** (20 mg, 0.05 mmol) in THF (2 ml) was added a brown solution of Cp<sub>2</sub>Co (37 mg, 0.20 mmol) in THF (2 ml), and the mixture allowed to react for 1 h. Filtration gave a brown precipitate of **2** (12 mg, 0.030 mmol, 30.1% yield). The green filtrate was concentrated to dryness to give a brownish green mixture, which was extracted with hexane (ca. 5 ml) to give a brown solution of unreacted Cp<sub>2</sub>Co (dried residue, 14 mg) and a green residue which recrystallised from THF/ether to give green crystals of **3** (20 mg, 0.031 mmol, 31.3% yield).

## 2.2. Electrochemical studies

Cyclic voltammetric studies were carried out using a platinum working electrode, a platinum bar counter electrode and an Ag/AgCl reference for which the ferrocene/ferrocenium couple was measured at 0.55 V. Measurements were made under an atmosphere of nitrogen.

### 2.3. VT NMR studies

Measurements were made on 0.02 M solutions of **1** in CD<sub>2</sub>Cl<sub>2</sub> and toluene-*d*<sub>8</sub> in serum-capped 5 mm NMR tubes in the temperature range +30 to -90°C.

### 2.4. Crystal structure analysis

Diffraction-quality single crystals of **1** were obtained as black prismatic crystals from toluene-THF after three days at ambient temperature.

All measurements were made as previously described [23] using a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation on a crystal mounted on a glass fibre. Details of the crystal parameters, data collection and structure refinement are given in Table 1.

Based on the systematic absences and the successful

solution and refinement of the structure, the space group was determined to be *P*2<sub>1</sub>/*n*. Lorentz-polarization and absorption corrections were applied [25].

The two metal atoms were located from a 3D Patterson based on all data. This phased the data sufficiently to locate the other atoms from difference Fourier maps. Full-matrix least-squares refinement [26] was carried out using the TEXRAY [27] program set, giving unweighted and weighted agreement factors of:

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.47,$$

$$R_w = \left[ \frac{(\sum w(|F_o| - |F_c|)^2)}{\sum wF_o^2} \right]^{1/2} = 0.048$$

The standard deviation of an observation of unit weight was 2.54 [28]. The weighting scheme was based on counting statistics and included a factor *p* = 0.01 to downweight the intense reflections. Plots of  $\sum w(|F_o| - |F_c|)^2$  vs.  $|F_o|$ , reflection order in data collection  $\sin \theta/\lambda$ , and various classes of indices showed no unusual trends. Neutral atom scattering factors were taken from Cromer and Waber [29]. Anomalous dispersion effects were included in *F*<sub>calc</sub> [30]; the values of Δ*f*' and Δ*f*" were those of Cromer [31]. Positional parameters are given in Table 2.

## 3. Results and discussion

### 3.1. VT NMR studies

Proton NMR studies of **1** in CD<sub>2</sub>Cl<sub>2</sub> and toluene-*d*<sub>8</sub> show the appearance of additional Cp and S-phenyl proton resonances with decrease of temperature. These changes, which are reversible, suggest a structural rearrangement to equilibrium mixtures of isomers **1A**, **1B** and **1C**, the relative proportions of which have been estimated from the integrals of their Cp resonances. Table 3 gives the percentage population of these isomers in CD<sub>2</sub>Cl<sub>2</sub>, as well as the chemical shifts of their Cp resonance. The corresponding spectral changes are illustrated in Fig. 1, which shows clearly both the Cp and phenyl proton signals. The predominant isomer **1A** possesses phenyl proton resonances at δ 8.03 (d, *J* = 7.0 Hz) for the *ortho*-Hs of the aromatic ring, δ 7.61 (t, *J* = 7.6 Hz) for the *meta*-Hs and δ 7.41 (d, *J* = 7.6 Hz) for the *para*-H atom at 25°C, with a slight shift to δ 8.22, 7.66 and 7.53 respectively at -60°C. As the temperature was progressively lowered from 30 to -55°C, the percentage population of **1A** decreased, while that of **1C** increased and that of **1B** remained almost invariant. The isomers **1A** and **1C** appear in

Table 2  
Positional parameters and  $B_{\text{eq}}$  for 3

Atom	x	y	z	$B_{\text{eq}}$	Occupancy
Co	0.83575(6)	0.8585(1)	0.84647(5)	3.79(4)	
Cr	0.42683(7)	0.8053(1)	0.72464(6)	3.08(5)	
S(1)	0.5465(1)	0.9467(2)	0.7759(1)	4.14(9)	
S(21)	0.453(2)	0.799(2)	0.621(1)	4.4(5)	0.620
S(22)	0.445(3)	0.823(4)	0.608(2)	3.9(7)	0.380
S(31)	0.522(2)	0.630(3)	0.777(1)	2.9(4)	0.480
S(32)	0.513(2)	0.620(3)	0.758(1)	3.1(4)	0.520
C(11)	0.5731(4)	0.9704(7)	0.8684(4)	4.0(3)	
C(12)	0.5945(5)	1.0892(8)	0.8968(5)	6.0(4)	
C(13)	0.6203(8)	1.114(1)	0.9677(8)	9.5(7)	
C(14)	0.6244(7)	1.019(1)	1.0144(6)	9.1(7)	
C(15)	0.6025(5)	0.893(1)	0.9887(5)	7.1(5)	
C(16)	0.5764(5)	0.8730(8)	0.9140(5)	5.3(4)	
C(21)	0.3850(5)	0.9252(7)	0.5546(4)	4.3(4)	
C(22)	0.2975(6)	0.9040(9)	0.5095(5)	6.7(5)	
C(23)	0.2476(6)	1.004(1)	0.4580(5)	8.7(7)	
C(24)	0.308(2)	1.116(2)	0.459(1)	7.6(6)	0.620
C(24A)	0.266(2)	1.108(3)	0.448(2)	6.3(8)	0.380
C(25)	0.397(1)	1.127(2)	0.494(1)	9.8(7)	0.620
C(25A)	0.357(2)	1.135(3)	0.499(1)	5.1(6)	0.380
C(26)	0.4236(7)	1.035(1)	0.5464(5)	8.5(6)	
C(31)	0.4519(5)	0.4888(6)	0.7286(5)	4.2(4)	
C(32)	0.3938(5)	0.4830(7)	0.6546(5)	5.4(4)	
C(33)	0.3475(5)	0.373(1)	0.6269(5)	7.0(5)	
C(34)	0.3579(7)	0.268(1)	0.6712(8)	9.0(7)	
C(35)	0.4141(7)	0.273(1)	0.7426(7)	9.0(7)	
C(36)	0.4609(5)	0.3831(8)	0.7720(5)	6.0(4)	
C(41)	0.3362(5)	0.9194(8)	0.7610(5)	5.1(4)	
C(42)	0.2932(5)	0.902(1)	0.6877(5)	5.3(4)	
C(43)	0.2783(5)	0.773(1)	0.6767(5)	5.7(5)	
C(44)	0.3128(5)	0.7118(7)	0.7426(6)	5.3(4)	
C(45)	0.3501(5)	0.803(1)	0.7966(4)	5.0(4)	
C(51)	0.8280(6)	0.6698(7)	0.8284(5)	6.0(4)	
C(52)	0.7430(6)	0.725(1)	0.7994(5)	6.2(5)	
C(53)	0.7400(5)	0.814(1)	0.7483(4)	5.9(4)	
C(54)	0.8264(6)	0.8199(8)	0.7459(4)	5.5(4)	
C(55)	0.8785(5)	0.7276(9)	0.7952(5)	6.1(5)	
C(61)	0.8079(5)	0.9359(8)	0.9280(4)	5.2(4)	
C(62)	0.8942(6)	0.8863(8)	0.9552(4)	5.4(4)	
C(63)	0.9441(5)	0.9431(9)	0.9190(4)	5.6(4)	
C(64)	0.8889(6)	1.0317(7)	0.8707(4)	5.4(4)	
C(65)	0.8047(6)	1.0267(8)	0.8772(4)	5.5(4)	
C(71)	0.935(2)	1.075(5)	0.476(3)	14(3)	1/2
C(72)	0.938(4)	0.977(6)	0.440(4)	14(3)	1/2
C(73)	0.991(4)	0.896(5)	0.527(3)	9(1)	0.333
C(74)	0.926(7)	1.04(1)	0.429(5)	19(3)	0.333
C(75)	0.914(4)	0.940(7)	0.468(4)	10(2)	0.333
C(76)	1.040(4)	1.115(4)	0.525(3)	9(1)	0.333
C(77)	1.007(5)	1.074(6)	0.544(4)	11(1)	0.333
C(78)	0.962(4)	0.946(6)	0.544(3)	12(2)	0.333
H(12)	0.5911	1.1640	0.8622	6.5	
H(13)	0.6347	1.1992	0.9918	9.1	
H(14)	0.6360	1.0325	1.0634	8.2	
H(15)	0.6067	0.8107	1.0261	8.1	
H(16)	0.5590	0.7800	0.8936	6.4	
H(22)	0.2636	0.8240	0.5101	8.6	
H(23)	0.1708	0.9796	0.4191	8.6	
H(26)	0.4914	1.0573	0.5736	9.5	
H(32)	0.3918	0.5590	0.6250	5.5	
H(33)	0.3088	0.3649	0.5721	7.8	
H(34)	0.3260	0.1926	0.6535	9.0	
H(35)	0.4238	0.1985	0.7767	11.8	
H(36)	0.5025	0.3872	0.8251	8.7	

Table 2 (continued)

Atom	x	y	z	$B_{eq}$	Occupancy
H(41)	0.3533	1.0044	0.7881	5.4	
H(42)	0.2677	0.9688	0.6465	5.5	
H(43)	0.2433	0.7335	0.6256	6.3	
H(44)	0.3047	0.6180	0.7477	5.6	
H(45)	0.3782	0.7803	0.8499	5.8	
H(51)	0.8504	0.5935	0.8629	6.8	
H(52)	0.6856	0.7022	0.8070	7.4	
H(53)	0.6862	0.8708	0.7165	6.0	
H(54)	0.8459	0.8785	0.7115	6.3	
H(55)	0.9357	0.7059	0.7997	7.1	
H(61)	0.7569	0.9181	0.9438	6.4	
H(62)	0.9173	0.8253	0.9940	5.6	
H(63)	1.0059	0.9282	0.9279	5.8	
H(64)	0.9001	1.0955	0.8356	6.4	
H(65)	0.7499	1.0784	0.8437	6.2	

approximately equal proportions between  $-25$  and  $-55^\circ\text{C}$ . Below  $-65^\circ\text{C}$ , considerable broadening at the base of the solvent peak at  $\delta$  5.40 renders it difficult to estimate relative isomer abundance. While the resonances of the *ortho*-, *meta*- and *para*-protons of the phenyl rings in **1A** remain well-defined and resolved throughout the temperature range studied, those of **1C** are ill-defined, generally appearing as unresolved multiplets, centred for instance at  $\delta$  7.27 at  $-50^\circ\text{C}$ , and becoming broader on further lowering of the temperature. In scans below  $-50^\circ\text{C}$ , the phenyl proton resonances of **1B** are discernible on the shoulder of the broad resonance of **1C**; their pattern [doublet ( $\delta$  7.25  $J = 7.0$  Hz, *ortho*-Hs) and triplets ( $\delta$  7.17,  $J = 7.6$  Hz, *meta*-Hs;  $\delta$  7.09,  $J = 7.6$  Hz, *para*-H)] shows a striking resemblance to that of **1A**.

The occurrence of geometrical *cis/trans* isomers of such thiolato- and selenolato-bridged dimetallic com-

plexes has been frequently encountered [6,16,32–34]. On account of facile pyramidal inversion at the bridging chalcogen atoms, *syn/anti* conformers are also possible. With *cis* and *trans* referring to the disposition of the Cp rings with respect to each other, and *syn* and *anti* referring to the disposition of the phenyl groups with respect to the S...S vector, there are three possible conformers for both the *cis* and *trans* configurations, as shown in Fig. 2. Our previously-determined solid state molecular structure of **1**, possessing *trans* Cp rings and *trans* carbonyl ligands and the two S-phenyl groups in an axial-equatorial relationship [19], conforms to the *trans/anti* structure **IIA** in the figure; likewise we may assume that the **1A** isomer, the predominant form at ambient temperature in solution, possesses a similar *trans* configuration. The occurrence of conformers **IIIB** (*trans/syn* (2)) and **IIIC** (*cis/syn*(2)) is unlikely, owing to steric interactions of the phenyl rings,

Table 3  
Temperature-dependent percentage population <sup>a</sup> of isomers <sup>b</sup> of **1** present in  $\text{CD}_2\text{Cl}_2$

Temperature ( $^\circ\text{C}$ )	<b>1A</b>	<b>1B</b>	<b>1C</b>
30	95 (5.98)	5 (5.09)	<sup>c</sup>
20	84 (5.91)	4 (5.11)	12 (4.99)
0	70 (5.84)	3 (5.13)	27 (5.01)
$-25$	53 (5.82)	3 (5.17)	44 (5.02)
$-55$	43 (5.82)	5 (5.18)	52 (5.05)

<sup>a</sup> Determined from integrals of Cp resonances of VT  $^1\text{H}$  NMR spectra.

<sup>b</sup> Chemical shifts of Cp resonances (given in parentheses) are referenced to residual non-deutero solvent. In toluene- $d_6$ , the isomers **1A**, **1B** and **1C** possess chemical shifts in the range  $\delta$  4.83–5.16, 3.79–4.16 and 4.40–4.59 respectively, with percentage population approximately the same as in  $\text{CD}_2\text{Cl}_2$ .

<sup>c</sup> Not observed.

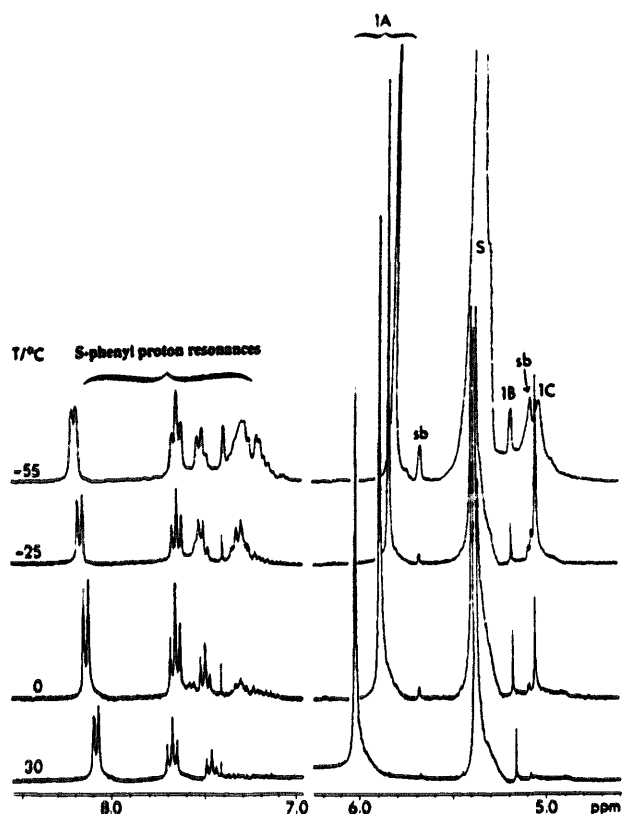


Fig. 1. Variable-temperature  $^1\text{H}$  NMR spectra of **1** in  $\text{CD}_2\text{Cl}_2$ ; isomers **1A**, **1B** and **1C**; S, solvent; sb, spinning side bands of solvent peak.

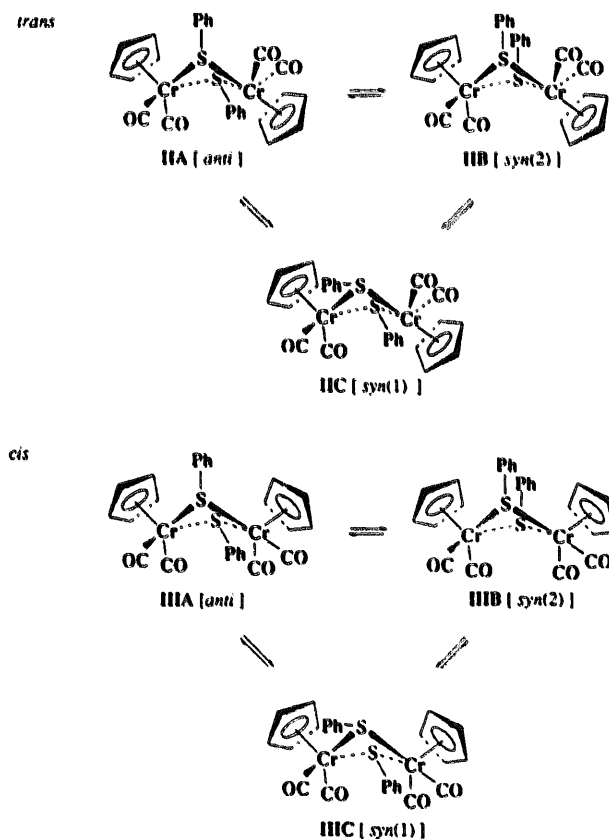
as observed for similar complexes of other transition metals. The conformer **II C** (*trans/syn(1)*) can be ruled out on the basis that neither the isomer **1B** nor **1C** is seen to possess inequivalent Cp resonances. That leaves **IIIA** (*cis/anti*) and **IIIC** (*cis/syn(1)*) as the probable isomeric forms. Of these, **IIIA** should show two sets of phenyl protons versus one set for **IIIC**. This would be in agreement with an assignment of structure **IIIA** for the isomer **1C**, wherein the observed broad unresolved nature of the phenyl proton signals results from the overlapping of two sets of resonances. The remaining probable structure **IIIC** then very likely pertains to the isomer **1B**. However, these assignments remain speculative. The overall results suggest the occurrence of *cis-trans* isomerisation for the system, though we had expected that the lower energy interconversions involving only Ph-group orientations would be more energetically favourable, as observed for similar Ru systems [16]. However, the steric course of the reaction will undoubtedly be influenced by the delicate balance between  $\text{Cp} \cdots \text{Cp}$ ,  $\text{Cp} \cdots \text{Ph}$  and  $\text{Ph} \cdots \text{Ph}$  interactions.

### 3.2. Electrochemical reduction

In 0.5 M  $(^n\text{Bu}_4\text{N})\text{PF}_6/\text{CH}_2\text{Cl}_2$  at 287 K, the complex **1** shows an electrochemically reversible one-electron

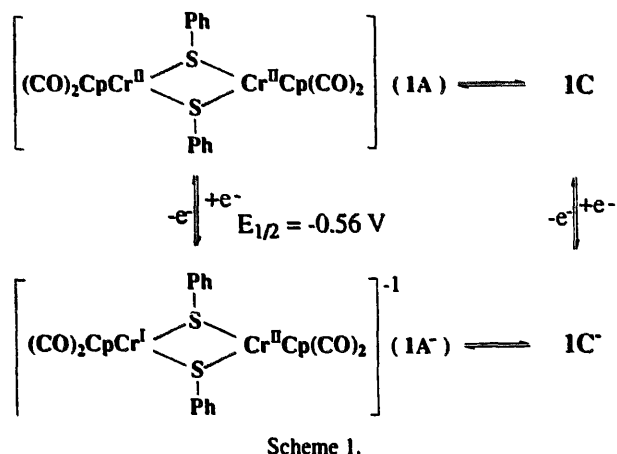
reduction at  $-0.56$  V. At faster scan rates a quasi-reversible process is distinguished (Fig. 3(a)), while the same effect is achieved by lowering the temperature (Fig. 3(b)). The anodic and cathodic peak potentials are separated by a difference of  $E_{p,a} - E_{p,c} = 0.060$  V at  $50 \text{ mV s}^{-1}$  scan rate and  $0.090$  V at  $500 \text{ mV s}^{-1}$  scan rate. These values are very close to the limit (57 mV) [35]. The quasi-reversible process is also centred at  $-0.56$  V, but with  $E_{p,a} - E_{p,c}$  increasing at lower temperature up to  $0.30$  V at 263 K, indicating a slower electron transfer rate. A further irreversible reduction at  $-1.25$  V generates a daughter process at  $-0.18$  V. Only an irreversible oxidation is observed at  $0.85$  V. A reversible one-electron reduction at  $-0.57$  V is observed in  $0.2 \text{ M } (^n\text{Bu}_4\text{N})\text{PF}_6/\text{C}_3\text{H}_7\text{CN}$ , but no other process is found at faster scan rates or at lower temperatures.

The electrochemical behaviour is represented in Scheme 1, wherein the species **1A** and **1C** conform to the structures **IIA** and **IIIA** respectively (Fig. 2), as discussed above. The one-electron reduction of **1A** at  $-0.56$  V produced the species **1A<sup>-</sup>**, which must undoubtedly be a mixed-valent dichromium(I,II) complex. In this connection, we note that the one-electron oxidation of the triply thiolato-bridged  $\text{Mn}(\text{CO})_6(\mu\text{-SPh})_3$



*cis* and *trans* refer to the disposition of the Cp ligands with respect to each other

Fig. 2. Possible geometric *cis/trans* and *syn/anti* isomers of complex **1** in solution.



Scheme 1.

complex had likewise produced a mixed-valent Mn(I,II) state [36]. The observations are consistent with the existence of a second process coupled to the first. As illustrated in the scheme, this second process is represented as an equilibrium of 1A with a species 1C. At 14°C, this quasi-reversible  $1\text{C} \rightleftharpoons 1\text{C}^-$  process is not observable as 1A is consumed at the electrode, owing to the fast  $1\text{A} \rightleftharpoons 1\text{C}$  equilibrium at this temperature. At lower temperatures, a slower equilibration allows the detection of the  $1\text{C}/1\text{C}^-$  redox couple. The large  $E_{p,a} - E_{p,c}$  separation indicates that the latter electrochemical process is accompanied by a structural rear-

angement, probably a geometrical isomerisation. Indeed, redox-initiated geometric rearrangement or isomerisation has been observed for a number of organic and inorganic systems [37]. In particular, the two-electron oxidation of the *trans* thiolato-bridged Mo analogue of 1 has effected a transformation to its *cis*-isomer [6,7]. The corresponding redox couple of 1B is apparently masked by the overlapping waves of 1A and 1C.

Similar studies demonstrate that the monocarbonyl and Te analogues of 1, i.e.  $[\text{CpCr}(\text{CO})(\text{SPh})_2]$  and  $[\text{CpCr}(\text{CO})_2(\text{TePh})_2]$  respectively, show no reversible electrochemistry.

### 3.3. Chemical reduction

Since the binuclear complex 1 shows a reversible one-electron reduction at  $-0.56$  V, we have utilised the one-electron reductant cobaltocene  $\text{Cp}_2\text{Co}$  (reduction potential  $-0.95$  V [38]) for the reduction of 1 in bulk. It was found that the reaction of an orange-brown solution of the compound with 2 or 4 molar equivalents of  $\text{Cp}_2\text{Co}$  resulted in a suspension of a brown precipitate of  $\text{Cp}_2\text{Co}[\text{CpCr}(\text{CO})_3]$  (2) in a green solution. A subsequent work-up involving filtration and crystallisation led to the isolation of 2 as brown crystals in 30–34% yield, and  $\text{Cp}_2\text{Co}[\text{CpCr}(\text{SPh})_3]$  (3) as green crystals in ca. 31% yield.

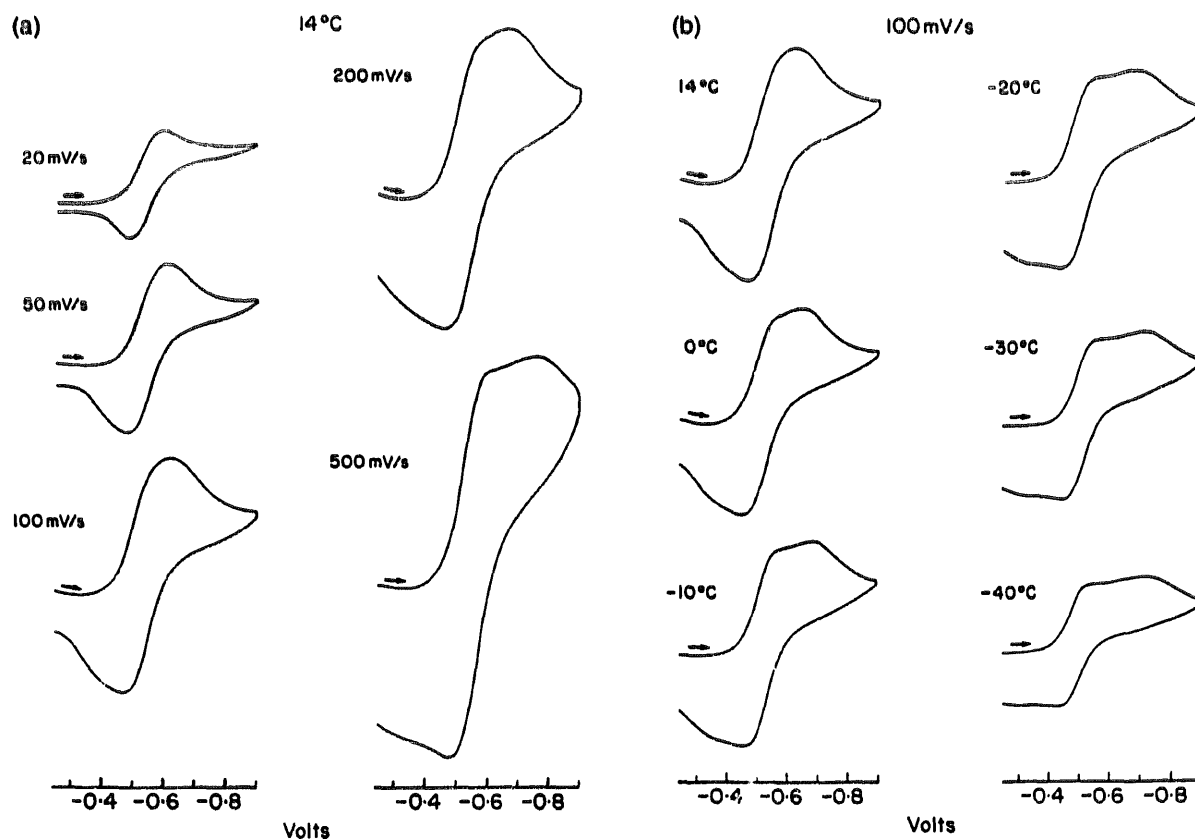


Fig. 3. Cyclic voltammograms of 1: (a) at 14°C and variable scan rate; (b) at variable temperature, 100  $\text{mV s}^{-1}$  scan rate.

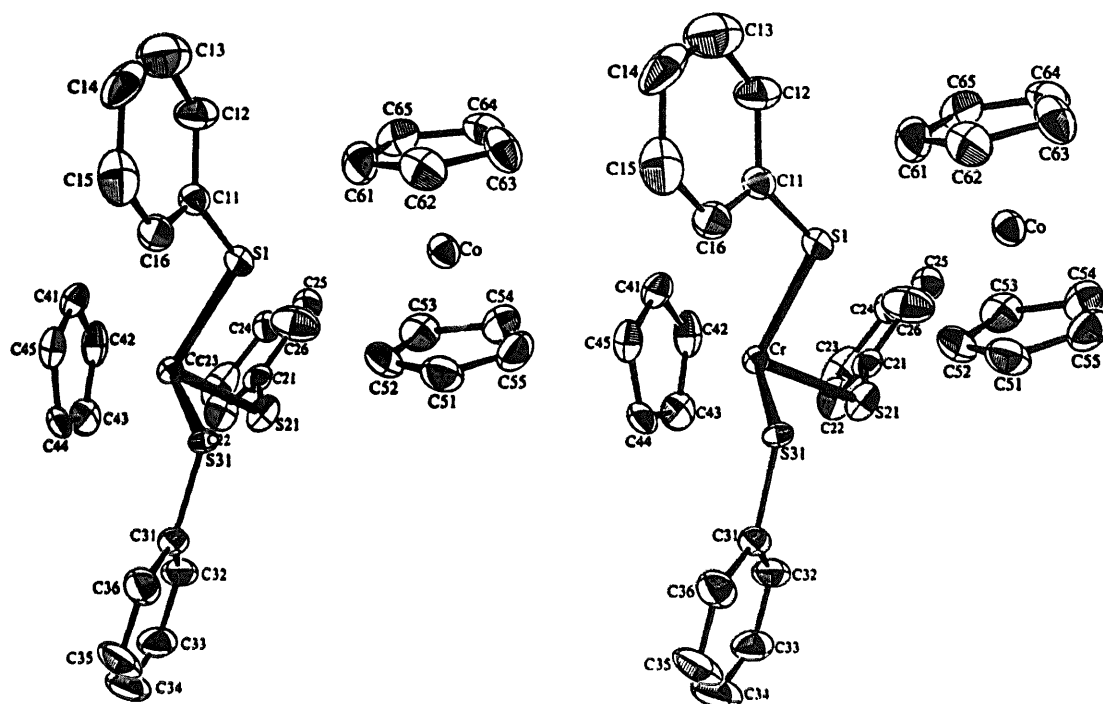


Fig. 4. Stereoview of complex 3.

Table 4  
Selected intramolecular distances (Å) and angles (deg) for 3

Atom	Atom	Distance	Atom	Atom	Distance
Co	Cp5 atoms	2.008(7)	Cr	S(32)	2.35(3)
Co	Cp6 atoms	2.010(7)	Cr	Cp4 atoms	2.242(7)
Co	Cp5 ring	1.619(8)	Cr	Cp4 ring	1.909(8)
Co	Cp6 ring	1.619(8)	S(1)	C(11)	1.743(8)
Cr	S(1)	2.339(2)	S(21)	C(21)	1.89(2)
Cr	S(21)	2.28(2)	S(22)	C(21)	1.56(3)
Cr	S(22)	2.48(4)	S(31)	C(31)	1.89(3)
Cr	S(31)	2.37(4)	S(32)	C(31)	1.67(3)

## Nearest intermolecular distances (Å)

C(62)	C(63)	3.35(1Xa)	C(63)	C(63)	3.25(1Xa)
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(a) Symmetry operation:  $2 - x, 2 - y, 2 - z$ 

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(51)	Co	C(61)	121.6(4)	S(22)	Cr	S(32)	93(1)
C(51)	Co	C(63)	123.2(4)	Cr	S(1)	C(11)	111.6(3)
C(52)	Co	C(62)	123.5(4)	Cr	S(21)	C(21)	110(1)
C(52)	Co	C(65)	122.3(4)	Cr	S(22)	C(21)	115(2)
C(53)	Co	C(61)	123.0(4)	Cr	S(31)	C(31)	104(1)
C(53)	Co	C(64)	122.6(4)	Cr	S(32)	C(31)	113(1)
C(54)	Co	C(63)	121.1(3)	S(1)	C(11)	C(12)	119.3(7)
C(54)	Co	C(65)	124.1(4)	S(1)	C(11)	C(16)	121.9(6)
C(55)	Co	C(62)	122.9(4)	S(21)	C(21)	C(22)	121(1)
C(55)	Co	C(64)	123.5(4)	S(21)	C(21)	C(26)	121(1)
S(1)	Cr	S(21)	89.5(8)	S(22)	C(21)	C(22)	123(2)
S(1)	Cr	S(22)	88(1)	S(22)	C(21)	C(26)	119(2)
S(1)	Cr	S(31)	91.6(7)	S(31)	C(31)	C(32)	126(1)
S(1)	Cr	S(32)	96.4(7)	S(31)	C(31)	C(36)	115(1)
S(21)	Cr	S(31)	92.9(8)	S(32)	C(31)	C(32)	117(1)
S(21)	Cr	S(32)	85.7(8)	S(32)	C(31)	C(36)	123(1)
S(22)	Cr	S(31)	100(1)				



Thus the reduced mixed valent Cr(I,II) dimeric species  $1A^-$  had given rise to a Cr(0) complex **2** and a Cr(III) complex **3**. It is probable that this could have resulted from the disintegration of  $1A^-$  to form the 15-electron Cr(I)  $CpCr(CO)_2$  and the 16-electron Cr(II)  $CpCr(SPh)_2$  moieties, followed by intermolecular ligand and scrambling. In this context, we observe that ligand exchange/substitution at paramagnetic metal centres has been reported to be much more facile than at diamagnetic centres [39–44]. It is noted that this secondary reaction is not featured in the voltammetric behaviour of **1**. This would suggest that it is much slower than the electrochemical reaction represented in Scheme 1.

### 3.4. Crystal structure

Fig. 4 gives an ORTEP [45] diagram for a stereoview of the molecule. The solid state structure shows a lattice consisting of two discrete ionic species,  $[Cp_2Co^{III}]^+$  and  $[CpCr^{III}(SC_6H_5)]^-$ . Selected intramolecular and intermolecular distances and bond angles are given in Table 4. The nearest Co–Cr separation is at 6.114(3) Å. Fig. 4 together with the dihedral angles between the least-squares planes of the Cp rings, i.e. 96.47° between the planes of Cp4 and Cp5 and 95.34° between the planes of Cp5 and Cp6, shows how this pair of ions approach each other with the Cp rings of the different metals being essentially orthogonal. The next nearest approach is 6.600(2) Å (from the Co–Cr of a cation transformed to  $1-x, -y, 1-z$ ). The shortest intermetallic approach between like ions is Co–Co at 6.483 Å (at  $1-x, 1-y, 1-z$  or  $1-x, -y, 1-z$ ).

In the anion sulphur atoms, two positions are possible with little change in the phenyl ring orientations. This possibility is realized for two of the S atoms which show two-fold positional multiplicity.

The Co–Cp(centroid) distances in the  $[CoCp_2]^+$  cation (1.62 Å) are shorter than that (1.73 Å) in the neutral cobaltocene molecule [46]. However, the  $[CpCr(SC_6H_5)_3]^-$  anion has a lengthened Cr–Cp separation (1.91 Å) compared with the neutral species **1** (1.861 Å, av.).

The complex **3** constitutes a new example of well-characterised homoleptic transition metal thiolates of the ionic type [1,2], wherein polymer formation has been prevented by its anionic character.

### 4. Supplementary material available

For  $[Cp_2Co][CpCr(SPh)_3]$  (**3**), structure factor tables (22 pages) and tables of  $U$  values, interatomic distances (Å), bond angles (deg) and least-squares planes.

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- $S$  = scan rate,  $C$  = total integrated peak count,  $R$  = ratio of scan time to background counting time,  $B$  = total background count,  $Lp$  = Lorentz-polarization factor, and  $p$  = p-factor.
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