

## Tuning the Interaction between Paramagnetic Metallocenes. Doubly Silyl-bridged Chromocenes

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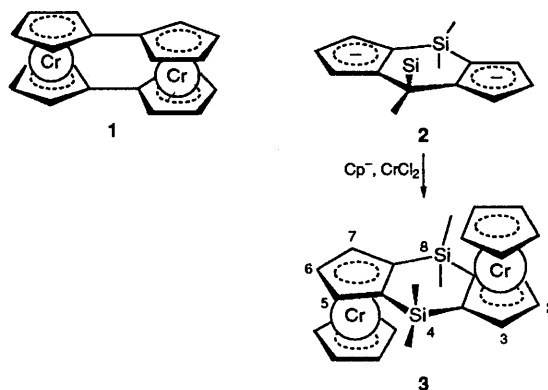
Doubly silyl-bridged cyclopentadienyl anion ( $L^{2-}$ ), chromium(II) chloride and cyclopentadienyl anion ( $Cp^-$ ) react to give the dinuclear chromocene  $CpCrLCrCp$  with a metal–metal distance of 5.831(1) Å (X-ray determination) that has magnetically probably isolated chromocene moieties (NMR, magnetic susceptibility) but which show interactions in cyclic voltammetry.

Extended interactions between metal ions<sup>1</sup> may be controlled by appropriate choice of the ligands, a task that is considerably facilitated when di-, tri-, or simple oligo-nuclear complexes can be used as model compounds. Examples are cooperative phenomena disclosed by the study of redox properties<sup>2</sup> or the design of magnetic properties.<sup>3</sup> Such properties should be of particular concern also for polymetallic arrays made up from paramagnetic metallocenes. However, nothing is known about a ligand-bridging approach (and metals other than iron<sup>4</sup>) as an alternative to stacked metallocenes.<sup>5</sup> The first example of a dinuclear model compound containing chromium is bis(fulvalene)dichromium **1**. Diamagnetism has been claimed for **1**,<sup>6</sup> but it is in fact strongly antiferromagnetic.<sup>7</sup> We now report on a compound where two  $Me_2Si$  groups function as spacers between two chromocenes.

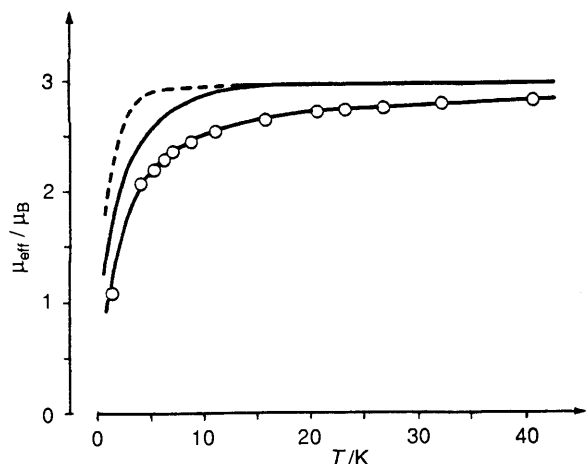
The silyl-bridged dianion **2**<sup>8</sup> was treated with cyclopentadienyl ( $Cp$ ) anion and chromium(II) chloride to form the dinuclear chromocene **3** (Scheme 1) which was isolated† by

fractional crystallization from hexane in 43% yield as dark-red air-sensitive needles.

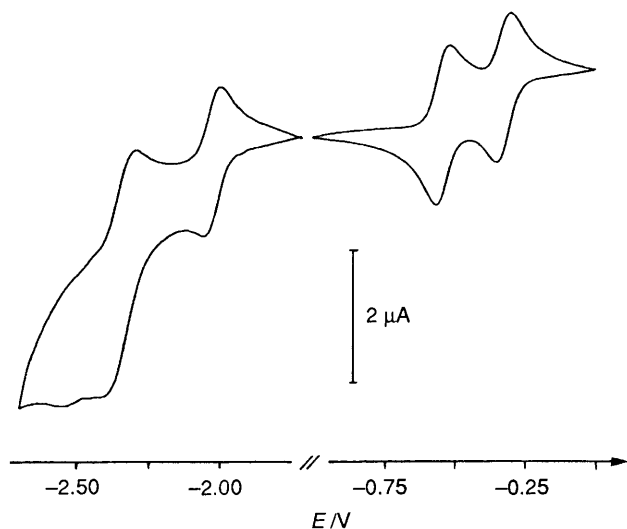
The NMR spectra show that **3** behaves like paramagnetic  $Cp_2Cr$  rather than like antiferromagnetic **1**. For instance, the NMR signals† of the terminal  $Cp$  of **3** appear at  $\delta(^1H)$  314 and  $\delta(^{13}C)$  –300 ppm, and those of  $Cp_2Cr^9$  at  $\delta(^1H)$  316.2 and  $\delta(^{13}C)$  –318.6 ppm (all at 298 K) whereas **1**<sup>7</sup> gives signals at



† A satisfactory elemental analysis was obtained for **3**. Selected spectroscopic data:  $^1H$  NMR (200 MHz,  $C_6D_5CD_3$ , 294.3 K)  $\delta$  317.6 (Cp), 259.4 (H-1/3), 211.6 (H-2) and –5.6 ( $CH_3$ ) ppm,  $\delta$  values relative to the signals of the analogous diiron derivative, shifts to high frequency are positive. EI mass spectrum,  $m/z$  (%) 476 (100)  $M^+$ , 410 (9)  $M^+ - Cp$ , 238 (14)  $M^{2+}$  and 117 (12)  $CpCr^+$ .



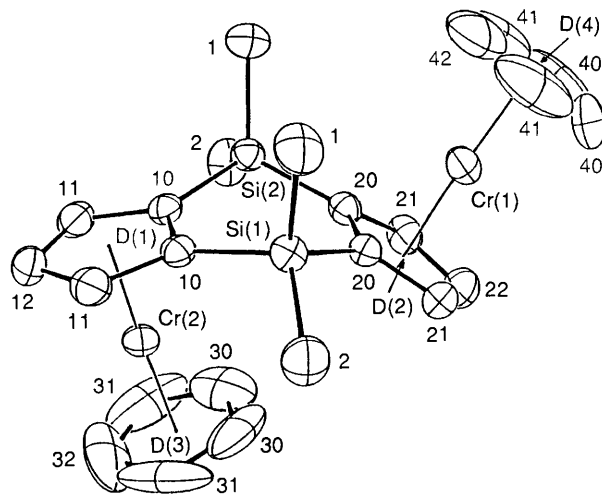
**Fig. 1** Temperature dependence of the effective magnetic moment per chromium for **3**. For comparison curves without experimental points are given for  $\text{Cp}_2\text{Cr}^{10a}$  (solid) and  $(\text{MeCp})_2\text{Cr}^{10b}$  (broken). Above 80 K all curves virtually coincide.



**Fig. 2** Cyclic voltammogram of **3** ( $7 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) in *n*-propionitrile; supporting electrolyte  $[\text{Bu}_4\text{NPF}_6]$  (0.1 mol  $\text{dm}^{-3}$ ); scan rate 200  $\text{mV s}^{-1}$ ;  $-20^\circ\text{C}$ ; potential vs.  $\text{Ag}/\text{AgCl}$

$\delta(^1\text{H})$  37.7 and 48.5 ppm at 287.6 K. The fact that the  $\delta$  values of **3** are somewhat smaller than those of  $\text{Cp}_2\text{Cr}$  may be attributed to slight antiferromagnetism and/or to changes in the dipolar signal shifts and in the spin delocalization. Therefore we have measured the magnetic susceptibility of **3** between 1.3 and 293.1 K and compared the temperature dependence of the effective magnetic moment ( $\mu_{\text{eff}}$ ) with that of  $\text{Cp}_2\text{Cr}^{10a}$  and  $(\text{MeC}_5\text{H}_4)_2\text{Cr}^{10b}$  (Fig. 1). There is a close similarity of all the curves which means that the magnetism of **3** may be explained in terms of a  $^3E_{2g}$  ground state from considerations of symmetry distortion, spin-orbit coupling, covalency and Jahn-Teller coupling as has been worked out previously.<sup>10b</sup> Thus, if there is any antiferromagnetic coupling operating in **3**, then it is small.

The interaction of the two chromocenes in **3** has also been studied by cyclic voltammetry (CV). Fig. 2 shows that each chromocene undergoes a separate oxidation (to give  $3^+$  and  $3^{2+}$ ) and reduction (to give  $3^-$  and  $3^{2-}$ ) resulting in two pairs of redox potentials  $E_{1/2}$ . Although the wave associated with the formation of  $3^{2-}$  is somewhat distorted by a parasite current it is clear that the influence of the neighbouring



**Fig. 3** Molecular structure of **3**. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{Cr}(2)\text{-D}(1)$  1.778,  $\text{Cr}(2)\text{-D}(3)$  1.806,  $\text{Cr}(1)\text{-D}(2)$  1.89,  $\text{Cr}(1)\text{-D}(4)$  1.804,  $\text{Si-C}(10)$  1.858(2),  $\text{Si-C}(20)$  1.856(3),  $\text{C}(1)\text{-Si-C}(2)$  107.7(1),  $\text{C}(10)\text{-Si-C}(20)$  104.0(1), plane  $\text{C}(10)$ ,  $\text{C}(11)$ ,  $\text{C}(12)$ -plane  $\text{C}(20)$ ,  $\text{C}(21)$ ,  $\text{C}(22)$  47.5; D is the centroid of the Cp rings.

chromocene anion is more pronounced [ $\Delta E_{1/2}(\text{red}) = 325$  mV] than that of the neighbouring chromocenium ion [ $\Delta E_{1/2}(\text{ox}) = 215$  mV] on the formation of  $3^{2+}$ . Experiments to clarify whether the effect is mainly due to a change in the solvation are under way. For the diiron compound analogous to **3**,  $\Delta E_{1/2}(\text{ox}) = 210$  mV,<sup>11</sup> *i.e.*, the same splitting of the oxidation potential within the error limits has been found. Hence the interaction between the metallocene units monitored by CV should be very similar for both metals. In fact, the NMR and magnetic data suggest that there is no magnetic exchange which could additionally influence the CV results of **3**.

In the solid state **3** possesses crystallographically $\ddagger$  imposed mirror symmetry, the mirror plane bisecting the bridging ligand and passing through atoms  $\text{Cr}(1)$ ,  $\text{Cr}(2)$ ,  $\text{C}(12)$ ,  $\text{C}(22)$ ,  $\text{C}(32)$  and  $\text{C}(42)$ . The  $\text{CrCp}$  fragments are bound to opposite faces of the bridging ligand. As Fig. 3 shows, one  $\text{CrCp}$  fragment [containing  $\text{Cr}(1)$ ] is bent away from the bridging  $\text{SiMe}_2$  groups, while the other is located closer to the midpoint of the ligand. This is clearly a consequence of the bent ligand

$\ddagger$  *Crystal structure data* for **3**: Enraf-Nonius CAD4 diffractometer,  $\text{Mo-K}\alpha$  radiation,  $\lambda = 0.71069$   $\text{\AA}$ , graphite monochromator,  $T = 23^\circ\text{C}$ .  $\text{C}_{24}\text{H}_{28}\text{Cr}_2\text{Si}_2$ ,  $M = 476.655$ , monoclinic, space group  $P2_1/m$  (No. 11) with  $a = 7.924(1)$ ,  $b = 11.082(1)$ ,  $c = 12.957(1)$   $\text{\AA}$ ,  $\beta = 92.59(1)^\circ$ ,  $U = 1136.6$   $\text{\AA}^3$ ,  $D_c = 1.393$   $\text{g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 10.4$   $\text{cm}^{-1}$ ,  $Z = 2$ ,  $F(000) = 496$ . A redundant data set of 5294 reflections was measured and merged to give 2588 unique data, 2291 of which were 'observed' with  $F_o \geq 2.0 \sigma(F_o)$  [ $R_{\text{int}} = 0.014$ ,  $(\sin \theta/\lambda)_{\text{max}} = 0.637$   $\text{\AA}^{-1}$ ,  $hkl$  range + 12,  $\pm 15$ ,  $\pm 17$ ,  $\theta/2\theta$  scans,  $\Delta\omega = 0.9 + 0.35 \text{ tg } \theta$ ]. Lorentz-polarisation corrections were applied, as was an empirical correction for absorption ( $\psi$  scans for 9 reflections, rel. transmission: 0.94–1.00). Crystal decay and stability of the diffractometer was monitored by means of the net intensity of three periodically measured standard reflexions (4 – 2 – 1, 0 – 27, 161) which indicated a marginal decay of 0.1% during data acquisition. The structure was solved by Patterson methods (SHELXS-86). The positions of 10 hydrogen atoms could be located in difference Fourier maps, the remainder were calculated at idealized geometrical positions. Large displacement ellipsoids of the unsubstituted Cp rings at  $\text{Cr}(1)\text{-Cr}(2)$  indicated substantial disorder which could not be resolved. Refinement converged at  $R(R_w) = 0.042$  (0.038),  $w = 1/\sigma^2(F_o)$  for 136 refined parameters (anisotropic, hydrogen atoms constant with  $U_{\text{iso}} = 0.05$   $\text{\AA}^2$ , SHELX76). The residual electron density was  $+0.48/-0.60$   $\text{e \AA}^{-3}$  with the maxima close to the disordered C atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

geometry (angle of fold between the Cp rings 1 and 2 = 45.7°, Fig. 3) which also renders the methyl groups at one Si atom inequivalent. Thus the axial methyl groups C(1) are closer to the unsubstituted Cp ring at Cr(1), while the equatorial ones leave more room for the CrCp fragment containing Cr(2). In summary, this leads to a Cr...Cr distance of 5.831(1) Å which is about 5% shorter than estimated for ideal  $C_{2h}$  symmetry with a planar geometry of the bridging ligand and it leads to an arrangement where the metallocenes are on the whole magnetically isolated but still show interaction when being oxidized or reduced.

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