

*Journal of Organometallic Chemistry*, 381 (1990) 349–356  
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands  
 JOM 20450

## Isolation of pentamethylcyclopentadienylchromium tricarbonyl dimer by two methods. X-Ray crystal structural study of two polymorphs

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(Received July 5th, 1989)

### Abstract

The  $[(C_5Me_5)Cr(CO)_3]_2$  dimer has been prepared by two methods, (i) oxidation of the anion  $[(C_5Me_5)Cr(CO)_3]^-$  by ferric ions in an aqueous acidic medium, and (ii) carbonylation of  $[(C_5Me_5)Cr(CO)_2]_2$  under high CO pressure at elevated temperatures. The complex crystallises in the monoclinic system in two polymorphic forms (I and II). Crystal structure data: I: space group  $P2_1/c$ ,  $a = 8.376(4)$ ,  $b = 19.397(6)$ ,  $c = 8.805(5)$  Å,  $\beta = 117.40(3)^\circ$ ,  $U = 1269.8$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.419$  g cm<sup>-3</sup>, and II: space group  $P2_1/n$ ,  $a = 9.333(2)$ ,  $b = 8.998(1)$ ,  $c = 15.297(3)$  Å,  $\beta = 95.86(2)^\circ$ ,  $U = 1277.9(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.37$  g cm<sup>-3</sup>.

### Introduction

There has been much recent interest in the chemistry of the metal–metal-bonded complex  $[CpCr(CO)_3]_2$  ( $Cp = C_5H_5$ ) because of its high reactivity [1–6], which is ascribable to the extreme weakness [7–9] of its unusually long Cr–Cr bond [10]. We thus thought it of interest to synthesise the permethylcyclopentadienyl analogue for comparative structural and reactivity studies. We were aware of Wrighton's report of its formation in solution [11] after high pressure carbonylation of  $Cp'(CO)_2Cr\equiv Cr(CO)_2Cp'$  ( $Cp' = C_5Me_5$ ) at ambient temperature and King's isolation of it [12] after similar reaction at elevated temperatures, but we were unable to use this approach because we did not have a high-pressure bomb available at that

time. Thus we used Manning's method [13], known to work very well for the cyclopentadienyl complexes of Group 6 elements, and were able to isolate crystalline  $[\text{Cp}'\text{Cr}(\text{CO})_3]_2$ . Since this product was found to possess chemical and spectral properties markedly different from those reported by King [12], we repeated the reaction under the conditions he used and obtained crystals of the  $[\text{Cp}'\text{Cr}(\text{CO})_3]_2$  dimer along with an unstable product. This paper describes both of the preparative and isolation procedures, and the results of single crystal X-ray diffraction studies of both sets of crystals, which were found to be different polymorphic forms. Full structural details are presented here only for polymorph I, since Baird [14] subsequently reported the isolation of crystals with space group and cell-dimensions corresponding to those of polymorph II.

## Experimental

### *Reagents*

$\text{Cr}(\text{CO})_6$  was obtained from Strem Chemicals, Inc. Pentamethylcyclopentadiene was synthesised from 2-bromo-2-butane (Fluka Chemicals Ltd.) by Bercaw's method [15].  $\text{K}[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3]$  was prepared as yellow solids from the reaction of  $\text{K}(\text{C}_5\text{Me}_5)$  with  $\text{Cr}(\text{CO})_6$  as described by King [16], and purified by removal of residual  $\text{Cr}(\text{CO})_6$  via vacuum sublimation.  $[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_2]_2$  was made as previously described [12]. Solvents were distilled from sodium/benzophenone prior to use.

### *General procedures and physical measurements*

All manipulations were performed either by conventional Schlenk line techniques under nitrogen or in a Vacuum Atmospheres DriBox equipped with a Model HE493 Dri-Train under argon. IR spectra were recorded on a Perkin-Elmer 1330 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL FX100 100 MHz spectrometer or a VARIAN XL200 200 MHz spectrometer in the Department of Chemistry, Texas A and M University, with residual  $\text{C}_6\text{H}_6$  in  $\text{C}_6\text{D}_6$  or  $\text{SiMe}_4$  in  $\text{C}_6\text{D}_5\text{CD}_3$  as reference. Mass spectra were performed on Kratos AEI MS 3074. Elemental analyses were performed by the Analytical Unit of the Research School of Chemistry, Australian National University, and by courtesy of Dr. K.C. Badri of the Universiti Pertanian Malaysia.

### *Preparation of $[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3]_2$ (I)*

(a) *Manning's method [13]: From  $\text{K}[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3]$ .* An aqueous solution (30 ml) of ferric sulfate (2 g, ca. 3.7 mmol) containing glacial acetic acid (1.5 ml) was added during 30 min to a yellow orange suspension of  $\text{K}[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3]$  (1.55 g, 5.0 mmol) in diglyme (30 ml). There was an immediate formation of a deep green precipitate suspended in a dark green solution. Further stirring for 1 h resulted in coagulation of the solid, which settled to the bottom of the flask as a dark green gluey mass. The supernatant dark green solution was removed through a cannula and the sticky precipitate triturated with water ( $3 \times 10$  ml) and methanol (10 ml) and then pumped dry. Exhaustive extraction of the dark solids with toluene (ca. 25 ml) gave a dark greenish brown solution, which on dilution turned via dark purplish brown to purplish pink. Concentration of the filtered solution to ca. 1 ml, followed by addition of n-hexane and overnight cooling at  $-30^\circ\text{C}$  gave lustrous black

crystals of **1** (0.28 g, 0.33 mmol, 13% yield). A second crop (0.10 g, 0.18 mmol, 7% yield) was subsequently obtained. Anal. Found for **1**: C, 57.27; H, 5.56; Cr, 19.1, 19.2.  $[(C_5Me_5)Cr(CO)_3]_2$  calc.: C, 57.56; H, 5.57; Cr, 19.17%. Ir:  $\nu(CO)$  1987vs and a very broad unresolved peak centered at 1877vs with 1907s sh and 1835w sh  $cm^{-1}$  ( $C_6H_6$ ) \* or 2020vw, 1890vsb with 1850vs sh and other peaks at 1575 wbr, 1070vw, 1025m, 720vw, 660wsh, 642m, 620w, 570s, 550m, 525m, 480m, 458vw, 410s  $cm^{-1}$  (nujol).  $^1H$  NMR (toluene- $d_8$ ):  $\delta(CH_3)$  ca. 30 (concentration dependent  $\nu_{1/2}$  ca. 200 Hz) (30 °C) and 1.53 (−90 °C).  $^{13}C$  NMR (toluene- $d_8$ , −90 °C):  $\delta(C_5Me_5)$  101.07, 9.94;  $\delta(CO)$  250.29. MS  $m/e$  458  $Cr_2(C_5Me_5)_2(CO)_3$ , 430  $Cr_2(C_5Me_5)_2(CO)_2$ , 402  $Cr_2(C_5Me_5)_2(CO)$ , 374  $Cr_2(C_5Me_5)_2$ , 322  $Cr(C_5Me_5)_2$ , 270  $(C_5Me_5)_2$ , 187  $Cr(C_5Me_5)$ , and numerous unassigned lower-mass fragments.

(b) *King's method* [12]: Carbonylation of  $[(C_5Me_5)Cr(CO)_2]_2$  (**2**).  $[(C_5Me_5)Cr(CO)_2]_2$ , 0.21 g in toluene (80 ml) in a 300 ml Parr Bomb was subjected to 1200 psi CO pressure for ca. 30 min at 175 °C, followed by 400 psi at 175 °C for a further 10 h. The brownish green solution formed was concentrated to ca. 15 ml and kept overnight at −30 °C to give dark purple crystals of **1** (30 mg, ca. 15% yield), from which diffraction-quality crystals of polymorph II were selected. The complex is sparingly soluble in benzene or toluene to give brownish purple solutions, which turn cherry red on exposure to air.

The purplish green mother-liquor on concentration to dryness gave a dark residue (0.16 g), consisting of a mixture of the starting material (**2**) ( $\delta(H)$  1.73) and an unknown species (**3**) with a broad resonance at  $\delta(H)$  1.54 in a molar ratio of 1/1.6. Attempted separation on a silica gel column with n-hexane/toluene as eluent showed that both components eluted together. Chromatography on an alumina column (1.2 × 20 cm) with n-hexane/toluene as eluent gave a yellowish green solution, which yielded a black residue (ca. 0.1 g) consisting of a 2/1 molar mixture of **2** and **3**. Further elution with methanol gave a light greenish yellow solution, which yielded dark green solids (ca. 40 mg) consisting of **2** and **3** in molar ratio 1/5. The IR spectrum in toluene showed the carbonyl stretching frequencies of **2** ( $\nu(CO)$  1873 and 1851  $cm^{-1}$ ) [Wrighton [7] reported  $\nu(CO)$  1876 and 1857  $cm^{-1}$  in  $C_6H_6$  for **2**], of  $Cr(CO)_6$  ( $\nu(CO)$  1998  $cm^{-1}$ ) and  $\nu(CO)$  1914  $cm^{-1}$  assigned to **3**.

Attempted crystallisation during ca. 10 d at −30 °C gave only white crystals of  $Cr(CO)_6$  and green crystals of **2**, while **3** remained in the mother-liquor. Vacuum sublimation at 40 °C/0.1 mmHg gave only **2**.

### Crystal structure determination

The complex crystallised in two polymorphic crystals. Crystal I was obtained by overnight recrystallisation in THF at −30 °C of the product from Manning's method, and crystal II from overnight cooling at −30 °C of the concentrated solution in toluene obtained by King's method.

*Crystal data.*  $C_{26}H_{30}Cr_2O_6$ ,  $M = 542.52$ , monoclinic. *Crystal I*: space group  $P2_1/c$ ,  $a = 8.376(4)$ ,  $b = 19.397(6)$ ,  $c = 8.805(5)$  Å,  $\beta = 117.40(3)^\circ$ ,  $U = 1269.8$  Å<sup>3</sup>, (by least-squares refinement of diffractometer setting angles for 25 automatically centred reflections),  $Z = 2$ ,  $D_c = 1.419$  g  $cm^{-3}$ . Black needle shaped crystals. Crystal

\* The IBM 32 FTIR spectrometer at Texas A&M gave  $\nu(CO)$  1995vs and a very broad unresolved band centered at 1893vs with shoulders at 1918s, 1889vs, 1870vs, and 1843m  $cm^{-1}$  ( $C_6H_6$ ).

dimensions  $0.24 \times 0.07 \times 0.11$  mm.  $\mu(\text{Mo-K}\alpha) = 8.43 \text{ cm}^{-1}$ ,  $\lambda(\text{Mo-K}\alpha) = 0.71069 \text{ \AA}$ ,  $F(000) = 564$ . *Crystal II*: space group  $P2_1/n$ ,  $a = 9.333(2)$ ,  $b = 8.998(1)$ ,  $c = 15.297(3) \text{ \AA}$ ,  $\beta = 95.86(2)^\circ$ ,  $U = 1277.9(1) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.37 \text{ g cm}^{-3}$ .  $\mu(\text{Mo-K}\alpha) = 8.66 \text{ cm}^{-1}$ ,  $\lambda(\text{Mo-K}\alpha) = 0.71703 \text{ \AA}$ .

*Data collection and processing. Crystal I.* Reflections were measured on an Enraf-Nonius CAD4-F four-circle diffractometer,  $\omega$ - $\theta$  scan mode with scan width ( $^\circ$ )  $1.00 + 0.35 \tan \theta$ , aperture width (mm)  $2.40 + 0.50 \tan \theta$ . 2475 reflections measured ( $2^\circ < 2\theta < 50^\circ$ ) ( $+h, +k, +l$ ), 1999 unique non-zero (merging  $R = 0.023$ ). Lorentz, polarization, crystal decay (less than 3%) and absorption (min. 1.06 to max. 1.19) effects corrected for. *Crystal II.* Data were collected on a Nicolet R<sub>3</sub>m X-ray diffractometer.  $R = 0.040$  ( $wR = 0.040$ ) for 1876 absorption corrected reflections ( $20^\circ \text{ C}$ ,  $\theta$ - $2\theta$  scans,  $4.0 \leq 2\theta \leq 50.0 \text{ deg}$ ,  $F \geq 4\sigma F$ ). The structure was solved by direct methods, with refinement by full matrix least-squares on  $F^2$ .

*Structure analysis and refinement of crystal I.* The structure was solved by direct methods. Hydrogen atoms were refined with individual isotropic thermal parameters, and all other atoms with isotropic thermal parameters. Full-matrix least-squares refinement converged at  $R[\Sigma(|F_o - F_c|)/\Sigma|F_o|] = 0.034$ ,  $R' = 0.038$  [weighting scheme of the form  $0.93/(\sigma^2 F_o - 0.00093 F_o^2)$ ], for 1608 reflections with  $I > 2.5\sigma(I)$ . Maximum peaks in a final difference map were less than  $+0.4$  and  $-0.2 \text{ e\AA}^{-3}$ . Scattering factors and anomalous dispersion terms were taken from ref. 17. All calculations were carried out by use of SHELX-76, [18] ORTEP, [19] and data reduction programs on a CYBER computer. Final atomic coordinates are listed in Table 1 and bond lengths and angles in Table 2. Tables of observed and calculated structure factors, thermal parameters, hydrogen positional, and thermal parameters and details of least-squares planes calculations are available from the authors.

## Results and discussion

### Preparation

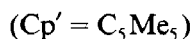
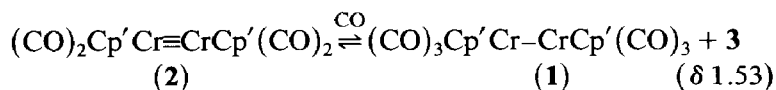
The  $[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3]_2$  dimer **1** was isolated as purplish-black crystals by two methods namely (a) the oxidation of the anion  $[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3]^-$  with ferric sulphate in aqueous acidic media, as described by Manning [13] for the  $[(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$  analogue, which gave a 20% yield, and (b) high-pressure carbonylation of  $[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_2]_2$  at elevated temperatures, which gave a 15% yield. During this work, Baird [14] reported a synthesis of **1** by dehydrogenation of the hydride  $(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3\text{H}$  with isoprene.

### Physical properties

The complex crystallises from THF or toluene or n-hexane/toluene as hexagonal plates, the colour of which changes reversibly from deep brownish purple at ambient temperature and deep brownish green below  $-30^\circ \text{ C}$ . It is moderately soluble in benzene or toluene, to give solutions which undergo similar reversible colour changes with temperature, being deep cherry red at  $90^\circ \text{ C}$  and a dark green when frozen at the temperature of liquid nitrogen. Colour variations with concentration range from brown when saturated through purplish brown to pink when very dilute. As observed by Baird [14] the solid is air-stable for short periods, whereas the solution is extremely air-sensitive, turning cherry red on exposure to air.

### Spectra

The  $^1\text{H}$  NMR concentration and temperature-dependent spectral features in  $\text{C}_6\text{D}_6$  or  $\text{C}_6\text{D}_5\text{CD}_3$  [ $\delta(\text{CH}_3)$  ca. 30, ( $\nu_{1/2}$  ca. 200 Hz) and  $\delta$  1.53 at  $-90^\circ\text{C}$ . Baird [14] reported  $\delta$  31.3 and 1.54, respectively for a 0.007 *M* solution] are in contrast to the peak ( $\delta$  1.56) reported by King [12]. The carbonyl region of the IR spectrum in  $\text{C}_6\text{H}_6$ , showing  $\nu(\text{CO})$  at 1987 vs and 1877 vs vbr with shoulders [1907 s and 1835 w  $\text{cm}^{-1}$ ] attributed to the dissociated monomer from **1** [14], is also markedly different from that reported by King for his isolated complex [ $\nu(\text{CO})$  (n-tetradecane) 1886 and 1915  $\text{cm}^{-1}$ ]. There is closer resemblance to Wrighton's spectrum [ $\nu(\text{CO})$  1985 and 1900  $\text{cm}^{-1}$  in  $\text{C}_6\text{H}_6$ ] for a product solution obtained by carbonylation of  $[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_2]_2$  at 300 atm. of CO at  $25^\circ\text{C}$ . These observed spectral differences raise the query whether the compound isolated by King might not have had the assumed formulation. A closer examination of the analytical results (C, 56.2; H, 6.30 and Cr, 18.00) shows that there is a closer fit to  $[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3]_2(\text{CO})$  (Calc. C, 56.84; H, 5.30 and Cr, 18.23) than to  $[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3]_2$  (Calc. C, 57.56; H 5.57 and Cr, 19.17%). To seek a clarification for these discrepancies we attempted the carbonylation of  $[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_2]_2$  at Texas A&M University and found that the reaction gave two products, viz. **1** and an unidentified complex (**3**) with a peak at  $\delta$  1.53 in the  $^1\text{H}$  NMR spectrum: as



Compound **1** crystallised out of the concentrated product solution, whereas **3**, remained in the mother liquor along with unchanged **2** or its decomposition products. Unfortunately all our attempts to isolate **3** failed, including column chromatography on  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ , fractional crystallization at  $-30^\circ\text{C}$ , and sublimation at ca.  $40^\circ\text{C}/0.1$  mmHg. All of these attempts eventually gave **2**, along with  $\text{Cr}(\text{CO})_6$  in the case of the last two methods. This facile decarbonylation as well as the extreme air-sensitivity of **3** are in agreement with King's observations. In contrast, we found that **1** survives sublimation conditions of  $110^\circ\text{C}/0.35$  mmHg. It is also observed that the IR spectrum of an 80% pure solution of **3** showed the presence of **2** and  $\text{Cr}(\text{CO})_6$ , and also a  $\nu(\text{CO})$  band at 1914  $\text{cm}^{-1}$  which is close to the value of  $\nu(\text{CO})$  1915  $\text{cm}^{-1}$  observed by King. These observations indicate that the complex **3** that we failed to isolate was the compound isolated by King.

### Structure of $[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3]_2$ (**1**)

The structures of both crystals I and II have been determined by X-ray diffraction analysis and found to involve different polymorphs. While attempting to isolate the elusive compound **3**, as discussed above, Baird [14], reported the cell-dimensions of a structure isomorphous with polymorph II and so we do not report here the structural details for this polymorph, except to state that it possesses the same molecular parameters as polymorph I.

The atomic coordinates for polymorph I are given in Table 1, and bonding parameters are given in Table 2. The molecular structure is shown in Fig. 1. The structural analysis confirms the presence of the  $[(\text{C}_5\text{Me}_5)\text{Cr}(\text{CO})_3]_2$  complex. These units lie on crystallographic centres of symmetry and are packed with no unusually

Table 1

Positional parameters ( $\times 10^4$ ) for  $[\text{Cr}(\text{C}_5\text{Me}_5)(\text{CO})_3]_2$  (crystal I)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cr(1)	-758(1)	9198(1)	-285(1)
C(1)	1043(5)	9271(2)	1940(4)
O(1)	2109(4)	9193(2)	3340(3)
C(2)	-2695(5)	9798(2)	-961(4)
O(2)	-4068(4)	10072(2)	-1455(4)
C(3)	-1854(5)	8867(2)	929(4)
O(3)	-2542(4)	8642(2)	1697(4)
C(4)	196(4)	8984(2)	-2264(4)
C(5)	986(4)	8508(2)	-893(4)
C(6)	-399(5)	8125(2)	-809(4)
C(7)	-2070(4)	8374(2)	-2126(4)
C(8)	-1681(4)	8904(2)	-3011(4)
C(9)	1203(7)	9422(2)	-2956(6)
C(10)	2963(6)	8362(3)	107(7)
C(11)	-146(11)	7511(2)	318(8)
C(12)	-3908(8)	8079(3)	-2642(9)
C(13)	-3028(6)	9244(3)	-4647(5)

short contacts between them. The closely related complex  $[(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$  crystallizes in the same space group with molecules at centres of symmetry [10], but the crystal lattices are in no sense isostructural.

Table 2

Bond lengths (Å) and angles ( $^\circ$ ) in  $[\text{Cr}(\text{C}_5\text{Me}_5)(\text{CO})_3]_2$ 

Cr(1)–Cr(1)	3.310(1)	C(1)–Cr(1)	1.848(3)
C(2)–Cr(1)	1.859(3)	C(3)–Cr(1)	1.818(3)
C(4)–Cr(1)	2.264(3)	C(5)–Cr(1)	2.221(3)
C(6)–Cr(1)	2.182(3)	C(7)–Cr(1)	2.179(3)
C(8)–Cr(1)	2.230(3)	O(1)–C(1)	1.152(4)
O(2)–C(2)	1.155(4)	O(3)–C(3)	1.157(4)
C(5)–C(4)	1.417(4)	C(8)–C(4)	1.406(4)
C(9)–C(4)	1.509(5)	C(6)–C(5)	1.409(4)
C(10)–C(5)	1.502(5)	C(7)–C(6)	1.429(5)
C(11)–C(6)	1.503(5)	C(8)–C(7)	1.415(5)
C(12)–C(7)	1.503(5)	C(13)–C(8)	1.513(5)
C(2)–Cr(1)–C(1)	117.3(1)	C(3)–Cr(1)–C(1)	77.9(1)
C(3)–Cr(1)–C(2)	78.9(1)	O(1)–C(1)–Cr(1)	167.8(3)
O(2)–C(2)–Cr(1)	168.6(3)	O(3)–C(3)–Cr(1)	178.6(3)
C(8)–C(4)–C(5)	108.1(3)	C(9)–C(4)–C(5)	125.5(3)
C(9)–C(4)–C(8)	125.9(3)	C(6)–C(5)–C(4)	108.3(3)
C(10)–C(5)–C(4)	125.5(3)	C(10)–C(5)–C(6)	125.6(3)
C(7)–C(6)–C(5)	107.6(3)	C(11)–C(6)–C(5)	125.7(4)
C(11)–C(6)–C(7)	126.3(4)	C(8)–C(7)–C(6)	107.7(3)
C(12)–C(7)–C(6)	126.9(4)	C(12)–C(7)–C(8)	125.0(4)
C(7)–C(8)–C(4)	108.3(3)	C(13)–C(8)–C(4)	125.5(3)
C(13)–C(8)–C(7)	125.5(3)		

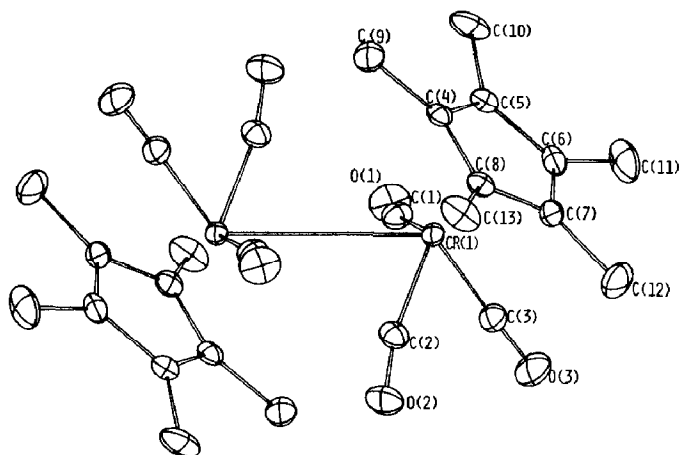


Fig. 1.

The Cp analogue is described as being highly strained, with an extraordinary long Cr–Cr bond of 3.281(1) Å. [10] The Cp' ligand is expected to be even more sterically demanding and this is reflected in an even longer Cr–Cr bond in the present structure [3.310(1) Å]. Baird [14] obtained a value of 3.3107(7) Å for the Cr–Cr distance in polymorph II. The increased strain is also reflected in the non-linearity of the Cr–C–O angles *cis* to the Cr–Cr bond. In the structure of the Cp derivative [10] these angles are 172.0(2) and 172.9(2)°, and in the present structure they are 167.8(3) and 168.6(3)°. This deformation is the result of interactions between the carbons of the carbonyl groups and the central atoms of the Cp group bonded to the same Cr [C(1)···C(5) 2.88 Å, C(2)···C(8) 2.90 Å] and the oxygens of the carbonyl groups bonded to one Cr with the methyls of the Cp' group bonded to the other Cr [O(1)···H(13C)' 2.34 Å, O(2)···H(10C)' 2.61 Å]. This also results in deformation of the Cp' group away from planarity. The methyl groups lie from 0.139 to 0.195 Å out of the plane defined by the central five carbon atoms (all deviations less than 0.006 Å). The Cr–C bond lengths to the bent carbonyl groups are significantly longer than that to the third carbonyl, which is at the short end of the range for Cr–C(O) bonds. A smaller but similar variation was observed in the structure of the Cp analogue [10]. Curiously the average Cr–C bond length in the Cp' structure [1.842 Å] is shorter than that in the less crowded structure [1.861 Å] [10], perhaps as a result of the longer Cr–Cr bond length and consequently an increased electron density on Cr. The Cr–C(Cp') bond lengths range from 2.179(3) to 2.264(3) Å, av. 2.215 Å, all longer than the analogous bonds in the structure of the Cp analogue, av. 2.195 Å. [10] The distance from the Cr to the least-squares plane through the five central carbon atoms of the Cp' is 1.858 Å. Bonds lengths and angles within the Cp' ligand are all normal.

### Acknowledgements

One of us (L.Y.G.) thanks the University of Malaya for financial support and for sabbatical leave spent in 1986/87 at Texas A&M University (L.Y.G.). We also thank the University of Sydney for support (T.W.H.) and the National Science Foundation for Grant CHE 88-17873 (to D.J.D.), and a grant for the X-ray diffraction equipment at Texas A&M University.

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