

# Crystal and molecular structure of chromocene ( $\eta^5\text{-C}_5\text{H}_5$ )<sub>2</sub>Cr

Kevin R. Flower \*, Peter B. Hitchcock

School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, UK

Received 18 May 1995

## Abstract

The crystal structure of chromocene has been determined by a low-temperature single-crystal X-ray diffraction study. The average chromium–carbon bond length is 2.151(13) Å.

**Keywords:** Chromocene; Chromium; Metallocenes; Crystal structure

## 1. Introduction

The first row transition metal metallocenes have been known for over 40 years [1], and their low-resolution crystal structures were determined in the mid 1950s [2]. Full refinements were later carried out for Cp<sub>2</sub>V [3], Cp<sub>2</sub>Mn [4], Cp<sub>2</sub>Fe [5], Cp<sub>2</sub>Co [6] and Cp<sub>2</sub>Ni [7], but surprisingly, no high-resolution determination has been reported for Cp<sub>2</sub>Cr. We report below the results of a low-temperature single-crystal X-ray diffraction study of the latter.

## 2. Experimental details

Chromocene was purchased from Strem and purified by vacuum sublimation. A red plate crystal with dimensions 0.4 × 0.4 × 0.25 mm (grown by slow vacuum sublimation at 35° and 10<sup>-5</sup> mbar) was used for data collection on an Enraf Nonius CAD4 diffractometer. Cell parameters were calculated from the setting angles for 25 reflections with  $\vartheta \cong 10^\circ$ . Intensities were measured by an  $\omega - 2\vartheta$  scan for 1924 reflections with  $+h + k \pm l$  and  $2 < \vartheta < 35^\circ$ . Corrections were made for Lorentz and polarisation effects and empirically for absorption based on psi scan data. Crystal data are shown in Table 1. The structure was solved by direct methods using SHELXS-86 [8]. Refinement using SHELXL-93 [9] was based on  $F^2$  using all 1792 unique reflections

( $R_{\text{int}} = 0.02$ ) with anisotropic thermal parameters for Cr and C. A difference map showed an alternative lower occupancy orientation of the cyclopentadienyl ring related by a rotation within the plane of 36°. This was modelled by including a rigid body set of isotropic carbon atoms with idealised geometry (C–C = 1.42 Å) without H atoms. The occupancies of the two alternative ring orientations were refined to 0.88:0.12. Hydrogen atoms for the major ring orientation were refined with isotropic thermal parameters. A variable extinction parameter was refined. The weighting scheme was that defined by the program. The final parameters were  $R1 = 0.042$ ,  $wR2 = 0.103$  (for 1329 reflections with  $I > 2\sigma(I)$ ) and  $R1 = 0.062$ ,  $wR2 = 0.116$  (for all

Table 1  
Crystal data for Cp<sub>2</sub>Cr

Formula	C <sub>10</sub> H <sub>10</sub> Cr
Molecular weight	182.2
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>a</i>	5.786(7) Å
<i>b</i>	7.815(9) Å
<i>c</i>	10.787(9) Å
$\beta$	124.04(8)
<i>D</i> (calc)	1.50 g cm <sup>-3</sup>
<i>F</i> (000)	188
$\mu$	1.34 mm <sup>-1</sup>
Radiation Mo K $\alpha$ (monochromated) $\lambda$	0.71073 Å
Temperature	173 K
<i>R</i> 1	0.042 ( $I > 2\sigma(I)$ )
<i>wR</i> 2	0.116 (all data)

\* Corresponding author.

Table 2  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Cp}_2\text{Cr}$

Atom	x	y	z	$U_{\text{eq}}$
Cr	0	0	0	27(1)
C(1)	-4252(5)	701(3)	-1681(3)	39(1)
C(2)	-3175(5)	1820(3)	-473(3)	37(1)
C(3)	-896(7)	2677(3)	-316(4)	49(1)
C(4)	-615(7)	2067(5)	-1463(5)	59(1)
C(5)	-2713(9)	848(4)	-2305(3)	49(1)
C(11)	-3852(30)	1241(22)	-1129(22)	37(4)
C(21)	-1788(37)	2490(21)	-241(17)	38(5)
C(31)	61(27)	2578(18)	-712(17)	27(3)
C(41)	-860(36)	1382(23)	-1891(19)	41(5)
C(51)	-3278(35)	556(20)	-2149(20)	35(5)
Cp	-2330	1622	-1248	
H(1)	-5552(79)	-59(37)	-1954(42)	44(9)
H(2)	-3762(77)	1896(45)	165(38)	55(9)
H(3)	199(65)	3399(48)	381(40)	54(10)
H(4)	547(108)	2359(72)	-1542(59)	109(18)
H(5)	-2877(95)	210(46)	-2980(55)	66(13)

<sup>a</sup> Occupancies for C(1) to C(5) 0.88 and for C(11) to C(51) 0.12, Cp is the centroid of C(1) to C(5).  $U_{\text{iso}}$ .

Table 3  
Interatomic distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for  $\text{Cp}_2\text{Cr}$

Cr–Cp	1.791(4)	Cr–C(1)	2.155(4)
Cr–C(2)	2.147(3)	Cr–C(3)	2.136(3)
Cr–C(4)	2.144(3)	Cr–C(5)	2.171(4)
C(1)–C(5)	1.389(5)	C(1)–C(2)	1.394(4)
C(2)–C(3)	1.402(4)	C(3)–C(4)	1.417(6)
C(4)–C(5)	1.404(6)		
C(5)–C(1)–C(2)	109.2(3)	C(1)–C(2)–C(3)	108.0(3)
C(2)–C(3)–C(4)	107.1(3)	C(5)–C(4)–C(3)	108.2(3)
C(1)–C(5)–C(4)	107.4(3)		

data),  $S = 1.107$ , maximum shift/e.s.d., 0.001, extrema on difference map +.080,  $-0.53 \text{ e}\text{\AA}^{-3}$ . The molecular drawing was generated using CAMERON [10]. Atomic coordinates are listed in Table 2.

### 3. Discussion

The molecular structure of  $\text{Cp}_2\text{Cr}$ , **1**, is shown in Fig. 1. The interatomic bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) are

Table 4  
Electron imbalance and average M–C bond length

Chemical	Electron configuration	Electron imbalance	R(M–C) $\text{\AA}$	Ref.
$(\text{C}_5\text{H}_5)\text{Fe}$	$a_{1g}^2 e_{2g}^4$	0	2.033	[5]
$(\text{C}_5\text{H}_5)\text{Co}$	$a_{1g}^2 e_{2g}^3 e_{1g}^1$	1	2.096	[6]
$(\text{C}_5\text{H}_5)\text{Cr}$	$a_{1g}^1 e_{2g}^3$	2	2.151	This work
$(\text{C}_5\text{H}_5)\text{Ni}$	$a_{1g}^2 e_{2g}^4 e_{1g}^2$	2	2.185	[7]
$(\text{C}_5\text{H}_5)\text{V}$	$a_{1g}^1 e_{2g}^2$	3	2.26	[3]
$(\text{C}_5\text{H}_5)\text{Mn}$	$a_{1g}^1 e_{2g}^2 e_{1g}^2$	5	<sup>a</sup>	[4]

<sup>a</sup> Because the Cp rings are not parallel in the crystal structure two different M–C bond lengths are observed.

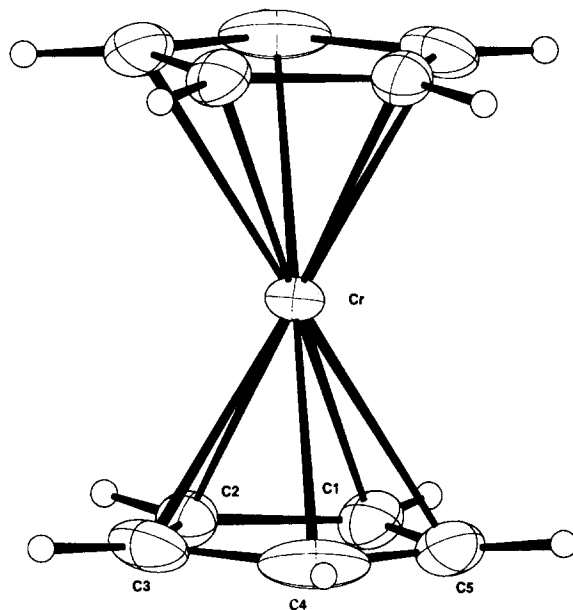


Fig. 1. The molecular structure of  $\text{Cp}_2\text{Cr}$  showing the numbering scheme. Cr and C shown as 50% thermal ellipsoids. (The lower occupancy orientation of the Cp ring is omitted.)

given in Table 3. The two cyclopentadienyl rings are parallel and staggered, with the chromium atom located between the two rings on a centre of inversion midway between the two rings. There is, however, a small amount of disorder in the cyclopentadienyl rings associated with two ring orientations with occupancies of 88% and 12% respectively. The average C–C bond lengths of 1.401(11)  $\text{\AA}$  are as expected. The average Cr–C bond length of 2.151(13)  $\text{\AA}$  is significantly longer than the Fe–C bond length in ferrocene. Some elongation would be expected because of the larger ionic radius of chromium than of iron, but the elongation is longer than would be expected for this reason alone.

Photoelectron spectroscopy has allowed assignment of the ground state electronic structures of the first row metallocenes [11,12]. These configurations suggest that the strongest metal-to-ligand bonds will be those in ferrocene. Further analysis by Haaland et al., led to the

definition of “electron imbalance” (based on the assumption that loss of an electron from the  $a_{1g}$  or  $e_{2g}$  orbitals weakens the metal Cp bond to the same extent as introduction of an electron into the anti-bonding  $e_{1g}$  orbital) as the number of holes in the  $a_{1g}$  and  $e_{2g}$  orbitals plus the number of electrons in the  $e_{1g}$  orbital [13]. The effect of electron imbalance vs. M–C bond length can be seen from Table 4, which shows that the M–C bond length increases regularly with increase in the electron imbalance, and that the M–C bond length for nickel is greater than for chromium, indicating that the  $e_{1g}$  orbital is more anti-bonding than the  $a_{1g}$  and  $e_{2g}$  orbitals are bonding: this was also observed from electron diffraction data [13].

### Acknowledgements

We thank the EPSRC for support and K.R.F. thanks Profs. F.G.N. Cloke and J.F. Nixon for their interest.

### References

- [1] (a) T.J. Kealy and P.L. Pauson, *Nature (London)*, 168 (1951) 1039; (b) S.A. Miller, J.A. Tebboth and J.F. Tremaine, *J. Chem. Soc.*, (1952) 632.
- [2] E.O. Fischer, *Recueil Trav. Chim.*, 75 (1956) 629.
- [3] R.D. Rogers, J.L. Atwood, D. Foust and M.D. Rauch, *J. Cryst. and Mol. Struct.*, 11 (1981) 183.
- [4] W. Bunder and E. Weiss, *Z. Naturforsch.*, B 33 (1978) 1235.
- [5] P. Seiler and J.D. Dunitz, *Acta Cryst., Sect. B* (1979) 1069.
- [6] W. Bunder and E. Weiss, *J. Organomet. Chem.*, 92 (1975) 65.
- [7] P. Seiler and J.D. Dunitz, *Acta Cryst., Sect. B* 36 (1980) 2255.
- [8] G.M. Sheldrick, *SHELXL-86, Program for the Solution of Crystal Structures*, Univ. of Gottingen, Germany, 1985.
- [9] G.M. Sheldrick, *SHELXS-93, Program for the Refinement of Crystal Structures*, Univ. of Gottingen, Germany, 1993.
- [10] D.J. Watkin and L.J. Pearce, *CAMERON, An interactive Graphics Editor*, Univ. of Oxford, England, 1993.
- [11] S. Evans, M.L.H. Green, B. Jewitt, A.F. Orchard and C.F. Pygall, *J. Chem. Soc. Faraday Trans II*, 68 (1972) 1847.
- [12] S. Evans, M.L.H. Green, B. Jewitt, G.H. King and A.F. Orchard, *J. Chem. Soc. Faraday Trans II*, 70 (1974) 356.
- [13] E. Gard, A. Haaland, D.P. Novak and R. Seip, *J. Organomet. Chem.*, 88 (1975) 181.