

### Preliminary communication

## CONFORMATIONAL ANALYSIS AND X-RAY CRYSTAL STRUCTURE OF $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CH}_2\text{CH}_3]$

STEPHEN G. DAVIES\*, ISABELLE M. DORDOR-HEDGECOCK, KEVIN H. SUTTON and  
 MARK WHITTAKER

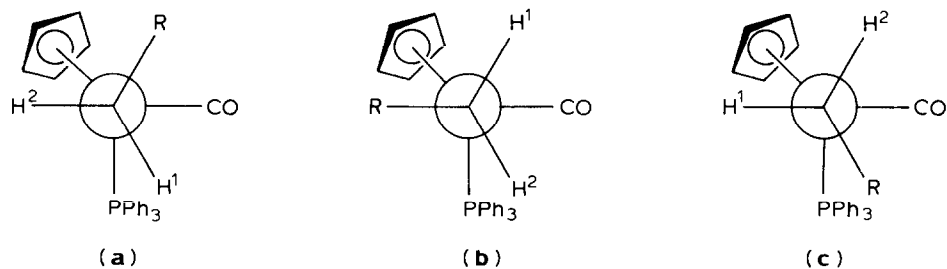
*The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY (Great Britain)*

(Received October 13th, 1986)

### Summary

The complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CH}_2\text{CH}_3]$  is shown by  $^1\text{H}$  NMR spectroscopy and an X-ray crystal structure analysis to adopt a single conformation with the methyl group residing between the cyclopentadienyl and carbon monoxide ligands.

In order to rationalise the remarkable stereocontrol observed in reactions of ligands attached to the chiral auxiliary  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)$  [1] we have proposed recently a conformational analysis for complexes of the type  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CH}_2\text{R}$  based on extended Hückel calculations [2]. This model predicted that for the pseudo-octahedral complexes of the type  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CH}_2\text{R}]$  (**1**) three stable conformations exist with the order of stability  $\mathbf{a} \gg \mathbf{b} > \mathbf{c}$ . It was further predicted that even for the complex **1** ( $\text{R} = \text{CH}_3$ ) only



conformer **a** ( $\text{R} = \text{CH}_3$ ) would be significantly populated although conformation **b** might be accessible. This analysis [2], which is at variance with the previous long

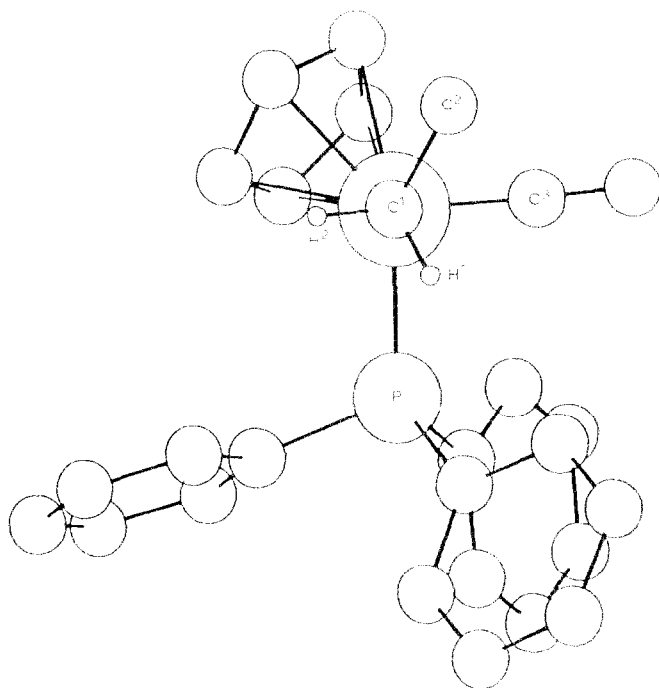


Fig. 1. Molecular structure of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CH}_2\text{CH}_3]$ .

standing model [3,4] has come in for considerable criticism [5] mainly on the basis of the observed variations with temperature of the  $^3J(\text{PH})$  coupling constants for **1** ( $\text{R} = \text{SiMe}_3$ , Ph) [4] which were assumed to indicate the population of several conformations for all complexes **1**. We describe here evidence in support of our conformational analysis which is consistent with essentially only conformer **a** being populated for complex **1** ( $\text{R} = \text{CH}_3$ ).

The ethyliron complex **1** ( $\text{R} = \text{CH}_3$ ) was prepared by photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{CH}_3$  in the presence of triphenylphosphine [6]. In the 300 MHz  $^1\text{H}$  NMR spectrum\* ( $\text{C}_6\text{D}_6$ ) of **1** ( $\text{R} = \text{CH}_3$ ) the diastereotopic methylene protons,  $\text{H}^1$  and  $\text{H}^2$ , appeared at  $\delta$  1.07 and 1.87 ppm and exhibited coupling constants to phosphorus of 12.1 and 2.0 Hz, respectively. This is entirely consistent with conformation **a** with  $\text{H}^1$  being shielded by one of the phenyl groups of the triphenylphosphine [7] and having, according to the Karplus equation [8] ( $\text{PFcCH}^1 \cong 30^\circ$ ), a large  $^3J(\text{PH})$  whereas  $\text{H}^2$  would be expected to show a small  $^3J(\text{PH})$  ( $\text{PFcCH}^2 \cong 90^\circ$ ). Of most significance however is the observation of a four bond coupling ( $^4J(\text{PH}) = 2.1$  Hz) between the phosphorus and the methyl protons. Such long range couplings only occur between atoms in a 'W' arrangement [9] which in this case is only achieved in conformations close to **a**. Monitoring the  $^3J(\text{PH})$  coupling constants of  $\text{H}^1$  and  $\text{H}^2$  over the temperature range 230–360 K showed,

\* (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.57–6.95 (15H, m, Ph), 4.13 (5H, d,  $J(\text{PH})$  1.1 Hz,  $\text{C}_5\text{H}_5$ ), 1.87 (1H, ddq,  $^3J(\text{PH})$  2.0 Hz,  $^2J(\text{HH})$  9.3 Hz,  $^3J(\text{HH})$  7.4 Hz,  $\text{FeCH}^2$ ), 1.58 (3H, dt,  $^4J(\text{PH})$  2.1 Hz,  $^3J(\text{HH})$  7.5 Hz,  $\text{CH}_3$ ), 1.07 (1H, ddq,  $^3J(\text{PH})$  12.1 Hz,  $^2J(\text{HH})$  9.2 Hz,  $^3J(\text{HH})$  7.4 Hz,  $\text{FeCH}^1$ ).

TABLE 1

SELECTED BOND AND TORSIONAL ANGLES FOR  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CH}_2\text{CH}_3$  (Degrees)

$\text{C}^3\text{-Fe}^1\text{-C}^1\text{-H}^1$	-65
$\text{C}^3\text{-Fe}^1\text{-C}^1\text{-H}^2$	-179
$\text{C}^3\text{-Fe}^1\text{-C}^1\text{-C}^2$	+57
$\text{P}^1\text{-Fe}^1\text{-C}^1\text{-H}^1$	+29
$\text{P}^1\text{-Fe}^1\text{-C}^1\text{-H}^2$	-85
$\text{P}^1\text{-Fe}^1\text{-C}^1\text{-C}^2$	+151
$\text{C}^1\text{-Fe}^1\text{-P}^1$	92.9(1)
$\text{C}^3\text{-Fe}^1\text{-P}^1$	93.4(1)
$\text{C}^3\text{-Fe}^1\text{-C}^1$	92.7(2)

within experimental error, no variation. This is in complete contrast to the reported results for **1** ( $\text{R} = \text{Ph}$ ,  $\text{SiMe}_3$ ) [4] and is consistent with only conformation **a** being populated for **1** ( $\text{R} = \text{CH}_3$ ): A significant change in the  $^3J(\text{PH})$  values with temperature would be expected if any other conformation were populated. An X-ray crystal structure analysis\* of **1** ( $\text{R} = \text{CH}_3$ ) (Fig. 1) shows that conformation **a** is also adopted in the solid state. Selected bond and torsion angles are given in Table 1 and show that complex **1** ( $\text{R} = \text{CH}_3$ ) is close to octahedral with  $\text{PFeCH}^1$   $29^\circ$  and  $\text{PFeCH}^2$   $-85^\circ$ .

The above results demonstrate the validity of our new conformational analysis for complexes of the type  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CH}_2\text{R}$  ( $\text{R} = \text{alkyl}$ ) where essentially only the conformer with  $\text{R}$  orientated between the cyclopentadienyl and the carbon monoxide ligand is populated.

**Acknowledgements.** We thank the British Petroleum Company p.l.c. for a Venture Research Award (to M.W.), the SERC for support (to I.M.D-H and K.H.S.) and Dr. Keith Prout for access to the facilities of the Chemical Crystallography Laboratory, Oxford.

## References

- 1 G.J. Baird and S.G. Davies, *J. Organomet. Chem.*, 248 (1983) C1; S.G. Davies, I.M. Dordor-Hedgecock and P. Warner, *ibid.*, 285 (1985) 213; L.S. Liebeskind and M.E. Welker, *Tetrahedron Lett.*, (1984) 1845; S.G. Davies and J.C. Walker, *J. Chem. Soc., Chem. Commun.*, (1985) 209; (1986) 495; (1986) 609.
- 2 J.I. Seeman and S.G. Davies, *J. Am. Chem. Soc.*, 107 (1985) 6522.
- 3 J. Thomson, W. Keeney, M.C. Baird and W.F. Reynolds, *J. Organomet. Chem.*, 40 (1972) 205; K. Stanley, R.A. Zelonka, J. Thomson, P. Fiess and M.C. Baird, *Can. J. Chem.*, 52 (1974) 1781; K. Stanley and M.C. Baird, *J. Am. Chem. Soc.*, 97 (1975) 6598; 99 (1977) 1808.

\* Crystal data for **1**,  $\text{C}_{26}\text{H}_{25}\text{POFe}$ ,  $M = 440.3$ , orthorhombic, space group  $Pbca$ ,  $a$  9.328(3),  $b$  17.218(5),  $c$  26.810(7) Å  $U$  4303 Å<sup>3</sup>,  $Z = 8$ ,  $D_c$  1.36 Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  ( $\lambda$  0.71069 Å) 7.86 cm<sup>-1</sup>, crystal size 0.75 × 0.51 × 0.19 mm. 2326 reflections  $I \geq 3\sigma(I)$ , final  $R = 0.035$ ,  $R_w = 0.037$ . Data were collected on an Enraf-Nonius CAD-4 diffractometer to  $\theta$  25°. The structure was solved by Patterson and electron density Fourier synthesis methods. 272 parameters including those for anisotropic thermal vibration (non-hydrogen atoms) were refined by full-matrix least squares refinement. Hydrogen atoms were allowed to "ride" on their respective carbon atoms except  $\text{H}^1$  and  $\text{H}^2$  ( $\alpha$ -methylene group) which were refined isotropically to satisfactory values. A Table of atom coordinates and a complete list of bond lengths and angles is available from the Cambridge Crystallographic Data Centre.

- 4 K. Stanley and M.C. Baird, *Inorg. Nucl. Chem. Lett.* 10 (1974) 1111; *J. Am. Chem. Soc.*, 97 (1975) 4292.
- 5 A.D. Cameron and M.C. Baird, *J. Chem. Soc., Dalton Trans.*, (1985) 2691; B.K. Hunter and M.C. Baird, *Organometallics*, 4 (1985) 1481.
- 6 S.R. Su, and A. Wojcicki, *J. Organomet. Chem.*, 27 (1971) 231.
- 7 J.S. Waugh and R.W. Fessenden, *J. Am. Chem. Soc.*, 79 (1957) 846.
- 8 M. Karplus, *J. Am. Chem. Soc.*, 85 (1963) 2870.
- 9 J. Meinwald and Y.C. Meinwald, *J. Am. Chem. Soc.*, 85 (1963) 2514; S.D. Robinson and A. Sahajpal, *Inorg. Chem.*, 16 (1977) 2718, 2722; Y. Wakatsuki, K. Aoki and H. Yamazaki, *J. Am. Chem. Soc.*, 101 (1979) 1123; S.G. Davies, S.D. Moon, S.J. Simpson and S.E. Thomas, *J. Chem. Soc., Dalton Trans.*, (1983) 1805.