Chemical Synthesis with Metal Atoms: Preparation and *X*-Ray Structure of (η^5-cycloheptadienyl)-(η^5-cycloheptatrienyl) Iron. A Bifluxional Molecule

By J. RICHARD BLACKBOROW,* KNUT HILDENBRAND, (the late) ERNST KOERNER VON GUSTORF, ALBERTO SCRIVANTI, and (in part) COLIN R. EADY and DANIEL EHNTOLT
(*Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung,* D-4330 *Mülheim a.d. Rhur, Stiftstrasse* 34-36)

and CARL KRÜGER
(*Max-Planck-Institut für Kohlenforschung,* D-4330 *Mülheim a.d. Ruhr, Lembkestrasse* 5 *B.R.D.*)

Summary $[Fe(\eta^5\text{-}C_7H_7)\ (\eta^5\text{-}C_7H_9)]$ has been prepared by cocondensation of iron vapour with cycloheptatriene; an *X*-ray analysis shows a sandwich structure with open faces of the two η^5-systems skew to each other, and in solution two types of fluxional behaviour are exhibited.

WE have prepared $[Fe(\eta^5\text{-}C_7H_7)\ (\eta^5\text{-}C_7H_9)]$ by co-condensation of iron atoms and cycloheptatriene at -196 °C. Laser-assisted thermal evaporation of iron (10^{-4} Torr, 10 g/h) was carried out in an apparatus described previously.[1] After workup at -20 °C under argon, dark red crystals,† m.p. 195 °C; M 248 (C_6H_6), m/e 240 (M^+), 148 ($M - C_7H_8$)$^+$, and 91 (C_7H_7)$^+$] were obtained in 4·2% yield from iron evaporated, which were structurally characterised by *X*-ray crystallography. *Crystal data:* monoclinic, space group $P2_1/c$, $a = 10{\cdot}991(1)$, $b = 8{\cdot}628(1)$, $c = 12{\cdot}594(1)$ Å, $\beta = 112{\cdot}11(1)°$, $Z = 4$. 2364 Diffractometer intensities were collected with graphite-monochromated Mo-K_α radiation from which 1951 reflections were deemed observed. The structure was refined by full-matrix least-squares methods to a conventional R-value of 0·049 including refined hydrogen parameters. Bond distances and hydrogen atom positions reveal a non-symmetrical system with two sp^2 [C(2)–C(3), 1·319(9) Å] and two sp^3 carbon atoms [C(11)–C(12), 1·484(6) Å] and the open faces of the two η^5-systems skew (60°) to each other.[2] The complexed ring fragments are planar to within 0·03 Å, the terminal carbon atoms [C(4) and C(10)] in a *trans* position to each other being bonded slightly more weakly than the other atoms to the central atom [Fe–C(4) 2·115, Fe–C(10) 2·136 Å] and therefore being removed from these planes by 0·10 and 0·24 Å respectively (Figure).

The structure of the molecule in solution (C_7D_8, $CDCl_3$) is fluxional and is represented by the three modifications (A) (-80 to -30 °C), (B) (-30 to 50 °C), and (C) (50 to 80 °C). The ^1H n.m.r. spectrum of (A) shows 16 different proton resonances (distinguishable where they overlap by ^1H–^1H double resonance experiments) and the ^{13}C proton-noise-decoupled (p.n.d.) n.m.r. spectrum shows 14 resonances. We believe this information is consistent with a structure for (A) which is similar to that observed in the solid with open faces of the two η^5-systems angled to each other. The ^{13}C-p.n.d. n.m.r. spectrum of (B) is derived from that of (A) by a pairwise coalescence of 12 of the 14 signals of the (A) form, two remaining unchanged; similarly the ^1H n.m.r. spectrum of (B) appears to be derived from that of (A) by a pairwise coalescence of signals as would be observed if each ring developed a mirror plane through atoms C(6) or C(8) bisecting the bonds C(2)–C(3) or C(11)–C(12) respectively. Form (B) must therefore contain two rings which rock or rotate with respect to each other in such a way that a pairwise equivalence of all but the C(6)–H and C(8)–H units is induced on the n.m.r. time scale.[3]

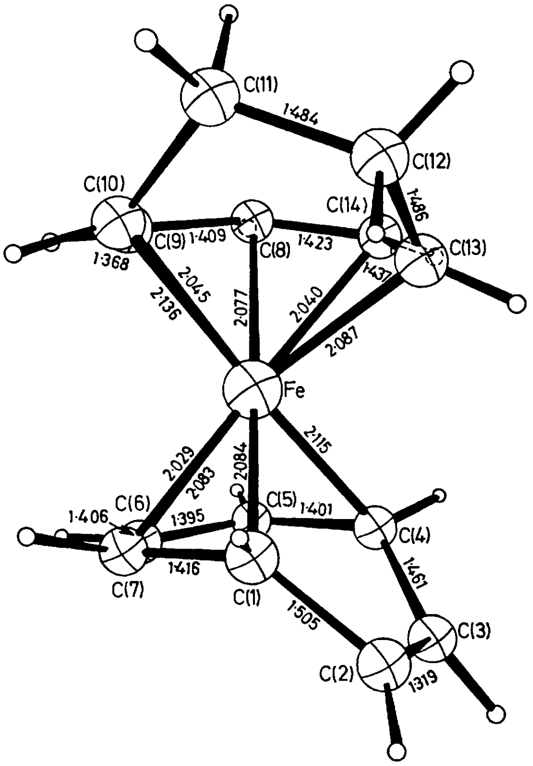

FIGURE. *X*-Ray structure of $[Fe(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$; bond lengths in Å.

The ^1H n.m.r. spectrum of (C) shows a coalescence of all the protons of the C_7H_7 ring (τ 5·6) and an equivalencing of the η-pentadienyl protons of the C_7H_9 ring (τ 5·65), the CH_2 resonances remaining the same as in (B) (τ 7·5 and 8·6).

---

† Satisfactory elemental analyses were obtained.

The ^{13}C-p.n.d. n.m.r. spectrum of the C_7H_9 ring of (C) remains the same as that of (B) but the 4 signals assignable to the C_7H_7 ring have coalesced. The incorporation of the free diene unit of the C_7H_7 ring of (B) in a further fluxional motion for C explains the equivalencing of the ^{13}C and ^{1}H n.m.r. signals, but both rings remain η^5-bonded because the ^{13}C n.m.r. spectrum of the C_7H_9 ring remains unchanged.

We thank our colleagues at the Max-Planck-Institute for support.

(*Received, 24th October* 1975; *Com.* 1202.)

---

[1] E. Koerner von Gustorf, O. Jaenicke, and O. E. Polansky, *Agnew. Chem. Internat. Edn.*, 1972, **77**, 532.

[2] For details of data collection and computing procedures see: D. J. Brauer, C. Krüger, P. J. Roberts, and Y.-H. Tsay, *Chem. Ber.*, 1974, **107**, 3706. A list of atomic parameters and structure factors may be obtained from the authors (C.K.)

[3] J. Müller, C. G. Kreiter, B. Mertschenk, and S. Schmitt, *Chem. Ber.*, 1975, **108**, 273; T. H. Whitesides and R. A. Budnik, *Chem. Comm.*, 1971, 1514; T. H. Whitesides and R. A. Budnik, *J.C.S. Chem. Comm.*, 1974, 302.