The Crystal Structure and Infrared Spectrum of a *cis*-Complex Derived from $[\pi\text{-}C_5H_5Fe(CO)_2]_2$

By P. McARDLE and A. R. MANNING*
(*Department of Chemistry, University College, Belfield, Dublin* 4)

and F. S. STEVENS
(*Department of Chemistry, University of Essex, Colchester, Essex*)

Summary The crystal structure and i.r. spectrum of $[\pi\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4]Fe_2(CO)_4$ are reported; the latter is similar to that predicted for *cis*-$[\pi\text{-}C_5H_5Fe(CO)_2]_2$.

It has been suggested that $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (I) and many of its derivatives exist in solution as solvent-dependent equilibrium mixtures of *cis*- and *trans*-bridged isomers,[1,2] whilst only the *trans*-species are normally present in the solid state.[1–3]

Although the i.r. spectrum[4] of $[\pi\text{-}(C_5Me_5)Fe(CO)_2]_2$ provides a convenient model for the *trans*-species in solution, a simple *cis*-isomer was not available. However, there have been two reports of complexes of the type $[\pi\text{-}C_5H_4CR^1R^2{\cdot}CR^1R^2C_5H_4]Fe_2(CO)_4$ where the cyclopentadienyl ligands are linked by two-carbon bridges.[5,6] These constrain the compounds to a *cis*-conformation. Our attempts to prepare the derivative reported by Weiss and Hubel, in which $R^1 = R^2 = Me$,[5] have been unsuccessful, but we have been able to obtain the compound in which $R^1 = H$ and $R^2 = NMe_2$, (II).[6]

Brown crystals of (II) were grown from benzene–hexane mixtures, and a three-dimensional *X*-ray crystal-structure analysis carried out on one of them. [Orthorhombic, $a = 14{\cdot}957 \pm 0{\cdot}024$, $b = 12{\cdot}792 \pm 0{\cdot}024$, $c = 20{\cdot}128 \pm 0{\cdot}030$ Å, $D_m = 1{\cdot}60$ (by flotation), $M = 466{\cdot}11$, $Z = 8$, $D_c = 1{\cdot}600$. Space group = *Pbca* (No. 61).] Unit-cell and intensity data were obtained from single-crystal precession photographs using Mo-K_α radiation. 2328 unique, non-zero reflections were recorded from layers 0—6, 0—5, and 0—2 precessing about *a*, *b*, and (1,1,0) respectively. The structure was solved by the usual Patterson and Fourier methods, and refined by full-matrix least-squares techniques with individual isotropic thermal parameters for each atom. The present *R* value is 0·095.

As can be seen from Figure 1, the molecule has the expected *cis*-configuration. All bond distances are normal, and similar to those found by Mills for $[\pi\text{-}C_5H_5Fe(CO)_2]_2$.[3] The $Fe_2(CO)_2$ bridging system is not planar, but is bent about the Fe–Fe axis away from the cyclopentadienyl rings.

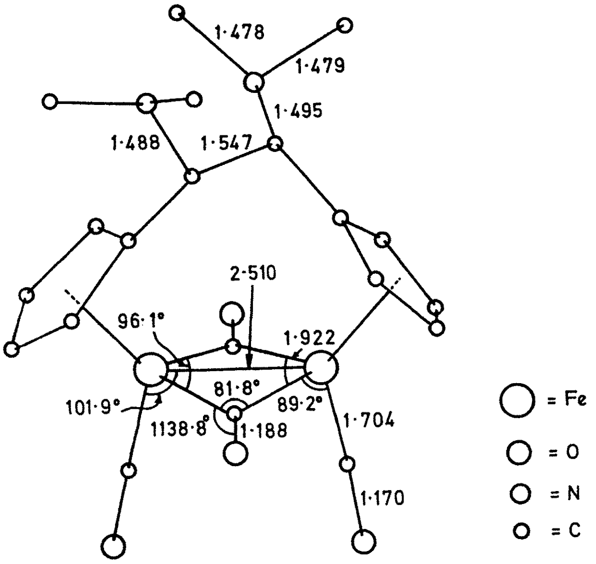

FIGURE 1. *The structure of* $[\pi\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4]\text{-}Fe_2(CO)_4$ (II). [σ Fe–Fe = 0·002 Å, Fe–CO = 0·010—0·013, C–O = 0·013—0·016, C–C *and* C–N = 0·014—0·017, ∠ C-C-C = ca. 1°, *and* ∠ Fe–C–CFe = ca. 0·4°].

The dihedral angle between the normals from the two Fe(CO)Fe planes is 19·9°.

In contrast to those of other dimeric π-cyclopentadienyliron dicarbonyl complexes,[1,2] the i.r. spectrum of (II) in solution is similar to that in the solid state, and is independent of the solvent. Furthermore the relative intensities and frequencies of the four absorption bands due to its ν(CO) vibrations are as predicted for *cis*-$[\pi\text{-}C_5H_5Fe(CO)_2]_2$[1] (Figure 2), and the spectrum is similar to that of (I) in dimethyl sulphoxide. This lends weight to the suggestion that although *cis*-$[\pi\text{-}C_5H_5Fe(CO)_2]_2$ predominates in such solvents, it is not only bridged species in solution.[1]

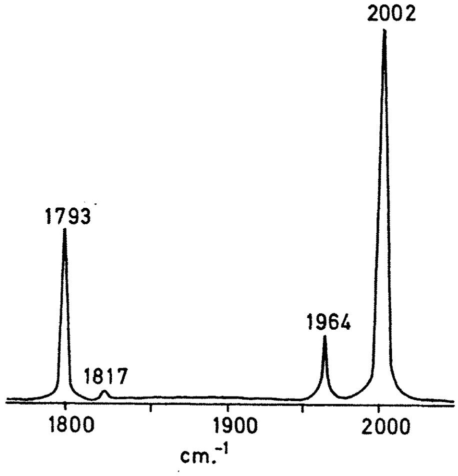

FIGURE 2. *The i.r. spectrum of* $[\pi\text{-}C_5H_4CH(NMe_2)CH(NMe_2)\text{-}C_5H_4]Fe_2(CO)_4$ *in heptane solution.*

There is a close resemblance between the i.r. spectra of (II) in the solid state and of solid films of (I).[1] Thus it is probable that the latter contain high proportions of *cis*-$[\pi\text{-}C_5H_5Fe(CO)_2]_2$ with ν(CO) = 1766, 1801, 1933, and 1975 cm.$^{-1}$.

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