Journal of Organometallic Chemistry, 174 (1979) 335—341

A BRIDGE OPENING SELECTIVITY IN THE ADAMS—COTTON MECHANISM: THE PREPARATION AND FLUXIONAL BEHAVIOUR OF $(\eta^5\text{-Cp})_2Fe_2(CO)_2(CNBu\text{-}t)_2$

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(Received March 3rd, 1979)

Summary

The title molecule exists in solution as a mixture of $(\eta^5\text{-Cp})_2Fe_2(\mu\text{-CO})_2(CNBu\text{-t})_2$ and $(\eta^5\text{-Cp})_2Fe_2(\mu\text{-CO})(\mu\text{-CNBu-t})(CO)(CNBu\text{-t})$ isomers. NMR studies show that interconversion by the Adams—Cotton mechanism proceeds by two different pathways having significantly different activation energies.

Introduction

Studies of the fluxional nature of transition metal carbonyl derivatives continues to attract attention [1]. For many dinuclear derivatives containing two bridging carbonyl ligands, considerable experimental evidence supports a mechanism proposed by Adams and Cotton [2] which involves initial pairwise opening of the bridge to yield an intermediate which may undergo rotation about the M—M bond, followed by reclosure to yield the doubly bridged derivative. The dimer $Cp_2Fe_2(CO)_4$ exists as a *cis—trans* mixture in solution. ^1H and ^{13}C NMR spectra at the lowest temperature studied (—85° C) show that while *cis—trans* interconversion and bridge—terminal CO exchange in the *cis* isomer is slow on the NMR time scale, bridge—terminal exchange in the *trans* isomer is still rapid. Warming results in the onset of *cis—trans* interconversion and bridge—terminal CO exchange in the *cis* isomer at equivalent rates [3a—c]. In terms of the Adams—Cotton mechanism, bridge—terminal exchange in the *trans* isomer may take place without M—M bond rotation in the unbridged intermediate, while bridge—terminal exchange in the *cis* isomer requires M—M bond rotation which also necessarily results in *cis—trans* interconversion. The significantly higher activation energy for the latter process is ascribed to the need for bond rotation. We wish to present here evidence which shows that with a suitably substituted derivative, a selectivity in pairwise bridge opening may also result in observation of more than one type of fluxional process.

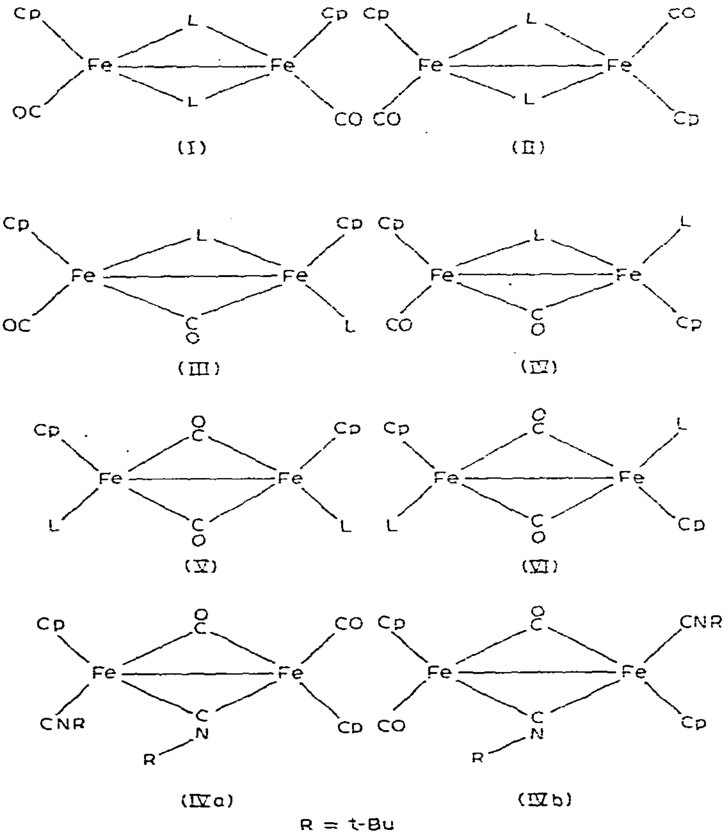

Fig. 1. Isomeric forms of $Cp_2Fe_2(CO)_2L_2$ (L = CNBu-t).

Results and discussion

The title complex was an unexpected product of the reaction of CNBu-t with the thiocarbonyl complex $Cp_2Fe_2(CO)_3(CS)$ [4] *, although we have also isolated it in small yield from the reaction of a large excess of CNBu-t with $Cp_2Fe_2(CO)_4$ in refluxing benzene. It is unusual in being green in colour, both in the solid state and in solution, rather than the purple-red colour of other derivatives of the type $Cp_2Fe_2(CO)_x(CNR)_{4-x}$ (x = 1—4). Satisfactory analytical and mass spectral data were obtained.

Isonitrile ligands are well known to function as both bridging and terminal ligands, and the six possible isomeric forms of this complex are shown in Fig. 1. The infrared spectrum (hexane) shows absorptions at 2099 (sh), 2050 (33), 1945(43), 1935(50), 1779(30), 1755(100) and 1715(26) cm^{-1} (relative intensities in parentheses). The two broad bands at highest frequency may be assigned to ν(C—N) (terminal) vibrations. Bands at 1945, 1935, 1779 and 1715 cm^{-1}

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* A full report of this reaction, and that with $Cp_2Fe_2(CO)_2(CS)_2$ will be published elsewhere.

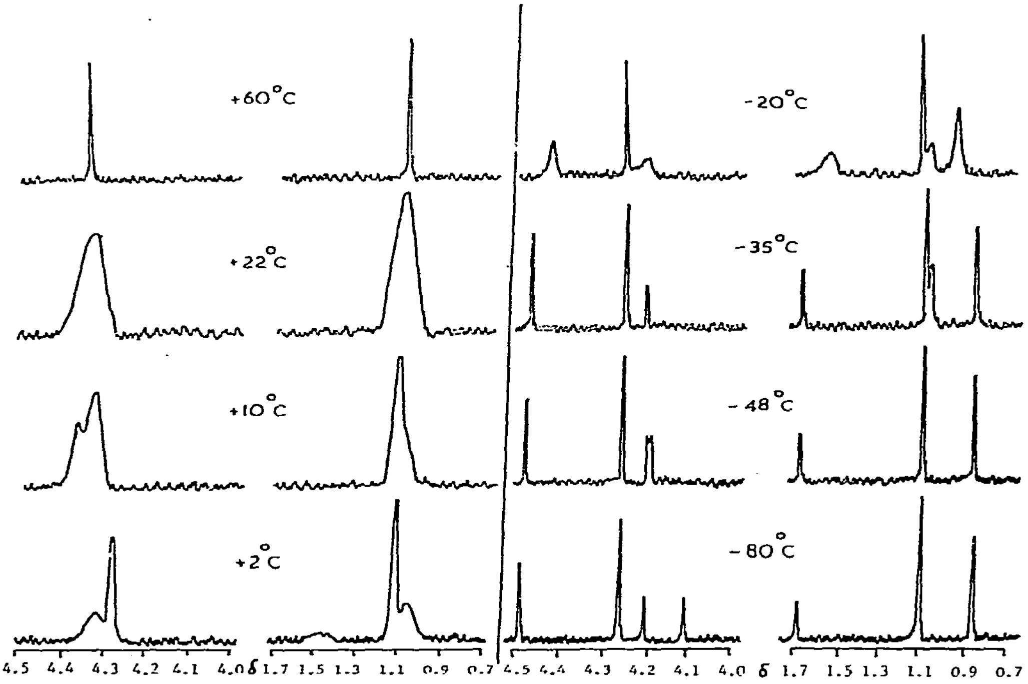


Fig. 2. ^{1}H NMR spectra of $Cp_2Fe_2(CO)_2(CNBu\text{-}t)_2$. Toluene-$d_8$; solvent peaks omitted.

may be assigned to ν(C—O) (terminal), ν(C—O) (bridging) and ν(C—N) (bridging) vibrations of either isomer III or IV. NMR results (vide infra) show only IV to be present, and the observation of two terminal ν(C—O) absorptions may be taken to indicate the presence of the two enantiomers IVa and IVb. A similar assignment has been made for the trisubstituted $Cp_2Fe_2(CO)(CNMe)_3$ derivative [5]. The remaining band at 1755 cm^{-1} may be assigned to the ν(C—O) (bridging) vibration of V and VI; NMR studies (vide infra) show both to be present. No detectable concentrations of isomers I and II are found. It is also interesting to note that in comparison, the monosubstituted complex $Cp_2Fe_2(CO)_3$-(CNBu-t) shows no evidence for detectable concentrations of an isonitrile-bridged isomer [6a,b] while in the case of the other disubstituted molecule to be studied in detail, [$Cp_2Fe_2(CO)_2(CNMe)_2$], only the isomers of structures I and IV are found in solution, with no detectable concentrations of V or VI [3b,5].

Proton NMR spectra in toluene-d_8 at various temperatures are shown in Fig. 2. In the spectrum obtained at the lowest temperature (—80°C), the doublet at δ4.15 ppm may be assigned to the non-equivalent cyclopentadienyl ligands of either III or IV, although consideration of the mechanism is consistent with IV only. The resonance at δ1.69 ppm may be assigned to the bridging CNBu-t group of IV, while that due to the terminal CNBu-t ligand is masked by the resonances due to V and VI, although it can be seen in the spectrum obtained at —35°C. By analogy with $Cp_2Fe_2(CO)_2(CNMe)_2$, cooling below —80°C should result in separation of individual resonances for IVa and IVb due to the slowing

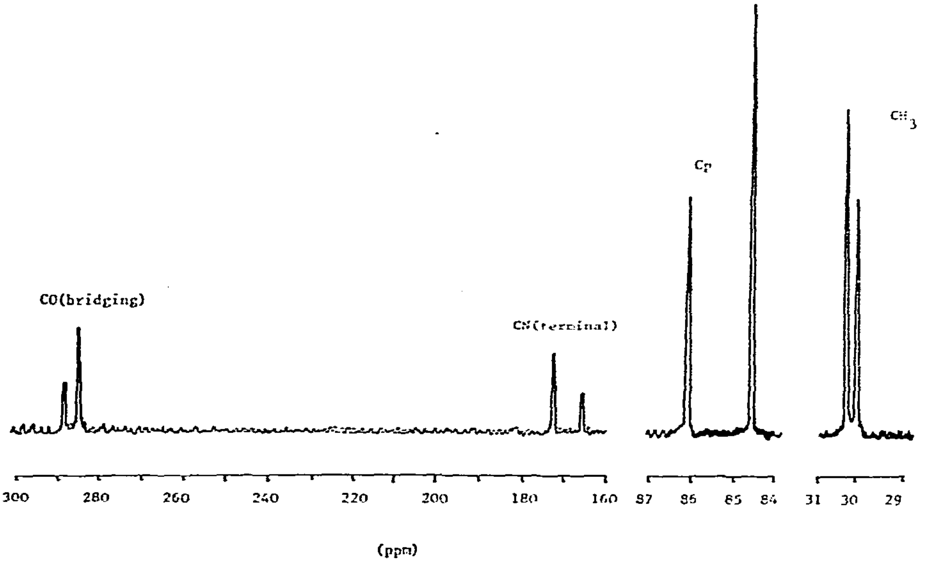


Fig. 3. ^{13}C NMR spectrum of $Cp_2Fe_2(CO)_2(CNBu\text{-}t)_2$: CD_2Cl_2/CH_2Cl_2, −20°C: proton decoupled; $Cr(acac)_3$ added. (Not to scale: quaternary carbon resonances under solvent peak at 54 ppm.)

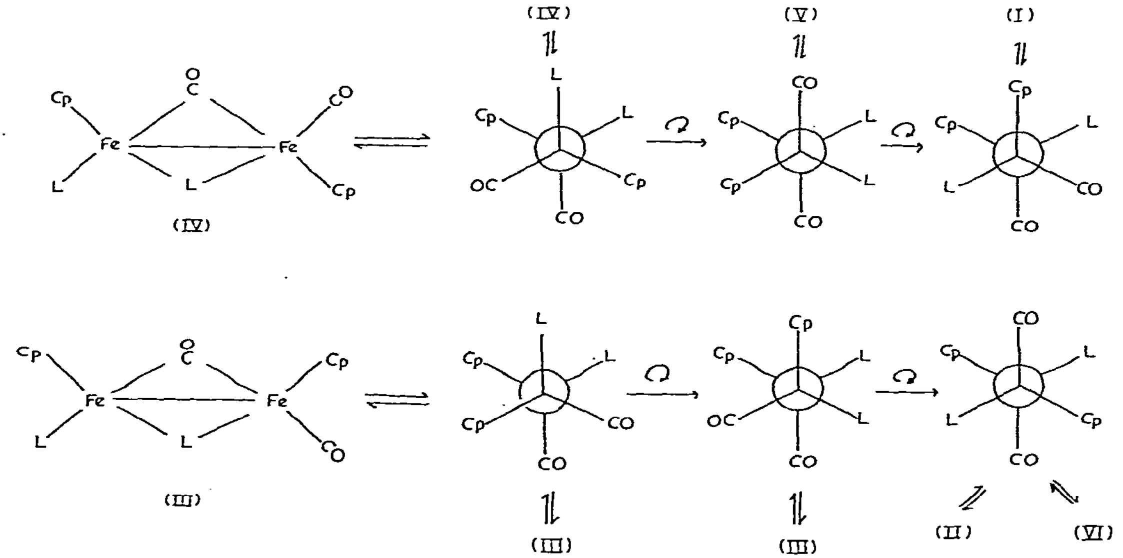
of nitrogen inversion [5]. This we have not done, however.

The cyclopentadienyl resonances at δ 4.48 and 4.26 ppm (ratio 1 : 1.2) and the t-butyl resonances at δ 1.12 and 0.78 ppm may be assigned to the *cis*/*trans* mixture of V and VI. A tentative assignment of signals may be made by comparison with the spectrum in CD_2Cl_2 at −80°C which shows two cyclopentadienyl resonances at δ 4.47 and 4.37 ppm in the ratio of 2 : 1. It has previously been shown for $Cp_2Fe_2(CO)_4$ [7] and $Cp_2Fe_2(CO)_3(CS)$ [4] that an increase in the polarity of the solvent medium increases the proportion of the more polar *cis* isomer. We thus assign the resonance at δ 4.48 ppm in the toluene spectrum to the *cis* isomer, and that at δ 4.26 ppm to the *trans*. It may be noted that only one t-butyl resonance (δ 1.20 ppm) is observed in CD_2Cl_2, and that isomer IV has been depopulated below the limits of detectability. The ^{13}C spectrum in CD_2Cl_2 (Fig. 3) is also consistent with a mixture of V and VI, and here two t-butyl resonances are observed.

Consideration of the variable temperature spectra show that two fluxional processes are occurring: (a) at lower temperature, both bridge—terminal isonitrile and, most probably cyclopentadienyl site exchange in the resonances attributed to IV, accompanied by interconversion with the *cis* isomer V only, and (b) at higher temperatures, a *cis*—*trans* interconversion of V and Vl which eventually yields the high temperature limiting spectrum at +60°C.

The behaviour outlined in (a) may be explained by the Adams—Cotton mechanism of Scheme 1 in which pairwise bridge opening yields the symmetrically substituted Cp(CO)(CNBu-t)FeFe(CO)(CNBu-t)(CO)Cp intermediate. By consideration of the isomers available from bridge closure of the various non-bridged rotamers, it is evident that the equilibria constitute closed sets. Thus, if the lower field cyclopentadienyl resonance is assigned to V, it follows

SCHEME 1 (L = CNBu-t)



that isomer IV is taking part in the fluxional process at lower temperature.

$$\begin{tikzcd} & \mathrm{II} \arrow[dr, leftrightharpoons] & \\ \mathrm{VI} \arrow[ur, leftrightharpoons] \arrow[rr, leftrightharpoons] & & \mathrm{III} \end{tikzcd} \quad \text{and} \quad \begin{tikzcd} & \mathrm{IV} \arrow[dr, leftrightharpoons] & \\ \mathrm{I} \arrow[ur, leftrightharpoons] \arrow[rr, leftrightharpoons] & & \mathrm{V} \end{tikzcd}$$

Note also that IV can undergo bridge—terminal isonitrile exchange and cyclopentadienyl site exchange without M—M bond rotation, whereas the interconversions IV $\rightleftharpoons$ V or IV $\rightleftharpoons$ I require rotation. This has been verified in the case of $Cp_2Fe_2(CO)_2(CNMe)_2$ [3a] where IV $\rightleftharpoons$ I interconversion has a higher activation energy (23.0 kcal mol^{-1}) than that found for bridge—terminal isonitrile exchange and cyclopentadienyl exchange in IV (19.8 kcal mol^{-1}). Because of the low population of IV and the overlap of signals, it is difficult to judge whether this is also true for the IV $\rightleftharpoons$ V interconversion observed here. The changes observed in the doublet at δ 4.15 ppm in the temperature range —80 to —35°C are not associated with a fluxional process, but are due to a temperature dependent chemical shift of the resonance at higher field. Spectra in this temperature range show a coalescence of these two resonances, but with no associated broadening, and we have observed similar behaviour in the cyclopentadienyl resonances of $Cp_2Fe_2(CO)_2(CS)(CNBu\text{-}t)$ and $Cp_2Fe_2(CO)(CS)_2$-(CNBu-t) *. From the coalescence of the bridge and terminal isonitrile resonances, an approximate ΔG^* value of 13.4 kcal mol^{-1} may be calculated (cf. 19.8 kcal mol^{-1} for the analogous process in $Cp_2Fe_2(CO)_2(CNMe)_2$ in *o*-dichlorobenzene as solvent [3a]).

Scheme 1 cannot account for the V $\rightleftharpoons$ VI interconversion observed at higher temperatures. However, bridge opening to give the asymmetrically substituted $Cp(CO)_2FeFe(CNBu\text{-}t)_2Cp$ intermediate outlined in Scheme 2 does provide a pathway. It can be seen that bridge opening in this fashion results only in equilibration between III and IV. However, since V $\rightleftharpoons$ IVand VI $\rightleftharpoons$ III from con-

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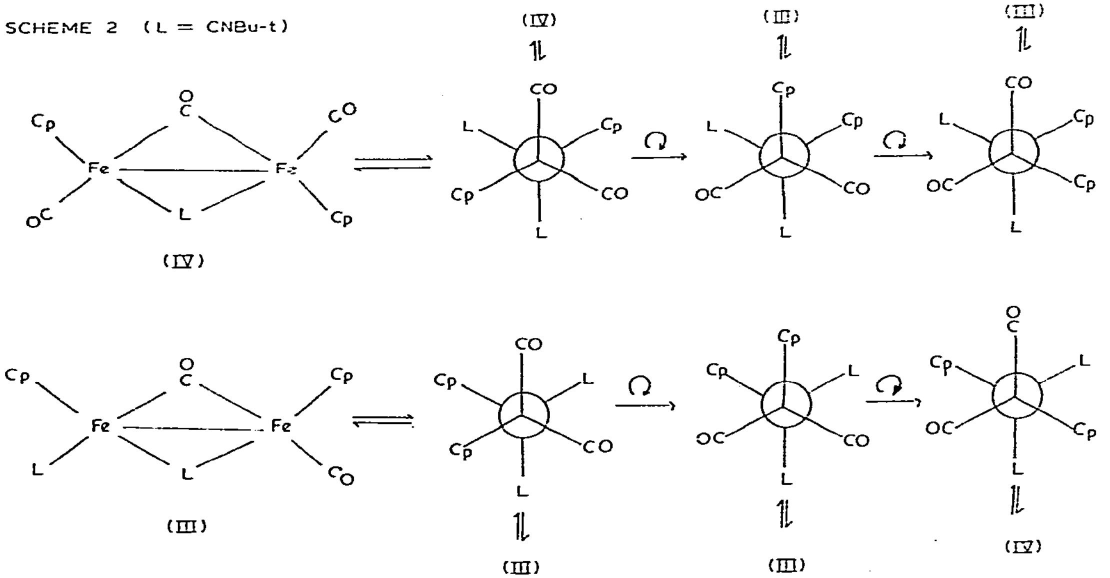
* See footnote on p. 336.

sideration of Scheme 1, it follows that interconversion of V and VI occurs, even though no concentration of III may actually be detected. Thus, Scheme 2



SCHEME 2 (L = CNBu-t)

provides a mechanism for linking of the two closed sets of Scheme 1. The possibility of asymmetric cleavage has been outlined by Adams and Cotton [3a], although these results provide the first experimental evidence. At least in this case, the statement by Adams and Cotton that "unsymmetrical intermediates may be too unstable to play a role in the rearrangements" seems unjustified. The significantly higher activation energy observed for V $\rightleftharpoons$ VI interconversion may perhaps be a consequence of the greater strain introduced on bridge opening to yield an intermediate in which the two sterically demanding CNBu-t ligands are bonded to the same iron atom.

It should also be noted that it is only in this unique situation of the interconversion IV $\rightleftharpoons$ V $\rightleftharpoons$ VI [or III $\rightleftharpoons$ V $\rightleftharpoons$VI] that a selectivity in bridge opening may be detectable. For both monosubstituted $Cp_2Fe_2(CO)_3(CNR)$ and trisubstituted $Cp_2Fe_2(CO)(CNR)_3$ complexes, pairwise bridge opening can yield only one structural isomer for the non-bridged intermediate, regardless of the isomeric form of the bridged dimer from which it was derived.

Experimental

NMR spectra were recorded on a JEOL FX-100 spectrometer. ^{13}C spectra were recorded in the presence of $Cr(acac)_3$ as relaxation agent. All chemical shifts are with respect to Me_4Si. Infrared spectra were recorded on a Perkin—Elmer 257 spectrometer using 1 mm NaCl cells.

Acknowledgement

We thank the S.R.C. and the University of Keele for financial support.

References

1 J. Evans, Adv. Organometal. Chem., 16 (1977) 319.
2 F.A. Cotton and L.M. Jackman, Dynamic NMR Spectroscopy, Academic Press, New York, 1975.
3 (a) R.D. Adams and F.A. Cotton, J. Amer. Chem. Soc., 95 (1973) 6589; (b) D.C. Harris, E. Rosenberg and J.D. Roberts, J. Chem. Soc. Dalton, (1974) 2398; (c) O.A. Gansow, A.R. Burke and W.D. Vernon, J. Amer. Chem. Soc., 94 (1972) 2550.
4 M.H. Quick and R.J. Angelici, J. Organometal. Chem., 160 (1978) 231.
5 R.D. Adams and F.A. Cotton, Inorg. Chem., 13 (1974) 249.
6 (a) R.D. Adams, F.A. Cotton and J.M. Troup, Inorg. Chem., 13 (1974) 257; (b) J.A.S. Howell, M.J. Mays and T.W. Matheson, J. Chem. Soc. Chem. Commun., (1975) 865.
7 A.R. Manning, J. Chem. Soc. A, (1968) 1319. Values obtained for the *cis/trans* ratio of $Cp_2Fe_2(CO)_4$ in xylene and CH_2Cl_2 at room temperature from infrared data are 1 : 1 and 1.5 : 1, respectively.