A Proof of the Validity of the Application of Woodward–Hoffmann Rules to the Fluxionality of $Fe(\eta^4-C_8H_8)(CO)_2(CNPr^i)$

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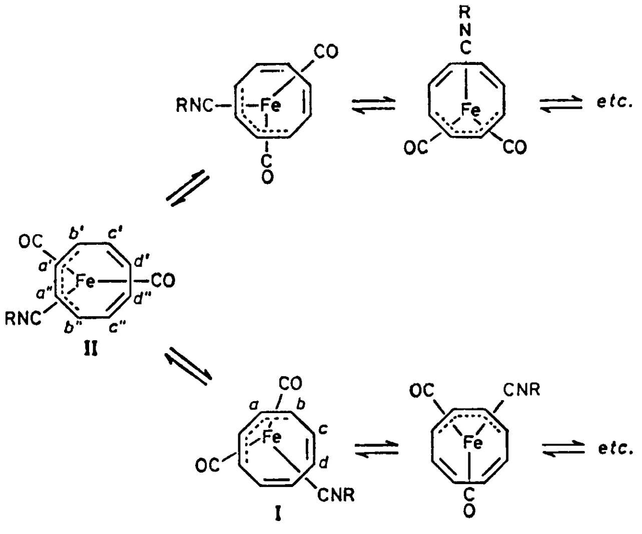
Magnetisation transfer measurements have been applied to the ^{13}C n.m.r. spectrum of $Fe(\eta^4-C_8H_8)(CO)_2(CNPr^i)$ to demonstrate specific transfer, completely consistent with the Woodward–Hoffmann mechanism, but inconsistent with the least motion mechanism.

There are currently two theories for the fluxionality of η-polyenes and η-polyenyls on metals, one based on the Woodward–Hoffmann rules and the other based on least motion coupled with carbonyl scrambling. It has been



Scheme 1

proposed that the observed shifts of π-systems on metals can be described in terms of the Woodward–Hoffmann rules if localized bonding descriptions are used to represent the polyene bonding,[1] and this approach permits the rationalisation of $Fe(\eta^4\text{-}C_8H_8)(CO)_3$ being highly fluxional[2] while $[Fe(\eta\text{-}C_5H_5)(\eta^2\text{-}C_8H_8)(CO)_2]^+$[3] and $[Fe(\eta\text{-}C_5H_5)(\eta^6\text{-}C_8H_8)]^+$[4] are static at room temperature. Subsequently this theory was extended to include the other ligands on the metal, which permitted the explanation of concomitant carbonyl scrambling and metal migration in $Fe(\eta^4\text{-}C_8H_8)(CO)_3$ and the increase in activation energy found in $Fe(\eta^4\text{-}C_8H_8)(\eta^4\text{-}C_4H_6)(CO)$.[5] Although this theory provides an attractive interpretation of experimental observations, the alternative interpretation of the observations based on the least motion of the metal producing [1,2]-shifts coupled with carbonyl scrambling[2] as observed for $Fe(\eta^4\text{-}C_4H_6)(CO)_3$[6] could not be dismissed as, prior to this work, the two theories were experimentally indistinguishable.

In order to provide the first direct experimental evidence which differentiates between these two mechanisms, a number of compounds $Fe(\eta^4\text{-}C_8H_8)(CO)_2L$, L = MeNC, Pr^{i}NC, Bu^{t}NC, PhNC, 2,4,6-$Me_3C_6H_2NC$, and $P(OMe)_3$, have been synthesised by reacting $Fe(\eta^4\text{-}C_8H_8)(CO)_3$[7] with L in MeCN at *ca.* 21 °C in the presence of Me_3NO.[8] After chromatography, $Fe(\eta^4\text{-}C_8H_8)(CO)_2L$ is isolated in better than 32% yield.[9]† The low temperature 100.6 MHz ^{13}C n.m.r. spectra of these compounds, L = CNR, in CD_2Cl_2–$CHFCl_2$ showed the presence of a mixture of two isomers, I and II, which are rapidly interconverting at room temperature. It was not possible to obtain limiting low temperature spectra when L = $P(OMe)_3$. In each case where L = CNR, no difference in rate was found between carbonyl exchange, cyclo-octatetraene rotation, and isomer interconversion after allowing for the difference in population of the various sites.

A more detailed mechanistic investigation was performed on $Fe(\eta^4\text{-}C_8H_8)(CO)_2(CNPr^i)$, using ^{13}C magnetisation transfer; this molecule being chosen as at low temperature isomers I and II are present in approximately equal concentration. The mechanism using the Woodward–Hoffmann rules[1,5] makes predictions as to the interconversion of isomers and the movement of specific carbon atoms in the cyclo-octatetraene ring, see Scheme 1. The 100.6 MHz ^{13}C n.m.r. spectrum at −118 °C is shown in Figure 1(a), where exchange is relatively fast, k = *ca.* 100 s^{-1}. At −150 °C, a limiting low temperature spectrum was obtained, and the assignments

Figure 1. (a) A partial 100.6 MHz ^{13}C n.m.r. spectrum of $Fe(\eta^4\text{-}C_8H_8)(CO)_2(CNPr^i)$ in CD_2Cl_2–$CHFCl_2$, 1 : 1, at −118 °C. In addition to the cyclo-octatetraene signals, there is a doublet at δ 104.9 due to $CHFCl_2$, a weak doublet at δ 89.5 due to solvent impurity coincident with the signals due to carbons *a′* and *a″*, a broad singlet at δ 54.6 due to CD_2Cl_2, and two signals at δ 49.2 and 48.4 p.p.m. due to the methine carbons of the isopropyl group. (b) The partial spectrum 1 μs after applying a selective 180° pulse at δ 55.5 p.p.m. A sideband, 5 kHz away perturbed the $CHFCl_2$ signal. (c) A difference spectrum obtained by subtracting spectrum (b) from that obtained 10 ms after applying a selective 180° pulse at δ 55.5 p.p.m.

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† Satisfactory analyses and mass spectra were obtained for all compounds.

are based on that, and literature data for Fe(η^4-C_8H_8)(CO)$_3$.[2] Isomer I has cyclo-octatetraene ^{13}C signals at δ 86.6, *a*; 61.1, *b*; 127.2, *c*; and 117.9 or 118.2 p.p.m., *d*; while isomer II has the signals at δ 88.2, 90.6, *a′*,*a″*; 55.5, 62.3, *b′*,*b″*; 128.8, 129.2, *c′*,*c″*; and 117.9 and/or 118.2 p.p.m., *d′*,*d″*. Using the DANTE pulse sequence,[10] a specific 180° pulse was applied to the signal *b′* or *b″* at δ 55.5 p.p.m.,‡ see Figure 1(b). At −118 °C the subsequent transfer of magnetisation was monitored as a function of time. Magnetisation transfer occurred first to the signals at δ 86.6, *a*, and δ 128.2 p.p.m., *c′* or *c″*, and was maximum after *ca.* 10 ms, see Figure 1(c) where it is displayed as the difference between this spectrum and that after 1 μs to emphasise the changes. This observation is completely consistent with Scheme 1 where the inverted magnetisation at carbon *b′* is first transferred to sites *c′* and *a*.§ The mechanism involving least motion would transfer magnetisation to *a′* and *c′* first while carbonyl scrambling would transfer it to *b* and *b″*. This is inconsistent with experimental observations and both the least motion and carbonyl scrambling mechanisms can be rejected as being the predominant mechanism for this compound. These meaurements provide a powerful check of mechanism and prove the validity of the Woodward–Hoffmann mechanism.

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‡ A sideband also perturbed the CHFCl$_2$ solvent resonance.

§ The assignment of the signal at δ 55.5 p.p.m. as *b′* is consistent with CNR being a weaker *trans*-influence ligand than CO.[11] Assignment of the signal at δ 55.5 p.p.m. to *b″* would not produce the observed magnetisation transfer.

References

1 D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1977, 31.
2 F. A. Cotton and D. L. Hunter, *J. Am. Chem. Soc.*, 1976, **98**, 1413.
3 A. Cutler, D. Ehntholt, W. P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, and D. Wells, *J. Am. Chem. Soc.*, 1976, **98**, 3495.
4 D. L. Reger and C. Coleman, *J. Organomet. Chem.*, 1977, **131**, 153.
5 J. A. Gibson and B. E. Mann, *J. Chem. Soc., Dalton Trans.*, 1979, 1021; B. E. Mann in 'Comprehensive Organometallic Chemistry,' ed. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Vol. 3, Chapter 20, p. 89, 'Non-rigidity in Organometallic Chemistry,' Pergamon, New York, 1982.
6 L. Kruczysnki and J. Takats, *Inorg. Chem.*, 1976, **15**, 3140.
7 T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc., London*, 1959, 90; *J. Am. Chem. Soc.*, 1960, **82**, 366.
8 Y. Shro and E. Hazum, *J. Chem. Soc., Chem. Commun.*, 1975, 829; D. J. Blumer, K. W. Barrett, and T. L. Brown, *J. Organomet. Chem.*, 1979, **173**, 71.
9 A multistep synthesis of Fe(η^4-C_8H_8)(CO)$_2$CNR has been previously described, H. Behrens, M. Moll, W. Popp, N-J. Seibold, E. Sepp, and P. Würstl, *J. Organomet. Chem.*, 1980, **192**, 389.
10 G. A. Morris and R. Freeman, *J. Magn. Reson.*, 1978, **29**, 433.
11 W. Strohmeier and H. Hellman, *Chem. Ber.*, 1964, **97**, 1877.