

FURTHER MECHANISTIC DETAIL ON THE FLUXIONAL BEHAVIOR OF (η^1 -CYCLOPENTADIENYL)IRON COMPLEXES

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Summary

NMR studies on several complexes of type $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{L}(\eta^1\text{-C}_5\text{H}_4\text{R})$ indicate that the fluxional process in these molecules involves a suprafacial migration with retention of configuration of the migrating group.

Introduction

It is well established that fluxional rearrangement of $\eta^1\text{-Cp}$ complexes (Cp = cyclopentadienyl) involves 1,2 shifts (so-called “ring-whizzing”), for all systems examined, both of main group and transition metals [1]. This result agrees with theoretical predictions both by the Woodward–Hoffmann rules (i.e., a 1,5-sigmatropic migration) [2] and a perturbation method treatment [3]. The former also require that an allowed 1,5 migration be suprafacial with retention at the migrating group, or, alternatively, antarafacial with inversion. While the former seems much more probable simply considering the geometry of the system, it seemed worthwhile to attempt to design a system which would test experimentally whether these rules are satisfied, particularly for a transition metal complex.

It has previously been pointed out [1,4] that the low temperature NMR spectrum of a $\eta^1\text{-Cp}$ complex which has a chiral metal center will show all five ring protons as nonequivalent. Since all five positions become equivalent when the fluxional rearrangement is fast, the chiral center does not provide new information which can be used to answer the questions raised above. However, if the ring is monosubstituted, then the remaining four protons will still be nonequivalent even in the fast-exchange region, unless the fluxional process involves one (not both) of the following: inversion of the metal center, or traversal of the migrating center from one face of the ring to the other. Either of these would interchange the two nonequivalent edges of the $\eta^1\text{-C}_5\text{H}_4\text{R}$ ring and thus simplify the ABCD system into AA'BB'. The system to be studied,

therefore, should be (for example) of type $(\eta^5\text{-Cp})\text{Fe}(\text{CO})\text{L}(\eta^1\text{-C}_5\text{H}_4\text{CH}_3)$. If, in addition, the ligand L contains a pair of diastereotopic groups, then inversion at the chiral metal center can be probed independently of the nature of the motion about the ring, allowing both aspects of the fluxional process to be determined.

Results and discussion

We have previously shown that the reaction of $(\eta^5\text{-Cp})\text{Fe}(\text{CO})_2(\eta^1\text{-Cp})$ (Ia) with phosphorus ligands gives substitution products only for certain types of ligand; $(\eta^5\text{-Cp})\text{Fe}(\text{CO})(\text{P}(\text{OPh})_3)(\eta^1\text{-Cp})$ (IIa) was prepared and its fluxional behavior examined [5]. In similar fashion, the methyl substituted analog $(\eta^5\text{-Cp})\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_4\text{CH}_3)$ (Ib) affords $(\eta^5\text{-Cp})\text{Fe}(\text{CO})(\text{P}(\text{OPh})_3)(\eta^1\text{-C}_5\text{H}_4\text{CH}_3)$ (IIb). Whereas the η^1 -ring proton region of the NMR spectrum of Ib (which has no chiral center) shows two peaks of equal area (resulting from an AA'BB' system which is not quite at the fast-exchange limit, thus giving only two broad, unresolved signals), the same region for IIb shows two peaks with intensity ratio 3/1 (Fig. 1). This is only consistent with an ABCD system wherein three of the protons are sufficiently close in shift to give one broad signal. Exactly the same pattern was observed in the low-temperature spectrum of $\text{SiHCl}(\text{n-Bu})(\eta^1\text{-Cp})$ [4]. On raising the temperature these peaks sharpen somewhat, and some fine structure begins to be visible; however, decomposition (leading to Ib, methylferrocene, and several unassigned new peaks) also becomes quite significant, making a limiting fast-exchange spectrum unattainable. However, as the temperature is raised, only sharpening and no broadening (until decomposition is so

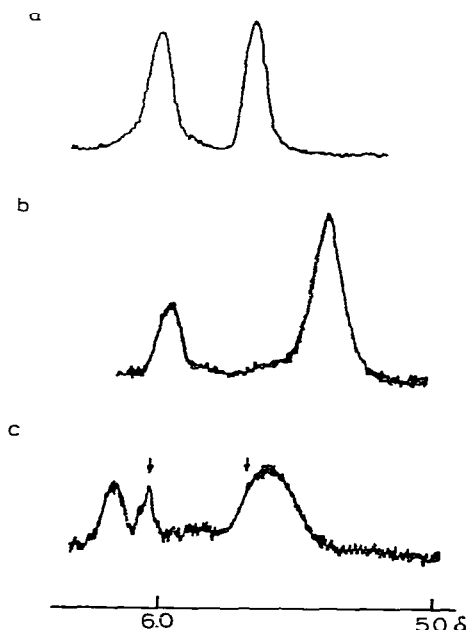


Fig. 1. ^1H NMR spectra (60 MHz, ambient temperature). (a) Ib (C_6D_6); (b) IIb (CDCl_3); (c) IIIb (C_6D_6), signals indicated with arrows are due to Ib.

extensive as to degrade the entire spectrum) was ever observed, indicating that any process causing exchange of these protons always remains slow on the NMR time scale.

In hopes of getting a better-resolved spectrum, we also ran the ^{13}C spectrum of Ib; however, the expected greater shift differences also mean that the broadening due to being below the fast-exchange limiting temperature will also be more severe; only a broad, featureless signal was observed up to 60°C , by which temperature decomposition is quite rapid. (The ^{13}C spectrum of Ib shows the expected three signals at 60°C , although they are still quite broad; decomposition appears much slower than for IIb.)

The low-temperature behavior of the ^1H spectrum of IIb shows the anticipated behavior: the two signals broaden and coalesce, then grow up as a very broad and complex set of signals as the temperature is lowered. The complexity results from the existence of three distinct isomers (depending upon the relative position of methyl and metal groups), each giving rise to three or four signals in this region; the possibility of restricted rotation about the Fe—C bond is an additional complicating factor [6]. Although accurate kinetic information cannot be obtained, the coalescence temperature appears fairly close to that observed for IIa [5].

Compounds $(\eta^5\text{-Cp})\text{Fe}(\text{CO})(\text{PF}_2\text{NMe}_2)(\eta^1\text{-C}_5\text{H}_4\text{R})$ ($\text{R} = \text{H}$, IIIa; $\text{R} = \text{CH}_3$, IIIb) were prepared from the corresponding dicarbonyl by irradiation in the presence of catalytic amounts of $[\text{CpFe}(\text{CO})_2]_2$; this method takes advantage of our knowledge of the radical chain mechanism for these substitution reactions [7]. These compounds appear to be even more liable to decomposition than the $\text{P}(\text{OPh})_3$ derivatives; even though the products appeared to separate cleanly from the unreacted parent dicarbonyl on chromatography, the NMR of the isolated product always shows a small amount of the parent. However, NMR spectral characterization appears unequivocal. The key region of the ^1H spectrum of IIIb (Fig. 1) again shows two broad signals in a 3/1 ratio, leading to the same conclusion as for IIb: all four protons are nonequivalent. (The presence of a small amount of Ib can be clearly seen, but this can be corrected for in determining peak intensities.)

The ^{19}F NMR of both IIIa and IIIb shows two sets of multiplets (Fig. 2), demonstrating that configuration at iron is always retained; otherwise the two diastereotopic fluorines would become equivalent. Using the rate estimated for the fluxional rearrangement of IIa [5], the shift difference between the two fluorines, and the usual simple formulas [8], if the rearrangement were always accompanied by inversion, the ^{19}F spectrum would be well on the fast-exchange side of the coalescence point. From the linewidths (compared to the reference standard), there is no evidence for broadening due to exchange at all.

From the proton spectra, then, the fluxional process must be either suprafacial migration with retention, or antarafacial with inversion. From the ^{19}F spectrum inversion does not occur; therefore the first alternative is confirmed. An analogous establishment of retention of configuration was recently reported for $\text{SiHCl}(\text{i-Pr})(\eta^1\text{-C}_5\text{H}_5)$ [9]; while the question of supra- vs. antarafaciality was not addressed, the former seems overwhelmingly more probable. Thus both a main group and a transition metal $\eta^1\text{-Cp}$ system have now been found to follow the orbital symmetry allowed path, although as noted earlier, this is also the

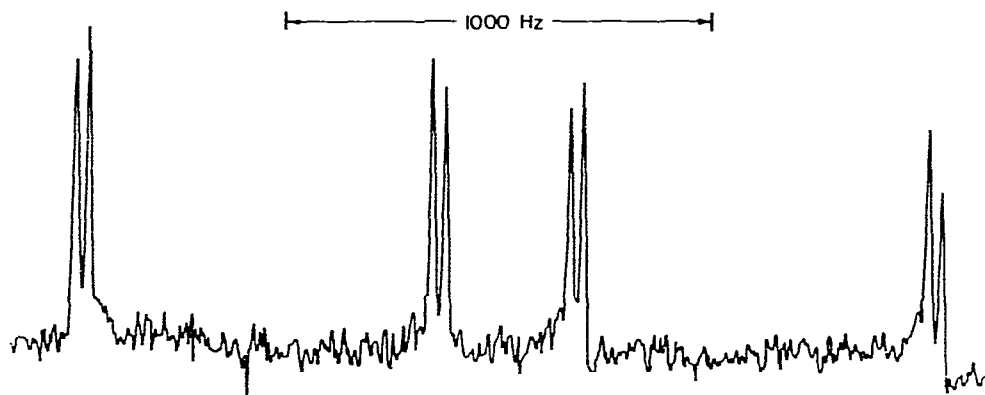


Fig. 2. ^{19}F NMR spectrum of IIIa (94.1 MHz, ambient temperature, C_6D_6).

path one would intuitively predict from the principle of least motion. These results may be contrasted with those found for $\eta^1\text{-C}_7\text{H}_7$ complexes: while $\text{Ph}_3\text{Sn}(\eta^1\text{-C}_7\text{H}_7)$ rearranges via orbital symmetry allowed 1,5 shifts [10], $(\text{CO})_5\text{-Re}(\eta^1\text{-C}_7\text{H}_7)$ follows 1,2-shifts (least motion) instead [11]. A reasonable, albeit still tentative, conclusion is that sigmatropic migrations of transition metal centers are governed by the principle of least motion; there is yet no clear evidence that orbital symmetry rules (in the form constituted for organic systems, that is) are applicable for transition metal systems as well.

Experimental

All manipulations were carried out under inert atmosphere using standard methods. NMR spectra were obtained on Varian A-60 and XL-100 instruments.

$(\eta^5\text{-Cp})\text{Fe}(\text{CO})(\text{P}(\text{OPh})_3)(\eta^1\text{-C}_5\text{H}_4\text{CH}_3)$ (IIb). IIb was prepared from Ib as previously reported for IIa [5]. The ^1H NMR (CDCl_3) shows singlets at 1.98 (CH_3) and 3.55 (Cp), a multiplet around 7.2 (Ph), and two broad, featureless signals at δ 5.4 and 6.0 ppm (Fig. 1), whose areas integrate (relative to each other as well as to the rest of the spectrum) for 3 and 1 protons, respectively. On raising the temperature these peaks sharpen somewhat; some fine structure may be seen by 55°C but the sample is over half decomposed (giving Ib, methylferrocene, and several additional peaks not assigned) after 20 minutes at this temperature. On lowering the temperature these two peaks coalesce around -25°C ; by -55°C a broad and complex multiplet extending over the range δ 6–7 ppm is observed.

The ^{13}C spectrum (CDCl_3) shows sharp signals at 15.6 (CH_3), 84.1 (Cp), 121.1, 124.6 and 129.3 (Ph), and 219.8 ppm (d, $^2J(\text{CP})$ 46 Hz, CO), plus a very broad signal (ca. 220 Hz full width) centered at δ 100 ppm; only marginal sharpening is found up to 55°C , when decomposition has become serious. For comparison, the ^{13}C spectrum of Ib (which does not appear to have been previously reported) consists of peaks at 15.6 (CH_3 ; appears as quartet with $^1J(\text{CH})$ 123 Hz in gated-decoupled spectrum), 85.6 (Cp; doublet of quintets, $^1J(\text{CH})$ 179, $^2J(\text{CH}) = ^3J(\text{CH}) = 6$ Hz), 215.8(CO); the η^1 -ring carbons give a signal which is poorly resolved at room temperature, but by 55°C three separate (but

still broad) peaks can be distinguished at δ 98.9, 111.6 and 117.6 ppm; only slight decomposition is observed at this temperature.

$(\eta^5\text{-Cp})\text{Fe}(\text{CO})(\text{PF}_2\text{NMe}_2)(\eta^1\text{-C}_5\text{H}_5)$ (*IIIa*). A solution of Ia in benzene (0.15 M) containing a three-fold excess of PF_2NMe_2 [12] and a few mg $[\text{CpFe}(\text{CO})_2]_2$ was irradiated (Rayonet photochemical reactor $\lambda_{\text{max}} \approx 360$ nm, Pyrex vessel) for about 1 h, when NMR monitoring showed that product signals had reached a maximum (continued irradiation results primarily in formation of more ferrocene). About 50% of starting Ia had been consumed. Evaporation of solvent and chromatography on neutral alumina, eluting with petroleum ether/toluene, gave three bands, identified as ferrocene, Ia, and product *IIIa*, successively. However, the last fraction still contained some Ia. All attempts at crystallization or repeated chromatography gave only a slightly impure orange oil, which did not give satisfactory C, H analyses (not surprisingly as it appears to be somewhat thermally unstable). IR: $\nu(\text{CO})$ 2020w, 1940s(br) cm^{-1} . ^1H NMR (C_6D_6): 2.34 (dt, $^3J(\text{HP})$ 11, $^4J(\text{HF})$ 3 Hz, F_2PNMe_2), δ 3.66 (s, $\eta^5\text{-Cp}$), 6.13 ppm (s, $\eta^1\text{-Cp}$). The last peak was fairly broad, as the spectrum (at room temperature) is not at the fast-exchange limit; also there is probably some coupling to phosphorus, although a definite splitting could not be resolved.

The ^{19}F spectrum shows two overlapping double doublets (Fig. 2); at higher resolution each peak appears as a multiplet due to coupling to the methyl protons. It is notable that the coupling constants, as well as the shifts, are distinctly different for the two diastereotopic fluorines: (shifts measured to external CF_3COOH and corrected to the CFCl_3 scale) δ 108.7 ($^1J(\text{PF})$ 1169.4, $^2J(\text{FF})$ 30.3, $^4J(\text{HF})$ 2.7 Hz), 117.6 ppm ($^1J(\text{PF})$ 1160.3, $^2J(\text{FF})$ 30.3, $^4J(\text{HF})$ 2.4 Hz). Allowing for the HF splitting, the peaks are virtually as sharp as the reference signal.

$(\eta^5\text{-Cp})\text{Fe}(\text{CO})(\text{PF}_2\text{NMe}_2)(\eta^1\text{-C}_5\text{H}_4\text{CH}_3)$ (*IIIb*). *IIIb* was prepared from Ib in the same manner; again a completely pure, crystalline sample could not be obtained. IR: $\nu(\text{CO})$ 2020w, 1940s(br) cm^{-1} . ^1H NMR (C_6D_6): δ 2.27 (s, $\text{C}_5\text{H}_4\text{CH}_3$), 2.36 (dt, $^3J(\text{HP})$ 11, $^4J(\text{HF})$ 3 Hz, F_2PNMe_2), 3.75 (s, $\eta^5\text{-Cp}$), 5.6 and 6.2 ppm (broad, $\text{C}_5\text{H}_4\text{CH}_3$). As noted earlier, some Ib is always present (see Fig. 1); after correcting for intensity due to the latter, the ratio of the two peaks at 5.6 and 6.2 is 3/1, within experimental uncertainty. The ^{19}F spectrum is completely analogous to that for *IIIa*, except that the upfield signal appears as a broad doublet (instead of a sharp double doublet) in which $J(\text{FF})$ cannot be completely resolved; apparently the difference between $J(\text{HF})$ coupling constants for the two fluorines is somewhat larger here, and the coupling constant for the upfield fluorine is large enough to give the observed unresolved signal. Parameters: δ 114.4 ($^1J(\text{PF})$ 1175 Hz), 124.9 ppm ($^1J(\text{PF})$ 1161.3, $^2J(\text{FF})$ 30.1 Hz).

Acknowledgements

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References

- 1 F.A. Cotton, in L.M. Jackman and F.A. Cotton (Eds.), *Dynamic Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York, 1975, p. 378—401, and ref. therein.
- 2 R.B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Academic Press, New York, 1970, p. 114—132.
- 3 C.-C. Su, *J. Amer. Chem. Soc.*, 93 (1971) 5653.
- 4 A. Bonny and S.R. Stobar., *J. Amer. Chem. Soc.*, 101 (1979) 2247.
- 5 J.A. Labinger, *J. Organometal. Chem.*, 136 (1977) C31.
- 6 K. Stanley, R.A. Zelonka, J. Thomson, P. Fiess and M.C. Baird, *Can. J. Chem.*, 52 (1974) 1781.
- 7 B.D. Fabian and J.A. Labinger, *J. Amer. Chem. Soc.*, 101 (1979) 2239.
- 8 G. Binsch, in ref. 1, p. 50.
- 9 R.D. Holmes-Smith and S.R. Stobart, *J. Amer. Chem. Soc.*, 102 (1980) 382.
- 10 R.B. Larrabee, *J. Amer. Chem. Soc.*, 93 (1971) 1510; B.E. Mann, B.F. Taylor, N.A. Taylor and R. Wood, *J. Organometal. Chem.*, 162 (1978) 137.
- 11 D.M. Henekey and W.A.G. Graham, *J. Amer. Chem. Soc.*, 101 (1979) 6115.
- 12 R.G. Cavill, *J. Chem. Soc.*, (1964) 1992.