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THE STEREOSPECIFIC RING PROTONATION OF DIINDENYLIRON

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Summary

Reactions of protonic acids (HCl, CF_3COOH) with diindenyliron give the h^5-indenyl-h^6-indeneiron(II) monocation, $[Fe(C_9H_7)(C_9H_8)]^+$, which can be isolated as a hexafluorophosphate salt. Two deuterium labeling experiments, the reaction of $Fe(C_9H_7)_2$ and DCl and the reaction 1,1′,3,3′-tetradeuteriobis-(indenyl)iron with HCl, confirm that the products in this reaction have been formed by stereospecific addition of the proton to the indenyl ring. Because of the wealth of data on metal protonations, including data on the protonation of ferrocene at the iron atom, preference is indicated here for *endo* ring protonation which is proposed to occur via an intermediate protonated metal species. Protonation of $Fe(C_5H_5)(C_9H_7)$ is also reported. Deprotonation with n-butyllithium regenerates diindenyliron. However, data on these reactions suggest preferential loss of an *exo*-proton, which is perhaps realistic in view of the known attack of nucleophiles on the *exo* position of coordinated hydrocarbon rings.

Introduction

The stereospecific protonation of hydrocarbon metal complexes at the hydrocarbon ligand is a well-documented phenomenon. Generally, the data available suggest that initial protonation occurs at the metal, which is presumably the basic site in the complex due to its electron rich character; intramolecular rearrangement of this intermediate then occurs with transfer of the proton to an *endo* position of the complexed ring.

This type of reaction appears most extensively studied with various (diene)-iron tricarbonyl complexes [1-4]. Low temperature NMR studies of (diene)iron tricarbonyl species in acid media have identified a proton coordinated to the metal [1]. At higher temperature rapid transfer of the proton to and from the hydrocarbon ligand is observed, and products associated with stereospecific transfer of this proton to the hydrocarbon ligand are identified in these systems

[1-4]. The recent, analogous work on the stereospecific *endo* protonation of h^4-1,3-cyclohexadiene(h^5-cyclopentadienyl)rhodium and the corresponding iridium complex is also noted [5].

The protonation of ferrocene [6-9] is specifically of interest to our work because ferrocene and diindenyliron are structurally similar. With respect to the ferrocene work, the greatest significance must be accorded to the isolation of the species $[Fe(C_5H_5)_2H]AlCl_4$, from ferrocene, aluminium chloride and HCl [6]; most other studies on ferrocene in acid concur with metal protonation [7, 8] though there is one contradictory report [9]. Studies on other electrophilic reactions such as Friedel—Crafts reactions [10] also are suggested to be metal-assisted.

In contrast to the protonation of ferrocene, the protonation of diindenyliron at the metal can be accompanied by an intramolecular proton transfer to the hydrocarbon ligand, in a manner generally similar to that observed with the metal diene complexes noted above. If this reaction were to occur with proton transfer to the five-membered ring of indene, it seems reasonable to anticipate the migration of the site of metal coordination to the six-membered ring. Indeed, such a result has been demonstrated here; protonation of diindenyliron with HCl in benzene, or with trifluoroacetic acid gives a h^5-indenyl-h^6-indeneiron(II) complex, isolated as the hexafluorophosphate salt. A similar conversion has been noted earlier using boron trifluoride etherate [11].

As a test of the presumed mechanism of this reaction, we have investigated the stereochemistry of this reaction. The details of this investigation are presented in this paper.

Experimental

Diindenyliron was prepared from $FeCl_2$ and $Na[C_9H_7]$ in tetrahydrofuran by a published method [12]; 1,1',3,3'-d_4-bis(indenyl)iron was also prepared by this route from sodium 1,3-d_2-indenide, obtained from 1,1,3-d_3-indene [13]. This iron complex was shown to be 95% deuterated in the 1 and 3 positions by NMR intensity measurements. Other reagents were commercial samples.

All reactions were carried out under nitrogen, and solvents were purged with nitrogen before use. Tetrahydrofuran was distilled from $LiAlH_4$, benzene from CaH_2, and hexane from Na/K alloy, before use.

Infrared spectra were recorded on a Beckman IR-10 instrument. PMR spectra were run on either the JEOL-NM-MH-100 or Varian XL-100 spectrometers. PMR data are presented in Table 1. Reported melting points were run in sealed capillaries and are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Mass spectra were recorded on an AEI MS-9 spectrometer.

Preparation of $[Fe(C_9H_7)(C_9H_8)]PF_6$. A 0.855 g sample of $Fe(C_9H_7)_2$ (3.0 mmol) was placed in a flask connected to a standard vacuum line and approximately 20 ml of toluene was distilled in, followed by 5.7 mmol of HCl (measured by volume). The reaction flask, still evacuated and sealed, was allowed to warm slowly with stirring. No reaction was evident until the temperature reached about 20°, but at that temperature the reaction occurred almost immediately, with an orange solid precipitating and the black solution becoming colorless.

TABLE 1

PMR ASSIGNMENTS FOR h^5-INDENYL-h^6-INDENEIRON(II) HEXAFLUOROPHOSPHATE[a]

Assignment[b]	Chemical shift (δ)	Coupling constant (Hz)
H(1), H(1′)	5.86 (2H)	
H(2)	4.91 (t)	^{J}[H(1)—H(2)] 2.5
H(3), H(3′)	7.35, 7.55	
H(4), H(4′)	7.52 (2H)	
H_{endo}[c]	2.68	^{J}[H_{endo}—H_{exo}] 24
H_{exo}[c]	3.15	
H(5)	7.03	^{J}[H_{endo}—H(5)] 2.0
H(6)	6.51	^{J}[H(5)—H(6)] 6
H(7), H(7′), H(8), H(8′)	6.26 (2H), 6.56, 6.72	^{J}[H_{exo}—H(5)] 2

[a] NMR spectra were recorded on a JEOL MH-100 or Varian XL-100 operating at 100 MHz and ambient probe temperature in acetone-d_6 solution with TMS as internal standard. [b] See Fig. 1 for assignments. [c] An AB pattern, centered at δ 2.91, $\Delta\nu$ = 47 Hz, $J/\Delta\nu$ = 0.51.

The solvent was distilled off and after the flask was detached from the vacuum line, the residue was dissolved in acetone. Excess NH_4PF_6 (≈1.1 g) was added and the mixture was stirred for 0.5 h. A white solid was filtered; then an additional 1.0 g of NH_4PF_6 in a few ml H_2O was added. After the mixture had been stirred for a short time, the solvent was evaporated until crystallization was observed. A red-orange solid was filtered and dried over H_2SO_4. The product, 0.150 g (12%), was purified by repeated crystallization from acetone/ether; m.p. 184-185° (dec.).

The same product can be obtained by bubbling HCl through a benzene solution of $Fe(C_9H_7)_2$ or by stirring a mixture of $Fe(C_9H_7)_2$ with CF_3COOH in benzene. Work-up in each case was the same as that given above, and the yields were comparable.

Found: C, 49.94; H, 3.73; Fe, 12.83; P, 7.16. $C_{18}H_{15}F_6FeP$ calcd.: C, 50.03; H, 3.50; Fe, 12.92; P, 7.32%.

Infrared spectrum (nujol mull): 3100w, 1570w, 1503w, 1340w, 1205w, 1180w, 1150w, 939w, 918w, 830s, 757w, 736w, 731w, 667w, 553m.

Preparation of $Fe(C_9H_7)(C_5H_5)$. This known compound [14] was prepared in considerably better yield by the reaction of diindenyliron (3.47 g, 12.1 mmol) and NaC_5H_5 (approx. 10 mmol, based on Na metal used, 0.23 g) in refluxing tetrahydrofuran. The solution color changed rapidly from black to purple. Refluxing was stopped after 3 h and solvent was removed to give a dark purple oil. This was extracted with 300 ml of pentane, and the extract was filtered, concentrated, and chromatographed on alumina with pentane. The red-violet fraction which eluted was concentrated to about 50 ml and cooled to −78° to give the crystalline product (2.2 g, 78%), identified by PMR and m.p. [14].

Preparation of $[Fe(C_5H_5)(C_9H_8)]PF_6$. Gaseous HCl was bubbled into a solution of 0.830 mg of $Fe(C_5H_5)(C_9H_7)$ (3.5 mmol) in benzene for 18 h, causing a precipitate to form. Saturated aqueous NH_4PF_6 (2 ml) was added and the mixture was stirred for 1 h. The reaction mixture was filtered and the water layer was separated and evaporated. This residue and the filtered material were combined, extracted with CH_2Cl_2, filtered, and evaporated to give a brown solid. Recrystallization from acetone/diethyl ether gave 0.080 g of product (6%), m.p. 180-184° (dec.).

Found: C, 45.42; H, 3.34. $C_{14}H_{13}F_6FeP$ calcd.: C, 44.01; H, 3.43%.

Infrared spectrum (nujol mull): 3120w, 1572w, 1337w, 1308w, 1226w, 1179w, 1147w, 830s, 734m, 668w, 653m, 456m.

PMR spectrum (Varian-XL-100; acetone-d_6): 4.88 (5H, C_5H_5); 3.85 (AB pattern $\Delta\nu$ = 37 Hz, $J/\Delta\nu$ = 0.65 CH_2); 6.75 and 6.90 (multiplets, each 1H, each olefinic hydrogen on the five-membered ring); 6.24 (m, 2H) and 7.03 ppm (br. s, 2H), protons on six-membered ring.

Reaction of [$Fe(C_9H_7)(C_9H_8)$]PF_6 with n-butyllithium. A slurry of 0.172 g of [$Fe(C_9H_7)(C_9H_8)$]PF_6 (0.398 mmol) in dry hexane was stirred with ≈0.4 mmol of n-butyllithium in hexane. After 5 min the reaction mixture turned black and the solid dissolved. Solvent was removed and the residue sublimed in vacuum at 130° to give 0.026 g of $Fe(C_9H_7)_2$ (23%) which was identified by NMR.

Discussion

The reaction of diindenyliron with protonic acids yielded a product wherein the proton had added to the five-membered ring of the coordinated indenyl group. A similar reaction with $Fe(C_5H_5)(C_9H_7)$ also was noted:

$$Fe(C_9H_7)_2 \xrightarrow{HX} \xrightarrow[(-NH_4X)]{NH_4PF_6} [Fe(C_9H_7)(C_9H_8)]PF_6$$

$$Fe(C_5H_5)(C_9H_7) \xrightarrow{HCl} \xrightarrow[(-NH_4Cl)]{NH_4PF_6} [Fe(C_5H_5)(C_9H_8)]PF_6$$

In each case the product was identified by standard analytical and spectroscopic methods. The proposed structure for [$Fe(C_9H_7)(C_9H_8)$]PF_6, involving iron(II) coordination to the five-membered ring of the indenyl group and the six-membered ring of the indene ligand, was assigned from analysis of the PMR spectrum of this species. Though not a unique assignment (the only reasonable structure in accord with the PMR data having the indene ligand remains coordinated to the metal by its five-membered ring, i.e., a 16 electron species), it certainly seems to be the most reasonable one. It may be noted that there is no evidence such as a high field PMR resonance, or ν(M—H) frequency in the infrared spectrum to suggest a metal hydride formulation.

The d_4 species, [$Fe(C_9H_5D_2)(C_9H_6D_2)$]PF_6, labeled in the 1 and 3 positions of each ligand, was prepared from 1,1′,3,3′-d_4-diindenyliron, which in turn was prepared from Na[1,3-d_2-$C_9H_5D_2$]. Labeling was accomplished to the extent of 95%. The reaction of $Fe(C_9H_7)_2$ and DCl was also carried out to give [$Fe(C_9H_7)(C_9H_7D)$]PF_6.

Necessarily, the PMR spectrum of [$Fe(C_9H_7)(C_9H_8)$]PF_6 is complex, since the 15 protons in this species are chemically non-equivalent. Twelve resonances in the PMR spectrum are observed, with three pairs of protons showing fortuitous though not unexpected magnetic equivalence. Fortunately, some of the assignments of the resonances shown in Table 1 could be made unambiguously as a

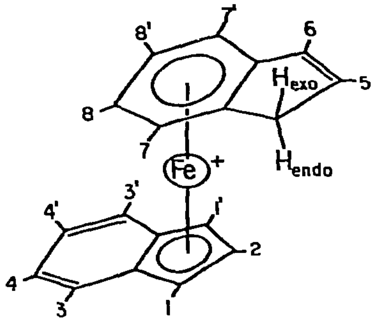

Fig. 1. The structure of the h^5-indenyl-h^6-indeneiron(II) monocation.

result of the deuterium labeled species prepared in this work, and all of the resonances crucial to an assignment of reaction stereochemistry were determined. The following assignments are noted (refer to Fig. 1 for numbering):

(a). The resonance at δ 5.86, intensity 2, absent in the d_4 species, was assigned to protons 1 and 1', of the coordinated indenyl ligand. Their magnetic equivalence is not particularly surprising. The singlet resonance at δ 6.51, intensity 1, also absent in the d_4 species must be due to the olefinic proton 6 in the indene ligand.

(b). The *endo* and *exo* protons of the methylene group of the indene ligand occur as an AB pattern centered at δ 2.91 with the appropriate parameters $\Delta\nu = 47$ Hz and $J/\Delta\nu = 0.51$. This position, widely separated from other resonances in this spectrum, is appropriate for a methylene group.

(c). The assignment of the singlet resonance at δ 4.91 to proton 2 was based on the similarity of its chemical shift value with chemical shift values for the 2 and 2' protons in $Fe(C_9H_7)_2$ (which occur at δ 3.92). Under optimum resolution, this broadened singlet at δ 4.91 resolved to a triplet, $J = 2.5$ Hz, a result of coupling to protons 1 and 1'. The chemical shift for proton 5, in the indene ring and consequently an olefinic proton, is shifted from this value; its value is δ 7.03. Evidence for these assignments comes from the spectrum of the d_4 species, $[Fe(C_9H_5D_2)(C_9H_6D_2)]PF_6$. Both the δ 4.91 and 7.03 proton absorptions sharpened markedly when the deuterium—proton spin coupling was removed in a double irradiation experiment.

Further evidence for the assignment of proton 5 resulted from another double irradiation experiment. In the spectrum of the d_4 species, the peak at δ 7.03 appeared as a doublet, $J = 2.0$ Hz. Upon irradiation at δ 2.68, it collapsed to a singlet. The value of the corresponding coupling constant in free indene is also 2.0 Hz [17].

(d). Unlike the quite unequivocal assignments for the protons on the five-membered rings, the assignments for protons on the six-membered rings were less definitive. Our preference for the assignments of H(3) and H(3') at δ 7.35 and 7.55 and of H(4) and H(4') at δ 7.52 (intensity 2H) is based on the similarity of these chemical shifts with the values for similar protons in $Fe(C_9H_7)_2$ (δ 6.80). Coordination of the metal to the six-membered ring in the indene ligand would be expected to shift the resonance of these protons to higher field. Thus the assignment of the remaining resonances at δ 6.26 (2H), 6.56, and 6.72 to H(7), H(7'), H(8) and H(8') is reasonable. A good case for the precise assignment of H(8) and H(8') to the δ 6.26 resonance can be made, assuming that these protons are more distant from the asymmetry of this ligand.

The same general pattern of PMR resonances for $[Fe(C_5H_5)(C_9H_8)]PF_6$ was noted; however deuterium labeling experiments were not carried out here so that the assignments were less definite. Tentative assignments are noted in the experimental section.

The PMR data on the two deuterated species provided definitive evidence concerning the stereospecificity of this protonation. The product of the reaction of DCl with $Fe(C_9H_7)_2$ shows, in the methylene portion of the PMR spectrum, only a relatively broad singlet at δ 3.14. Conversely the product derived from HCl protonation of $Fe(C_9H_5D_2)_2$ gives a singlet at δ 2.68. These results uniquely define the reaction to be stereospecific. In particular, it is possible to rule out both random *endo* and *exo* addition which would necessarily give two singlets for each of these reaction products. Also it is clear that random intermolecular H—D exchange is impossible, since this would give a mixture of CD_2, CHD (2 isomers) and CH_2 species in solution and lead to a superposition of the anticipatedspectra for each group.

We cannot uniquely define the stereochemistry of this reaction from the data in hand. Nonetheless we offer our distinct prejudice in favor of *endo* protonation, which presumably would occur via an intermediate metal hydride complex. This would be in accord with most of the data on ferrocene protonations [5-8], and on the protonation of iron carbonyl complexes of dienes [1-4].

It is important to stress that this conclusion regarding stereospecificity may be made invariant to the low yields observed in these reactions. There is no realistic way to obtain different isomers in both reactions unless they were necessarily formed in a stereospecific manner. It is not conceivable that a mixture of isomers could initially form and that one of the two isomers then degrades. Of course this does not explain the reason for the low yields in these reactions (isolated yields ≈10%). Our evidence indicates that these protonated products, once formed, are stable. Thus, it is only reasonable to conclude that some alternative reaction must also be occurring which does not involve protonation on the indenyl ligand (at least on the five-membered ring). One realistic possibility is that the protonation occurs via an intermediate metal hydride (see above), with this species being extremely susceptible to oxidative degradation. It has been shown recently that protonated ferrocenes are in fact exceedingly sensitive to oxidation [7, 8]. However, our most careful work, described in the experimental section, involving vacuum line manipulation of reagents, did not improve the product yield. A second possibility is that the acid itself can serve as the oxidizing agent and that oxidation and protonation occur concurrently and at comparable rates. Indeed, we have observed oxidation to occur as the only reaction between 1,1',3,3'-$Fe[C_9H_5Me_2]_2$ with HCl [15]. The species resulting from oxidation of $[Fe(C_9H_7)_2]$ is apparently (surprisingly) not stable [15].

One suggestion that we do not particularly like is that protonation occurs randomly in the *exo* position and at the metal, and that the protonated metal complex then degrades leaving only the stereospecifically protonated *exo* species. The thinking behind this suggestion is that protonation in the *endo* position would almost necessarily imply a metal hydride intermediate. However, this mechanism avoids the arguments concerning the fortuitous rate coincidence mentioned above.

Deprotonation of $[Fe(C_9H_7)(C_9H_8)]PF_6$ was carried out using n-butyllithium as a base, regenerating diindenyliron in 23% yield. However the reaction is apparently not the reverse of the stereospecific protonation reported above; this fact is clearly established in analogous reactions of n-butyllithium with the d_1 and d_4 species, $[Fe(C_9H_7)(C_9H_7D)]PF_6$ and $[Fe(C_9H_5D_2)(C_9H_6D_2)]PF_6$.

To establish this fact, we looked at mass spectral data on four compounds (Table 2). The mass spectrum for $Fe(C_9H_7)_2$ contains the predominate parent mass peak with *m/e* 286 ($^{12}C_{18}{}^{1}H_{14}{}^{56}Fe$), having a relative intensity 100; in addition there is a peak at *m/e* 287 which arises due to the presence of ^{13}C in the molecule in its natural abundance ($^{13}C^{12}C_{17}{}^{1}H_{14}{}^{56}Fe$), relative intensity found, 22; calcd. 20.2). The mass spectrum for the d_4 species, approximately 95% enriched according to PMR data, contains a peak at *m/e* 290, four mass units above that of the undeuterated complex, and a *m/e* 291 peak of the expected intensity. There is also a peak at *m/e* 289 which must be due to a d_3 species, though its intensity is somewhat higher than expected from abundances estimated by NMR. (The intensity of this peak suggests ≈70% deuterium incorporation in the 1,1′,3 and 3′ positions.)

We may next consider the reaction product derived from $[Fe(C_9H_7)(C_9H_7D)]PF_6$ on treatment with n-butyllithium. The mass spectrum of this product shows a peak at *m/e* = 297 of relative intensity 100; clearly this indicates that the product obtained in this reaction must have substantial amounts of the d_1 compound $Fe(C_9H_7)(C_9H_6D)$. In addition, there is also a *m/e* 286 peak of lesser intensity (50), which is presumably due to a lesser amount of undeuterated species, $Fe(C_9H_7)_2$. A rough estimate based on the intensities suggests a ratio of the d_1 complex to the d_0 complex of 2/1.

The mass spectrum of the reaction product derived from the d_4 species, $[Fe(C_9H_5D_2)(C_9H_6D_2)]PF_6$, and n-butyllithium contains a peak of highest intensity at *m/e* 289. However, in addition, there is a peak of *m/e* 290, of relative intensity 44. This former peak must be assigned to the d_3 product. The increased intensity of the *m/e* 290 peak, over the value expected on the basis of ^{13}C incorporation, seems to be assignable logically to the d_4 species. A very approximate calculation based on the intensities of the *m/e* 289 and *m/e* 290 peaks suggest a ratio of d_3 to d_4 species of about 3.5/1.

TABLE 2

MASS SPECTRA (20 eV RELATIVE INTENSITIES)

m/e	284	285	286	287	288	289	290	291	292
$Fe(C_9H_7)_2$	6.5	1.6	100	22	2.6				
$\underset{\rightarrow}{\text{DCl}}$ $\underset{\rightarrow}{\text{n-BuLi}}$	3.8	7.1	50	100	41	12	3.3		
$Fe(C_9H_5D_2)_2$			1.0	3.7	14	42	100	22	2.8
$\underset{\rightarrow}{\text{HCl}}$ $\underset{\rightarrow}{\text{n-BuLi}}$				3.7	46	100	44	10.7	3.1

These two results on the deuterio complexes can be explained in the following way. Assume that the initial protonation occurs in an *endo* position. Then the deprotonation reactions, in each example, appear to proceed with loss of a proton from either *exo* or *endo* position. Qualitative evidence suggests, however, that loss of an *exo* proton or deuterium ion appears to predominate by a factor of about two or three to one. The actual values found here are 2/1 and 3.5/1 but these are quite imprecise. Thus the d_1 species, assigned the structure [Fe(h^5-C_9H_7)(h^6-*endo*-1-d-C_9H_7D)]PF_6, loses its *exo* proton preferentially to give the d_1 species Fe(C_9H_7)(1-d_1-C_9H_6D), and the d_4 species, i.e., [Fe(h^5-1,3-d_2-$C_9H_5D_2$)(h^6-3,*exo*-1-d_2-$C_9H_6D_2$)]PF_6, looses its *exo* deuterium ion preferentially to yield Fe(1,3-d_2-$C_9H_5D_2$)(1'-d_1-C_9H_6D), the d_3 species. The two reactions appear consistent in this process.

These results were not expected at the outset of this work, yet in retrospect they seem reasonable. n-Butyllithium is clearly a very strong base, and so its non-selectivity in the deprotonation reaction should not be surprising. Moreover we note the propensity of alkyllithium reagents for *exo*-attack at a coordinated hydrocarbon [16]; such a result is implied here. Clearly further experiments with milder bases are suggested.

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