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π-ARENE-π-CYCLOPENTADIENYLIRON CATIONS FROM SOME SUBSTITUTED NAPHTHALENES

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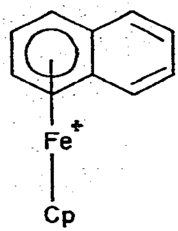
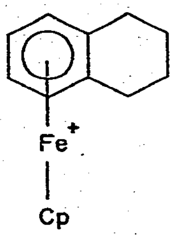
Summary

Reaction of 1-fluoro-, 1-chloro- or 1-bromo-naphthalene with ferrocene and $AlCl_3/Al$ in refluxing cyclohexane gave the π-1-halonaphthalene-π-cyclopentadienyliron cation (III, IV or V) in which the (Cp)Fe group is complexed only to the unsubstituted aromatic ring. A similar reaction with 2-methylnaphthalene, however, gave rise to both π-2-methylnaphthalene-π-cyclopentadienyliron cations in which either the substituted or the unsubstituted aromatic ring was complexed to (Cp)Fe. With 1-bromonaphthalene under these reaction conditions, in addition to ion V, both the dehalogenated π-naphthalene-π-cyclopentadienyliron cation (I) and the hydrogenated π-tetralin-π-cyclopentadienyliron cation (II) were obtained. When the reaction was carried out in the presence of I_2 or DPPH as radical scavenger, the formation of II was eliminated, thus strongly implicating radical reactions in the hydrogenation process. Moreover, when perdeuteronaphthalene was converted to II, extensive H—D exchanges were observed. To account for these results, a hydrogenation mechanism involving radical ions as key intermediates is proposed.

Introduction

Recently, we reported the observation of a novel hydrogenation of the aromatic ligand during the synthesis of π-arene-π-cyclopentadienyliron mono- and di-cations [1]. Thus anthracene reacted with ferocene in the presence of $AlCl_3/Al$ to give the same mono- and di-cations as those derived from 9,10-dihydroanthracene, while naphthalene yielded a mixture of the naphthalene and tetralin complexes I and II, with greater amounts of II being formed at higher reaction temperatures. The present paper describes an extension of these studies, including the work with 1-fluoro-, 1-chloro-, 1-bromo- and 2-methyl-naphthalenes. The data led to the suggestion of a mechanism for the hydrogenation process, involving the formation of radical ions as key intermediates.


(I)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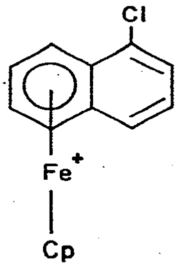
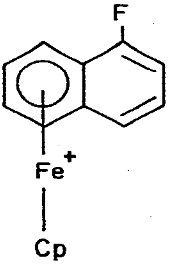
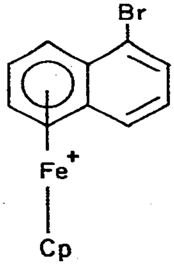
Discussion

1-Halonaphthalenes

Nesmeyanov and coworkers [2] reported that the $AlCl_3/Al$ catalyzed ligand exchange between ferrocene and chlorobenzene gave, beside the π-chlorobenzene-π-cyclopentadienyliron cation, a coupling product, π-biphenyl-π-cyclopentadienyliron cation, while from bromobenzene, both π-bromobenzene-π-cyclopentadienyliron and π-benzene-π-cyclopentadienyliron cations were obtained. In our previous work [1], we found that the reaction of 1-chloronaphthalene, at the relatively mild temperature of about 80° C (refluxing cyclohexane), gave the π-1-chloronaphthalene-π-cyclopentadienyliron cation (III) in which the unsubstituted aromatic ring was complexed to the (Cp)Fe group. At about 190° C, however, a mixture of I and II was obtained, indicating both dehalogenation and hydrogenation. In the present study, the milder temperature of 80° C was utilized in an attempt to minimize the formation of mixed products. When 1-fluoronaphthalene was treated with ferrocene and $AlCl_3/Al$ in refluxing cyclohexane, the only product was the expected π-1-fluoronaphthalene-π-cyclopentadienyliron cation (IV), with the complexing taking place on the unsubstituted ring. With 1-bromonaphthalene, however, even at 80° C, a mixture of π-1-bromonaphthalene-π-cyclopentadienyliron cation (V) and the dehalogenated ion I as well as the hydrogenated ion II were obtained, the relative product composition, for a reaction time of 6 h, being about 15:65:20 for V/I/II.


(III)


(IV)


(V)

In the identification of ions III, IV and V, ^{13}C NMR proved to be extremely useful. As illustrations, the ^1H-decoupled ^{13}C NMR spectra for III and IV are given in Fig. 1. Since the carbon atoms of the complexed ring give absorptions at higher field than the carbon atoms of the uncomplexed ring [1,3], the appearance of 4 lines at higher field and 3 lines at lower field corresponds to 4 carbon atoms with nuclear Overhauser enhancement in the complexed ring and 3 car-

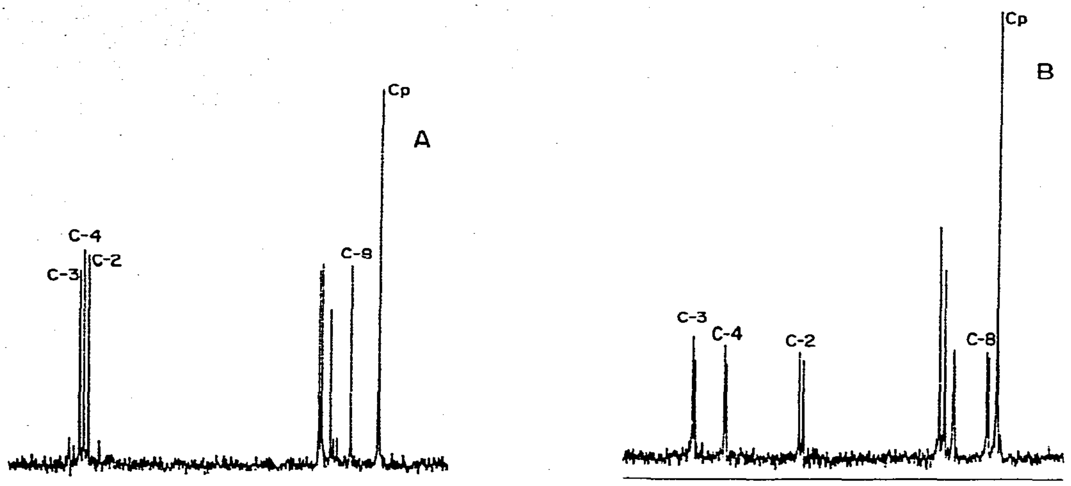
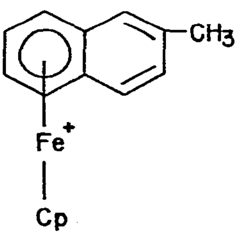


Fig. 1. ^{1}H-Decoupled ^{13}C NMR spectra: A, π-chloronaphthalene-π-cyclopentadienyliron cation (III); B, π-1-fluoronaphthalene-π-cyclopentadienyliron cation (IV).

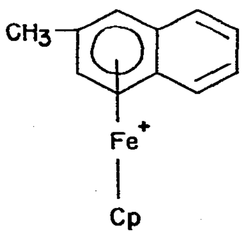
bon atoms with such enhancement in the uncomplexed ring. Clearly, this fits the assigned structures III, IV and V. Moreover, in ion IV, ^{13}C—^{19}F coupling gives rise to well defined doublets, and from the magnitudes of the coupling constants, assignments of these lines to C(2,3,4) and C(8) can be made [4]. The chemical shifts in the ^{13}C NMR spectra and their assignments for III, IV and V are summarized in Table 1.

2-Methylnaphthalene

For comparison with the 1-halonaphthalenes, 2-methylnaphthalene * was treated with ferrocene and $AlCl_3/Al$ in refluxing cyclohexane. A 55:45 mixture of π-2-methylnaphthalene-π-cyclopentadienyliron cations VIA and VIB was obtained, with the (Cp)Fe group complexing to a somewhat greater extent to the



(VIA)



(VIB)

unsubstituted ring. The ^{13}C NMR spectra (Fig. 2, A and B) again were extremely useful for structural differentiation. Thus ions VIA and VIB gave 3 and 4 lines, respectively, in the uncomplexed aromatic region, and 4 and 3 lines, respectively, in the complexed aromatic region.

Nesmeyanov [2] has concluded that the effect of substituents in the benzene

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* A commercial sample of 1-methylnaphthalene was found to be contaminated with 2-methylnaphthalene, hence pure 2-methylnaphthalene was utilized.

TABLE 1

^{13}C MAGNETIC RESONANCE DATA [a]

Ion	Uncomplexed ring			Complexed ring		
	C(2)	C(3)	C(4)	C(5,6,7)	C(8)	Cp
IV	113.6 (18.4 Hz) [b]	133.1 (7.6 Hz) [b]	127.4 (5.0 Hz) [b]	88.4, 87.5, 85.8	79.6 (6.1 Hz) [b]	77.7
III	131.0	132.5	131.8	88.6, 88.2, 86.5	82.7	77.6
V	131.1	135.3	132.2	87.9 [c], 85.8	84.6	76.8

[a] δ(Acetone-d_6)(ppm) from TMS. [b] $J(^{13}C-^{19}F)$. [c] Overlapping of two lines.

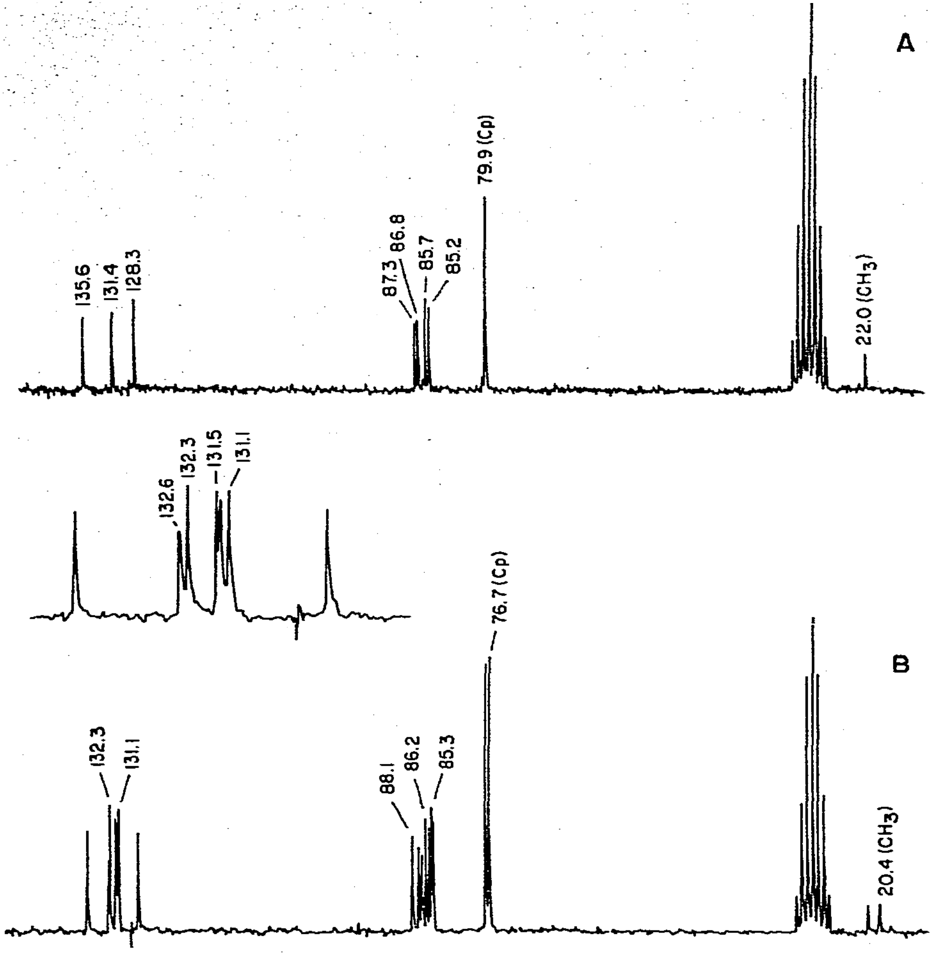


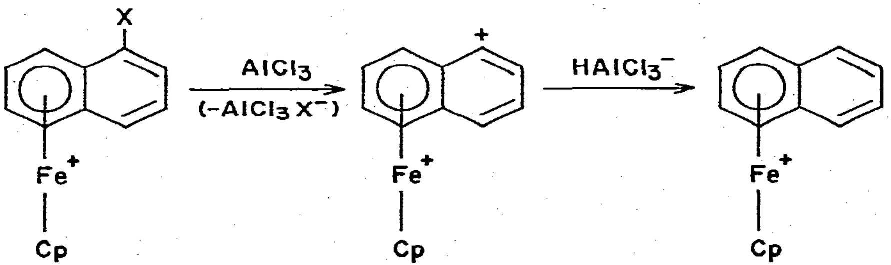
Fig. 2. ^{1}H-Decoupled ^{13}C NMR spectra: A, π-2-methylnaphthalene-π-cyclopentadienyliron cation (VIA); B, mixture of π-2-methylnaphthalene-π-cyclopentadienyliron cations (VIA and VIB), the inset shows the expanded spectrum of the uncomplexed aromatic region (chemical shifts given for VIB only in Fig. 2B).

ring on the reactivity of the ligand exchange reaction with ferrocene is similar to such substituent effects in the Friedel—Crafts reaction. Besides the electronic factor, steric effects have also been suggested as playing a part [5]. Since the fluoro-, chloro- and bromo- substituents are electron-withdrawing, it is not surprising to find that ligand exchanges occur with the unsubstituted ring in the π-1-halonaphthalene-π-cyclopentadienyliron cations III, IV and V. With 2-methylnaphthalene, however, the electron-donating effect of the methyl group is weak and it is unable to limit the ligand exchange only to the substituted ring. Indeed a somewhat greater amount of complexing of the (Cp)Fe group to the unsubstituted ring was observed, and possibly this may be attributed to the influence of a steric factor. Thus a direct parallel in reactivity to the Friedel—Crafts reaction does not hold, and this is further demonstrated by the observation that attempts to bring about ligand exchange reactions with 1-methoxy- or 2-methoxynaphthalene resulted only in decomposition, with no isolable product.

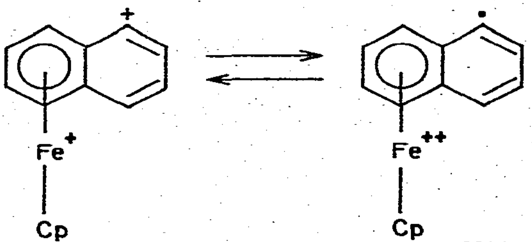
Mechanism of hydrogenation and dehalogenation

The ready formation of the hydrogenated ion II as one of the products from the reaction of bromonaphthalene at a relatively low temperature is a departure from the behavior of naphthalene or 1-chloronaphthalene, which require a higher reaction temperature to give hydrogenation. However, the reaction of anthracene at relatively low temperatures also gave hydrogenated products [1]. Since the complexing of two (Cp)Fe groups to anthracene leaves two unpaired electrons, and since the formation of the biphenyl complex from chlorobenzene presumably arises from coupling with the phenyl radical [2], the possibility of an involvement of radical processes is clearly worthy of investigation. When bromonaphthalene was treated with ferrocene and $AlCl_3/Al$ in cyclohexane in the presence of iodine or diphenylpicrylhydrazyl (DPPH) as radical scavenger, it was found that the products were a mixture of V and the dehalogenated ion I, with no detectable amount of the hydrogenated ion II. This finding clearly implicated radicals as being involved in the hydrogenation process.

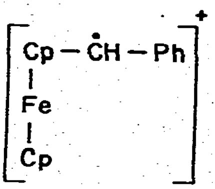
In our previous and current work, the reactants were generally employed in the molar ratio of 1 : 1 : 2 : 1 for arene/ferrocene/$AlCl_3/Al$. When napthalene was treated in the usual way [1], but with increasing amounts of $AlCl_3$ the extent of formation of the hydrogenated ion II was found to increase. For example, with 10 molar equivalents of $AlCl_3$ at 140°C, the only product obtained was ion II. When perdeuteronaphthalene was treated under these conditions (1 : 1 : 10 : 1 for arene/ferrocene/$AlCl_3/Al$ at 140°C), extensive H—D exchange, as indicated by ^1H NMR, was observed in ion II (see Experimental). Apparently, under the conditions of ligand exchange reactions, $AlCl_3$, being a strong Lewis acid, is capable of abstracting hydride (or deuteride) ions, presumably as $HAlCl_3^-$ (or $DAlCl_3^-$), from naphthalene. Recombination with hydride ions derived, for example, from the hydrocarbon solvent would lead to H—D exchange. Such a mechanism could also explain the dehalogenation observed with 1-chloro- and 1-bromonaphthalene.



(III or V) (VII) (I)

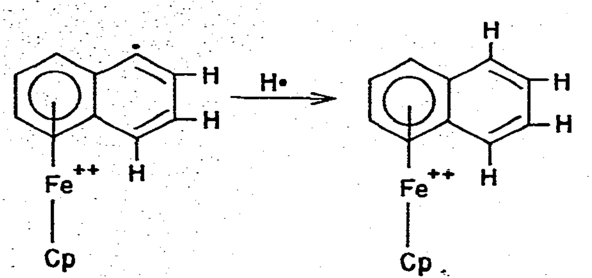


(VII) (VIII)



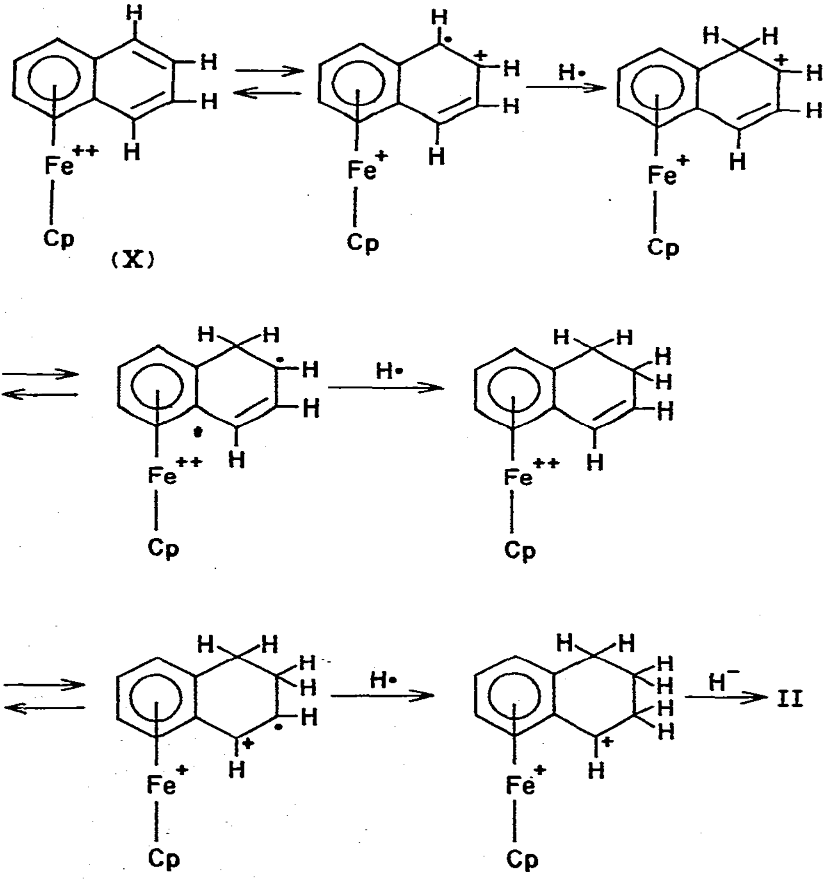
$$\left[\begin{array}{l}\mathrm{Cp-\dot{C}H-Ph}\\ \mid\\ \mathrm{Fe}\\ \mid\\ \mathrm{Cp}\end{array}\right]^+$$

(IX)



(VIII) (X)

To account for the hydrogenation process, as a working hypothesis, it may be suggested that after abstraction of H⁻ or X⁻ to VII, an intramolecular oxidation—reduction takes place to give a radical ion as a key intermediate (VII ⇌ VIII). Such an intramolecular oxidation—reduction has an analogy in the formation of the ferrocenylphenylcarbinyl cation which gave rise to radical ion IX, and this radical ion would subsequently undergo radical reactions [6,7]. Abstraction by VIII of H· , probably from the hydrocarbon solvent, will give the ferricinium-type ion X. Previously, it has been noted [1] that the hydrogen did not arise from D_2O added during work up. Since ferricinium ions are known to undergo radical reac-



(X)

tions [8,9], the subsequent hydrogenation step could be formulated as a series of intramolecular oxidation—reduction and radical reactions, the final step being a recombination with the hydride ion to give the iron(II) complex ion.

Since the formation of ferricinium-type ions and their conversion to radical ions are key steps in the mechanism suggested above, it may be argued that in the presence of Al powder, formation of ferricinium ions could be inhibited. In the original ligand exchange reaction carried out by Nesmeyanov and coworkers [10,11], Al powder was added in order to minimize the oxidation of ferrocene to the ferricinium cation. As a control test, ferrocene was treated with $AlCl_3/Al$, in the molar ratio of 1 : 2 : 1, in cyclohexane at room temperature. The blue ferricinium ion was formed and isolated as the hexafluorophosphate. Thus under the conditions of ligand exchange reactions, formation of ferricinium ions is indeed feasible.

As already pointed out, we regard the proposed hydrogenation mechanism as a working hypothesis. Further work is currently underway in order to obtain more data which may be relevant to the mechanism for the hydrogenation of the aromatic ligands. Included in the additional work are studies with other arenes such as phenanthrene and pyrene. which, according to preliminary results, also give rise to some hydrogenation. These and other results will be reported in later communications.

Experimental

π-1-Fluoronaphthalene-π-cyclopentadienyliron cation (IV)

The reaction of 1-halonaphthalene with ferrocene in the presence of $AlCl_3/Al$ in cyclohexane was carried out as previously described for 1-chloronaphthalene [1]. After treatment of 4.4 g (30 mmol) of 1-fluoronaphthalene, 5.6 g (30 mmol) of ferrocene, 8.0 g (60 mmol) of $AlCl_3$ and 0.8 g (30 mmol) of Al powder in refluxing cyclohexane (100 ml) under N_2 for 6 h, the resulting mixture was worked up [1] to give 2.7 g (22%) of the hexafluorophosphate of IV. Recrystallized from acetone/ether, it melted with decomposition at 140—145°C, ^{1}H NMR (acetone-d_6) δ 4.90 (5H, Cp, s), 6.7 (2H, arom., m), 7.6 (3H, arom., m), and 8.0 ppm (2H, arom., m). Its ^{13}C NMR spectral data and their assignments are given in Table 1.

Reaction with 1-bromonaphthalene

1-Bromonaphthalene (6.2 g, 30 mmol), ferrocene (5.6 g, 30 mmol), $AlCl_3$ (8.0 g, 60 mmol) and Al powder (0.8 g, 30 mmol) were refluxed in cyclohexane (100 ml) under N_2 for 6 h. After work-up in the usual manner [1], 3.5 g of a mixture of the hexafluorophosphate salts of π-1-bromonaphthalene-π-cyclopentadienyliron cation (V), π-naphthalene-π-cyclopentadienyliron cation (I), and π-tetralin-π-cyclopentadienyliron cation (II) was obtained, the relative amounts of V/I/II, based on the ^{1}H NMR absorption of the Cp peaks of V, I and II at δ 4.83, 4.78 and 5.10 ppm, respectively, were about 15 : 65 : 20. Separation by column chromatography over alumina using acetone as eluant gave pure samples of the hexafluorophosphate salts of I and II [1], but no isolable amount of V.

When the same reaction with 1-bromonaphthalene was carried out except that the reaction time was decreased from 6 to 3 h, 3.0 g of a mixture of the hexafluorophosphate salts of V and I, in the ratio of about 70 : 30, was obtained. Repeated recrystallizations from acetonitrile/ether gave the pure hexafluorophosphate salt of V as fine orange needles, m.p. 140—143°C (dec), ^{1}H NMR (acetone-d_6) δ 4.83 (5H, Cp, s), 6.7 (2H, arom., m), 7.6 (3H, arom., m), and 8.1 ppm (2H, arom., m). The ^{13}C NMR data and their assignments are given in Table 1.

When the reaction of 1-bromonaphthalene was carried out again under the same conditions for 6 h but in the presence of 100 mg of I_2 or DPPH as radical scavenger, about 2.0 g of hexafluorophosphate salts were obtained and ^{1}H NMR showed the presence of about a 50 : 50 mixture of the hexafluorophosphate salts of V and I, but no hydrogenated product II.

Reaction with 2-methylnaphthalene

A mixture of 5.0 g (35 mmol) of 2-methylnaphthalene, 6.6 g (35 mmol) of ferrocene, 9.4 g (70 mmol) of $AlCl_3$ and 1.0 g (35 mmol) of Al powder in 100 ml of cyclohexane was refluxed under N_2 for 20 h. After work-up in the usual manner [1], 2.5 g (17%) of a mixture of the hexafluorophosphate salts of π-2-methylnaphthalene-π-cyclopentadienyliron cations (VIA) and (VIB) was obtained. The ratio of VIA (unsubstituted ring complexed to (Cp)Fe) to VIB (CH_3-substituted ring complexed to (Cp)Fe) was estimated to be 55 : 45 on the basis of the intensities of the ^{1}H NMR absorptions of the Cp groups (δ 4.73 and 4.70 ppm, respectively, for VIA and VIB) and the CH_3 groups (δ 2.55 and 2.70 ppm, respectively, for VIA and VIB). After repeated recrystallizations from acetone/ether, the pure hexafluorophoshate salt of VIA was obtained, m.p. 190—192°C (decomp), ^{1}H NMR (acetone-d_6) δ 2.55 (3H, CH_3, s), 4.73 (5H, Cp, s), 6.5 (2H, arom., m), 7.4 (2H, arom., m), and 8.0 ppm (3H, arom., m). The more soluble component was assigned to VIB, which gave ^{1}H NMR absorptions at δ 2.70 and 4.70 ppm for the CH_3 and Cp groups. The ^{13}C NMR spectra for VIA and a mixture of VIA and VIB are shown in Fig. 2.

Reaction with perdeuteronaphthalene

In preliminary trials, it was found that the use of a large excess of $AlCl_3$ in the naphthalene/ferrocene/$AlCl_3$/Al reaction mixture greatly increased the relative proportion of the hydrogenated π-tetralin-π-cyclopentadienyliron cation (II). In order to investigate the extent of exchange in the formation of II, the following experiment was carried out.

A mixture of perdeuteronaphthalene ($C_{10}D_8$, Merck, Sharp and Dohme Canada Ltd., 1.36 g, 10 mmol), ferrocene (1.86 g, 10 mmol), $AlCl_3$ (13.3 g, 100 mmol) and Al powder (0.27 g, 10 mmol) in 25 ml of dried and redistilled decalin was heated under N_2 at 140°C for 4 h. After work up in the usual manner [1], a 30% yield of the hexafluorophosphate salt of II was obtained as the only product. Its ^{1}H NMR spectrum, except for the difference in relative intensities, was the same as that previously observed for II [1]. On the assumption that the Cp absorption at 5.10 ppm corresponds to 5H (i.e. assuming no exchange of H for D in the Cp group), the complexed aromatic ring showed absorptions at δ 6.32 ppm corresponding to about 3H (instead of 4H if no D), and the uncomplexed saturated ring showed absorptions at δ 3.00 and 2.10 ppm corresponding to nearly 8H, indicating almost complete exchange of all D for H.

Ferricinium hexafluorophosphate

A mixture of 4.7 g (25 mmol) of ferrocene, 6.7 g (50 mmol) of $AlCl_3$ and 0.7 g (25 mmol) of Al powder in 50 ml of dried and redistilled cyclohexane was stirred under N_2 at room temperature (20° C). The reaction mixture turned blue, and after 7 h of stirring the resulting material was cooled in an ice-bath, and ice was slowly added to decompose the $AlCl_3$. The aqueous layer was separated, washed twice with cyclohexane and then filtered into 10 ml of a saturated solution of NH_4PF_6. Upon cooling in a refrigerator, about a 10% yield of the blue ferricinium hexafluorophosphate was obtained. Its UV and ESR spectra were essentially identical to those previously reported for this ion [12].

It is of interest to note that in ligand exchange experiments which gave extensive hydrogenation under relatively mild conditions, such as in the reaction with anthracene at 80° C or with naphthalene at 140° C with 10 molar excess of $AlCl_3$, the aqueous filtrate after the isolation of the hydrogenated π-arene-π-cyclopentadienyliron complex was blue, suggesting the probable presence of the ferricinium ion as a by-product. Under conditions which gave only some hydrogenation at high temperature, the blue color was not observed; presumably, any ferricinium ion that may have been formed would have decomposed.

Acknowledgement

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