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LIGAND EXCHANGE REACTIONS OF FERROCENE WITH PHENANTHRENE OR 9,10-DIMETHYLPHENANTHRENE IN THE PRESENCE OF ALUMINUM CHLORIDE AND ALUMINUM

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Summary

Ligand exchange reactions between phenanthrene or 9,10-dimethylphenanthrene with ferrocene effected in the presence of $AlCl_3$-Al were carried out under a variety of conditions. With phenanthrene (I), hydrogenation at the C-9 and C-10 positions could take place during the reaction and the cationic products obtained were the η^6-phenanthrene-η^5-cyclopentadienyliron and η^6-9,10-dihydrophenanthrene-η^5- cyclopentadienyliron moncations (II and III), and the η^6-phenanthrene-trans-bis-η^5- cyclopentadienyliron and η^6-9,10-dihydrophenanthrene-trans-bis-η^5-cyclopentadienyliron dications (IV and V). With 9,10-dimethylphenanthrene (VI), reactions carried out in refluxing cyclohexane gave the non-hydrogenated η^6-9,10-dimethylphenanthrene-η^5-cyclopentadienyliron monocation (VII) and η^6-9,10-dimethylphenanthrene-trans-bis-η^5-cyclopentadienyliron dication (VIII). When higher temperatures were used in an attempt to promote hydrogenation, decomposition predominated and no cationic product could be obtained. These findings are discussed and contrasted with previous results obtained from similar reactions using anthracene or 9,10-dimethylanthracene.

Introduction

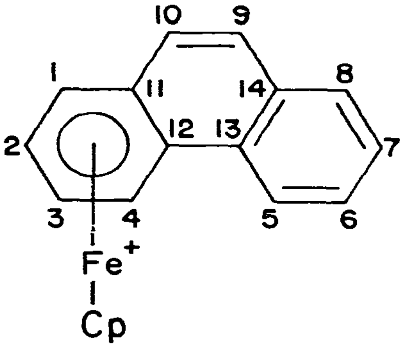
In our studies on the partial hydrogenation of the aromatic ligands observed during ligand exchange reactions between ferrocene (FcH) and polycyclic arenes effected in the presence of $AlCl_3$-Al (for a recent summary, see [1]), anthracene was found to be the most easily hydrogenated, giving rise to 9,10-dihydroanthracene complexes [2]. In the reaction of 9,10-dimethylanthracene with FcH, the stereospecific hydrogenation to give the η^6-cis-(endo-9,10-dihydro)-9,10-dimethylanthracene-η^5-cyclopentadienyliron cation led to the formulation of a possible mechanism for the hydrogenation process [3,4]. In the present work, reactions of ferrocene with phenanthrene or 9,10-dimethylphenanthrene in the presence of $AlCl_3$-Al are investigated in order to obtain data for comparison with the results from anthracene and 9,10-dimethylanthracene.

Results and Discussion

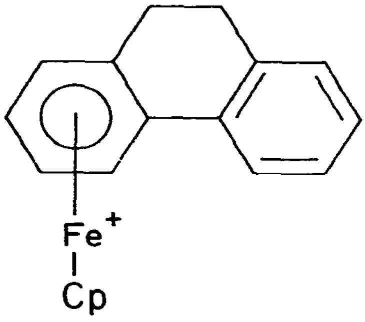
η^6-Phenanthrene-η^5-cyclopentadienyliron and η^6-9,10-dihydrophenanthrene-η^5-cyclopentadienyliron cations (II and III)

The reaction of phenanthrene (I) with FcH and $AlCl_3$-Al (molar ratio of 1:1:2:1 for I:FcH:$AlCl_3$:Al) in refluxing cyclohexane (81°C) under N_2 for 16 h gave a 10% yield of the

η^6-phenanthrene-η^5-cyclopentadienyliron cation (II). In contrast, under similar conditions, reaction with anthracene gave only the hydrogenated η^6-9,10-dihydroanthracene-η^5-cyclopentadienyliron cation [2]. In fact, the non-hydrogenated η^6-anthracene-η^5-cyclopentadienyliron cation has so far not been prepared. It has been pointed out [2] that since anthracene is a 14-π-electron system, if the two terminal rings were complexed to cyclopentadienyliron (CpFe) groups, the 9,10-positions would become a diradical. Similarly, if only one terminal ring were complexed to CpFe and the other terminal ring aromatized, the 9,10-positions again would be a diradical. Since the mechanism of the hydrogenation apparently involves attack of H atoms on free radical centers [3,4], the facile formation of hydrogenated products in ligand exchange reactions with anthracene is readily understandable. On the other hand, although phenanthrene (I) is isoelectronic with anthracene, after one or both terminal rings are complexed with CpFe, the 9,10-positions can still form a double bond instead of a diradical. Hence at the relatively mild temperature of refluxing cyclohexane, the non-hydrogenated cation II could be obtained.



II



III

In previous work on the reaction of naphthalene with FcH and $AlCl_3$-Al [1,2], hydrogenation to give the η^6-tetralin-η^5-

Table 1

Extents of hydrogenation in the reaction of phenanthrene with FcH-$AlCl_3$-Al at different temperatures.

Solvent	Temp. °C	Yield[a] of II & III, %	Relative amount of III, %[b]
Decalin	105	31	23
	120	34	26
	135	21	35
	145	22	37
	155	23	41
	170	31	15
	180	27	13
n-Octane	126	31	21
n-Nonane	151	18	30
n-Decane	174	35	3

[a] Cations II and III were isolated as their hexafluorophosphate salts.

[b] Based on the absorptions of the Cp singlets in the ^1H NMR spectra of the mixture of ions II and III.

cyclopentadienyliron cation was found to be highly dependent on reaction conditions such as temperature and the relative amounts of the various reactants. The extent of hydrogenation is increased by an increase in the amount of $AlCl_3$, and is decreased by an increase in the amount of FcH [1]. Using this information, cation II was prepared with an increased yield of about 30% by using a molar ratio of 1:5:2:1 for I:FcH:$AlCl_3$:Al and heating the mixture under N_2 in decalin at 185°C for 4 h.

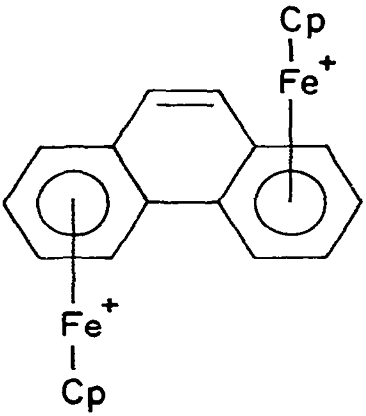
When a molar ratio of 1:1:2:1 for I:FcH:$AlCl_3$:Al was heated under N_2 in decalin at different temperatures for 16 h, mixtures of cations II and III were obtained as the hexafluorophosphate salts and these could be separated by passage through an alumina column with acetone as eluant. The relative amounts of II and III were determined by ^1H NMR and the results are summarized in Table 1. For comparison, experiments using refluxing n-octane, n-nonane or n-decane as solvent were carried out and the results are also given in Table 1. In general, it appears that at temperatures above 125°C, the use of normal alkanes as solvent gave rise to somewhat lesser extents of hydrogenation than in decalin at comparable temperatures. This finding apparently supports the previous suggestion [1] that the solvent may be a major source of hydrogen for the hydrogenation and that decalin is a better hydrogen donor than the long chain normal alkanes.

From the work with naphthalene on the effect of varying the amount of $AlCl_3$ on the extent of hydrogenation, interpolation of the data indicated that a reaction carried out with a molar ratio of 1:1:5.6:1 for naphthalene:FcH:$AlCl_3$:Al at 140° C for 4 h would give about a 50:50 mixture of non-hydrogenated and hydrogenated products [1]. However, using these conditions with phenanthrene (molar ratio of 1:1:5.6:1 for I:FcH:$AlCl_3$:Al at 140° C for 4 h), the hydrogenated cation III in 32% yield was obtained as the only product. Pure cation III was also obtained with 9,10-dihydrophenanthrene as the arene in the ligand exchange reaction. From the above experiments, it may be concluded that during the ligand exchange reaction, phenanthrene, while less susceptible to hydrogenation than anthracene, is more susceptible to hydrogenatio than naphthalene.

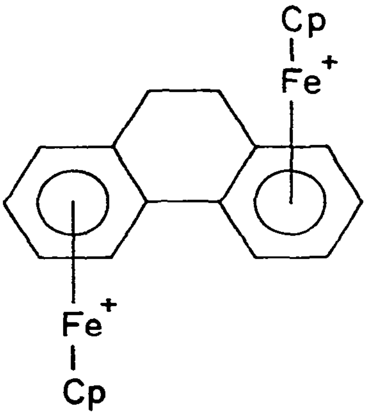
The hydrogenation to give ion III may be formulated via the ion-radical mechanism as previously proposed [3,4]. After I is complexed with CpFe to give II, abstraction of a hydride ion by $AlCl_3$ from the 9- or 10-position would give rise to a carbonium ion. An intramolecular oxidation-reduction would then take place through the transfer of an electron from Fe(II) to give Fe(III), while at the same time the carbonium ion center would be reduced to a radical, and this is followed by reactions with H atoms in th same manner as previously described [3,4]. It is also of interest to note that in a recent communication on the synthesis of *bis*-(η^6-naphthalene)chromium(0) [5], it was stated in a footnote tha control experiments with naphthalene-$AlCl_3$-Al-$CrCl_3$ in C_6H_5Cl as solvent or with $Li^{+}C_{10}H_8^{\overline{\cdot}}$-$CrCl_3(THF)_3$-THF gave *bis*-($\eta^6$-tetralin)-chromium(0) as the main product. Thus possible hydrogenations that may take place in the formation of organometallic complexes containing transition metals other than Fe may be worthy of further investigation.

η^6-Phenanthrene-*trans*-*bis*-η^5-cyclopentadienyliron and η^6-9,10-dihydrophenanthrene-*trans*-*bis*-η^5-cyclopentadienyliron dications (IV and V)

The complexing of certain arenes with two CpFe groups to give dications can be effected in a one-step ligand exchange react using an excess of ferrocene and $AlCl_3$ [2,6]. With anthracene, onl the hydrogenated η^6-9,10-dihydroanthracene-*trans*-*bis*-η^5-cyclopentadienyliron dication could be obtained [2]. However, with phenanthrene (I), a mixture of the non-hydrogenated and hydrogenat dications IV and V were produced. For example, heating a mixture of I:Fc:AlCl$_3$:Al in a molar ratio of 1:5:10:1 at 135° C in decalin under N_2 for 16 h gave a 12% yield of a mixture consisting of 70% IV and 30% V. Dication V so obtained was identical with that prepared directly from 9,10-dihydrophenanthrene. Morrison *et al.* [6] have previously reported the formation of dication IV from a one-step ligand exchange reaction. On repeating the experiment using the conditions of Morrison *et al.* (molar ratio of 1:20:100:33 for I:FcH: AlCl$_3$:Al in refluxing cyclohexane for 16 h), we obtained a 40% yield of mixed products consisting of 80% IV and 20% V.



IV



V

^1H and ^{13}C magnetic resonance spectra of ions II, III, IV and V

The identification of the structures of ions II, III, IV and V was greatly assisted by their ^1H and ^{13}C NMR spectra, and these spectral data are summarized in Tables 2 and 3. The assignments of various absorptions were facilitated by the steric interaction between the H atoms at C-4 and C-5 (numbering as shown in structure II), which would result in a steric downfield shift for the ^1H absorptions at C-4 and C-5, and a coincident steric upfield shift for the ^{13}C absorptions at these positions [7,8]. For example, in the ^1H spectrum of cation II, the 1H multiplet at the lowest

Table 2.

^{1}H magnetic resonance data for various mono- and dications

Ion	δ(acetone-d_6) ppm from TMS			
	Uncomplexed aromatic	Complexed aromatic	Cp	CH_2 or CH_3
II	8.00(m) (C-6-10) (6H) 8.80 (m) (C-5) (1H)	6.64 (m) (C-2,3) (2H) 7.25 (m) (C-1) (1H) 8.00(m) (C-4)[a]	4.62 (s) (5H)	
III	7.50 (m) (C-6-8) (3H) 8.00 (m) (C-5) (1H)	6.55 (m) (C-1-3) (3H) 7.03 (m) (C-4) (1H)	5.11 (s) (5H)	3.17 (m) (C-9,10) (4H)
IV	7.84 (s) (C-9,10) (2H)	6.65 (m) (C-2,3,6,7) (4H) 7.00 (m) (C-1,8) (2H) 7.55 (m) (C-4,5) (2H)	4.73 (s) (10H)	
V		6.74 (m) (C-1-3,6-8) (6H) 7.20 (m) (C-4,5) (2H)	5.24 (s) (10H)	3.52 (s) (C-9,10) (4H)
VII[b]	7.90 (m) (C-6,7) (3H) 8.20 (m) (C-8) (1H) 8.75 (m) (C-5) (1H)	6.60 (m) (C-2,3) (2H) 7.35 (m) (C-1) (1H) 7.90 (m) (C-4)[c]	4.58 (s) (5H)	2.67 (m) (CH_3) (6H)
VIII[b]		6.60 (m) (C-2,3,6,7) (4H) 7.20 (m) (C-1,8) (2H) 7.55 (m) (C-4,5) (2H)	4.66 (s) (10H)	2.72 (s) (CH_3) (6H)

[a] As part of the multiplet for C-6-10.

[b] CD_3CN instead of acetone-d_6 was the solvent.

[c] As part of the multiplet for C-6,7.

field (8.80 ppm) is assigned to C-5, a downfield shift of about 0.8 ppm from the uncomplexed aromatic proton absorptions centered at 8.0 ppm. For the complexed aromatic ring, a 2H multiplet at 6.64 ppm and a 1H multiplet at 7.25 ppm are assigned, respectively, to C-2,3 and C-1. Since the C-5 proton is shifted downfield by about 0.8 ppm, a similar shift for the C-4 proton relative to C-1 would place it in the 8.0 ppm region, and this is confirmed by the integration of the 8.0 ppm multiplet as 6H, corresponding to C-4 and C-6-10. Similarly, in the ^{13}C spectrum of cation II, for the complexed aromatic carbons, the absorption at the highest field (80.2 ppm) is assigned to C-4, the result of a steric upfield shift. The quaternary carbons (C-11, 12) at 93.1 and 93.7 are easily recognized and the remaining complexed aromatic carbons at 86.4, 86.8 and 87.5 ppm are assigned to C-1-3.

When hydrogenation occurs at C-9,10, these carbon positions become methylene groups, and only in the hydrogenated ions III and V do methylene absorptions in the aliphatic region appear in both the ^{1}H and ^{13}C spectra (Tables 2 and 3). For dications IV and V, the symmetry of the structures greatly simplified both the ^{1}H and ^{13}C spectra. The two CpFe groups are assigned a trans geometry by analogy with similar assignments in dications formed from other polycyclic arenes [4, 6, 9]. Moreover, if the two CpFe groups were cis, in dication V, two of the C-9,10 protons would be on the same side (endo) and the other two would be on the opposite side (exo) relative to the two CpFe groups, and it would be unlikely that the 4 protons at C-9,10 would give a singlet in the ^{1}H spectrum [9], as was observed (Table 2).

η^6-9,10-Dimethylphenanthrene-η^5-cyclopentadienyliron cation (VII) and η^6-9,10-dimethylphenanthrene-trans-bis-η^5-cyclopentadienyliron dication (VIII)

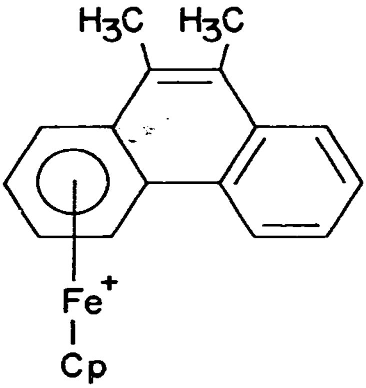
9,10-Dimethylphenanthrene (VI) was prepared via a series

Table 3.

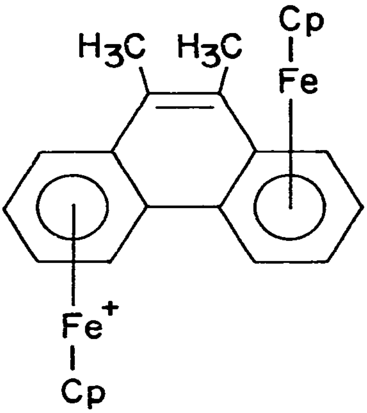
^{13}C magnetic resonance data for various mono- and dications

	δ(DMSO-$\underline{d}_6$) ppm from TMS			
Ion	Uncomplexed aromatic	Complexed aromatic	Cp	CH_2 or CH_3
II	124.3, 126.1, 128.7 129.0, 129.5, 130.0, 132.2, 133.0 (C-5-10, 13,14)	80.2 (C-4) 85.5, 86.1, 86.5 (C-1-3) 93.1, 93.7 (C-11,12)	76.4	
III	125.6, 127.6, 129.1, 129.3, 130.5, 138.0 (C-5-8,13,14)	80.0 (C-4) 86.4, 86.8, 87.5 (C-1-3) 96.7, 102.6 (C-11, 12)	77.0	26.5, 27.1 (C-9,10)
IV	131.5 (C-9,10)	82.6 (C-4,5) 87.2, 87.3, 88.2 (C-1-3,6-8) 92.2, 94.0 (C-11-14)	77.9	
V		81.4 (C-4,5) 86.2, 87.1, (C-1-3,6-8) 91.1, 102.2 (C-11-14)	76.7	24.6 (C-9,10)
VII	123.5, 125.4, 127.2, 127.4 127.9, 129.0 (C-5-10) 132.8, 135.4 (C-13,14)	79.5 (C-4) 81.5, 85.3, 85.9 (C-1-3) 91.8, 94.7 (C-11,12)	75.9	14.6, 15.1 (CH_3)
VIII	134.0 (C-9,10)	82.5 (C-4,5) 84.0, 87.1, 88.2 (C-1-3,6-8) 91.4, 96.1 (C-11-14)	77.9	16.4 (CH_3)

of reactions as described by Rabideau and Harvey [10] involving the conversion of I to 9-bromophenanthrene to 9-methylphenanthrene to 9-bromo-10-methylphenanthrene and then to VI. When a mixture of VI:FcH:$AlCl_3$:Al in the molar ratio of 1:1:2:1 was heated under N_2 in refluxing cyclohexane for 16 h, conditions which usually favor the formation of a monocation, the η^6-9,10-dimethylphenanthrene-η^5-cyclopentadienyliron cation (VII) was obtained in 34% yield, and there was no evidence of any hydrogenation. In a similar reaction in refluxing cyclohexane but with a molar ratio of 1:10:20:1 for VI:FcH:$AlCl_3$:Al, conditions which usually favor the formation of a dication, the η^6-9,10-dimethylphenanthrene-trans-bis-η^5-cyclopentadienyliron dication (VIII) was produced in 68% yield, again without any evidence of hydrogenation. The ^1H and ^{13}C NMR data for ions VII and VIII are included in Tables 2 and 3. When ligand exchange reactions using VI as the arene were attempted at temperatures of about 140° C with various molar combinations of the reactants in order to promote hydrogenation, only decomposition occurred and no cationic product could be obtained.



VII



VIII

The finding that 9,10-dimethylphenanthrene (VI) gave rise to only the non-hydrogenated ions VII and VIII is in complete contrast to the results observed with 9,10-dimethylanthracene [3, 4]. With 9,10-dimethylanthracene, the minimum temperature required for reaction to occur was 130 - 140° C and the mono- or dicationic product obtained was hydrogenated at the C-9 and C-10 positions [3,4]. As pointed out earlier for anthracene, the ready formation of radical centers at C-9 and C-10, which leads to hydrogenation, also applied to 9,10-dimethylanthracene. It has been suggested [4] that the higher temperature required for reaction with 9,10-dimethylanthracene may be related to the mechanism of the hydrogenation process, which is initiated by hydride abstraction by $AlCl_3$. Since a primary hydrogen has to be abstraced from a CH_3 group, a higher temperature is required for 9,10-dimethylanthracene than for anthracene. In the case of 9,10-dimethylphenanthrene (VI), since a double bond can be formed between C-9 and C-10 in place of radicals, at the relatively low temperature of refluxing cyclohexane cations VII and VIII, without hydrogenation, were obtained in relatively good yields. When the temperature has to be raised to allow for hybride abstraction from a CH_3 group in order to initiate the hydrogenation process, apparently decomposition predominated at such higher temperatures and no cationic product was obtainable.[*]

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[*] The referees raised some questions on our suggested mechanism, especially on the role of $AlCl_3$ in abstracting a hydride ion from the coordinated arene in initiating the hydrogenation process [3,4]. A number of experimental observations should be cited. Firstly, the amount of $AlCl_3$ used was found to influence pronouncedly the extent of hydrogenation in the reaction with naphthalene [1]. When perdeuteronaphthalene was used as the arene, extensive H-D exchange took place [11]. With 1-bromonaphthalene as the arene, there was debromination to give the naphthalene complex as well as debromination and hydrogenation to give the tetralin complex, the latter being suppressed by the presence of radical scavengers [11]. All of these findings suggest an important role for $AlCl_3$, likely as a hydride abstractor. For the present systems, a referee has also pointed out that hydride abstraction from C-9 or C-10 of II would give a vinyl cation, while removal of a hydride from one of the CH_3 groups in VII would give a benzylic type of cation. It was stated that a benzylic cation would be more stable than a vinyl cati hence one would expect a more facile hydrogenation for 9,10-dimethyl phenanthrene (VI) than for phenanthrene (I), opposite to what was

Experimental

The ligand exchange reactions were carried under a variety of experimental conditions as discussed in the preceding section. The following descriptions of experimental procedure are given as illustrations of typical experiments.

η^6-Phenanthrene-η^5-cyclopentadienyliron cation (II)

A mixture of 4.4 g (25 mmol) of phenanthrene (I), 4.7 g (25 mmol) of ferrocene, 6.7 g (50 mmol) of $AlCl_3$ and 0.65 g (25 mmol) of Al powder in 50 ml of cyclohexane was heated under N_2 and under reflux for 16 h. After cooling to room temperature, 50 ml of H_2O was added and the mixture was filtered under vacuum to remove all solid material. The aqueous layer was separated, washed with hexane (2 x 50 ml) and then filtered into a solution of ammonium hexafluorophosphate (4.0 g, 25 mmol, in 10 ml H_2O). The hexafluorophosphate salt of II that precipitated was recovered by filtration under vacuum, redissolved in acetone, dried over $MgSO_4$, concentrated and then crystallized from acetone-ether to give 1.15 g (10%) of the hexafluorophosphate salt of II as orange-yellow plates. (Found: C, 50.94; H, 3.45; Fe, 12.58. $C_{19}H_{15}F_6PFe$ calcd: C, 51.38; H, 3.40; Fe, 12.57%). The ^1H and ^{13}C NMR spectral data are given in Tables 2 and 3.

The hexafluorophosphate salts of the various cations obtained in the present work generally melted with decomposition over a temperature range and this temperature range may also change

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observed. These arguments of the referee, however, may not be valid. It is known that α-ferrocenyl substituted carbocations are extraordinarily stable. Thus calorimetry has shown that the primary ferrocenylmethyl cation is more stable than the well-known tertiary triphenylmethyl cation [12]. We have also demonstrated that a tertiary cation, such as $FcCH_2(Ph)_2C^+$, can rearrange to the more stable secondary $(Ph)_2CH(Fc)CH^+$, which has an α-ferrocenyl substituent [13, 14]. A hydride abstraction from a position α to the complexed aromatic ring, such as a removal of hydride from C-10 of II, would give a cation analogous to an α-ferrocenyl substituted cation and its stability would most probably be greater than that of a benzylic type of cation, hence the ease of hydrogenation is greater for I than for VI, as was observed.

after each recrystallization. Hence the melting points are not recorded. Samples for analysis usually were obtained after furth purification by passage through an alumina column (chromatographi activated alumina F-20, Sargent-Welch Scientific Co.) with aceton or acetonitrile as eluant. In the experiments where mixtures of cations II and III were obtained (Table 1), the hexafluorophospha salt of III is eluted first.

η^6-9,10-Dihydrophenanthrene-η^5-cyclopentadienyliron cation (III)

A mixture of 4.4 g (25 mmol) of I, 4.7 g (25 mmol) of ferrocene, 18.6 g (140 mmol) of $AlCl_3$ and 0.65 g (25 mmol) of Al powder in 50 ml of decalin was heated with stirring under N_2 at 140° C for 4 h. Work-up as described in the preparation of II ga the hexafluorophosphate salt of III which crystallized from acetone-ether as a fine yellow powder, weighing 3.5 g (32%). (Found: C, 49.95; H, 3.84; Fe, 12.52. $C_{19}H_{17}F_6PFe$ calcd: C, 51.15; H, 3.84; Fe, 12.52%).

In an experiment in which a mixture of 25 mmol of 9,10-dihydrophenanthrene, 25 mmol of ferrocene, 50 mmol of $AlCl_3$ and 25 mmol of Al powder in 50 ml of cyclohexane was heated under reflux and under N_2 for 16 h, a 22% yield of cation III was obtained as its hexafluorophosphate salt.

η^6-Phenanthrene-*trans*-*bis*-η^5-cyclopentadienyliron and η^6-9,10-dihydrophenanthrene-*trans*-*bis*-η^5-cyclopentadienyliron dications (IV and V)

A mixture of 4.4 g (25 mmol) of I, 23.3 g (125 mmol) of ferrocene, 33.3 g (250 mmol) of $AlCl_3$ and 0.65 g (25 mmol) of A powder in 100 ml of decalin was heated with stirring under N_2 at 135° C for 16 h. The usual work-up gave 2.1 g (12%) of a mixture of the dihexafluorophosphate salts of dications IV and V, consisti of 70% IV and 30% V as measured by the Cp absorptions in the ^1H

NMR spectrum. Fractional crystallization from acetone-ether gave the less soluble dihexafluorophosphate salt of IV, the ^{1}H and ^{13}C NMR spectral data of which are given in Tables 2 and 3. On passage through an alumina column, IV apparently decomposed, monocation II being among the decomposition products. Therefore, no C and H analysis on the dihexafluorophosphate salt of IV was carried out.

When a mixture of the dihexafluorophosphate salts of dications IV and V was passed through an alumina column with acetonitrile as eluant, monocation II arising from the decomposition of IV and some impurities were first eluted. The pure dihexafluorophosphate salt of V was then recovered and was recrystallized from acetonitrile-ether as a fine yellow powder. (Found: C, 40.13; H, 3.11; Fe, 15.69; $C_{24}H_{22}F_{12}P_{2}Fe_{2}$ calcd: C, 40.48; H, 3.11; Fe, 15.69%).

When a mixture of 5.0 mmol of 9,10-dihydrophenanthrene, 25 mmol of ferrocene, 50 mmol of $AlCl_3$ and 5.0 mmol of Al powder in 50 ml of cyclohexane was heated under reflux and under N_2 for 12 h, the usual work-up and crystallization from acetone-ether gave a 50% yield of the dihexafluorophosphate salt of V.

η^6-9,10-Dimethylphenanthrene-η^5-cyclopentadienyliron cation (VII) and η^6-9,10-dimethylpheananthrene-trans-bis-η^5-cyclopentadienyliron dication (VIII)

A mixture of 1.03 g (5.0 mmol) of 9,10-dimethylphenanthrene (VI), 0.93 g (5.0 mmol) of ferrocene, 1.33 g (10 mmol) of $AlCl_3$ and 0.14 g (5.0 mmol) of Al powder in 50 ml of cyclohexane was heated under reflux and under N_2 for 16 h. Work-up in the usual manner gave 0.80 g (34%) of the hexafluorophosphate salt of VII. (Found: C, 53.19; H, 4.14. $C_{21}H_{19}F_{6}PFe$ calcd: C, 53.41; H, 4.06%).

In a similar reaction using 1.03 g (5.0 mmol) of VI, 9.3 g (50 mmol) of ferrocene, 13.3 g (100 mmol) of $AlCl_3$ and 0.14 g (5.0 mmol) of Al powder in refluxing cyclohexane for 16 h, 2.5 g

(68%) of the dihexafluorophosphate salt of dication VIII was obtained. (Found: C, 41.97; H, 3.21. $C_{26}H_{24}F_{12}P_2Fe_2$ calcd: C, 42.31; H, 3.28%).

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