Journal of Organometallic Chemistry, 101 (1975) 221—229
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

HYDROGENATION OF AROMATIC LIGANDS DURING THE SYNTHESIS OF π-ARENE-π-CYCLOPENTADIENYLIRON MONO- AND DICATIONS. EVIDENCE FROM ^{1}H AND ^{13}C MAGNETIC RESONANCE STUDIES

R.G. SUTHERLAND, S.C. CHEN, J. PANNEKOEK and C.C. LEE*

Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Sask. S7N OWO (Canada)

(Received April 23rd, 1975)

Summary

Anthracene reacts with ferrocene in the presence of $AlCl_3/Al$ to form the same mono- and dications derived from 9,10-dihydroanthracene. Naphthalene yields arene complexes of both naphthalene and tetralin, the product formed being dependent on the reaction temperature.

Introduction

In 1963, Nesmeyanov [1,2] reported that π-arene-π-cyclopentadienyliron cations could be prepared by the reaction of benzene and substituted benzenes with ferrocene and $AlCl_3$, Al powder being added to convert any ferricenium ion formed back to ferrocene. Later work showed that benzene could be replaced by other arenes including naphthalene and fluorene [3]. Much interesting chemistry has developed in this area and the early studies have been reviewed [4,5]. Our interest in this area was aroused by the observation that the cyclopentadienyl ligand of ferrocene could be intramolecularly displaced by an arene, this being exemplified by the reaction of bisindenyliron with BF_3·etherate to give the corresponding π-arene-π-cyclopentadienyliron cation [6]. These studies led to our attempts to prepare dications from arenes such as fluorene by treating the π-fluorene-π-cyclopentadienyliron cation with excess ferrocene, whereby the corresponding dication was isolated [7]. While further studies on other arene systems were in progress in this laboratory, Hendrickson et al. [8] used a slight modification of our procedure to extend the observations to other arene systems. Subsequently, these workers [9] reported extensively on the electronic properties of these dications. In the present paper, we report the results of our studies with both anthracene and naphthalene.

Discussion

Anthracene

Anthracene (I) is a 14-π-electron system, and so would not be expected to form a dication since each coordinated arene ring is required to donate six π-electrons to each iron atom, and formation of such a species would leave an odd electron on both the 9- and 10-positions. Hendrickson et al. [8] have reported that anthracene binds two (Cp)Fe moieties and ascribed the symmetrical structure II to the dication. The ^{13}C NMR spectrum of this species was discussed in some detail with particular emphasis on the problem of identifying the 9,10-anthracene carbon resonances and their possible accidental degeneracies. The ^{1}H NMR spectrum was also held to be consistent with II, the resonance at 32 Hz higher field than the Cp ring being ascribed to the 9,10-protons. In our work, the reaction of anthracene with ferrocene and $AlCl_3/Al$ under mild conditions produced a monocation which was identical in all respects with monocation IV,

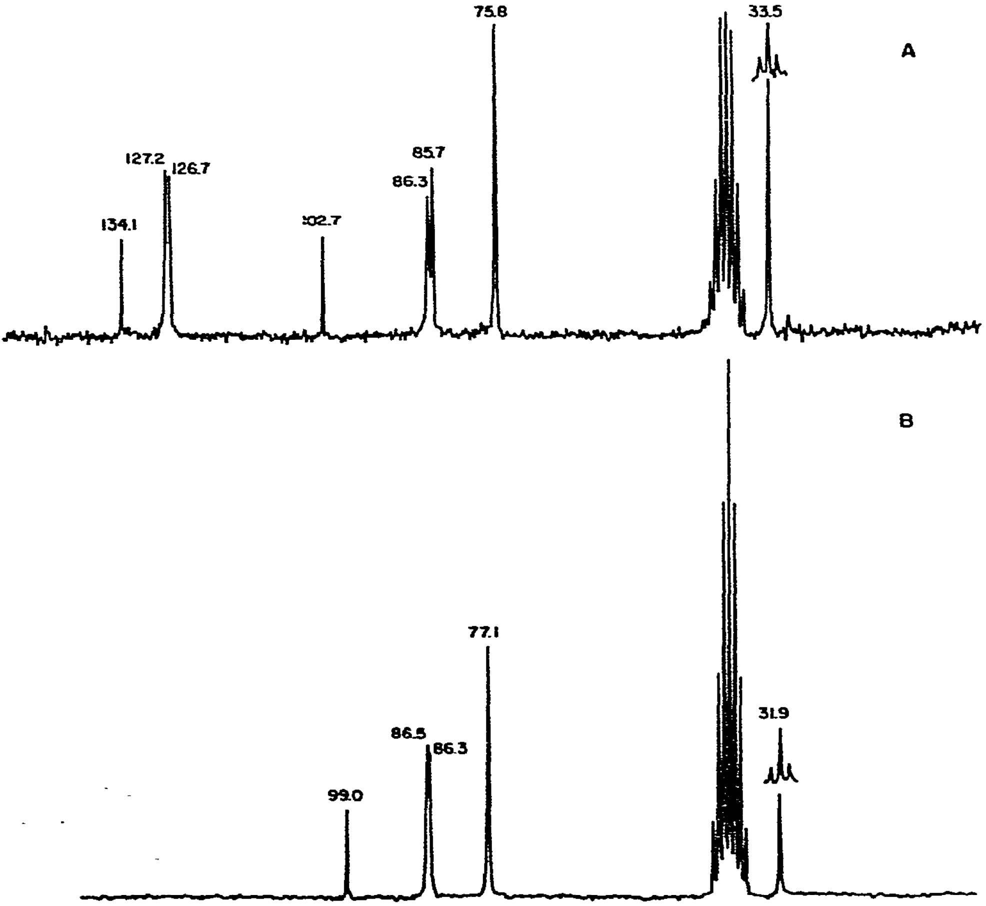


Fig. 1. ^{1}H-Decoupled ^{13}C NMR spectra: a, π-9,10-dihydroanthracene-π-cyclopentadienyliron monocation (IV); b, bis-(π-9,10-dihydroanthracene-π-cyclopentadienyliron) dication (V). Insets show ^{1}H—^{13}C coupling of CH_2 from off resonance experiments.

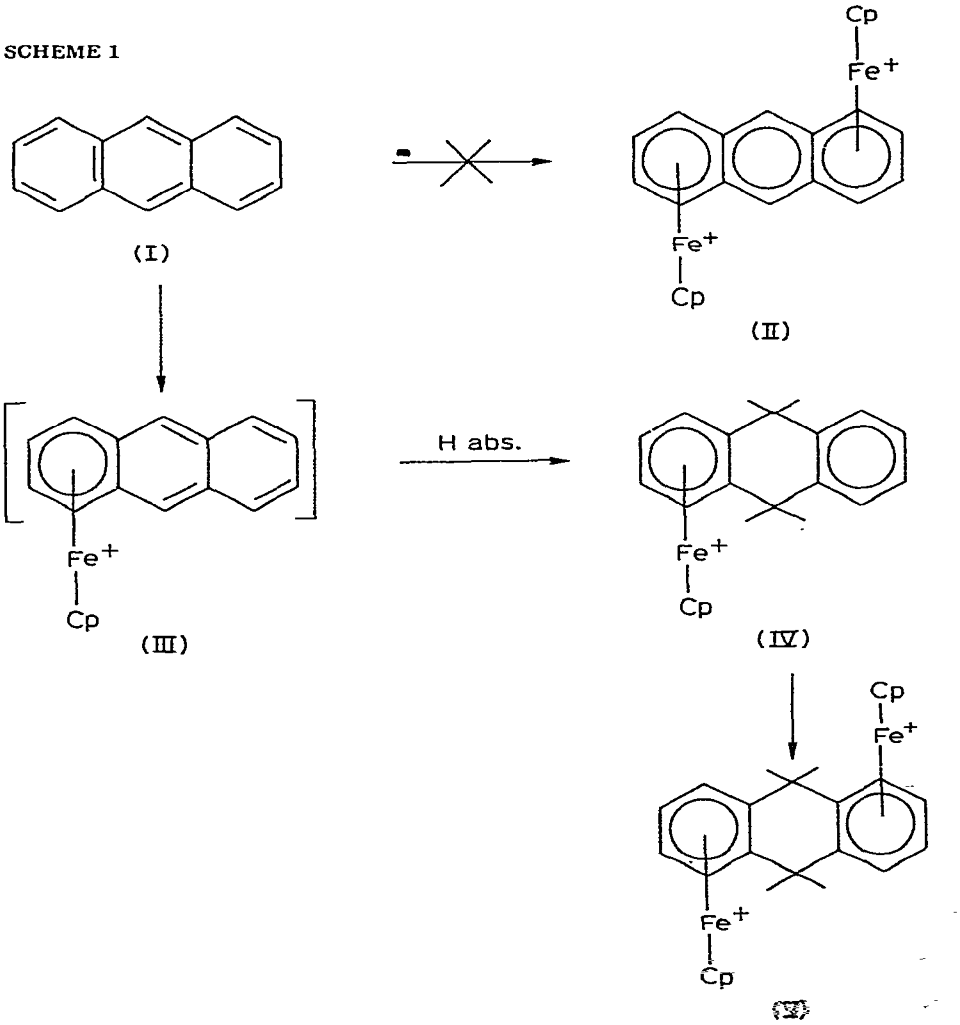
TABLE 1

^{13}C MAGNETIC RESONANCE DATA

	δ (DMSO-d_6), ppm from TMS			
Ion	Uncomplexed aromatic	Complexed aromatic	CH_2	Cp
IV	134.1 (quat)[a] 127.2, 126.7	102.7 (quat) 86.3, 85.7	33.5	75.8
V		99.0 (quat) 86.5, 86.3	31.9	77.1
VII		102.8 (quat) 87.6, 86.9	28.8 22.4	77.7
VIII	132.7, 131.8	96.6 (quat) 87.6, 86.0		77.2

[a] Denoting quaternary carbons.

SCHEME 1



previously obtained from 9,10-dihydroanthracene [10]. Its ^1H NMR spectrum consisted of four groups of resonances at δ 7.51 (4H, uncomplexed ring, m), 6.51 (4H, complexed ring, m), 4.67 (5H, Cp, s), and 4.12 (4H, two CH_2, s). Its ^{13}C NMR spectrum, shown in Fig. 1a, is also consistent with a 9,10-dihydroanthracene moiety as the arene ligand. The chemical shifts of the ^{13}C spectrum are summarized in Table 1. An important feature is the signal at 33.5 ppm, diagnostic of a saturated carbon and it is established as a methylene group by off resonance experiments.

A dication could be formed directly from anthracene or from the monocation by further treatment with ferrocene and $AlCl_3/Al$. Again the spectra are consistent with the conversion of the ligand to 9,10-dihydroanthracene. The ^1H NMR spectrum now consists of three signals, δ 6.60 (complexed ring, m), 5.02 (Cp, s), and 4.55 (CH_2, s) with an integral ratio of 4/5/2. The ^{13}C NMR spectrum is shown in Fig. 1b, with the chemical shifts also summarized in Table 1. Of interest is the aliphatic line at 31.9 ppm, again shown to be due to CH_2 groups by off resonance experiments.

In addition to the NMR studies, both the mono- and dicationic species were photolyzed using 253.7 nm radiation in THF. The resulting material, after being chromatographed over alumina, gave a mixture of ferrocene anf 9,10-dihydroanthracene. From the present work, it is concluded that anthracene does not function as a stable ligand in Nesmeyanov's reaction; probably, the monocation III is unstable and abstracts hydrogen to give the same species, IV, as that isolated from 9,10-dihydroanthracene. The monocation IV can then be converted to dication V (Scheme 1).

Naphthalene

The observation of hydrogenation in the reaction with anthracene led to a search for other such reactions, and the reaction of naphthalene (VI) with ferrocene and $AlCl_3/Al$ described by Nesmeyanov [3] and later by Hendrickson [8] was reinvestigated. The course of the reaction was found to be temperature dependent. When the reaction was carried out in refluxing decalin, only product VII was isolated. This proved to be identical with the product obtained when tetralin was treated under these conditions. Its ^{13}C NMR spectrum is shown in Fig. 2a and the chemical shifts are again summarized in Table 1. The features of interest are the two lines at 28.8 and 22.4 ppm, which are assigned to the saturated carbons of the tetralin ligand; off resonance (inset) shows that they are methylene groups. The ^1H NMR spectrum shows four sets of signals at δ 6.32 (complexed ring, s), 5.10 (Cp, s), 3.00 (protons at C-2,3, m), and 2.10 (protons at C-1,4, m) with integral ratio of 4/5/4/4.

As the temperature of the reaction of naphthalene with ferrocene and $AlCl_3/Al$ was lowered, a mixture of products was obtained. These were the tetralin complex VII and the naphthalene complex VIII. The mixture could be separated over alumina using acetone as eluant, with the tetralin complex being eluted first. At temperatures of about 140°C, an approximately 1/1 mixture of the complexes was obtained, while reaction in refluxing methylcyclohexane (b.p. 101°C) gave the pure naphthalene complex VIII. The ^{13}C NMR spectrum of VIII is given in Fig. 2b (chemical shifts given in Table 1), and the ^{13}C spectrum of a representative mixture is shown in Fig. 2c. The ^1H NMR spectrum of

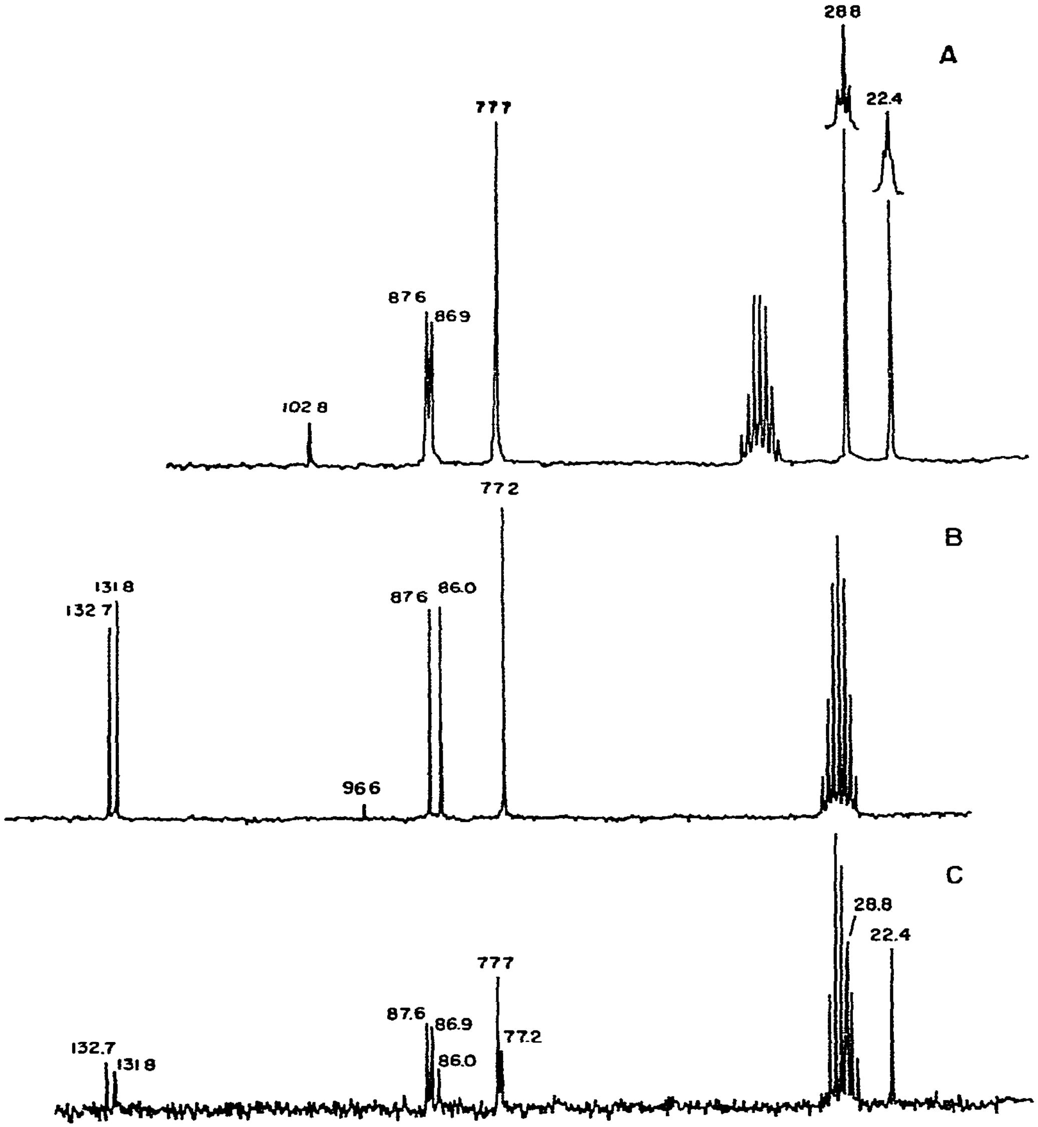
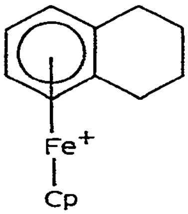
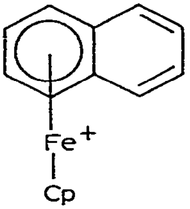


Fig. 2. ^{1}H-Decoupled ^{13}C NMR spectra; a, π-tetralin-π-cyclopentadienyliron monocation (VII); b, π-naphthalene-π-cyclopentadienyliron monocation (VIII); c, mixture of VII and VIII. Insets show ^{1}H—^{13}C coupling of CH_2 from off resonance experiments.

VIII shows absorptions at δ 8.04 (4H, uncomplexed ring, m), 7.48 (2H, α-H of complexed ring, m), 6.60 (2H, β-H of complexed ring, m) and 4.78 (5H, Cp, s). Photolysis of VIII gave, as expected, a mixture of ferrocene and naphthalene, which could be separated chromatographically. Thus it can be seen that the nature of the reaction occurring between naphthalene and ferrocene, in the presence of $AlCl_3/Al$, is temperature dependent, with higher temperatures favoring hydrogenation. 1,2-Dihydronaphthalene as well as 1,4-dihydronaphthalene treated under similar conditions at 160 or 180°C in decalin also gave the tetralin complex VII.



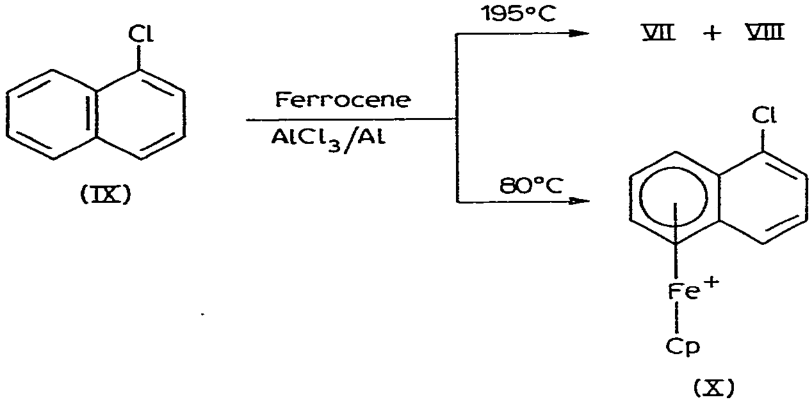
(VII)



(VIII)

α-Chloronaphthalene

Earlier studies by Nesmeyanov [3] have shown that halobenzenes are sometimes dehalogenated during the formation of π-arene-π-cyclopentadienyliron cations, and it is thus of interest to investigate the reaction with α-chloronaphthalene (IX). IX reacts in refluxing cyclohexane to give X in which the unsubstituted ring was complexed to the (Cp)Fe group. When refluxing decalin was used as solvent in this reaction, a mixture of VII and VIII was obtained in yields of 18 and 6%, respectively, showing that dehalogenation as well as hydrogenation could take place. The dehalogenation differs from that observed previously [3] in that it is the uncomplexed aromatic ring which loses halogen.



Some preliminary experiments have been carried out in an attempt to obtain information on the mechanism of this novel hydrogenation. A final step in the reaction work-up involves quenching with water and isolation of the hexafluorophosphate salt from the aqueous phase. Replacement of the water by D_2O did not cause any incorporation of deuterium into the product, thus indicating that the hydrogenation took place during the reaction, and not during the work-up of the reaction mixture. Attempts to hydrogenate VIII using hydrogen and Pt as catalyst caused no reaction, VIII being recovered unchanged. Thus the double bonds in the uncomplexed ring are not "localized" by the formation of the complex; i.e., it is not a dienoid system. This conclusion is reinforced by the lack of reactivity of VIII with tetracyanoethylene under Diels—Alder conditions or with triplet O_2 in the presence of $AlCl_3$ [11]. $AlCl_3$ in decalin at 160 or 180°C does convert VIII to VII; but a Lewis acid under these conditions would be expected to disproportionate the π-arene-π-cyclopentadienyliron cation to ferrocene and the arene, and thus this conversion, although synthetically useful, does not provide any mechanistic information.

Experimental

π-9,10-Dihydroanthracene-π-cyclopentadienyliron cation (IV)

(a) From 9,10-dihydroanthracene. 9,10-Dihydroanthracene (10.8 g, 60 mmol), ferrocene (11.2 g, 60 mmol), $AlCl_3$ (16.0 g, 120 mmol) and Al powder (1.6 g, 60 mmol) were refluxed in methylcyclohexane (150 ml) for 20 h under N_2. The mixture was cooled and ice (50 g) was added. The organic layer was separated and extracted with H_2O (3 X 100 ml). The combined aqueous phase was washed with cyclohexane (2 X 30 ml) and then filtered into a concentrated solution of ammonium hexafluorophosphate. The hexafluorophosphate salt of IV precipitated (9.5 g, 36%) and was recrystallized from acetone/ether as greenish needles, m.p. 84-86°C (dec.). (Found: C, 50.97; H, 3.97. $C_{19}H_{17}F_6FeP$ calcd.: C, 51.15; H, 3.84%.)

(b) From anthracene. Anthracene (5.0 g, 28 mmol), ferrocene (5.2 g, 28 mmol), $AlCl_3$ (7.5 g, 56 mmol) and Al powder (0.76 g, 28 mmol) were refluxed in methylcyclohexane (100 ml) under N_2 for 20 h. The mixture was worked up as described above to give a greenish crystalline precipitate (4.9 g, 39%) which was recrystallized from acetone/ether to give a product identical with that obtained in *a*.

Bis-(π-9,10-dihydroanthracene-π-cyclopentadienyliron) dication (V)

(a) From IV. The hexafluorophosphate salt of IV (2.0 g, 4.5 mmol), ferrocene (1.7 g, 9.0 mmol), $AlCl_3$ (1.80 g, 13.5 mmol) and Al powder (0.25 g, 9.0 mmol) were refluxed in methylcyclohexane (80 ml) under N_2 for 20 h. The hexafluorophosphate salt of dication V (2.0 g, 62%) was obtained upon work-up and was recrystallized from acetonitrile/ether as yellow needles, m.p. 190°C (sintering) with dec. at 210°C. (Found: C, 40.54; H, 3.02. $C_{24}H_{22}F_{12}Fe_2P_2$ calcd.: C, 40.48; H, 3.12%.)

(b) From 9,10-dihydroanthracene or anthracene. When 9,10-dihydroanthracene or anthracene was treated with two equivalents of ferrocene in the presence of excess $AlCl_3/Al$ as described in *a*, the same hexafluorophosphate salt of V was obtained in yields of 29 and 28%, respectively.

π-Tetralin-π-cyclopentadienyliron cation (VII) and π-naphthalene-π-cyclopentadienyliron cation (VIII)

The reactions of naphthalene, ferrocene, $AlCl_3$ and Al, in molar ratios of 1/1/2/1, respectively, were carried out under N_2 in either methylcyclohexane or decalin as solvent at different temperatures ranging between 80-195°C. The work-up procedure was the same as that described for the isolation of the hexafluorophosphate salt of IV. The products obtained were dependent on the reaction temperature, and the yields were generally around 30%, but varied between 10-50%. In refluxing decalin (195°C), the only product that could be isolated was the hexafluorophosphate salt of VII, which was identical with that obtained from the reaction in which tetralin was used in place of naphthalene. The yellow hexafluorophosphate of VII crystallized from acetonitrile/ether, m.p. 202-204 °C. (Found: C, 45.60; H, 4.30; F, 28.5; Fe, 14.1; P, 8.0. $C_{15}H_{17}F_6FeP$ calcd.: C, 45.26; H, 4.30; F, 28.6; Fe, 14.0; P, 7.8%.)

At lower temperatures of 80-100°C, the hexafluorophosphate salt of VIII was obtained. A typical experiment is as follows. A mixture of naphthalene (5.25 g, 41 mmol), ferrocene (7.63 g, 41 mmol), $AlCl_3$ (10.9 g, 82 mmol) and Al powder (1.1 g, 41 mmol) was refluxed in methylcyclohexane (120 ml) under N_2 for 16 h. After work-up in the usual manner, the hexafluorophosphate salt of VIII (5.4 g, 33%) was obtained which crystallized from acetone/ether as orange flakes, m.p. 166-168°C (dec.). (Found: C, 45.70; H, 3.35; F, 28.9; Fe, 14.4; P, 7.6. $C_{15}H_{13}F_6FeP$ calcd.: C, 45.72; H, 3.32; F, 28.9; Fe, 14.2; P, 7.9%.)

When the reaction was carried out at temperatures intermediate between 100 and 195°C, a mixture of VII and VIII was obtained; for example, after heating the reaction mixture in decalin at 160°C for 16 h, the ratio of VII to VIII, separated as the hexafluorophosphate salts by column chromatography over alumina using acetone as eluant, was about 3/2.

At temperatures of 160 or 180°C in decalin, when the hexafluorophosphate salt of VIII was treated with $AlCl_3$, or when 1,2- or 1,4-dihydronaphthalene was treated with ferrocene and $AlCl_3/Al$ in the usual way, the hexafluorophosphate salt of VII was obtained in yields of 20-50%.

Reaction with α-chloronaphthalene

(a) π-Chloronaphthalene-π-cyclopentadienyliron cation (X). α-Chloronaphthalene (4.9 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 (80 ml) under N_2 for 6 h. The reaction mixture was worked up in the usual way to give the hexafluorophosphate salt of X (2.5 g, 19%) which crystallized from acetone/ether as orange-brown needles, m.p. 140-145°C (dec.), ^1H NMR (acetone-d_6) δ 4.85 (5H, Cp, s), 6.7 (2H, complexed aromatic, m), 7.6 (2H, complexed aromatic, m), and 7.9-8.4 (3H, uncomplexed aromatic, m). (Found: C, 41.18; H, 2.83. $C_{15}H_{12}ClF_6FeP$ calcd.: C, 42.04; H, 2.82%.)

(b) Mixture of VII and VIII from α-chloronaphthalene. When a similar reaction as described in *a* was carried out in decalin at 190°C for 28 h, after work-up, a yellowish-orange product was obtained which was separated by column chromatography over alumina with acetone as eluant to give the hexafluorophosphate salts of VII and VIII in yields of 18 and 6%, respectively.

Photolysis experiments

A solution of the hexafluorophosphate salt of IV (650 mg, 1.46 mmol) in THF (50 ml) was photolyzed under N_2 in a Rayonet reactor using 253.7 nm radiation. The reaction was shown by TLC analysis to be complete in 1.5 h. The deep green solution was poured into H_2O (200 ml) and then extracted with methylene chloride (3 × 30 ml). After drying over $MgSO_4$, the solvent was removed and the residue subjected to column chromatography over neutral alumina using hexane as eluant. A first fraction obtained gave about 300 mg of a mixture of ferrocene and 9,10-dihydroanthracene while a second fraction gave 70 mg of pure 9,10-dihydroanthracene, whose identity was confirmed by spectroscopic comparison with an authentic sample.

When a solution of the hexafluorophosphate salt of V or VIII was photolyzed in a similar manner as described above, but with reaction times of 5 and 3 h, respectively, for V and VIII, 9,10-dihydroanthracene was obtained from V and naphthalene was obtained from VIII.

NMR spectra

The ^{1}H and ^{13}C NMR spectra were obtained, respectively, using the HA-100 and XL-100 spectrometers.

Acknowledgments

We thank Miss M. Vetter for technical assistance; the financial support given by the National Research Council of Canada and by the President's Research Fund of the University of Saskatchewan are gratefully acknowledged.

References

1 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Dokl. Akad. Nauk SSSR, 140 (1963) 615.
2 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Tetrahedron Lett., (1963) 1725.
3 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Dokl. Akad. Nauk SSSR, 166 (1966) 607.
4 A.N. Nesmeyanov, Adv. Organometal. Chem., 10 (1972) 44.
5 M.I. Bruce, Organometal. Chem. Rev., 6 (1970) 705.
6 C.C. Lee, R.G. Sutherland and B.J. Thomson, J. Chem. Soc. Chem. Comm., (1971) 1071.
7 C.C. Lee, R.G. Sutherland and B.J. Thomson, J. Chem. Soc. Chem. Comm., (1972) 907.
8 W.H. Morrison, E.Y. Ho and D.N. Hendrickson, J. Amer. Chem. Soc., 96 (1974) 3603.
9 W.H. Morrison, E.Y. Ho and D.N. Hendrickson, Inorg. Chem., 14 (1975) 500.
10 B.J. Thomson, unpublished results.
11 D.H.R. Barton, R.K. Haynes, P.D. Magnus and I.D. Menzies, J. Chem. Soc. Chem. Comm., (1974) 511.