LIGAND EXCHANGE OF SOME HETEROCYCLIC ANALOGUES OF FLUORENE AND ANTHRACENE WITH FERROCENE

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Summary

The preparation of some new complexes of the type (heteroarene)(cyclopentadienyl)iron hexafluorophosphate and (heteroarene)bis(cyclopentadienyliron)-bis(hexafluorophosphate) are described where heteroarene is dibenzofuran, dibenzothiophene, xanthene, thioxanthene, phenothiazine, dihydrophenazine, acridan or carbazole. Bonding is to the benzo ring in all cases and hydrogenation at the 9,10-positions is observed in the reaction with phenazine and acridine. ^{1}H and ^{13}C NMR spectra of the complexes were used extensively for characterization.

Introduction

The aluminum chloride-catalysed exchange reaction between arenes and ferrocene, first described by Nesmeyanov and co-workers [1] has been used to prepare a wide range of complexes of the type $[(\eta^6$-arene)$(\eta^5$-cyclopentadienyl)iron]$^+$ X$^-$, where X is usually PF$_6$ or BF$_4$ [2]. In certain polycyclic systems both mono- and di-substitution can be effected [3,4] and, in addition, the reaction may be accompanied by hydrogenation at unsaturated positions not involved in complexation [5,6].

As part of our current interest in the application of these systems in organic synthesis, we have examined the exchange reaction of some polycyclic heteroaromatic systems with ferrocene. Previous to this work the preparation has also been reported of $(\eta^6$-carbazole)- and $(\eta^6$-benzimidazole)-$(\eta^5$-cyclopentadienyl)-iron hexafluorophosphate [7]. Other related complexes include the (N-methylindole)-, (indole)-, and (tetramethylthiophene)(cyclopentadienyl)-iron cations [8,9]. A review of π-heterocyclic complexes has also recently appeared [10].

Results and discussion

Monocations

Equimolar quantities of dibenzofuran (9-oxafluorene), dibenzothiophene (9-thiafluorene), xanthene (10*H*-9-oxaanthracene), thioxanthene (10*H*-9-thia-anthracene) or phenothiazine (10*H*-9-thia-10-azaanthracene), ferrocene and aluminum metal powder were treated with four equivalents of aluminum chloride (or two in the case of phenothiazine) in decalin at approximately 140°C for 4 h. Hydrolysis and precipitation as the hexafluorophosphate salt produced the monocationic species I to V as yellow or orange solids in yields ranging from 22 to 48%. Under similar conditions no complex formation was observed using pyridine, indole, quinoline or isoquinoline. Instead, the only salts obtained were those of the conjugate acids. With acridine (9-azaanthracene) or phenazine (9,10-diazaanthracene) the product obtained, depending on the conditions, was either the salt of the conjugate acid (refluxing cyclohexane) or the dicationic species described below (decalin at 150°C).
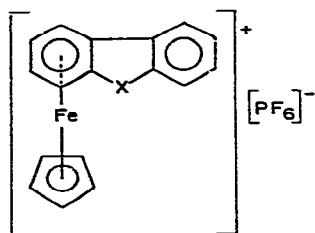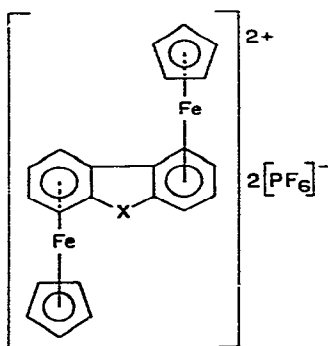
I : X = O
II : X = S
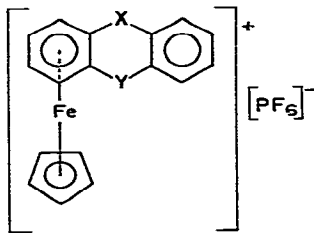
III : X = CH$_2$, Y = O
IV : X = CH$_2$, Y = S
V : X = NH, Y = S

VI : X = O
VII : X = S
VIII : X = NH
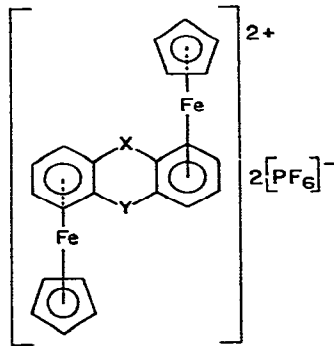
IX : X = CH$_2$, Y = O
X : X = CH$_2$, Y = S
XI : X = CH$_2$, Y = NH
XII : X = NH, Y = S
XIII : X = Y = NH

Dications

Using a five-fold excess of ferrocene and correspondingly more aluminum chloride (i.e., 12 equivalents for mono-heteroatomic and 14 equivalents for

TABLE 1

YIELDS AND ANALYTICAL AND IR DATA

Complex	Yield (%)	Analysis (Found (calcd.) (%))			$K(NH)^a$ (cm^{-1})
		C	H	N	
I	48	46.94 (47.04)	3.02 (3.02)	—	—
II	42	45.11 (45.36)	2.88 (2.93)	—	—
III [b]	45	45.97 (46.38)	3.53 (3.68)	—	—
IV [b]	29	44.99 (44.84)	3.99 (3.55)	—	—
V	22	42.61 (43.89)	2.95 (3.03)	3.11 (3.01)	3415
VI	35	36.64 (37.75)	3.10 (2.59)	—	—
VII	48	38.25 (36.90)	3.07 (2.53)	—	—
VIII [b]	70	39.45 (39.96)	3.20 (3.20)	2.13 (2.12)	3450
IX	40	38.32 (38.69)	3.01 (2.82)	—	—
X	95	37.57 (37.84)	2.97 (2.76)	—	—
XI	60	39.28 (38.73)	3.07 (2.97)	2.01 (1.96)	3430
XII	40	38.96 (36.14)	3.42 (2.62)	1.65 (1.92)	3395
XIII	99	36.45 (37.01)	3.15 (2.82)	3.64 (3.92)	3390

a Nujol mull. b Monohydrate.

di-heteroatomic systems) under otherwise similar experimental conditions, the dicationic complexes VI to XIII were obtained from dibenzofuran, dibenzo-thiophene, carbazole (9H-9-azafluorene), xanthene, thioxanthene, acridine, phenothiazine and phenazine respectively. Yields ranged from 33 to 99% based on the arene used. Analytical data and yields are given in Table 1. Note that in the case of the acridine and phenazine reactions, hydrogenation occurs at the 9,10 positions. This is in line with the similar behavior observed for the anthracene system [5].

NMR spectra

The site of complexation and stoichiometry of the complexes were readily determined by examination of the ¹H and ¹³C NMR spectra. The data are presented in Tables 2 and 3. For the monocationic complexes the resonances for the protons on the complexed ring are shifted upfield by approximately 1 ppm compared to those of the uncomplexed ring and the carbon chemical shifts of the complexed ring are likewise found at about 35 ppm to higher field. These shifts are typical for this mixed sandwich system [4—6] and will be dealt with in more detail in a subsequent publication. No complexation to the central ring which contains the heteroatoms is observed (this would give rise to much

TABLE 2

^{1}H NMR DATA (δ, ppm)

Complex	$\delta(C_p)$	Complexed aromatic	Uncomplexed aromatic	Other
I	4.8(s)	6.3(m); 7.4(m)	7.6—8.3(m)	—
II	4.8(s)	6.6(m); 7.6(m)	7.5—8.5(m)	—
III	5.0(s)	6.4(m)	7.4(m)	$\delta(CH_2)$ 4.3(s) ^{c}
IV	4.7(s)	6.6(m)	7.6(m)	$\delta(CH_2)$ 4.1(q) [^2J(HH) 16.7 Hz]
V	5.0(s)	6.2(m)	7.1(m)	$\delta(NH)$ 8.2(br, s)
VI	5.0(s)	6.4—7.4(m)	—	—
VII	4.9(s)	6.6(m); 7.4(m)	—	—
VIII	4.8(s)	6.3(m); 7.1(m); 7.5(m)	—	$\delta(NH)$ not observed
IX	5.1(s)	6.5(m)	—	$\delta(CH_2)$ 4.7(s)
X	5.0(s)	6.6(m)	—	$\delta(CH_2)$ 4.6(s)
XI	4.9(s)	6.2(m)	—	$\delta(CH_2)$ 4.6(s) $\delta(NH)$ 7.5(br,s)
XII	5.1(s)	6.2(m)	—	$\delta(NH)$ 7.4(br,s)
XIII	5.0(s)	5.9(m)	—	$\delta(NH)$ 8.0(br,s)

^{a} Recorded in acetone-d_6 (I—V, XIII), nitromethane-d_3 (VI—XII). Shifts in ppm relative to internal TMS.
^{b} s = singlet, q = quartet, br,s = broad singlet, m = multiplet. ^{c} Chemical shifts of both protons coincide.

TABLE 3

^{13}C NMR data ^{a} (δ, ppm)

Complex	(C_p)	Complexed aromatic	Uncomplexed aromatic	Other
I	76.5	72.7; 78.2; 82.9(2) 88.8*; 121.7*	111.7; 122.1; 124.1; 130.1 127.9*; 158.7*	—
II	77.4	78.8; 80.9; 83.4; 84.0 97.7*; 108.7*	123.0(2); 125.6; 129.7 132.2*; 140.5*	—
III	76.1	76.7; 83.7; 84.4; 85.0 88.6*; 125.4*	115.9; 124.5; 127.9; 128.3 117.7*; 149.4*	$\delta(CH_2)$ 25.8
IV	76.3	84.6; 85.1; 85.7; 86.5 100.9*; 104.0*	126.6; 127.2; 127.8; 128.0 129.3*; 133.3*	$\delta(CH_2)$ 35.0
V ^{b}	76.6	72.9; 81.7; 82.8; 84.1 112.7*; 89.5*	116.0; 124.0; 126.0; 128.1 113.0*; 137.3*	—
VI	78.1	74.5; 80.2; 84.4; 85.0 87.9*; 131.3*	—	—
VII	78.8	80.9; 82.3; 84.9; 86.2 95.6*; 110.0*	—	—
VIII	76.9	72.4; 79.4; 81.8; 84.5 86.2*; 116.4*	—	—
IX	77.5	76.2; 85.1(2); 85.7 123.3* ^{c}	—	$\delta(CH_2)$ 25.6
X	77.8	85.1; 85.9(2); 86.8 97.8*; 100.8 *	—	$\delta(CH_2)$ 34.0
XI	76.6	72.5; 82.6; 84.6; 85.0 81.8*; 100.2*	—	$\delta(CH_2)$ 27.8
XII	78.3	73.0; 82.0; 83.0; 84.4 85.0*; 107.9*	—	—
XIII	76.9	70.8; 80.7 100.6*	—	—

^{a} Recorded in CH_3NO_2. Shifts are reported relative to central solvent resonance = 60.55 ppm (external TMS [15]). Absorptions marked with asterisk are due to quaternary carbons. ^{b} Recorded in $(CD_3)_2CO$. Shifts are reported relative to central solvent resonance = 28.05 ppm (external TMS [15]). ^{c} Other quaternary signal obscured.

simpler NMR spectra). This may be easily understood since it involves loss of the resonance stabilization of both benzene nuclei. In the dicationic systems all the proton and carbon chemical shifts for the complexed rings occur at the higher field positions. A *trans*-configuration is assumed for all cases and is supported for the complexes IX to XI by the observation that the methylene bridge protons give rise to a singlet rather than an AB quartet (unless, of course, the resonances coincide). Also, purely from steric considerations, a *trans*-configuration is much more likely. The hydrogenation of acridine and phenazine is indicated by both NMR and IR evidence. A medium strong infrared absorption at ca. 3400 cm^{-1} is characteristic of ν(N—H) and broad proton resonances at 7.5 ppm (acridan) and 8.0 ppm (dihydrophanazine) are typical of the N—H proton. The CH$_2$ group in complex XI also give rise to a singlet in the ^{1}H NMR at 4.6 ppm and a ^{13}C NMR signal at 27.8 ppm, both being consistent with this assignment.

General comments

The mechanism of the hydrogenation is unclear and the complex nature of the reaction system makes a conclusive study difficult, but the driving force is presumably, as proposed for the anthracene system, the instability of a diradical species which would be required if no hydrogenation occurred [5].

The reason for the failure to obtain a monocation of either acridine or phenazine is also not immediately obvious. It is possible, however, that any such monocationic system may be unstable to the reaction or work-up conditions and it is also not as susceptible as the dication, or the anthracene system, to hydrogenation which might be expected to produce a more stable complex.

Preliminary studies on the chemistry of some of these systems indicate that they are open to modification by a variety of means. Details of these have been, or will be, published elsewhere. They include the deprotonation and alkylation at α-positions [11,12], oxidation of α-methylene groups to the ketone [13] and ring cleavage of the oxygen and sulfur heterocycles by nucleophilic reagents [14].

Experimental

All reactants were obtained commercially and used as received. Reactions were carried out with protection from moisture by CaCl$_2$ drying tubes. ^{1}H NMR spectra were recorded on Varian T-60 and Bruker WP-60 instruments. ^{13}C NMR spectra were recorded on the Bruker WP-60 at 15.08 MHz. Infrared spectra were recorded using a Beckman IR 8 instrument.

Monocations

A typical procedure is described. A mixture of ferrocene (5.5 g, 30 mmol), AlCl$_3$ (16.0 g, 120 mmol), Al powder (0.81 g, 30 mmol) and dibenzofuran (5.1 g, 30 mmol) was heated with stirring in decalin (50 ml) for 4 h at 135—145°C. After cooling to 60—70°C the reaction mixture was poured with stirring onto ice-water (500 ml). Any residual solid was washed out of the reaction flask with water and ether. After stirring for about 10 min, solid materials were filtered off and the aqueous layer separated, washed with ether (2 ×,

200 ml) and filtered into a concentrated aqueous solution of NH_4PF_6. After stirring for 30 min the crude solid product was filtered off, air-dried, dissolved in CH_2Cl_2 and residual water removed by allowing to stand over anhydrous $MgSO_4$. Filtration, concentration of the filtrate and addition of ether precipitated a yellow crystalline solid which was collected, washed with ether and dried. A yield of 6.2 g (48%) of (η^6-dibenzofuran)(η^5-cyclopentadienyl)iron hexafluorophosphate (I) was obtained.

The complexes II, III and IV were prepared by a similar procedure. V was also prepared similarly except that half the amount of $AlCl_3$ was used. The yields and analytical data are recorded in Table 1.

Dications

As an example the preparation of VI is described. Ferrocene (18.6 g, 100 mmol), $AlCl_3$ (32.0 g, 240 mmol), Al powder (0.54 g, 20 mmol) and dibenzofuran (3.35 g, 20 mmol) were heated with stirring in decalin (75 ml) at 135—155°C for 4 h. The work-up procedure was the same as described for the monocations except that the crude solid obtained initially was dissolved in nitromethane and then dried over anhydrous $MgSO_4$, filtered, concentrated and the purified solid precipitated with ether to give a yellow powder. A yield of 4.9 g (35%) of (η^6, η^6-dibenzofuran)bis(η^5-cyclopentadienyliron) bis(hexafluorophosphate) VI was obtained.

The dicationic complexes VII to XI were prepared analogously. For complexes XII and XIII the amount of $AlCl_3$ used was increased to 280 mmol but otherwise the procedure was the same. The analytical data for some of the dicationic complexes are not very good, probably resulting from contamination with the monocation. The NMR spectra indicate, however, that the purity is >95% in all cases.

Acknowledgement

References

1 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Dokl. Akad. Nauk SSSR, 149 (1963) 615.
2 R.G. Sutherland, in D. Seyferth et al. (Eds.), Journal of Organometallic Chemistry Library 3. Elsevier Scientific Publ. Co, Amsterdam, 1977, p. 311.
3 C.C. Lee, R.G. Sutherland and B.J. Thomson, J. Chem. Soc. Chem. Commun., (1972) 907.
4 W.H. Morrison, E.Y. Ho and D.N. Hendrickson, J. Amer. Chem. Soc., 96 (1974) 3603.
5 R.G. Sutherland, S.C. Chen, J. Pannekoek and C.C. Lee, J. Organometal. Chem., 101 (1975) 221.
6 R.G. Sutherland, W.J. Pannekoek and C.C. Lee, J. Organometal. Chem., 129 (1977) C1.
7 J.F. Helling and W.A. Hendrickson, J. Organometal. Chem., 141 (1977) 99.
8 K.K. Joshi, P.L. Pauson, A.R. Quazi and W.H. Stubbs, J. Organometal. Chem., 1 (1964) 471.
9 P. Bachmann and H. Singer, Z. Naturforsch. B, 31 (1976) 525.
10 K.H. Pannell, B.L. Kalsotra and C. Parkanyi, J. Heterocyclic Chem., 15 (1978) 1057.
11 C.C. Lee, B.R. Steele, K.J. Demchuk and R.G. Sutherland, Can. J. Chem., 57 (1979) 946.
12 R.G. Sutherland, B.R. Steele, K.J. Demchuk and C.C. Lee, J. Organometal. Chem., 181 (1979) 411.
13 Work of U.S. Gill, to be published.
14 Work of B.R. Steele, to be published.
15 E. Breitmaier, G. Jung, W. Voelter and L. Pohl, Tetrahedron, 29 (1973) 2485.