Journal of Organometallic Chemistry, 142 (1977) 89—93
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SYNTHESIS AND STRUCTURE OF THE 1,1'-TRIMETHYLENEBENZENE-CYCLOPENTADIENYLIRON CATION

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(Received June 28th, 1977)

Summary

1,1'-Bis(3-phenylpropyl)ferrocene reacts with $AlCl_3/Al$ in heptane to yield 1,1'-trimethylenebenzenecyclopentadienyliron hexafluorophosphate (I). The structure of complex I was established by X-ray analysis.

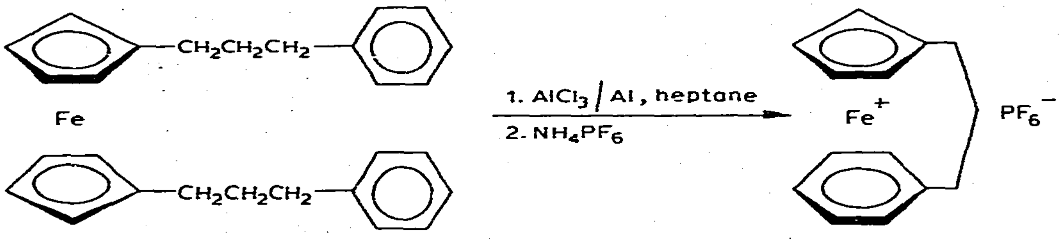
Results and discussion

Continuing our previous investigations in the field of bridged metallocenes [1—4], we have carried out the synthesis of the benzenecyclopentadienyliron cation [5,6], in which benzene and cyclopentadienyl rings are linked by a trimethylene bridge (complex I).

It was recently reported [7] that one ligand of 1,1'-bis(2-phenylethyl)ferrocene can be replaced by a phenyl ring of the other molecule by heating in heptane in the presence of $AlCl_3/Al$, the following cation being obtained: $[C_6H_5(CH_2)_2C_5H_4Fe^+C_6H_5(CH_2)_2C_5H_4FeC_5H_4(CH_2)_2C_6H_5]$. Products containing intramolecular bridges were not isolated.

The bridged compound appears to be unstable in this case because of the ring-tilt distortion which can be induced by the too short CH_2CH_2 bridge. Such a distortion was found in the molecule of [2]ferrocenophane [8]. One could expect that a bridge expansion to $CH_2CH_2CH_2$ would relax the molecular strain and the preparation of the bridged complex would became possible. In fact we found that 1,1'-bis(3-phenylpropyl)ferrocene when treated with $AlCl_3$ in the presence of Al in heptane produced the 1,1'-trimethylenebenzenecyclopentadienyliron cation, which was isolated in the form of the PF_6^- salt (yield ca. 10%).

The salt I is a rather stable yellow crystalline substance, which is soluble in CH_2Cl_2, acetone, and 1,2-dichloroethane. In the PMR spectrum of this compound (in acetone-d_6) the coordinated benzene ring appears as a multiplet cen-



(I)

tered at δ 6.40 ppm, and the cyclopentadienyl ring exhibits a slightly broadened singlet at δ 5.15 ppm. There are two multiplets in the region of CH_2 proton absorption (2.20–2.40, 2H; 2.40–2.65, 4H). The high field multiplet appears to be due to the central CH_2 group of the bridge. The IR spectrum of complex I shows a strong absorption band at 825 cm^{-1} (PF_6^-).

In order to confirm the composition of complex I and to compare its structure with that of the [3]ferrocenophane system we carried out an X-ray analysis *.

Atomic coordinates, bond distances and angles are given in Tables 1, 2 and 3 respectively.

The crystal structure is composed of $[C_5H_4(CH_2)_3C_6H_5]Fe^+$ cations and PF_6^- anions. The latter possesses a C_i symmetry and the former has a C_2 symmetry with the Fe and C(1) atoms lying on the rotation axis (Fig. 1).

Thus the cations are disordered, their benzene and cyclopentadienyl rings being statistically equivalent. This may occur because the benzene and cyclopentadienyl rings have rather close spatial arrangements and their difference does

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) OF 1,1'-TRIMETHYLENEBENZENECYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE

Atom	x	y	z
Fe	0	1770(30)	1/4
P	1/4	1/4	0
F(1)	2280(80)	3420(90)	−1410(120)
F(2)	2470(90)	3510(80)	1160(130)
F(3)	1320(70)	2320(100)	−780(140)
C(1)	0	4790	1/4
C(2)	890	4330	3260
C(3)	1060	2990	3940
C(4)	690	2550	4880
C(5)	680	1390	5110
C(6)	1110	740	4270
C(7)	1480	1160	3340
C(8)	1430	2330	3270
C(9)	−760	4070	590
C(10)	−950	2910	760
C(11)	−1480	2340	1820
C(12)	−1430	1070	1390
C(13)	−950	750	430
C(14)	−790	1860	−20

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* The X-ray analysis of I was carried out by N.G. Bokii, A.S. Batsanov and Yu.T. Struchkov.

TABLE 2

BOND LENGTHS d (Å) IN 1,1'-TRIMETHYLENEBENZENECYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE

Atom	d	Atom	d
Fe—C(3)	2.06	C(10)—C(11)	1.70
Fe—C(4)	2.14	C(11)—C(12)	1.53
Fe—C(5)	2.17	C(12)—C(13)	1.48
Fe—C(6)	2.05	C(13)—C(14)	1.41
Fe—C(7)	2.11	C(10)—C(14)	1.50
Fe—C(8)	2.04		
Fe—C(10)	2.03	C(3)—C(10)	3.03
Fe—C(11)	2.13	C(3)—C(11)	3.37
Fe—C(12)	2.06	C(4)—C(10)	3.42
Fe—C(13)	2.11	C(4)—C(11)	3.13
Fe—C(14)	2.05	C(5)—C(11)	3.38
		C(5)—C(12)	3.38
C(1)—C(2)	1.29	C(6)—C(12)	3.47
C(2)—C(3)	1.64	C(6)—C(13)	3.40
C(1)—C(9)	1.78	C(7)—C(13)	3.36
C(9)—C(10)	1.39	C(7)—C(14)	3.41
		C(8)—C(14)	3.29
C(3)—C(4)	1.37	C(8)—C(10)	3.26
C(4)—C(5)	1.35		
C(5)—C(6)	1.47	P—F(1)	1.60(1)
C(6)—C(7)	1.34	P—F(2)	1.61(1)
C(7)—C(8)	1.36	P—F(3)	1.58(1)
C(3)—C(8)	1.28		

not affect the crystal packing.

Such disorder was not observed in the crystal structure of (η^5-cyclopentadienyl)(η^6-fluorenyl)iron [9], where iron is bonded to the benzene ring of the bulky fluorenyl ligand.

TABLE 3

BOND ANGLES (°) IN 1,1'-TRIMETHYLENEBENZENECYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE

Angle		Angle	
C(2)—C(1)—C(9)	110	C(9)—C(10)—C(11)	130
C(1)—C(2)—C(3)	121	C(9)—C(10)—C(14)	128
C(1)—C(9)—C(10)	113	C(11)—C(10)—C(14)	103
		C(10)—C(11)—C(12)	97
C(2)—C(3)—C(4)	124	C(11)—C(12)—C(13)	121
C(2)—C(3)—C(8)	113	C(12)—C(13)—C(14)	100
C(4)—C(3)—C(8)	122	C(10)—C(14)—C(13)	119
C(3)—C(4)—C(5)	120		
C(4)—C(5)—C(6)	112	F(1)—P—F(2)	90.8(6)
C(5)—C(6)—C(7)	128	F(1)—P—F(3)	90.9(6)
C(6)—C(7)—C(8)	111	F(2)—P—F(3)	90.5(6)
C(3)—C(8)—C(7)	127		

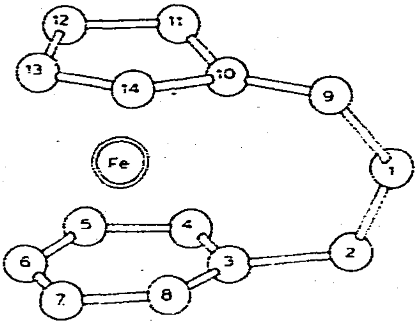

Fig. 1. The structure of the $[C_5H_4(CH_2)_3C_6H_5]Fe^+$ cation.

Unfortunately, the non-bridged benzenecyclopentadienyliron cation (which is more appropriate for comparison with the one discussed here) has not yet been studied crystallographically.

The trimethylene bridge draws cyclic ligands together so that the benzene and cyclopentadienyl rings are inclined to each other at an angle of 7°, which is similar to the ring-tilt distortion in the molecule of [3]ferrocenophanone-1 [10]. The iron atom is located at 1.59 Å from the benzene and at 1.62 Å from the cyclopentadienyl plane. The Fe ...C distances for benzene and cyclopentadienyl carbon atoms vary in the range of 2.04—2.17 Å and 2.03—2.13 Å, respectively. These distances for the two rings are almost identical confirming once more the similarity of their spatial arrangements.

The geometry of the anion is almost regular octahedral, the mean P—F bond distance of 1.60(1) Å being in good agreement with previously reported values of 1.58 Å [11] and 1.585 Å [12].

Analogous to I we prepared the bridged complex II using 1,1'-bis(1-methyl-3-phenylpropyl)ferrocene as starting compound (yield 8%).

Experimental

1,1'-Trimethylenebenzenecyclopentadienyliron hexafluorophosphate (I)

A mixture of 2.11 g (6.55 mmol) of 1,1'-bis(3-phenylpropyl)ferrocene, 0.18 g (6.65 mmol) of Al dust, 1.75 g (13.1 mmol) of $AlCl_3$ and 200 ml of heptane was refluxed for 2 h. After treating the reaction mixture with water, a saturated solution of NH_4PF_6 was added to the aqueous phase. The precipitated salt was extracted with CH_2Cl_2, purified by TLC on alumina (eluent acetone) and recrystallized from CH_2Cl_2 hexane. 0.25 g (10%) of compound I was prepared, decomposing at temperatures above 200°C. Found: C, 42.83; H, 4.31. $C_{14}H_{15}FePF_6$ calcd.: C, 43.78; H, 3.94%.

1,1'-(α-Methyltrimethylene)benzenecyclopentadienyliron hexafluorophosphate (II).

This compound was prepared analogously from 6.9 g of 1,1'-bis(1-methyl-3-phenylpropyl)ferrocene, 0.4 g of Al dust and 4.1 g of $AlCl_3$. 0.48 g (8%) of compound II was obtained, dec. >200°C. Found: C, 45.36; H, 4.32%. $C_{15}H$ $C_{15}H_{17}FePF_6$ calcd.: C, 45.53, H, 4.30%.

The X-ray experiment was carried out with a Syntex P2_1 four-circle computer-controlled diffractometer using the graphite-monocromated Cu-K_α radiation.

Crystal data: $C_{14}H_{15}PF_6Fe$, mol. wt. 384.1, monoclinic, a 15.325(5) Å, b 11,508(3) Å, c 9.413(3) Å, β 120.33(2)°, V 1433(1) Å^3, D_m 1.76 g/cm^3, D_c 1.78 g/cm^3, $Z = 4$, space group $C2/c$.

Of the total 867 reflections measured by the $\theta - 2\theta$ scan technique for $2\theta_{max}$ 115°, those 753 having $F^2 \geqslant 2\ \sigma(F^2)$, were considered as observed and used in the analysis.

The structure was solved by the heavy-atom technique. Least-squares refinement of the total structure was unsuccessful because of its disorder. Thus an anisotropic refinement was restricted to iron, phosphorus and fluorine atoms, while carbon atoms were located by difference-Fourier synthesis.

From several options of this synthesis (with different atomic groups of the cation excluded), one was selected with the best bond distances and angles and the smallest $R = 0.105$ (assuming B 3.00 Å^2 for all carbon atoms). All computations were carried out with a "Nova-1200" computer using XTL programmes.

Acknowledgement

The authors wish to thank Dr. M.Yu. Antipin for help with the X-ray measurements and solving the structure.

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