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sym-POLYMETHYLFERRICINIUM HEXAFLUOROPHOSPHATES

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Summary

A series of salts of the general formula $[(CH_3)_nC_5H_{5-n}]_2FePF_6$ with $n = 0$—5 has been synthesized. Elemental analysis of the compounds was carried out and their IR spectra recorded

Compared to neutral derivatives of ferrocene, the salts of substituted ferricinium cations have attracted little attention. Studying these salts can, however, help to solve a number of problems, like the nature of the metal—ligand bond, the mechanisms of reactions involving ferrocene and ferricinium-type systems, distribution of electron density in such systems, etc. With this in mind, we have synthesized a series of *sym*-polymethylferricinium hexafluorophosphates of general formula $[(CH_3)_nC_5H_{5-n}]_2FePF_6$ with $n = 0$—5, the salts with $n = 2$—4 not having been reported before.

Ferricinium salts are usually obtained by the action of various oxidants on corresponding ferrocenes (see for instance [1—4]). In order to find the best laboratory techniques which provide for simplicity of the experiment, high yields, and purity of the resulting alkylferricinium salts we have studied the interaction of ferrocene homologues of the $[(CH_3)_nC_5H_{5-n}]_2Fe$ type with bromine and with sulphuric acid. The reaction with bromine was carried out in hexane or heptane at —20 to —40°C for 1 h, the reaction with concentrated sulphuric acid at 20°C for 10—12 h. In both cases the yield of ferricinium salts increases with the number of methyl groups in the molecule. However, when bromine is used the yield is 25—50% of the calculated value, whereas H_2SO_4 gives high yields (80—95%) of practically pure salt. Only ferricinium and 1,1'-dimethylferricinium were found to contain insignificant amounts of decomposition products, and had thus to be filtered after dilution with water (see experimental section). It is noteworthy that spontaneous oxidation of polymethylferrocenes dissolved in organic media in air accelerates when the number of CH_3 groups in the molecule increases. In contrast, oxidation in concentrated sulphuric acid decelerates.

TABLE 1

sym-POLYMETHYLFERRICINIUM HEXAFLUOROPHOSPHATES

Compound	Initial components		Yield (%) of $(Me_nCp)_2FePF_6$ in the reaction with:		Analysis (%)		Decomposition temperature (°C)
	$(Me_nCp)_2Fe$ (mol)	H_2SO_4 (ml)	H_2SO_4	Br_2	Found	Calculated	
$(Cp_2Fe)PF_6$ [a]	0.027	5	78	25			160
$(MeCp)_2FePF_6$ [a]	0.025	3	83	20			183—184
$(1,3\text{-}Me_2Cp)_2PF_6$	0.020	3	83	20			193—194
$(1,2,4\text{-}Me_3Cp)_2FePF_6$	0.014	3	93	40	C, 45.80 H, 5.25 Fe, 13.50	C, 46.27 H, 5.30 Fe, 13.50	214—216
$(Me_4Cp)_2FePF_6$	0.018	6	95	40	C, 48.20 H, 5.90	C, 48.75 H, 5.87	214—216
$(Me_5Cp)_2FePF_6$ [a]	0.018			45	C, 49.90 H, 6.12	C, 50.95 H, 6.37	226—227

[a] Obtained in [4,5,9].

sym-Polymethylferricinium hexafluorophosphates are green crystals. As the number of methyl groups increases, the colour varies from dark green to light green. The salts obtained display excellent solubility in acetonitrile, acetone, nitromethane and dimethylformamide and modest solubility in methylene chloride and ethanol. They are virtually insoluble in ethyl ether, chloroform, aliphatic hydrocarbons, and water. Only ferricinium- and 1,1′-dimethylferricinium hexafluorophosphate are slightly water-soluble. On heating in a sealed capillary, hexafluorophosphates decompose without melting in the 160—230°C interval. As

TABLE 2

IR ABSORPTION SPECTRA OF *sym*-POLYMETHYLFERRICINIUM HEXAFLUOROPHOSPHATES $[(CH_3)_nC_5H_{5-n}]_2FePF_6$ (cm^{-1})

$n = 0$ [a]	$n = 1$ [a]	$n = 2$	$n = 3$	$n = 4$	$n = 5$ [a]
1010m			996w	980w	
	1032s	1027s	1030s	1028s	1025s
	1045w (sh)	1040s			
1057w	1058w				1070w
1110vw				1110vw	
	1240w				
	1370m		1372s	1365m	1380s (sh)
	1388m	1385s	1389s	1388s	1388s
1419s			1420w	1420w	1422w
	1440m (sh)	1433s	1450m	1450s (sh)	1450w (sh)
	1460s	1458m	1470m (sh)	1465s	
	1484s	1490s	1490m	1485s	1480m
	2850w	2890vw	2860vw	2867vw	2865w
	2915w	2920vw	2925w	2924w	2920w
	2930w (sh)		2965w	2970w	2967w
	2940w	2960vw	2983vw	2980w	2983w
3105s	3120m	3105m	3084m	3095w	

[a] Cf. [9].

seen from Table I, the decomposition temperature rises with the number of methyl groups in the molecule. The oxidative stability of *sym*-polymethylferricinium hexafluorophosphates in their solution increases in the same manner.

The IR spectra of the ferricinium salts in the 600—3600 cm^{-1} region were recorded with the UR-20 spectrometer in KBr discs. The results are given in Table 2. The PF_6^- anion possesses adsorption bands at 560 and 833 cm^{-1} which are not shown in the table. Its last band is very intense and wide, covering the bands of cations in the 700—900 cm^{-1} region.

Compared to analogous *sym*-polymethylferrocenes [6—8] the salts display a marked decrease in band intensity for C—H stretching modes of methyl groups. In contrast, the intensities and the frequencies of the corresponding bonds for the ring C—H stretching modes are higher.

Experimental

Preparation of 1,2,4,1',2',4'-hexamethylferricinium hexafluorophosphate by the action of concentrated sulphuric acid

3 ml (0.054 mol) of concentrated H_2SO_4 was added to 0.4 g (0.018 mol) of 1,2,4,1',2',4'-hexamethylferrocene. The solution was allowed to stand overnight, then diluted with water to 35—40 ml and treated with concentrated $NaPF_6$ solution. The solids were washed with ice water (4 × 10 ml) and dried. The yield of hexamethylferricinium hexafluorophosphate was 0.57 g (93% of the calculated value).

The hexafluorophosphates of the other *sym*-polymethylferriciniums were obtained in the same manner.

Preparation of sym-polymethylferricinium hexafluorophosphates by the action of bromine

A portion of *sym*-polymethylferrocene (0.018—0.027 mol) was dissolved in 30—40 ml heptane (or hexane). 25 ml of a hexane solution of a small excess of bromine (0.002—0.004 mol) was added dropwise to the initial solution for 1 h at —20 to —40° C. The green precipitate was filtered, washed four times with hexane, dried and dissolved in the minimum amount of water. The corresponding hexafluorophosphate was then precipitated by the action of $NaPF_6$ solution at 0°C. The product was washed four times with water and dried.

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