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COMPLEXATION OF α-FERROCENYLMETHYLCARBENIUM TETRAFLUOBORATES BY ETHERS; AN NMR STUDY

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Summary

The tetrafluoborates of the primary, secondary, and tertiary ferrocenylmethyl carbenium ions have been prepared from the corresponding carbinols in ethyl ether, tetrahydrofuran and t-butyl methyl ether by adding HBF_4. The NMR spectra of these salts, which dissolve in $CDCl_3$, are characterized by the presence of very strong signals attributed to the ether used in the preparation, the solubility depending upon the structure of the cation and that of the ether. The NMR data suggest that α-ferrocenylcarbenium ions undergo two distinct types of solvation with ether-like donor molecules: one involves a much stronger interaction than the other.

Introduction

Quantitative evidence of the remarkable stability of the α-ferrocenylmethyl carbenium ions, $Fc{-}\overset{+}{C}R_1R_2$, has been obtained from solvolysis experiments [1] and determination of the pK_{R^+}'s from the alcohol-ion equilibria [2]. Direct ^1H [3] and ^{13}C [4] NMR spectroscopic examination of these ions produced from alcohols in CF_3COOH or H_2SO_4 provided information about their structure and the distribution of the positive charge. The solutions of the ions are moderately stable for secondary and tertiary ions but rather unstable for the primary cation, which is more conveniently generated from the ether $FcCH_2{-}O{-}CH_2Fc$ [4a].

Despite the current interest in this field, isolation of salts of the ferrocenylalkylium ions as solids and study of their solutions have received little attention. Tertiary diphenyl ($R_1=R_2=C_6H_5$) tetrafluoborate [5] and tertiary dialkyl

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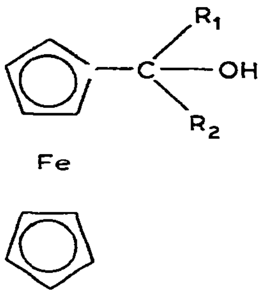
(R_1=R_2=alkyl) tetraphenylborates [6] have been isolated in form of light microcrystalline powders which are fairly stable on storage. On the other hand, secondary phenyl and alkyl tetrafluoborates have been obtained as dark crystalline precipitates but their immediate use is recommended as they decompose on exposure to air [5]. Decomposition also occurs in solution and the ^{1}H NMR spectrum of the fluoborate of the ferrocenyl(phenyl)methyl carbenium ion in acetone-d_6 could not be studied in detail for this reason [3b]. To our knowledge, salts of the parent cation, $Fc—\overset{+}{C}H_2X^-$, have not previously been isolated.

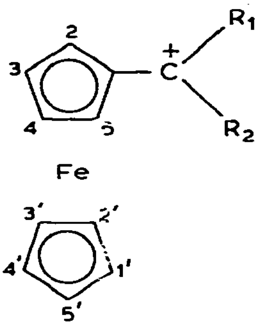
Recent evidence has shown that strong cation—oxygen interactions, responsible for the formation of stable complexes between alkali metal ions and cyclic ethers [7], can also occur between anilinium [8], arenediazonium [9] and benzoyl cations [9] and macrocyclic polyethers. This molecular complexation enables the salts to be dissolved in weakly polar media ($CHCl_3$) and causes changes in the ^{1}H NMR chemical shifts of the crown ethers. Moreover, the complexes are markedly more thermally stable than the uncomplexed salts [10]. We thus decided to look for the existence of such an interaction between ferrocenylmethyl carbenium ions and alkyl ethers with the aim of obtaining stable solutions of the salts. This paper deals with the results obtained on changing the structure of the cation as well as that of the ether.

Results

The tetrafluoborates of the ions IIa—f were prepared from solutions of the corresponding carbinols, Ia—f in Et_2O, THF or MeOt-Bu, by adding fluoboric acid in ethyl ether in the presence of small amounts of acetic anhydride [5]. The precipitates were filtered off under nitrogen, washed with the appropriate ether, and at least twice with cold pentane. Finally, they were carefully dried in a stream of dry nitrogen.



(I)



(II)

(Ia,IIa) $R_1 = R_2 = H$
(Ib,IIb) $R_1 = H, R_2 = CH_3$
(Ic,IIc) $R_1 = H, R_2 = CH(CH_3)_2$
(Id,IId) $R_1 = H, R_2 = C_6H_5$
(Ie,IIe) $R_1 = R_2 = CH_3$
(If,IIf) $R_1 = R_2 = C_6H_5$

The salt of IIa precipitates as an orange powder at —50° C (at room temperature or at —20° C a dark red oil was formed; this did not crystallize on cooling and decomposed rapidly giving a black residue). The orange powder dissolves in anhydrous acetonitrile, acetone and methylene chloride to give red solutions which are stable if kept at —30° C or below under nitrogen. Treatment of these solutions with nucleophiles (water, diethylamine and cyanide ion) gave the expected derivatives in high yields.

The fluoborates of IIb and IIc were obtained as dark orange powders at —30° C, and those of IId and IIf at 0° C, as dark, crystalline precipitates. The chemical and physical characteristics of the secondary and tertiary salts agree with those previously described [5,6]. The NMR spectrum of the primary cation is in agreement with the expected structure (see below).

Solubility in chloroform and ^1H NMR spectra

It is noteworthy that only some of the fluoborates prepared by this procedure are markedly soluble in anhydrous $CDCl_3$; the solubility depends upon the structure of the cation and of the ether used for its precipitation.

The tetrafluoroborate of IIa is very soluble (0.6—0.8 M) whatever ether it is precipitated from. The salts of IIb and IIc are also very soluble in $CDCl_3$ (except for IIb as precipitated from THF, which is less soluble); the salts of IId and IIe are much less soluble when isolated from Et_2O, and almost insoluble from THF; finally, the salt of IIf is almost insoluble even when precipitated from Et_2O.

It is striking that in the weakly polar $CDCl_3$ the tertiary ferrocenylmethyl salts are much less soluble than the primary and secondary alkyl fluoroborates; this is contrary to what would be expected on the basis of structural and charge dispersion considerations. These apparent anomalies will be explained below.

Solutions of primary and secondary cations show appreciable thermal stability, which allows their detailed investigation by the NMR technique. At —30° C IIaBF_4 is stable for hours, and IIb, c for days. At room temperature concentrated solutions of these ions are stable for sufficient time (10—20 min) to allow NMR spectra to be recorded with good accuracy. The less concentrated solutions of IId—f are fairly stable at room temperature.

The ^1H NMR spectrum of a ca. 0.6 M solution of IIaBF_4 precipitated from Et_2O in $CDCl_3$ at —30° C is shown in Fig. 1. The chemical shifts of the signals

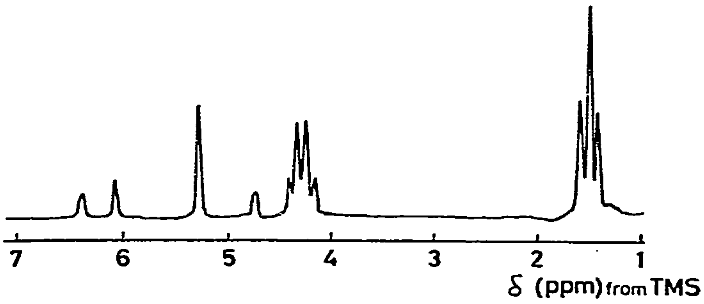


Fig. 1. ^1H NMR spectrum of a ca. 0.6 M solution of $FcCH_2^+BF_4^-$, precipitated from Et_2O, in $CDCl_3$ at —30° C.

TABLE 1

^{1}H-NMR CHEMICAL SHIFTS OF IIa—f FLUOBORATES [a] IN $CDCl_3$ AT 243°K

Cation	δ (ppm) [b]						
	H_{exo}	H_2	H_5	H_3	H_4	H'_{1}–$'_{5}$	Other protons
IIa	6.00	4.72	4.72	6.34	6.34	5.28	—
IIb	7.39	5.27	5.82	6.59	6.42	5.27	CH_2, 2.24
IIc	7.22	5.07	4.52	6.43	6.33	5.22	CH_3, 1.51 and 1.31; CH, 2.67
IId	8.22	5.44	4.89	6.52	6.28	4.89	C_6H_5, 7.11—6.62
IIe	—	5.11	5.11	6.37	6.37	4.92	CH_3, 2.29
IIf	—	5.26 [c]	5.26 [c]	6.74 [c]	6.74 [c]	4.93 [c]	C_6H_5, 7.8—7.3 [c]

[a] Obtained from Et_2O.

[b] Me_4Si as internal reference.

[c] These signals were assigned to the various protons by comparison with those of IId and from integral ratios.

attributed to the protons of IIa cation are listed in Table 1; the assignment was made on the basis of the chemical shifts, peak areas and spin-spin decoupling experiments. Moreover, comparison with the ^{1}H NMR spectra given by solutions of the alcohol Ia in CF_3COOH [2c] and in aqueous H_2SO_4 [3b] reveals only small, if any, change in the chemical shifts, and these can be attributed to solvent effects. The most important feature of the spectrum is the presence of two intense signals at δ 4.26 (quartet) and δ 1.49 (triplet) which, on the basis of the spin multiplicity and integral ratio, were attributed to the methylene and methyl protons of diethyl ether, respectively. At the same concentration and temperature, Et_2O in $CDCl_3$ resonates at δ 3.47 and δ 1.21. Thus, both the methylene and methyl protons of the ether in the solution of the salt are shifted considerably downfield. The molar ratio ether : salt, based on NMR integration, is ca. 4:1.

Useful information is obtained when the initial concentration is progressively diminished to 1% of its initial value by adding pure $CDCl_3$. The proton chemical shifts of the cation do not change; but in contrast, the signal at δ 4.26 splits into two signals: a more intense quartet which moves gradually upfield toward the chemical shift value of the methylene protons of the ether in the absence of salt, and a second quartet centered at δ 4.29 which does not shift on dilution and gives on integration a 1 : 1 molar ratio with the signals of the cation. We assign these two signals to two types of complexed ether, "mobile" and "fixed", respectively. Analogous behaviour was observed for the triplet of the methyl protons; however, the splitting of the two triplets observed on dilution was too small and a satisfactory separation could not be obtained. Dilution experiments carried out in $CDCl_3$ solutions of Et_2O under the same conditions indicate an overall shift for methylene and methyl protons of ca. 1 Hz.

When the same salt is precipitated from methyl-t-butyl ether, the ethereal peaks are present in the $CDCl_3$ solution with an ether : salt molar ratio of ca. 6 : 1. The methyl and t-butyl protons, which in the absence of the salt resonate at δ 3.32 and 1.22, respectively, are shifted to δ 3.76 and 1.56. On dilution of the solution the singlet of the methyl protons splits into two singlets, one "fixed" at δ 3.77 which does not shift with further dilution and gives on inte-

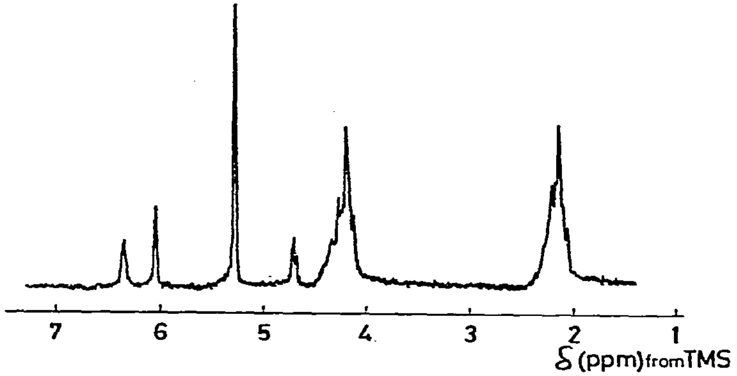


Fig. 2a. ^{1}H NMR spectrum of a ca. 0.7 M solution of $FcCH_2^+BF_4^-$, precipitated from THF, in $CDCl_3$ at −30°C.

gration a 1 : 1 molar ratio with the salt, and the other "mobile" towards the chemical shift of the ether in "pure" $CDCl_3$. No splitting of the t-butyl proton resonance is observed on dilution, the signal gradually moving upfield.

The most convincing results were obtained with THF as a solvent. As shown in Fig. 2a, the multiplet of the α-CH_2 protons of the ether (δ 3.77 in pure $CDCl_3$) appears in the concentrated solution at δ 4.20 associated with a partially overlapped smaller multiplet centered at δ 4.37; the ether : salt ratio is ca. 4 : 1. When the solution is diluted from one-half to one-fifth of the initial value, the more intense multiplet shifts upfield, while the peak centered at δ 4.37 does not shift and increases in height (see Figure 2 b). This signal gives on integration a 1 : 1 molar ratio with the cation. Similar, though less marked, changes are shown by the β-CH_2 protons of THF (δ 1.88 in pure $CDCl_3$): they exhibit a "fixed" absorbance at δ 2.24 and a "mobile" one which shifts on dilution towards the 1.88 limit.

The tetrafluoroborates of IIb and IIc, which are also very soluble in $CDCl_3$ (except for the salt of IIb precipitated from THF), exhibit NMR characteristics

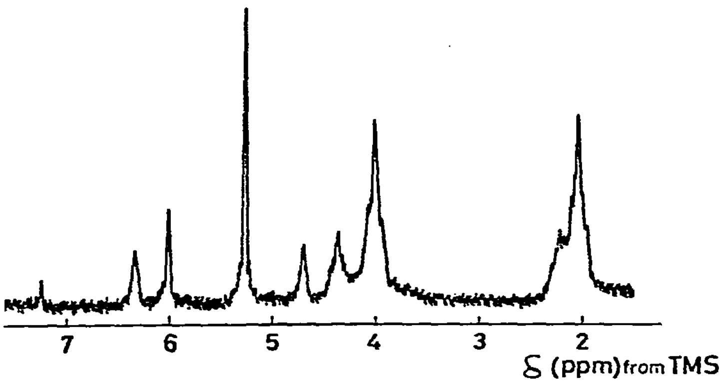


Fig. 2b. ^{1}H NMR spectrum of a ca. 0.15 M solution of $FcCH_2^+BF_4^-$, precipitated from THF, in $CDCl_3$ at −30°C.

TABLE 2

^{1}H NMR CHEMICAL SHIFTS (δ ppm)[a] OF THE PROTONS α TO THE ETHEREAL OXYGEN FOR THE "FIXED"[b] Et_2O, THF AND MeOt-Bu IN $CDCl_3$ AT 243°K IN PRESENCE OF IIa—f FLUOBORATES

Cation	Et_2O		THF		MeOt-Bu	
	CH_2	$\Delta\delta$[c]	α-CH_2	$\Delta\delta$[c]	CH_3	$\Delta\delta$[c]
none	3.47	—	3.77	—	3.23	—
IIa	4.29	0.82	4.37	0.60	3.77	0.54
IIb	4.30	0.83	4.36[d]	0.59[d]	3.70	0.47
IIc	4.24	0.77	4.33	0.56	3.70	0.47

[a] Me_4Si as internal reference.
[b] The "fixed" ethers have been defined in the text.
[c] $\Delta\delta$ is the variation of the chemical shift induced by the presence of the salt.
[d] In $CDCl_3$ containing 30% of CD_2Cl_2 (see text).

very similar to those shown by the primary cation, IIa. The chemical shifts of the organometallic residue are listed in Table 1. Their values are very similar to those obtained from the alcohols in strong acidic media [2c,3b,11]. Even in the solutions of these salts the absorptions due to the ether used in their precipitation are present. The ether : salt molar ratio based on NMR ranges between ca. 3 : 1 and 8 : 1, except for $IIbBF_4$, precipitated from THF, for which the ratio is ca. 1.2 : 1. On dilution, the ether signals split into a "fixed" signal whose chemical shift does not change appreciably on varying the structure of the alkyl group of the secondary cation from methyl to isopropyl and a "mobile" one.

The chemical shifts associated with the α-ethereal protons of the "fixed" ethers in $CDCl_3$ in presence of IIa—c cations are listed in Table 2.

In $CDCl_3$, the tetrafluoroborate of IId is much less soluble than the salts considered above, expecially when precipitated from THF. The NMR spectra were then recorded in a 1 : 1 v/v $CDCl_3$-CD_2Cl_2 mixture. The spectrum is identical to that reported for the same salt in acetone-d_6 [3b], and no ethereal signals were detected. In contrast, if after precipitation from Et_2O the salt is not washed with pentane, but only with ether and subsequently carefully dried with nitrogen, the precipitate is soluble in chloroform and the NMR spectrum indicates the presence of ca. six molecules of Et_2O per molecule of cation; the $\Delta\delta$'s are 0.22 and 0.07 ppm downfield for the methylene and methyl proton resonances, respectively. The NMR spectra of the tetrafluoroborates of the tertiary cations IIe and IIf, which are very poorly soluble in $CDCl_3$, were recorded with pulsed-FT technique and do not indicate the presence of any ethereal signal. Table 1 gives the NMR data for the protons for these cations.

Lastly, the behaviour shown by the fluoroborates of IIa and IIb when prepared as described by Cais [15] is significant. In this procedure, the carbinols are dissolved in propionic anhydride, aqueous HBF_4 is added, and the salt precipitated with cold ethyl ether. The precipitates after washing with pentane are insoluble in $CDCl_3$ ($IIaBF_4$ in CD_2Cl_2 also) and their ^{1}H NMR spectra in acetone-d_6 or CD_2Cl_2 exhibit only the signals of the cations and not those of the ether used as a precipitant.

Discussion

The results clearly show that the solubility of ferrocenylmethyl fluoroborates in the weakly polar $CDCl_3$ is strictly related to the presence of molecules of ether. In fact, solutions of the very soluble cations IIa—c show a molar ether : salt ratio varying from 3 : 1 to 8 : 1; in contrast, the NMR spectra of the very poorly soluble salts do not shows ether signals, and neither do the salts obtained by the Cais' procedure. An intermediate case is that of IIbBF_4 when precipitated from THF: its relatively low solubility in $CDCl_3$ can be explained by the low ether : salt molar ratio 1.2 : 1.

When the salts are precipitated with Et_2O from a non-ethereal medium, they appear completely insoluble in $CDCl_3$. The NMR spectra in CD_2Cl_2 do not show the presence of ether molecules, and thus, it appears that complexation, when present, occurs at the moment of forming the cations.

The most interesting feature of the NMR spectra of the soluble salts is the variation of the values of the chemical shifts of the ethereal protons compared to the values shown by the same ethers in "pure" $CDCl_3$: they are noticeably shifted downfield, and the extent of the shift is larger for the nuclei α than for those β to the oxygen.

In dilute solutions of IIaBF_4, the "fixed" and "mobile" ethereal signals from the α protons of the ethers indicate the existence of two different interactions of the ether with the cation. The signal of the "fixed" ether, which on integration gives a 1 : 1 molar ratio with the salt, can be attributed to one ether molecule coordinated with an electron deficient center of the ferrocenylmethyl cation. This complexation is expected to cause a large downfield shift ($\Delta\delta$) of the ethereal protons, as shown by the $\Delta\delta$ value found, for example, for the $Et_2O \cdot BF_3$ adduct in $CDCl_3$ ($\Delta\delta$ 0.72 ppm [12]) a value which is very close to those found for the Et_2O adducts of IIa—c cations ($\Delta\delta$ 0.77 + 0.83 ppm). Thus, the cation-ether complex is a Lewis-type adduct, the basic oxygen atom of the ether coordinating at an acidic site of the cation probably the exocyclic sp^2-carbon. However, it should be remembered that the positive charge in the ferrocenylmethyl cations is largely spread over the whole organometallic residue [13] so one cannot exclude the possibility that the coordination takes place at another electrophilic center, specifically the iron atom. Comparison can be made with the values of $\Delta\delta$ observed for the $Et_3O^+BF_4^-$-Et_2O system ($\Delta\delta$ 1.32 ppm in $CDCl_3$ [12]) and the recent values taken from a study by Scorrano [14] on the protonation equilibria of ethers in aqueous H_2SO_4: for $Et_2\overset{+}{O}H$-Et_2O system $\Delta\delta$ 1.02, and for $THFH^+$-THF $\Delta\delta$ 0.50 ppm. (For ethyl ether the $\Delta\delta$ value seems higher than that observed in this work.)

As far as the thermal stability of $CDCl_3$ solutions is concerned, it seems strictly related to the presence of the complexing agent, in analogy to the behaviour observed for arenediazonium salts, which are stabilized by complexing to macrocyclic polyethers [10]. In fact, the solutions of the salts obtained by the Cais' procedure exibit a much lower thermal stability than the corresponding solutions of "complexed" IIa, bBF_4. In addition, qualitative observations, based on NMR data, suggest that the thermal stability of the IIaBF_4 adducts decreases in the order $Et_2O > THF >> MeOt$-Bu, showing that the stability parallels the basicity of the ethers, whose pK_{BH^+} values are —2.39 and

—1.34 for Et_2O and THF, respectively. (For MeOt-Bu the pK_{BH^+} is not available because of the rapid decomposition in H_2SO_4 [16]). In the case of MeOt-Bu steric effects cannot, a priori, be excluded as the explanation of the relatively low stability of the complexes with this cation.

Inspection of the $\Delta\delta$ values of Table 2 suggests that the secondary-alkyl cations, IIb, c, form complexes with the ethers in the same way as the primary ion IIa. In spite of the fact that the secondary, methyl-containing ion IIb ($pK_{R^+} = -0.64$) [2] is thermodynamically more stable than the IIa cation ($pK_{R^+} = -1.49$), the complexing ability is still very high, suggesting that the positive charge at the "acid" centre is not much delocalized by the alkyl substituent. In contrast, the tertiary cations IIe ($pK_{R^+} = 0.00$) and IIf ($pK_{R^+} = 0.75$), which are much more stable than IIa, do not form complexes with ethers because of the large charge dispersion on the substituents at the exocyclic carbon.

A borderline case seems that of IId ($pK_{R^+} = +0.40$), which forms weak adducts with Et_2O. The phenyl substitutent has about the same steric size of the isopropyl group but a higher ability to delocalize the charge, which makes the cation less able to complex the ether.

Finally, steric effects on the cation-ether interaction can be invoked to explain the results obtained with IIe. This tertiary cation, which is thermodynamically less stable than the secondary phenyl-containing ion IId, does not form complexes, probably because high steric requirements involved in the complexation process.

Finally we comment on the more intense NMR signal, which we have attributed to a second type of ether, the "mobile" ether, present in all $CDCl_3$ solutions of primary and of secondary alkyl-containing cations. As described in the Results Section this signal is always shifted downfield with respect to the ether in "pure" chloroform and is strongly concentration dependent. This indicates the existence of a rapid chemical exchange between ether molecules belonging to a particular solvation sphere of the cation and molecules of "free" ether in solution. On dilution a higher fraction of ether no longer belongs to the solvation shell and becomes "free" in solution. The observed chemical shift is a weighted average between the two limiting situations.

In summary, we have shown that α-ferrocenylmethylcarbenium ions undergo two distinct types of solvation processes with ether-like donor molecules. One involves one molecule of ether per molecule of cation and has a large association constant, and the exchange rate is slow on the NMR time scale. It is tempting to attribute this interaction to a Lewis acid-base conjugation between the ether oxygen and the cation carbon center. The second interaction is characterized by fast exchange on the NMR time scale, which prevents assessment of the stoichiometry and so of the limiting ether chemical shift, and is indicative of a weaker interaction. The solvation center in this case may be different from that in the preceding one.

Studies on the structure of these adducts and on the dynamic equilibria in solution are in progress.

Experimental

The various ferrocenyl carbinols were synthesized by standard literature methods [15,17]. The ethers and pentane were dried over Na-K alloy and distilled under nitrogen immediately before use, the NMR spectra were recorded on a Bruker HFX-90 MHz spectrometer equipped with a Bruker B-ST 100/700 temperature control unit.

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