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Ferrocenyl Carbonium Ions and Related Cationic Complexes. Structure and Stabilisation Mechanism

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The review presents data on the structure and mechanism of the stabilisation of ferrocenyl carbonium ions and related cationic complexes with different types of hydrocarbon ligands. The results obtained in the study of complex carbonium ions by X-ray diffraction, ^{57}Fe Mössbauer spectroscopy, and ^{1}H, ^{13}C, ^{19}F, ^{57}Fe, and ^{187}Os NMR are compared. It is shown that the ability of the metal atom to interact directly with the carbonium ion centre generated in the β-position relative to it is a general property of transition metal complexes.
The bibliography includes 132 references.

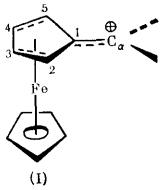
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I. INTRODUCTION

Over a quarter of a century has elapsed since the discovery of the unusually high stability of α-ferrocenylcarbonium ions.[1] It was found subsequently that the enhanced stability is a characteristic property of complex carbonium ions in which the transition metal is present in the β-position relative to the carbonium ion centre. α-Ferrocenylcarbonium ions remain the most thoroughly investigated among complex carbonium ions because of their comparatively high stability, the ready availability of ferrocene, and the wide variety of its chemical behaviour.

Throughout all these years, a lively controversy has continued concerning the structure and mechanism of the stabilisation of the α-ferrocenylcarbonium ions (see the earlier reviews[2-6]). In the explanations put forward for the stability of these ions, one can see two main concepts differing in the role which the transition metal atom plays in the stabilisation. According to one of them, the high stability of the carbonium ions (I) is achieved by the overlap of the *d* orbitals of the metal atom with the unoccupied *p* orbitals of the α-carbon atom. On the other hand, it has been claimed that the delocalisation of the positive charge of the ferrocenyl group takes place via a system of carbon–carbon bonds without the direct involvement of the iron atom in the stabilisation of the carbonium ion centre.



(I)

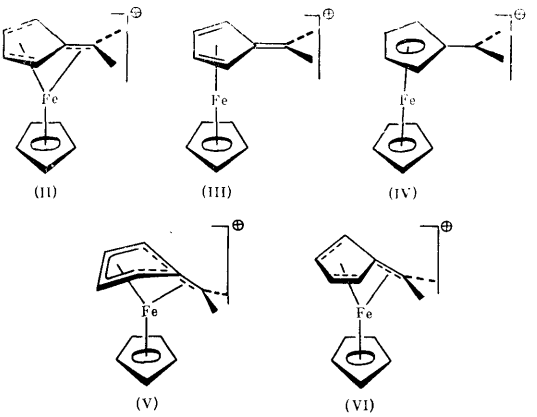
A wide range of physicochemical methods have been used to solve the problem of the structure and mechanism of the stabilisation of α-ferrocenylcarbonium ions. The data obtained recently have led to a considerable advance in our understanding of the causes of the enhanced stability of these cationic complexes. However, there are no reviews in the literature in which the experimental data obtained by different methods have been examined critically.

We therefore thought it useful to discuss the available data on the structure and mechanism of the stabilisation of ferrocenylcarbonium ions and also, bearing in mind the general nature of the problem, the corresponding information about related complex cations.

II. FERROCENYLCARBONIUM IONS

1. Structural Models of α-Ferrocenylcarbonium Ions

The unusually high ability of the ferrocenyl group to stabilise the neighbouring carbonium ion centre was demonstrated at an early stage in ferrocene chemistry. In particular, this was manifested by the high rate of solvolysis of α-acetoxyalkylferrocenes (comparable to that of trityl acetate)[1,7,8] and the ease of addition of weak acids to α-vinylmetallocenes.[9] Hill and Richards[7] suggested that structure (II) can reasonably explain the high stability of α-ferrocenylcarbonium ions. In this structure the FeC_5H_5 fragment is displaced towards the exocyclic carbon atom and the *d* orbitals of the metal atom overlap the *p* orbital of the C_α atom.



(II) (III) (IV) (V) (VI)

According to Traylor,[10,11] there is no need to postulate the direct participation of the iron atom in stabilisation to account for the experimental data and the best description of the structure of α-ferrocenylcarbonium ions is provided by the

resonance hybrid (III) ↔ (IV) with the predominant contribution by the canonical fulvene structure (III). Subsequently this concept was invoked to account for the mechanism of the stabilisation of other complex carbonium ions.

Both models have been frequently criticised. The criticism of model (II) is based on data obtained in a comparative ^{1}H NMR study of various α-ferrocenylcarbonium ions—of the kind for which a shift of the FeC_5H_5 fragment is possible and others where such a shift is prevented by the presence of a heteroannular bridge.[12] Traylor's model[10,11] has been criticised because the metal atom in structure (III) [which makes a dominant contribution to the (III) ↔ (IV) resonance hybrid] has a 16-electron configuration unusual for such an atom. Furthermore, structure (III) was proposed as a model for α-ferrocenylcarbonium ions on the basis of a comparison of ^{1}H NMR data for these cations and related tricarbonyliron(η-cyclobutadienyl)-substituted carbonium ions for which η^3-binding of the cyclic ligand has been erroneously postulated.[13] However, this structure was rejected after an X-ray diffraction study of the BF_4^- salt of the bis[tricarbonyliron-(η-cyclobutadienyl)]benzyl cation.[14]

A further two structural models of α-ferrocenylcarbonium ions, in which there is a direct Fe–C_α interaction, have been proposed. These are Cais's structure (V) with a non-planar cyclic ligand [bent at the C(II) and C(V) atoms][2,3] and structure (VI) in which the exocyclic bond is displaced from the plane of the five-membered ring and inclines towards the metal atom.[15] According to Cais, model (V) explains satisfactorily both the data on the solvolysis of ferrocene derivatives and the ^{1}H NMR data for α-ferrocenylcarbonium ions. However, a distortion of the cyclic ligand of this kind has not been observed in any of the X-ray diffraction studies of both cationic and uncharged cyclopentadienyl or fulvene metal complexes.

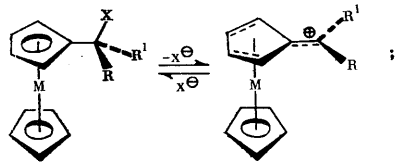
Model (VI) has been proposed on the basis of a calculation for $[FcCH_2]^\oplus$ (Fc = ferrocenyl) by the extended Hückel method.[15] According to the calculation, a 40° inclination of the C(I)–C_α bond in the direction of the iron atom corresponds to the minimum energy and the five-membered rings deviate from a parallel arrangement by 10°. The distortion of the fulvene ligand (the substituted ligand in α-metallocenylcarbonium cations is frequently regarded as a fulvene ligand[7,16]) is a consequence of the interaction of the unoccupied π* molecular orbital of the fulvene ligand with the d_{z^2} orbital of iron, which is non-bonding in ferrocene. According to the calculation, in contrast to model (VI), the model with a planar fulvene ligand should have a triplet ground state.

Model (VI) is consistent with many experimental data. However, one should note that a subsequent calculation[17] for $[FcCH_2]^\oplus$ by an analogous method led to a structure in which the angle of inclination of the C(I)–C_α bond is only 6°.

2. Kinetics and Stereochemistry of Solvolytic Reactions

After the first communications about the hydrolysis of the carbinols of the ferrocene series via the S_N1 mechanism, demonstrating the high stability of α-ferrocenylcarbonium ions,[1,8] several groups of investigators measured the rate of solvolysis in order to elucidate the role of the metallocenyl group in the acceleration of these reactions.[7,10,11,18–23]

Together with a high rate of the reactions of the metallocenyl-substituted substrates in solvolysis, the preferential *exo*-elimination of the leaving group was then demonstrated (the attack by the nucleophile on the carbonium ion also takes place in the *exo*-position).[8,18]

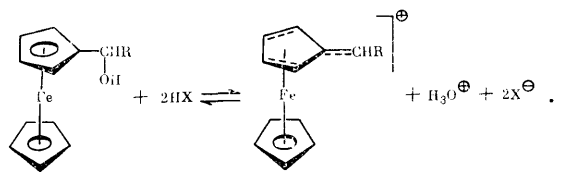


M = Fe, Ru, Os.

The increase of the solvolytic reaction in the series of iron, ruthenium, and osmium derivatives is regarded as evidence for the direct nucleophilic cooperation of the metal atom in these reactions. The stereochemical result of these reactions is also explained by the direct involvement of the metal atom.[8,18] On the other hand, the high rate of these reactions has been attributed to the effect of σ,π-conjugation (vertical stabilisation) and the stereochemical result has been attributed to steric causes.[10,11,21,22]

In considering the kinetic data it has usually been assumed that the α-ferrocenylcarbonium ion is closely related to the transition state in the heterolytic process. However, a very interesting observation has been made: the thermodynamic stability of α-ferrocenylcarbonium ions is much higher than would follow from the rate of their formation in solvolytic reactions.[24]

The thermodynamic stabilities of a series of α-ferrocenylcarbonium ions have been determined in a quantitative study of the ionisation equilibria involving ferrocenylcarbonium ions in aqueous solutions of inorganic acids:



The equilibrium constants of the above reaction have been determined in $H_2SO_4(HClO_4)$–H_2O systems. The pK_{R^+} were obtained from linear plots of lg $[R^+]/[ROH]$ against the acidity function H_{R^+}.

The discrepancy between the data for the stability of ferrocenylcarbonium ions obtained from measurements of the equilibrium constants and the reaction rates suggests that a significant electronic and evidently a structural rearrangement of the ferrocenyl group takes place in the pathway from the transition state to the α-ferrocenylcarbonium ions in the heterolytic process.[24]

3. X-RAY DIFFRACTION STUDY OF THE SALTS OF COMPLEX CARBONIUM IONS

It was to be expected that X-ray diffraction study of the salts of α-ferrocenylcarbonium ions or related cationic complexes would provide a final unambiguous answer to the question whether there is a direct interaction of the metal atom with the carbonium ion centre. However, the problem was not found to be quite so simple.

No significant interaction of any kind between the iron atoms and the carbonium ion centre has been observed in the structure of the BF_4^- salt of bis[tricarbonyliron(η-cyclobutadienyl)]benzyl cation,[14] where the Fe...C_α distances amounted to 2.85 and 2.94 Å. The C_α atom is coplanar with the cyclobutadiene rings, which have been somewhat rotated (by 5° and 8°) relative to the molecular plane; the benzene ring has undergone a rotation by 43°. This shows that the organometallic groups make a larger contribution to stabilisation than the benzene ring.

Nor has a significant Fe...C_α interaction been observed in the BF_4^- salt of the ferrocenyldiphenylcyclopropenyl cation.[25] The Fe...C_α distance is 2.96 Å and the angle of inclination of the C(I)–C_α atom in the direction of the iron atom is 6.3°. The deviation of the C_α atom relative to the plane of the ligand by 0.16 Å exceeds only slightly the value (~0.1 Å) observed in certain uncharged ferrocene derivatives. One cannot therefore agree with the authors' claim[25] that the Fe–C_α interaction takes place in this complex. Furthermore, bearing in mind the aromatic character of the cyclopropenyl cation, one can hardly expect any significant Fe–C_α interaction, leading to the delocalisation of the positive charge.

In the study of the structure of the BF_4^- salt of the diferrocenylmethyl cation it was observed[26,27] that the C_α atom has deviated from the plane of the five-membered rings but the Fe...C_α distances have been reduced to 2.69 and 2.81 Å, which corresponds to inclinations of the exocyclic bonds towards the iron atoms by 19.9° and 17.9° respectively. The authors suggest that the observed deviations may be the result of the interaction of the *d* electrons of the iron atom with the fulvene system, although the Fe...C_α distances are too large to permit the presence of a strong bond.

Yet another dinuclear complex with unequal Fe...$\overset{\oplus}{C}$H distances (2.59 and 2.72 Å) is $\{[Fe(\eta\text{-}C_5H_5)(CO)_2CH_2]_2CH\}.[BF_4]$.[28] In the precursor of this complex $[Fe(\eta\text{-}C_5H_5).(CO)_2CH_2]_2CH_2$ (the complex is generated from the latter by the abstraction of a hydride ion) the Fe...$C_\beta H_2$ distances are 3.07 Å.[29] It has been suggested that the difference between the Fe...$\overset{\oplus}{C}$H distances in the cationic complex are due to forces associated with the crystal packing.

The results of a study of the structure of the BF_4^- salt of the ferrocenyldiphenylmethyl cation were published in 1979.[30] The angle of inclination of the C(I)–C_α bond in this complex is 20.7° and the Fe...C_α distance is 2.715 Å.† The metal atom occupies an asymmetric position under the substituted ring, being displaced somewhat (by 0.008 Å) in the direction of the exocyclic C_α atom. As a result, the Fe–C(1) distance is somewhat shorter (2.009 Å) and the Fe–C(4) and Fe–C(5) distances are somewhat longer (2.095 and 2.085 Å) than the average length of the bond between the iron atom and the carbon atoms of the unsubstituted ring (2.056 Å). The planes of the five-membered rings are at an angle of 9.3°. The length of the exocyclic C(1)–C_α bond (1.416 Å) is significantly smaller than would be expected for a single bond between sp^2-hybridised carbon atoms (1.48 Å) indicating an appreciable proportion of double bond character. According to Behrens,[30] the structure can be fully regarded as one corresponding to the diphenylfulvenylcyclopentadienyliron cation.

Here it is appropriate to recall that the possibility of an appreciable deviation of the exocyclic bond of the fulvene ligand had been demonstrated earlier in a study of diphenylfulvenechromium tircarbonyl;[32] a similar deviation of the *exo*-bond has been observed recently for the complex $C_5H_5FeC_2B_9H_{10}CHC_6H_5$.[33]

Compared with the complex $(OC)_3CrC_5H_4C(C_6H_5)_2$, in which the angle of inclination of the *exo*-bond is 31°, in the zwitter-ionic chromium complex $(OC)_3\overset{\ominus}{C}rC_5H_4CH{=}\overset{\oplus}{N}(CH_3)_2$ with a planar imine group the corresponding angle of inclination is only 10°.[34] The decrease of the degree of deviation of the fulvene ligand from planarity with increasing ability of the substituent to delocalise the positive charge on the C_α atom also follows from data obtained for the complex $FcCH{=}\overset{\oplus}{N}(CH_3)_2$ where the "distortion is minimal".[35] The influence of complex formation with the metal and of the nature of the substituent at the C_α atom on the distortion of the fulvene ligand and on the barrier to rotation about the *exo*-bond has been examined.[35]

Thus structural studies on salts of α-ferrocenylcarbonium ions and related complexes have provided much valuable information about the structure of these interesting systems in the crystal state and the results of Cais et al.[26] and Behrens[30] can be regarded as evidence for the direct Fe–C_α interaction. However, it remains obscure to what extent the Fe...$C^\oplus$ distances found for the complex cations, which occur in the wide range from 2.59 to 2.96 Å, should be regarded as "bonding" and what the situation is in this respect on passing from the crystal to the solution. It would be desirable to answer this question also in connection with the fact that hitherto there have been no structural data for the carbonium ion $[FcCH_2]^\oplus$ in which the strongest Fe–C_α bond is to be expected.

4. ^{57}Fe Mössbauer Spectroscopy

The study of frozen solutions (137 K) of the carbonium ion $[FcCH_2]^\oplus$ in concentrated sulphuric acid and of the carbinol $FcCH_2OH$ in benzene by ^{57}Fe Mössbauer spectroscopy[36,37] showed that the isomer shifts δ of the complexes differ little and are close to that for ferrocene (0.56, 0.57, 0.53 mm s^{-1} respectively). According to the author's data, another parameter, namely the quadrupole splitting Δ, for the carbinol $FcCH_2OH$ is the same as for ferrocene, whereas Δ for the carbonium ion is greater by 15% than for the carbinol—1.99 and 2.29 mm s^{-1} have been quoted for $FcCH_2OH$ and $[FcCH_2]^\oplus$. It is known that the chemical shifts for the ferrocene derivatives vary little and are observed in the range 0.48–0.60 mm s^{-1} at 80 K; the quadrupole splittings are somewhat more sensitive to the influence of the substituent (2.05–2.55 mm s^{-1}) and diminish as the electron-accepting properties of the substituent are enhanced.[38,39] Accordingly, the substituent in model (IV) of α-ferrocenylcarbonium ions should manifest pronounced electron-accepting properties, which would diminish Δ. Model (II) with participation of the iron atom, in which one of the cyclopentadienyl ligands has been substituted by the fulvene ligand, linked to the metal atom the six carbon atoms, is consistent with experimental data according to Dannenberg and co-workers.[36,37]

A series of studies have been published recently (see Roberts and Silver[40] and the references quoted therein) concerning the application of Mössbauer spectroscopy to the study of derivatives of ferrocene and α-ferrocenylcarbonium ions. Neshvad et al.[41] studied the carbonium ion $[FcCH_2]^\oplus$ and $[FcCHCH_3]^\oplus$ and criticised the earlier investigations.[36,37] It was found that Δ for $FcCH_2OH$ and $[FcCH_2]^\oplus$ are not 1.99 and 2.29 mm s^{-1} but 2.40 and 2.70 mm s^{-1} respectively.[41] Furthermore, in discussing their own data, Dannenberg and Richards[36] used an erroneous, unduly low, value of Δ for ferrocene.

Overall, the reasoning the conclusions arrived at by both groups of investigators were analogous. A new factor in the study of Neshvad et al.[41] is that, in contrast to $[FcCH_2]^\oplus$, for which the Fe–C_α interaction has been postulated, in the tertiary carbonium ion $[FcC(CH_3)_2]^\oplus$ the possibility of this interaction is ruled out on the grounds of the similarity of the values of δ and Δ for this complex (0.51 and 2.41 mm s^{-1} respectively) and for ferrocene (0.53 and 2.42 mm s^{-1}). It has been suggested that the stabilisation in the complex

†It is remarkable that the Fe...$C^\oplus$ distances found in a number of studies,[26–28,30] are close to that between the bridging μ-CO ligand and the most remote iron atom in the cluster $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CO)]^{2\ominus}$; the distance 2.72(1) Å is believed to correspond to the presence of a bond between them.[31]

$[FcC(CH_3)_2]^{\oplus}$ is achieved through the inductive and hyperconjugation influences of the two methyl groups and also the resonance influence of the cyclopentadienyl ligand (see, however, Section II).

5. ^{1}H NMR Spectroscopy

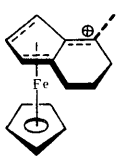
^{1}H NMR spectroscopy makes it possible to detect readily the formation of α-ferrocenylcarbonium ions when the traditional precursors of these ions, namely α-ferrocenylcarbinols[42-45] and α-vinylferrocenes[46] are treated with acids, usually CF_3COOH or H_2SO_4.

The formation of α-ferrocenylcarbonium ions is accompanied by a downfield shift of the signals due to the cyclopentadienyl protons. The greatest shift is then undergone by the signals of the H(3,4) protons of the substituted ring, while the H(2,5) protons are less deshielded [in contrast to acylferrocenes and other ferrocene derivatives with substituents exhibiting the $-R$ effect, in which the H(2,5) protons are more deshielded than the H(3,4) protons]. Thus, signals at δ = 5.45 (CH_2), 4.72 [H(2,5)], 6.32 [H(3,4)], and 5.27 (C_5H_5) p.p.m. have been observed[45] in the spectrum of a solution of the cation $[FcCH_2]^{\oplus}$ in CF_3COOH (δ = 4.04 p.p.m. for ferrocene in CCl_4).

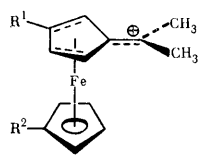
The difference between the relative shieldings of the H(2,5) and H(3,4) protons depends on the character of the substituent at the carbonium ion centre C_α and diminishes with increase of the ability of the substituent to delocalise the charge. For non-identical substituents at the C_α atom, four protons of the substituted ligand in the spectrum of α-ferrocenylcarbonium ions give separate signals, indicating that the rotation about the exocyclic C(1)–C_α bond is hindered.

The fact that the H(2,5) protons of the substituted ligand are more shielded in α-ferrocenylcarbonium ions (in contrast to, for example, acylferrocenes) has been regarded as evidence in support of model (II): when the FeC_5H_5 group shifts towards the C_α atom, its anisotropic effects leads to a greater shielding of the H(2,5) protons.[37]

To test the possibility of the displacement of the FeC_5H_5 fragment along the fulvene ligand, the carbonium ions (VII)–(X) have been investigated[12] assuming that such a shift is possible in the complexes (VII)–(IX) but not in the complex (X), where this is prevented by the heteroannular bridge consisting of three methylene units.



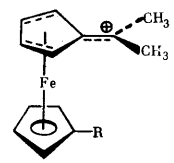
(VII)



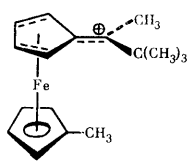
(VIII): $R^1 = R^2 = H$
(IX): $R^1 = R^2 = CH_3$
(X): $R^1, R^2 = (CH_2)_3$

The average difference $\Delta\nu$ between the shieldings of the H(2,5) and H(3,4) protons in the complexes (VII)–(X) is 72, 80, 86 and 65 Hz respectively, which is believed to be inconsistent with model (II) [a greater difference $\Delta\nu$ is expected if the model is applied to the complexes (IX) and (X)]. One can therefore assume that α-ferrocenylcarbonium ions undergo a deformation which is different from that postulated by the above model; otherwise one would have to assume that the metal–ring interaction and the character of the charge distribution in α-ferrocenylcarbonium ions and ferrocene differ significantly.

Data consistent with the distortion from planarity of the fulvene ligand have been published.[47] The protons of the alkyl-substituted ring in the carbonium ion (XI) are manifested in the ^{1}H NMR spectrum by a single narrow signal, which indicates the ease of the relative rotation of the rings. However, the H(2,5) and H(3,4) protons of the methylcyclopentadienyl ligand give rise to two multiplets at δ = 4.78 and 5.15 p.p.m. in the spectrum of the cation (XII), which is believed to be due to the restriction of the rotation of the cyclic ligands as a consequence of the contact between the t-butyl group at the C_α atom and the methyl group of the $C_5H_4CH_3$ ligand.



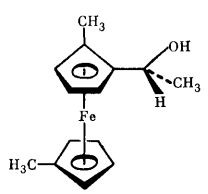
(XI): R = CH_3, C_2H_5, $CH(CH_3)_2$, $C(CH_3)_3$



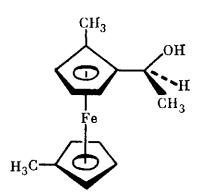
(XII)

Such a difference between the relative rotations of the ring in the isomeric complexes (XI, R = t-butyl) and (XII) was not to be expected for planar fulvene ligands. The spectroscopic differences between the isomeric cations noted above are therefore explained by the distortion of the fulvene ligand similar to that postulated in models (V) and (VI).

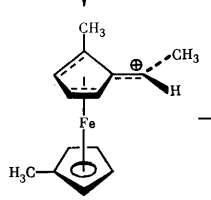
^{1}H NMR has been used to study the barrier to rotation about the exocyclic bond in α-ferrocenylcarbonium ions.[48] When the diastereoisomeric carbinols (XIII) and (XIV) are dissolved in acid, the isomeric carbonium ions (XV) and (XVI) are generated respectively and it is possible to follow the slow transformation of the carbonium ion (XV) into the sterically less strained isomer (XVI).



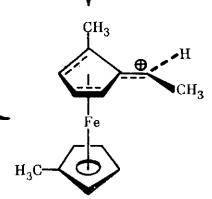
(XIII)



(XIV)



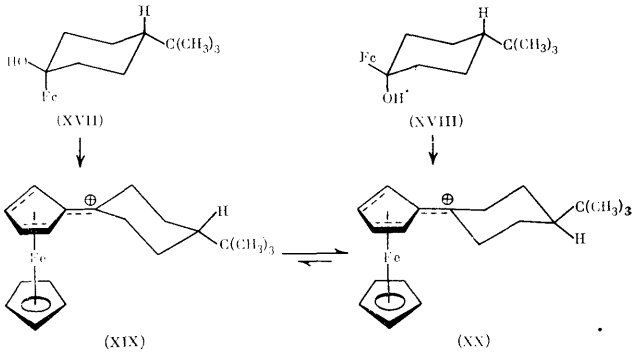
(XV)



(XVI)

The barrier to rotation about the C(1)–C_α bond is sufficiently large to detect the optically active carbonium ions generated from the enantiomeric carbinols *R*-(−)-$FcCH(OH).CH_3$ and *S*-(+)-$FcCH(OH)CH_3$; the racemisation of these ions has been investigated by the polarimetric method.[48]

The carbonium ions (XIX) and (XX) are formed from the tertiary carbinols (XVII) and (XVIII) respectively; the complexes isomerise slowly, giving rise to an equilibrium mixture consisting mainly (approximately 90%) of the carbonium ion (XX).



The lower stability of the carbonium ion (XIX) compared with (XX) has been explained by the more marked steric repulsion between the conformationally rigid t-butylcyclohexyl ring and the unsubstituted cyclopentadienyl ligand.[48]

The torsional barrier in the equilibrium (XIX) ⇌ (XX) between the tertiary carbonium ions is appreciably lower than in the equilibrium (XV) ⇌ (XVI) between the secondary carbonium ions (69.4 ± 2 and 88.7 ± 2.0 kJ mol^{-1} respectively). Consequently the difference between the energy barriers to rotation about the C(1)–C_α bond is not determined by steric causes due to contacts between the substituents at the C_α atom and the unsubstituted ring in the transition state. It is believed that these differences reflect the role of the electronic factors characteristic of the substituents at the C_α atom.[48]

The estimated torsional barriers (~100 kJ mol^{-1}) in the α-ferrocenylcarbonium ions show that the exocyclic bond of the fulvene ligand does not have an appreciable double bond character and this is inconsistent not only with model (III) but also with the appreciable contribution of the canonical structure (III) to the (III) ↔ (IV) resonance hybrid.[48]

6. ^{13}C NMR Spectroscopy

The study of α-ferrocenylcarbonium ions by ^{13}C NMR showed that the signals of all the carbon atoms in the cyclic ligand have undergone a downfield shift compared with the neutral precursors, which indicates the delocalisation of the charge over the entire ferrocenyl unit.[49–56] The deshielding of the carbon nuclei in the ferrocenyl group is relatively insensitive to the nature of the substituents at the C_α atom, so that the ferrocenyl group makes the main contribution to the stabilisation of the carbonium ion.

The relative shielding of the C(2,5) and C(3,4) atoms in the ^{13}C NMR spectra of α-ferrocenylcarbonium ions is the same as that of the H(2,5) and H(3,4) atoms: the signals of the nuclei in the 3,4-positions are less shielded. Thus signals at δ = 87.7 (CH_2), 110.6 [C(1)], 84.6 [C(2,5)], 94.4 [C(3,4)], and 82.3 (C_5H_5) p.p.m. have been observed in the spectrum of the cation $[FcCH_2]^\oplus$ (δ = 67.7 p.p.m. for ferrocene in dichloroethane). Similar relative shielding of the carbon atoms of the substituted ligand has been observed in the ferrocene derivatives FcR, where R = CHO, $COCH_3$, CN, or other substituents with a *–R* effect.[57]

The cause of the smaller shielding of the C(3,4) atoms compared with C(2,5) may be the known sensitivity of the former to the *–R* effect of the substituents in ferrocene derivatives.[57] Another factor which also favours the observed spectral picture may be the shift of the FeC_5H_5 fragment to the exocyclic C_α atom. Such a shift would weaken the bond between the metal atom and the C(3,4) carbon atoms and hence should entail a smaller shielding of the latter as a consequence of the diminution of the effect of the "coordination shift"#. At the same time the displacement of FeC_5H_5 towards the C_α atom should favour a greater shielding of the C(2,5) atoms as a consequence of the effect of the magnetic anisotropy of the FeC_5H_5 fragment.[37]

In the discussion of the ^{13}C NMR spectra of α-ferrocenylcarbonium ions, attention was drawn to the relatively small downfield shift of the C_α signal on passing from carbinols to carbonium ions.[51] For example, on formation of the $[FcCH_2]^\oplus$, $[FcCHCH_3]^\oplus$, and $[FcCHC_6H_5]^\oplus$ carbonium ions from the corresponding carbinols, the quantities $\Delta\delta(^{13}C_\alpha)$ are 26.2, 52.1, and 49.9 p.p.m. respectively. On the other hand, they are much greater for organic systems, $\Delta\delta(^{13}C_\alpha)$ amounting to 127.4 p.p.m. in the case of the 3,5-$(F_3C)_2C_6H_3$.$CH(OH)CH_3$/3,5-$(F_3C)_2C_6H_3\overset{\oplus}{C}HCH_3$ pair for example.[58] This difference between the $\Delta\delta(^{13}C_\alpha)$ for organometallic and organic systems may be the result of the more effective delocalisation of the positive charge in the organometallic carbonium ions and the occurrence of the metal–C_α interaction.

The ^{13}C–^{1}H spin–spin interaction constants (SSIC) for α-ferrocenylcarbonium ions, which are in the range 160–165 Hz, are consistent with the sp^2 hybridisation of the C_α atom but not with the formation of the Fe–C_α σ-bond.[49,51–53,55]

7. The ^{57}Fe NMR Chemical Shifts and the ^{13}C–^{57}Fe Spin–Spin Interaction Constants for α-Ferrocenylcarbonium Ions

Since it is impossible to resolve the question of the mechanism of the stabilisation of α-ferrocenylcarbonium ions within the framework of traditional methods for the investigation of carbonium ions, it became necessary to seek a new approach. Such an approach, consisting in the study by the $^{13}C\{^1H\}$ and $^{13}C\{^1H, ^{57}Fe\}$ methods of organoiron compounds enriched in the ^{57}Fe isotope (natural abundance 2.2%, nuclear spin 1/2), has been used in an investigation carried out at the Institute of Organoelemental Compounds of the USSR Academy of Sciences.[59,60] It was found that the ^{13}C–^{57}Fe SSIC for ferrocene derivatives is relatively insensitive to the nature of the substituent and usually occurs in the range 4.2–5.2 Hz; the signal of the exocyclic C_α carbon atom in the $^{13}C\{^1H\}$ NMR spectrum is manifested by a narrow singlet.[59,61]

In contrast to ferrocene derivatives, the ^{13}C–^{57}Fe SSIC for α-ferrocenyl carbonium ions are clearly not the same for different carbon atoms, being greatly reduced for C(3,4), while the signal of the C_α atom is either broadened or (when the resolution is sufficiently good) is observed as a doublet with a $^{13}C_\alpha$–^{57}Fe constant up to 2.7 Hz.[59,60]

The assignment of the observed broadening (splitting) of the signal of the $^{13}C_\alpha$ atom to interaction via only one bond ($^{13}C_\alpha$–^{57}Fe) and not via two bonds [$^{13}C_\alpha$–C(1)–^{57}Fe] has been justified[60] on the basis of the ^{13}C–^{57}Fe SSIC obtained for ^{57}Fe complexes with a wide variety of hydrocarbon ligands.

The broadening (splitting) of the $^{13}C_\alpha$ signal in the spectra of α-ferrocenylcarbonium ions is accompanied by a decrease of the ^{13}C(3,4)–^{57}Fe SSIC, which suggests that the "non-bonding" hybrid *d* orbitals of iron undergo a rehybridisation, which promotes the Fe–C_α interaction.

The data on the shielding of ^{57}Fe in the α-ferrocenylcarbonium ions $[FcCH_2]^\oplus$ (XXI) and $[FcCHCH_3]^\oplus$ (XXII) published in 1978 [59] confirmed this hypothesis. It has been

#The term "coordination shift" denotes the upfield shift of the NMR signals of the hydrocarbon ligand on coordination to the transition metal.

shown beforehand that the ^{57}Fe chemical shift for ferrocenes is very sensitive to the nature of the substituent, electron-accepting substituents of the *-R* type leading to a marked deshielding of iron. Thus the $\delta(^{57}Fe)$ are 215.5 and 425.6 p.p.m. for acetyl- and 1,1'-diacetyl-ferrocenes respectively (relative to ferrocene as the standard).[59]

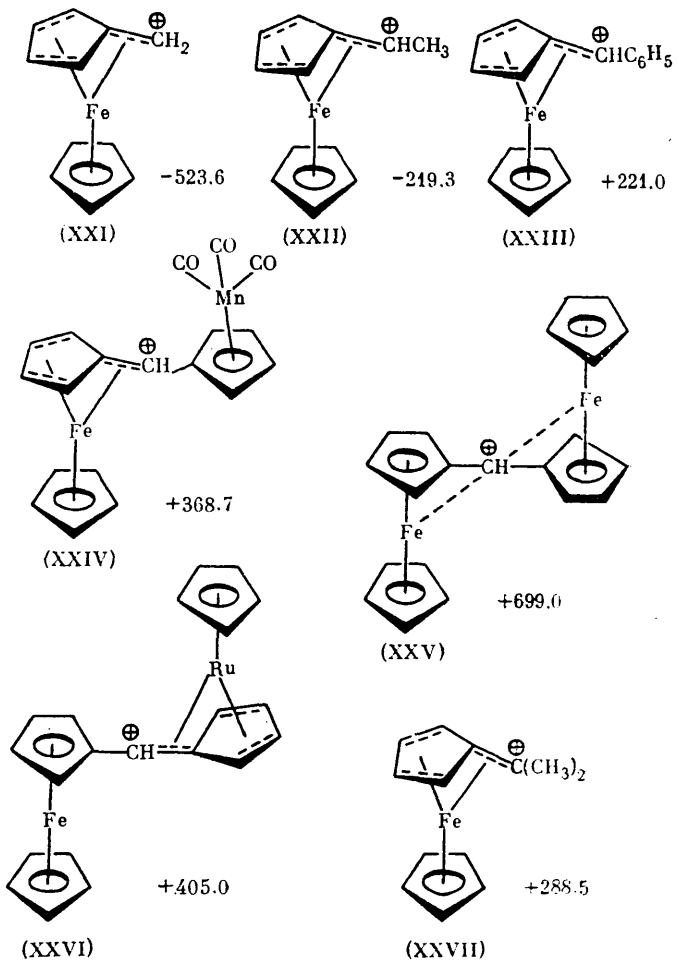


Figure 1. The ^{57}Fe NMR chemical shifts (p.p.m.) of α-metallocenylcarbonium ions.[60]

However, despite the "electron-accepting" character of the substituent, the ^{57}Fe signals of the carbonium ions (XXI) and (XXII) are observed in strong fields—at -523.6 and -219.3 p.p.m. respectively. The conclusion that the *d* orbitals are rehybridised in α-ferrocenylcarbonium ions has been supported by the following observations. The shift of the iron signal to a very strong field (-1098.8 p.p.m.) has also bee noted[61] for the protonated ferrocene $[HFe(C_5H_5)_2]^{\oplus}$, where the above rehybridisation is known to take place.[62,63] In addition an upfield shift has been observed also for those "uncharged" ferrocenophanes in which the rehybridisation of the "non-bonding" *d* orbitals is induced by the breakdown of the parallel arrangement of the rings as a consequence of the inadequate lengths of the hydrocarbon bridge.

It has been found that the ^{57}Fe NMR signal undergoes consecutive upfield shifts with increase of the degree of deviation of the cyclopentadienyl rings of ferrocene from the parallel arrangement: the $\delta(^{57}Fe)$ chemical shifts for 1,1'-diethylferrocene, [4]ferrocenophane, and [3]ferrocenophane are +72.5, -56.5, and -272.5 p.p.m. respectively. In ferrocene derivatives containing a heteroannular bridge made up of three or four carbon atoms, the five-membered rings are known to deviate from the parallel arrangement by approximately 9° and approximately 4° respectively as a consequence of the tightening (in the former case) and expanding (pushing apart) (in the latter case) effects respctively. Thus the ^{57}Fe signal of [3]ferrocenophane has undergone an upfield shift of approximately 350 p.p.m. compared with 1,1'-diethylferrocene containing parallel ligands.[60,64]

The study of the carbonium ions (XXI)–(XXVII) showed that their ^{57}Fe chemical shifts cover a range of 1200 p.p.m. and constitute a sensitive measure of the direct involvement of the iron atom in the stabilisation of the carbonium ion centre (Fig.1). The relative shielding of the ^{57}Fe nucleus in carbonium ions is determined by the sum of two opposed effects: the rehybridisation of the "non-bonding" *d* orbitals of iron promotes shielding, while the electron-accepting influence of the substituent promotes the deshielding of the ^{57}Fe nucleus.

Thus the ^{57}Fe chemical shifts for the series (XXI)–(XXVI) undergoes a consecutive [with the exception of the complex (XXV)] downfield displacement with increasing ability of the substituent R to delocalise the positive charge in the carbonium ions $[FcFHR]^{\oplus}$. The explanation is that, with increase in the ability of the group R to delocalise the charge, the contribution of the direct involvement of the metal to the stabilisation (i.e. the factor promoting the rehybridisation of its *d* orbitals, the ^{57}Fe shielding factor) diminishes.[60,65]

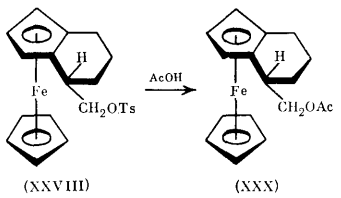
In the symmetrical complex $[(Fc)_2CH]^{\oplus}$(XXV) both ferrocenyl units make equal contributions to the delocalisation of the charge and the orbitals of each of the iron atoms are therefore less rehybridised [compared, for example, with the complex (XXIV)]; there is a simultaneous increase of the fraction of the charge delocalised via the system of carbon–carbon bonds of the cyclopentadienyl ligands. As a result, the complex (XXV) exhibits the most marked "carbenium ion" character among all the complexes (XXI)–(XXVII) investigated, which explains the marked deshielding of the iron nucleus in it (+699.0 p.p.m.). Data on the shielding of the C_α nuclei in the dinuclear complexes (XXIV), (XXV), and (XXVI) (122.4, 147.2, and 116.9 p.p.m. respectively) also agree with this finding.[60,65]

On the basis of the $^{13}C-^{57}Fe$ SSIC data for the shielding of the ^{57}Fe nucleus in the cationic complexes (XXI)–(XXVII), one may assume that the strongest $Fe-C_\alpha$ bond obtains in the primary carbonium ion (XXI), although in this case too the strength of the $Fe-C_\alpha$ bond should be smaller than that of the bond with the carbon atoms of the five-membered ring. The greatest $^{13}C_\alpha-^{57}Fe$ shielding, amounting to 2.7 Hz, has been noted for the [3]ferrocenophan-7-yl cation,[60] which may be accounted for by the distortion of the fulvene ligand as a consequence of the additional tightening influence of the heteroannular bridge. The minimum $Fe-C_\alpha$ interaction evidently takes place in $[(Fc)_2CH]^{\oplus}$, whereas the results obtained indicate the occurrence of the $Fe-C_\alpha$ interaction in the tertiary carbonium ion $[FcC(CH_3)_2]^{\oplus}$[in contrast to the claim based on the Mössbauer spectra of this complex:[41] being highly sensitive, ^{57}Fe NMR spectroscopy should indicate the occurrence of a weak $Fe-C_\alpha$ interaction in those cases where Mössbauer spectroscopy fails to record a change in the ligand environment of the metal on passing from the tertiary carbinol to the ion (XXVII)].

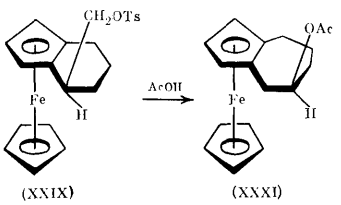
8. β-Ferrocenylcarbonium Ions

In view of the unusually high stability of α-ferrocenylcarbonium ions, it was of interest to discover how the ferrocenyl group influences the stabilisation of the carbonium centre in the β-position relative to it.

It has been observed[66] that *endo*-α-tosyloxymethyl-1,2-tetramethyleneferrocene (XXVIII) undergoes acetolysis 2780 times faster than its *exo*-isomer (XXIX). The corresponding acetate (XXX) is then formed from the *endo*-isomer, while the *exo*-isomer gives rise to the rearrangement product (XXXI), with a seven-membered ring:



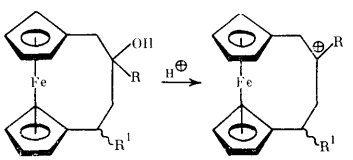
(XXVIII) (XXX)



(XXIX) (XXXI)

The difference between the rates of solvolysis of the complexes (XXVIII) and (XXIX) and also between the structures of the resulting products can be accounted for by the effective involvement of interannular electrons (in essence, the electrons of the iron atom) in the stabilisation of the β-ferrocenylcarbonium ion. The retention of configuration in the solvolysis of the optically active 1-ferrocenyl-2-propyl tosylate is consistent with the involvement of iron.[67]

The stability of β-ferrocenylcarbonium ions has been demonstrated in a ^{1}H NMR study of the cationic complexes (XXXIII) generated from carbinols of the [4]ferrocenophane series (XXXII):[68–70]



(XXXII) (XXXIII)

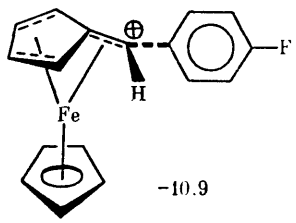
The effect of conjugation with the metallocenyl group is ruled out in the carbonium ions (XXXIII) where the electron-deficient centre is separated from the ferrocenyl group by the methylene unit. It is therefore natural to suppose that the stabilisation is achieved by the direct involvement of the iron atom.[69] The comparatively strong field of the C(7) hydrogen atom signal in complexes (XXXIII) (5.36–5.55 p.p.m.) agrees with this assumption.

III. RELATED COMPLEX CARBONIUM IONS

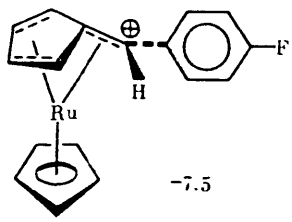
This Section does not deal with heteroatomic systems (for example, those generated by the protonation of acylferrocenes). These were partly considered in a previous review.[5] The presence of a heteroatom next to the carbonium ion centre can significantly reduce the role of the metallocenyl group in its stabilisation. Although these systems have been considered as models of α-ferrocenylcarbonium ions, this study has made little contribution towards the elucidation of the role of the transition metal atom in stabilisation.

1. Ruthenocenyl- and Osmocenyl-carbonium Ions

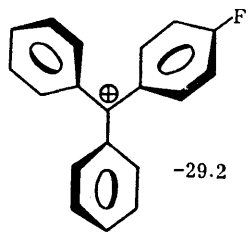
The rates of the S_N1 acetolysis of α-acetoxyethylmetallocenes[7] and of the non-catalysed addition of acetic acid to vinylmetallocenes[9] indicate an increase of carbonium ion stability in the sequence $[FcCHCH_3]^{\oplus} < [RucCHCH_3]^{\oplus} < [OscCHCH_3]^{\oplus}$ (where Ruc and Osc denote ruthenocenyl and osmocenyl). This stability series can be accounted for by the improvement of the overlap of the metal atom orbitals and the π orbitals of the fulvene ligand as the volume and polarisability of the valence shell of the metal increase.[2,3,7,71] The pK_{R^+} for $[RucCHCH_3]^{\oplus}$ and $[FcCHCH_3]^{\oplus}$ are 1.20 and −0.65 respectively.[71]



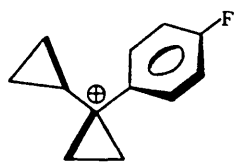
(XXXIV)



(XXXV)



(XXXVI)



(XXXVII)

Figure 2. The ^{19}F NMR chemical shifts (p.p.m.) of the p-fluorophenyl-substituted carbonium ions.[75,76]

It has been shown for the optically active carbonium ions $[RucCHCH_3]^{\oplus}$ that the torsional barrier is so high that racemisation does not take place even when the solution in CF_3COOH is heated at 70 °C for several days.[48]

The signals of the protons at C_α in the ^{1}H NMR spectra of the carbonium ions $[McCHCHC(CH_3)_2]^{\oplus}$ (Mc = Fc, Ruc, Osc) as well as $[McCHCH_3]^{\oplus}$ (Mc = Fe or Ruc) undergo successive upfield shifts, which can be accounted for by the decrease of the positive charge on the C_α atom in the isostructural series of metallocenylcarbonium ions.[54,72]

According to ^{13}C NMR data, the positive charge in the complex $[FeCHRuc]^{\oplus}$ (XXVI) is largely delocalised over the ruthenocenyl unit. The spectrum exhibits a temperature dependence due to the rotation about the Fe–C_α bond.[60,65] It is of interest to compare these results with data concerning the electronic influence of the corresponding metallocenyl

groups. It has been shown that, according to ^{19}F NMR data for the complexes *m*- and *p*-Fc_6H_4Mc, characterising the influence of the metallocenyl groups in the ground state of the uncharged substrates, the metallocenyl groups Fc, Ruc, and Osc show insignificant differences in their electronic influences, which are close to those of the alkyl substituents in the benzene ring.[73] Furthermore, estimation of the effective charges in metallocenes (also on the basis of the shielding of the ^{19}F nucleus) yielded the following values for the cyclopentadienyl ligand in ferrocene, ruthenocene, and osmocene: −0.26, −0.25, and −0.25 a.u. respectively.[74] In the light of these data, it is reasonable to postulate that the results obtained for the complex $[FcCHRuc]^{\oplus}$ agree with the direct involvement of the ruthenium atom in stabilisation.[60]

The ^{19}F NMR signals of the carbonium ions (XXXIV) and (XXXV) are observed at −10.9 and −7.5 p.p.m. respectively (in a weak field relative to fluorobenzene). Thus the ruthenocenyl group is more effective in delocalising the charge than the ferrocenyl group[75] (Fig.2).

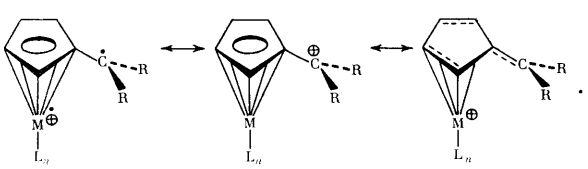
Comparison of the shielding of ^{19}F in the complexes (XXXIV) and (XXXV) and in the carbenium ions (XXXVI) and (XXXVII) [76] demonstrates to what extent the metallocenyl groups are superior to the phenyl and cyclopropyl groups as regards the delocalisation of the positive charge. The similarity of the ^{19}F chemical shifts for the complexes (XXXIV) and (XXXV) to those for *p*-fluoronitrobenzene and *p*-cyanofluorobenzene (−11.1 and −9.2 p.p.m. respectively) has also been noted.[75] Hence it follows that the treatment of the C_α atom as a "carbonium ion" centre is to a considerable extent arbitrary.

2. Cymantrenylcarbonium Ions

The cymantrenyl group is less effective in stabilising the cationic centre than the ferrocenyl group, but it is superior to the phenyl group in this respect.[77–80]

The substitution of the CO ligands by phosphine ligands increases the stabilisation of the corresponding ions, as might have been expected on the basis of the donor–acceptor properties of CO and PR_3 groups.[81]

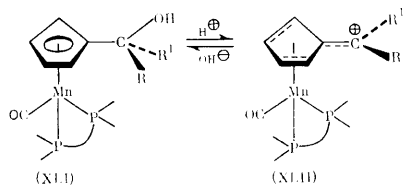
The similarity of the ultraviolet[80] and ^1H NMR [80,82,83] spectra of α-cymantrenyl- and α-ferrocenyl-carbonium ions suggested the similarity of the mechanisms of their stabilisation. A distinctive feature of the ^{13}C NMR spectra of cymantrenylcarbonium ions is that the signal due to the C(1) atom exhibits the greatest degree of shielding. According to Loim et al.,[84] the structure of α-metallocenyl carbonium ions (including cymantrenyl ions) may be described by the resonance of the structures (XXXVIII), (XXXIX), and (XL), in which the exocyclic bond is inclinded in the direction of the metal atom.



(XXXVIII) (singlet state) (XXXIX) (XL)

The contribution of each structure depends on the nature of the metal, its lipand environment, and the substituents at the C_α atom. With increase of the number of electron-donating substituents at this atom the stabilisation due to the $M-C_\alpha$ interaction diminishes owing to steric hindrance. The "approach of the cationic centre" to the plane of the five-membered ring diminishes the contribution of the structure (XXXVIII) with the direct involvement of the metal atom and correspondingly increases the contribution of the structures (XXXIX) and (XL). Overall, these considerations agree with those presented previously[37] for α-ferrocenylcarbonium ions and are not open to objection. However, it has not been explained why the exocyclic bond in the structures (XXXIX) and (XL), where a direct involvement of the metal atom in stabilisation is not implied, should nevertheless be inclined towards the metal atom.

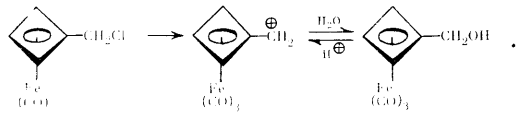
Two ^{31}P signals are sometimes observed when the cationic complexes (XLII), generated from the diphosphine derivatives of the cymantrenyl carbinols (XLI), are investigated by ^{31}P NMR, which is explained by hindrance to free rotation of the $Mn(CO)P_2$ group about the metal–ring axis, possibly owing to the inclination of the exocyclic bond.[85]



(XLI) (XLII)

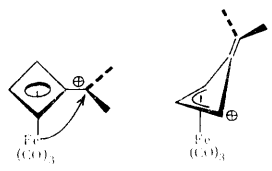
3. Tricarbonyliron(η-cyclobutadienyl)carbonium Ions

It has been shown that tricarbonyliron(α-chloromethylcyclobutadiene) (XLIII) undergoes rapid solvolysis in water or methanol, giving rise to the carbinol (XLV) or the corresponding methyl ether. These reactions have been explained by the intermediate involvement of the stable carbonium ion (XLIV). The latter has been isolated in the form of the $SbCl_6^-$ salt on treatment of the complex (XLIII) with antimony pentachloride.



(XLIII) (XLIV) (XLV)

In order to account for the pronounced shielding of the exocyclic protons in the ^1H NMR spectrum of the carbonium ion (XLIV) (signals at δ = 6.68, 5.91, and 5.09 p.p.m. with the relative intensities 1 : 2 : 2) and also of the secondary carbonium ion generated from tricarbonyliron(η-α-hydroxyethylcyclo butadiene), the structures (XLVI) and (XLVII) were examined and preference was given to the π-allyl structure (XLVII).[13]

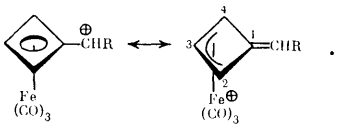


(XLVI) (XLVII)

On the basis of the results of X-ray diffraction analysis of the tetrafluoroborate salt of the cation $\{[(OC)_3Fe(\eta\text{-}C_4H_3)]_2.CC_6H_5\}$, the authors later concluded[14] that the main contribution to stabilisation comes from the interaction between the occupied orbitals of the metal atom and the four carbon

atoms of the cyclobutadiene ring with subsequent electron transfer to the electron-deficient centre via π,π interaction.

In the study of the cationic complexes $[(OC)_3Fe(\eta\text{-}C_4H_3).CHR]^{\oplus}$(R = H, CH_3, or C_6H_5) by ^{13}C NMR, it was noted[86] that $\Delta\delta(^{13}C_\alpha)$ is comparatively small for the transition from the carbinol to the carbonium ion (in contrast to organic systems). Furthermore, an appreciable downfield shift of the signal of the C(3) carbon atom (42–46 p.p.m.), compared with 3–13 p.p.m. for the C(2) and C(4) atoms, has been observed. These data can be accounted for in terms of hyperconjugation with participation of the metal–carbon bond.[11,87] It is believed[87] that the hyperconjugation effect weakens the bond between the metal and the C(1) atom, which increases the contribution of the π-allyl structure to the resonance hybrid (XLVIII)↔(XLIX):



(XLVIII) (XLIX)

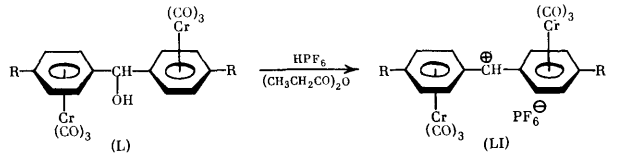
However, the above spectroscopic features may be a result of the rehybridisation of the iron atom, which ensures the Fe–C_α direct interaction.

4. Benchrotrenylcarbonium Ions

The study of tricarbonylarenechromium-substituted systems has the advantage that it makes possible a direct comparison with the corresponding non-coordinated arenes. The solvolysis of $(OC)_3Cr(\eta\text{-}C_6H_5CH_2Cl)$ is approximately 10^5 times faster than that of benzyl chloride, while the solvolysis of η-chlorodiphenylmethanechromium tricarbonyl is approximately 10^3 times faster than that of diphenylmethyl chloride.[88] A slight increase (only by a factor of 28) of the rate of solvolysis of α-chlorocumene on coordination to the $Cr(CO)_3$ group can be explained by the influence of steric factors.[89]

Data obtained from measurements of the pK_{R^+} for benchrotrenylcarbonium ions also indicate the ability of the $Cr(CO)_3$ group to delocalise the charge.[90,91]

The attempts to obtain stable salts of carbonium ions from $(OC)_3Cr(\eta\text{-}C_6H_5CH_2X)$ (X = Cl or CH_2OH) were unsuccessful.[86] The stable PF_6^- salts of the carbonium ions (LI, R = H or CH_3) have been synthesised only from the dimetallic carbinols (L):[92]



(L) (LI)

The 1-(tricarbonyl-*p*-tolylchromium)ethyl and bis(tricarbonyl-*p*-tolylchromium)methyl cations, generated from the corresponding carbinols in HSO_3F at −50 °C, have been identified by ^1H NMR.[93] ^{13}C NMR data for the same carbonium ions were published later.[92,94] Although the results presented did not enable the authors[94] to make a choice between the resonance-stabilised structure and the structure involving the direct participation of the metal atom, preference was given to the latter.

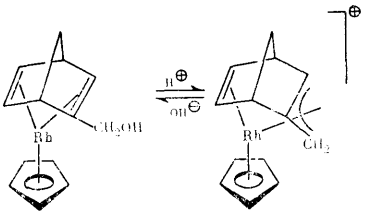
In a study of the ^{13}C NMR spectrum of the tricarbonylcumenylchromium cation (LII), it was noted[95] that, whereas the *ortho*- and *para*-carbon atoms in benchrotrenes and non-coordinated monosubstituted benzenes are usually more sensitive to the influence of substituents than the *meta*-carbon atoms, in the carbonium ion (LII) the opposite situation is observed: the *meta*-carbon atoms proved to be the most deshielded. On this basis, the authors regard the direct involvement of the metal atom and delocalisation via the overlap of the π,π type as unlikely; a significant role of the σ,π conjugation is also rejected (the appearance of a signal due to C_i in a very weak field would be expected in such a case). The authors merely state that the charge is delocalised over the $Cr(CO)_3$ group, although the mechanism of the delocalisation remains obscure.

According to a calculation by the LCAO-MO SCF method, the stability of the $[(OC)_3Cr(\eta\text{-}C_6H_5CH_2)]^{\oplus}$ ion is the result of the supply of the electrons from the $d_{x^2-y^2}$ orbital of chromium to the non-bonding π orbital of the benzyl ligand.[96] The mechanism corresponds to the direct participation of the metal atom but not via the formation of a specific Cr–C_α bond but as a result of the interaction with the π-benzyl ligand as a whole. The angle of inclination of the exocyclic bond towards the metal is 40°.

5. Carbonium Ions Stabilised by Olefins and Dienes Bound in Complexes

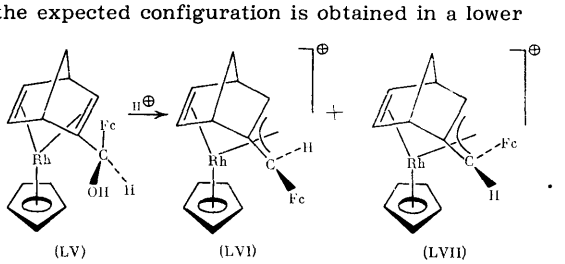
In the chemistry of transition metal π-complexes, it is well known that the generation of a carbonium ion centre next to a coordinated π-olefinic linkage transforms the olefin complex into a cationic π-allyl complex.

The stereochemistry of similar reactions and the influence of the character of the substituents at the exocyclic carbinol carbon atom has been investigated in detail in relation to norbornadiene carbinols.[97–100] Treatment of the carbinol (LIII) with acid results in the formation of the cationic complex (LIV) in which the bicyclic ligand is linked to the metal via π-ethylenic and π-allyl bonds.[98] The structure of this complex, proposed on the basis of ^1H and ^{13}C ^1H NMR data, has been confirmed by X-ray diffraction.[97]



(LIII) (LIV)

It has been shown for the diastereoisomeric 2-(α-hydroxyethyl)norbornadienecyclopentadienylrhodium complexes with the ψ-*exo*- and ψ-*endo*-configurations of the OH group that the elimination of the hydroxy-group is highly stereospecific and leads to the *syn*- and *anti*-allyl cationic complexes respectively.[97–100] The stereospecificity is retained also in the reaction of the phenyl-substituted ψ-*endo*-carbinol, while a mixture of the *syn*- and *anti*-isometric complexes (LVI) and (LVII) is obtained from the ferrocenyl-substituted ψ-*endo*-carbinol (LV) in proportions of 4:1, i.e. the complex having the expected configuration is obtained in a lower yield:

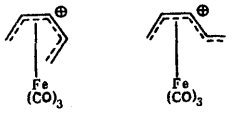


(LV) (LVI) (LVII)

The breakdown of stereospecificity in the reaction involving the elimination of the hydroxy-group from the carbinol (LV) can be accounted for by the competition between the iron and rhodium atoms in the stabilisation of the carbonium ion centre in the transition state of the reaction.[97]

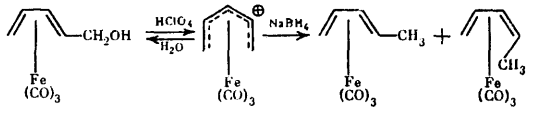
Considerable efforts have been devoted to the elucidation of the structure and mechanism of the stabilisation of the carbonium ions generated from dieneiron tricarbonyl complexes.[101]

The cationic pentadienyl complexes can exist in both the *cis*-form (LVIII) and the *trans*-form (LIX):



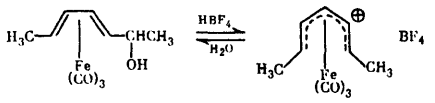
(LVIII) (LIX)

Although the formation of complexes of type (LIX) has been postulated in many reactions, for a long time they could not be detected owing to the ease of their rearrangement to the more stable *cis*-isomers (LVIII). Thus treatment of the complex (LX) with perchloric acid yielded the salt of the *cis*-cation (LVIII):[102]



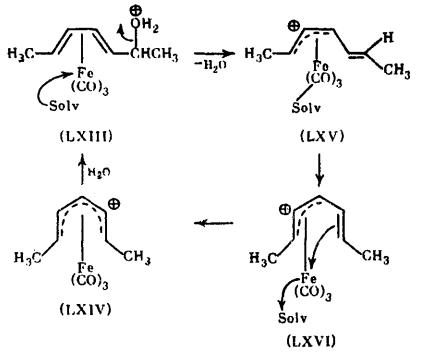
(LX) (LVIII) (LXI) (LXII)

The carbonium ion (LVIII) reacts with water, regenerating the *trans*-pentadienecarbinol (LX).[102] Such stereoselectivity does not always obtain in the reaction of the cation (LVIII) with nucleophiles. Treatment of salts of the carbonium ion (LVIII) with sodium tetrahydroborate yielded a mixture of the isomers (LXI) and (LXII) in proportions of 1:4.[102] The tricarbonyl-*syn*,*syn*-1,5-dimethylpentadienyliron cation (LXIV) has been regenerated from the diastereoisomeric carbinols (LXIII) by treatment with acids. Its hydrolysis is stereospecific and involves the formation of one of the isomeric carbinols:



(LXIII) (LXIV)

The following mechanism has been postulated to account for the stereochemistry of these reactions:[102]



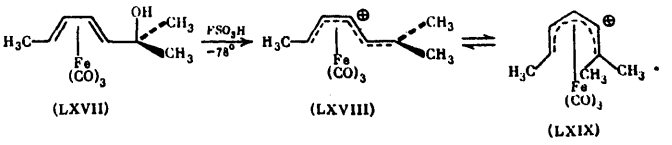
(LXIII) (LXV) (LXIV) (LXVI)

In the first stage both diastereoisomeric carbinols are converted (albeit at different rates) to the hydrated vinylallyl complex (LXV). Rotation about the single bond in compound (LXV) affords compound (LXVI) and subsequent displacement of the solvent molecule and coordination to the vinyl bond leads to compound (LXIV). The *exo*-attack on the cation (LXIV) by the $OH^{\ominus}$ion regenerates one of the carbinols (LXIII).

The study of the solvolysis of the 3,5-dinitrobenzoates of the diastereoisomeric carbinols of the butadieneiron tricarbonyl series showed that the solvolysis proceeds via the S_N1 mechanism with retention of configuration.[103] The study of the reaction products by spectroscopic methods indicates the retention of the initial carbon skeleton in the carbinols formed: thus the intermediate species in these reactions are tricarbonyl-*trans*-η-pentadienyliron cations.

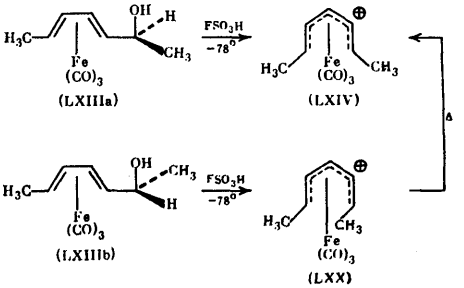
According to the authors,[103] the solvolytic data agree both with the direct nucleophilic involvement of the metal atom and with the hyperconjugation of the metal–carbon bond.

The direct detection of the *trans*-pentadienyl cations by ^{1}H NMR was achieved after many attempts[104–107] by employing appropriately substituted dienol complexes.[105,106] After dissolving the carbinol (LXVII) in cooled fluorosulphonic acid, the formation of the *trans*-cation (LXVIII), in equilibrium with its *cis*-isomer (LXIX), was observed:[105]



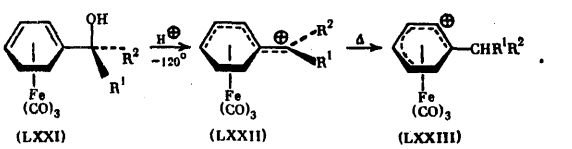
(LXVII) (LXVIII) (LXIX)

In the same study[105] it was shown that, when the reaction of the diastereoisomeric carbinols (LXIII) is carried out at a low temperature, a stereospecific conversion into the *cis*-ions (LXIV) and (LXX) takes place [in contrast to the data of Mahler and Pettit[102] who isolated only the cation (LXIV) from both carbinols]. The *trans*-cations could not be detected in this case. It was therefore assumed that the structure of the carbonium ions generated is determined not only by steric but also by electronic factors.[105]



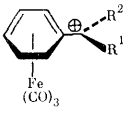
(LXIIIa) (LXIV) (LXIIIb) (LXX)

Cyclic *trans*-cations (LXXII), generated at −120 °C in solution in the FSO_3H–SO_2ClF mixture from the carbinols (LXXI), have been detected by ^{1}H NMR.[108] On raising the temperature of the solution, the complexes (LXXII) rearrange to the more stable cyclohexadienyl cations (LXXIII):



(LXXI) (LXXII) (LXXIII)

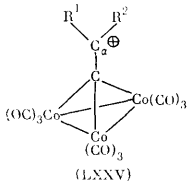
The rate of the rearrangement of the secondary ion (LXXII, $R^1 = H$, $R^2 = CH_3$) is much higher than that of the tertiary ion (LXXII, $R^1 = R^2 = CH_3$). On this basis, it has been suggested that the positive charge is localised on the exocyclic carbon atom. The authors therefore believe that the tetrahapto-structure (LXXIV) makes an important contribution to the overall structure of the complex and the stability of these cationic complexes should be a result of the delocalisation of the charge via a conjugation mechanism.[108]



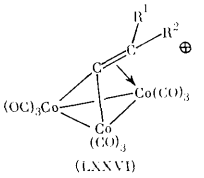
(LXXIV)

6. Carbonium Ions Stabilised by the $Co_3(CO)_9C$ and $Os_3H_3(CO)_9C$ Clusters

Seyferth and co-workers[109] investigated thoroughly the cationic complexes stabilised by the nonacarbonyltricobaltmethinyl group. The cationic complexes $[Co_3(CO)_9CCR^1R^2]^{\oplus}$ were isolated in the form of stable salts with the $PF_6^{\ominus}$ anion. The structure of the carbenium ion (LXXV) with the Co_3C-C_α bond directed at right angles to the plane of the Co_3 triangle was postulated for them. The high stability of the cationic complex was accounted for by the σ,π conjugation mechanism.[110-112]

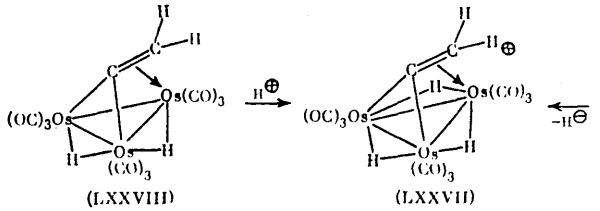


(LXXV)

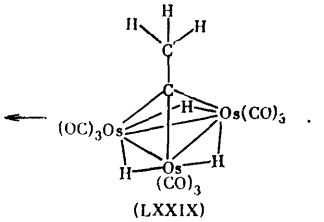


(LXXVI)

An alternative structure (LXXVI) with an inclined μ_3-η^2-hydrocarbon ligand has been suggested on the basis of ^1H NMR data for the related osmium complex $[Os_3H_3(CO)_{10}\cdot(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)^{\oplus}]$ (LXXVII), generated by protonating the dihydride complex (LXXVIII) or by eliminating a hydride ion from the methyl group of the complex (LXXIX).[113]



(LXXVIII) (LXXVII)



(LXXIX)

The spectrum of the complex (LXXVII) in the $CF_3COOH-CDCl_3$ mixture at −10 °C contains two hydride signals with relative intensities in proportions of 2 : 1 at −18.36 and −20.58 p.p.m. When the solution is heated, the hydride signals are broadened and merge into a singlet at 70 °C. It has been suggested[113] that the temperature dependence of the spectrum can be a consequence of either the migration of the hydride ligands relative to the Os_3 triangle or of the formation of a carbenium ion at an elevated temperature, as in the case of the complex (LXXV). Yet another explanation of the stereochemical non-rigidity of the complex (LXXVII) in relation to its cobalt analogue has been proposed. It consists of the rearrangement of the μ_3-η^2-hydrocarbon ligand. This process has been examined theoretically by Schilling and Hoffmann,[114,115] who state that the inclined structure (LXXVI) corresponds to the ground state of the complex $[Co_3(CO)_9CCH_2]^{\oplus}$. The experimental data obtained in a ^{13}C NMR study of the complex $[Co_3(CO)_9CCHCH(CH_3)_2]^{\oplus}$ are consistent with this finding. The signals of the methyl carbon atoms are anisochronic at −65 °C, in conformity with the structure (LXXVI), where they are diastereotopic. With increase of temperature, the signals of the methyl carbon atoms in the isopropyl substituent coalesce, possibly as a consequence of the correlated rotation about the $Co_3(CO)_9-C$ and $C-CHCH(CH_3)_2$ axes. However, spectroscopic data do not rule out a non-correlated rotation [i.e. the rotation of the $CHCH(CH_3)_2$ fragment without the simultaneous rotation of the $Co_3(CO)_9$ unit] or the formation of the carbenium ion structure (LXXV) at elevated temperatures.

The observation of satellites due to the $^{187}Os-^1H$ spin–spin interaction (natural abundance of the ^{187}Os isotope 1.64%, nuclear spin 1/2) in the ^1H NMR spectra of the cationic complexes $[Os_3H_3(CO)_9CR^1R^2]^{\oplus}$ established that the temperature variation of the spectrum is due to the migration of the hydrocarbon and not the hydride ligands.[117,118] One hydride signal at δ = 19.63 p.p.m. has been observed in the ^1H NMR spectrum of the complex $[Os_3H_3(CO)_9C\overline{C(CH_2)_2CH_2}]^{\oplus}$ at 30 °C. Two pairs of satellites (with 28.8 and 32.0 Hz splittings) have been noted on either side of the signal. It has been demonstrated by the method of double homonuclear resonance that the $^{187}Os-^1H$ SSIC is 30.4 Hz and the double set of satellites in the spectrum is explained by the further splitting of the satellite signal as a consequence of the spin–spin interaction with the third hydrogen atom which is not linked to the ^{187}Os isotope. The $^{187}Os-^1H$ SSIC, amounting to 30.4 Hz, lies in the range 27–35 Hz characteristic of saturated osmium complexes with stereochemically rigid (bridging) hydride ligands.

IV. CONCLUSION

Examination of the literature data presented above permits the conclusion that the structure of some of the cationic complexes and the role of the transition metal atom in their stabilisation have now been reliably established. This applies in the first place to the α-metallocenylcarbonium ions and also to cationic complexes of the type $[Co_3(CO)_9CCR_2]^{\oplus}$ and $[Os_3H_3(CO)_9CCR_2]^{\oplus}$. Although the available data for other related complexes are not quite so unambiguous, they are in overall agreement with the direct involvement of the metal atoms in the stabilisation of the carbonium ion centre.

One can therefore assume that the *ability (tendency) of the transition metal atom to enter into a direct interaction with the carbonium ion centre generated in the β-position relative to its is a general property of transition metal complexes.* Exceptions are possible in those cases where the need for the direct interaction with the metal atom does not arise because of the presence of heteroatomic substituents at the carbonium ion centre.

The validity of this generalisation can be confirmed by studying cationic complexes whose structure and the mechanism of the stabilisation of which have not yet been established. For example, stable complexes having the compositions $[(RC{\equiv}CCR^1R^2)Co_2(CO)_6][BF_4]$ [119,120] and $[(HC{\equiv}CCR^1.R^2)M_2(CO)_4(C_5H_5)_2][BF_4]$ (M = Mo or W) [121] and obtained from the corresponding complex ethynylcarbinols[121-123] are now known; they are usually regarded as carbenium ions. However, the spectroscopic characteristics and the set of available data for the related cationc complexes suggest that in these complexes too the metal atom interacts directly with the "carbonium ion centre".

In connection with the structure and the stabilisation mechanism mention should be made of the "redox tautomerism" of ferrocenylcarbonium ions.[124,125] It has been suggested[125] that ferrocenylcarbonium ions can readily undergo an intraionic oxidation-reduction reaction in which an electron is transferred from the metal atom to the "carbonium ion centre" C_α with formation of the ferricenium biradical cation. Calculation by the MO method[15] predicted that this type of reaction should be accompanied by a change in the geometry of the fulvene ligand—the latter should be planar in the triplet ferricenium cation.

Experiments with a spin trapping agent seemingly confirmed the hypothesis of the possible redox tautomerism,[125] but subsequently it was noted[126] that the formation of nitroxyradicals following the addition of nitrosobenzene to the ferrocenylcarbonium ion can also proceed via other pathways not involving the biradical redox tautomer.

Nevertheless one can assume that, in the presence of a suitable ligand environment, it is possible to achieve an intraionic oxidation-reduction reaction of the metallocenylcarbonium ion. Studies on these lines are being prosecuted by Rybinskaya and co-workers.[127]

The general assessment of the long controversy concerning the structure and mechanism of the stabilisation of α-ferrocenylcarbonium ions is that it has been extremely useful. Numerous studies of the factors influencing the stability of organic carbonium ions (the involvement of neighbouring groups in solvolytic reactions, the "problem of non-classical ions",[128] the σ- and π-donation of electron density by heteroatomic substituents,[129] the possibility of the donation of π electrons by the electron-accepting substituents CN, CHO, CF_3, and $\overset{\oplus}{N}H_3$,[130] and other problems) are being continued. It is therefore evident that the understanding of the mechanism of the delocalisation of the positive charge in the α-ferrocenylcarbonium ions and related cationic complexes extends our overall ideas about carbonium ions—these most important species in organic chemistry.

Furthermore, the elucidation of the way in which the transition metal atom influences the delocalisation of the positive charge (reactivity) of the organic ligand bound to it is now particularly timely, an increasing number of cationic complexes finding applications in the synthesis of organic compounds.[131,132]

In conclusion, we have to consider the names of the cationic complexes $[FcCR^1R^2]^{\oplus}$. The following notation has been adopted for them in the literature: α-ferrocenylcarbenium ion, α-ferrocenylcarbonium ion, and fulvenecyclopentadienyliron cation.

According to ^{57}Fe NMR and X-ray diffraction data, the exocyclic C_α atom in these complexes usually interacts with the metal atom. Consequently it is not tervalent and the term "carbenium ion" is not applicable to these systems.

Judging from the ^{19}F NMR chemical shifts, the fraction of the positive charge localised on the C_α atom in the complex $[FcCHC_6H_4F\text{-}p]^{\oplus}$ is so small that the term "fulvenecyclopentadienyliron cation" must be recognised as adequately justified, being particularly valid for the complex $[FcCH_2]^{\oplus}$. However, the ^{13}C and ^{57}Fe NMR studies of the complex enriched in the ^{57}Fe isotope have shown that the Fe–C_α interaction weakens with increasing capacity of the groups R^1 and R^2 to delocalise the charge and the fraction of the charge delocalised via the system of carbon–carbon bonds increases. In this case the term "α-ferrocenylcarbonium ion" appears more suitable. Although the latter term cannot be regarded as adequate, it has the advantage that it reflects the genesis of these complexes.

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