Journal of Organometallic Chemistry, 117 (1976) 265—276

α-CYMANTRENYLCARBENIUM IONS

II *. ^{13}C NMR SPECTRA AND STABILIZATION MECHANISM OF METALLOCENYLCARBENIUM IONS

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(Received March 20th, 1976)

Summary

^{13}C NMR spectra of some α-cymantrenylcarbenium ions and corresponding carbinols are reported. The data obtained are compared with the characteristics of the ^{13}C NMR spectra of ferrocenyl-, phenyl- and cyclopropyl-carbenium ions. The mechanism of the carbenium centre stabilization by the adjacent metallocenyl radical is discussed.

Introduction

Elucidation of the mechanism by which the cationic centre is stabilized by the adjacent metallocenyl groupings is an important but not yet solved problem in the chemistry of metallocenyl carbenium ions. It may be expected that a comparative study of metallocenyl carbocations which differ both in the nature of the transition metal and in the surrounding ligands will contribute to the solution of this problem. In recent years, besides extensive studies of the properties of α-ferrocenylcarbenium ions [1—3], systematic investigations of carbenium ions of cymantrenylic [4,5] and benchrotrenylic [6,7] series have been started.

In our previous communication [4] it was suggested that stabilization of the α-carbenium centre by cymantrenyl and ferrocenyl radicals having an isoelectronic structure proceeds by a common mechanism. This idea was prompted by the similarity of the PMR and UV spectra of ferrocenyl- and cymantrenylcarbenium ions [4].

Similarities in the properties of the cations of both types can also be established by a consideration of their thermodynamic stability. Similar to ferrocenyl

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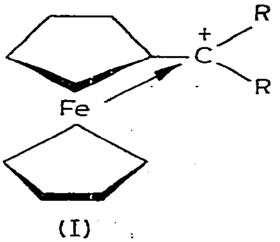
* For part I see ref. 4.

ions [2,8,9], alkyl and aryl substituents at the carbenium centre have little effect on the stability of cymantrenylcarbenium ions [4]. While the stability of the trityl cation increases by seven orders of magnitude as compared with the benzhydryl cation [10], when passing over from phenyl- to diphenyl-substituted ferrocenyl- and cymantrenyl-carbenium ions, pK_{R^+} values change, respectively, only by 0.5 and 2 units in terms of the pK_{R^+} scale. Consequently, stabilization of the adjacent carbenium centre in the metallocenyl ions under consideration is determined, mainly by the interaction of the metallocenyl fragment with the carbenium centre.

The small influence of the aryl radical on the stability of cymantrenylcarbenium ions becomes particularly apparent from consideration of the following facts. It has been shown [4,11] that the donor effect of the cymantrenyl radical is stronger than that of phenyl. Thus, the pK_{R^+} value for the α-cymantrenylbenzyl ion is —8.7 [4], while that for the benzhydryl cation is —13.3 [10]. However, when passing from the cymanthrenylbenzyl ion to the cymantrenylanisylbenzyl ion (pK_{R^+} —5.3), the stability only increases by 3.5 orders of magnitude, whereas when passing from the benzhydryl cation to the anisylbenzhydryl cation (pK_{R^+} —3.4 [10]) the pK_{R^+} value changes by 10 orders of magnitude. Thus, though the cymantrenyl radical is a stronger stabilizing group than phenyl, stability of the cymantrenylanisylbenzyl ion proves to be unexpectedly lower than the stability of its aryl analogue.

In spite of the similarity in a number of properties of ferrocenyl- and cymantrenyl-carbenium ions, the degree of cation stabilization in these related systems is essentially different. pK_{R^+} values for the α-cymantrenylmethyl ions studied by us are 6 to 9 orders of magnitude lower than the thermodynamic stability values for ferrocenyl carbocations having similar substituents at the carbenium centre. Evidently, this difference must manifest itself, particularly in the nature of delocalization of the positive charge and in the distribution of electron density in metallocenyl radicals.

At present a great deal of attention in the literature is paid to the two models of the structure of these ions, which were suggested in order to describe the properties of ferrocenylcarbenium ions. One of the models I assumes direct interaction of the filled nonbonding metal orbital and the unoccupied orbital of the carbenium centre [9,12,13]. The other model II treats the conjugation of the C^+ atom with the π-system of the cyclopentadienyl ring as the only factor stabilizing the positive charge [14,15].



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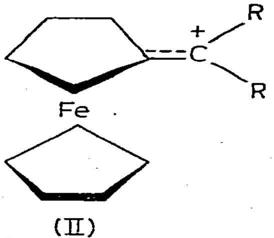
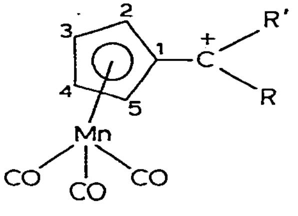


(II)

With a view to further study of the properties of metallocenylcarbenium ions and the character of electron distribution in them, we obtained ^{13}C NMR spectra for a series of α-cymantrenylcarbenium ions and compared these spectra with the data for ferrocenylmethyl, benzyl and cyclopropylmethyl carbocations.

Results and discussion

Table 1 shows the ^{13}C NMR spectra of carbenium ions IIIa—IIIe obtained by dissolving corresponding carbinols IVa—IVe in concentrated sulphuric acid [4].



(III)

	IIIa	IIIb	IIIc	IIId	IIIc
R =	H	CH_3	CH_3	C_6H_5	C_6H_5
R' =	C_6H_5	C_2H_5	C_6H_5	C_6H_5	C_6H_4-p-OCH_3

The assignment of resonance signals given in Table 1 is based on the analysis of the spectra obtained with and without proton suppression. The ^{13}C NMR spectra of the starting carbinols IVa—IVe are given in Table 2. Comparative ^{13}C NMR spectroscopic data for ferrocenylmethyl ions were taken from [1,16—18], those for benzyl and cyclopropyl ions were taken from [19,20], and for methylphenylferrocenylcarbenium, $C_5H_5FeC_5H_4—\overset{+}{C}(CH_3)C_6H_5$ (V), from our own experiments.

Carbenium centre

Signals due to the carbenium centre, C^+, of cations IIIa—IIIe appear downfield (δ 144—201 ppm) from those due to ferrocenyl ions of a similar structure (δ 116—161 ppm). In the case of benzyl cations, C^+ values are observed still further downfield (δ 200—255 ppm).

From the data cited, in agreement with the NMR theory of ^{13}C nuclei [21], it follows that the π-electron density at the carbenium centre increases in the series benzyl- < cymantrenyl- < ferrocenyl-carbenium ions.

From comparison of δC^+ and $\Delta\delta C^+$ ($\Delta\delta C^+$ being the difference between chemical shifts for the separate carbon atom in the cation and alcohol), it can be seen that for four carbenium ions with the same substituents at the C^+ atom (Table 3), in all the cases as we pass from the secondary to the tertiary cations, the values of both δ and Δδ increase. However, while for tertiary phenyl- and cyclopropyl-carbenium ions the nature of the substituents can significantly alter the δ values (δ 50—55 ppm), for ferrocenylcarbeniums and ions IIIb—IIId this value only changes by δ 3 and 12 ppm respectively. Therefore cymantrenylcarbenium ions, as regards the character of δ and Δδ changes for C^+, to a greater extent correspond to the ferrocene derivatives than to the purely organic methylcations.

Furthermore, in trishomocyclopropenyl (VI) [22], cyclopropylmethyl (VII) [20], ethylenebromonium (VIII), and tetramethylethylenebromonium (IX)

TABLE 1

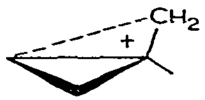
THE ^{13}C NMR SPECTRA OF CYMANTRENYLCARBENIUM IONS IIIa—IIIe AND THE METHYLPHENYLFERROCENYLCARBENIUM ION (V) IN CONCENTRATED H_2SO_4 AT 15°C (δ (ppm) FROM TMS, EXTERNAL STANDARD $CHCl_3$ (77.2 ppm FROM TMS), J(CH) (Hz) IN PARENTHESES)

R	R′	C(1)	C(2) [a]	C(3) [a]	C(4) [a]	C(5) [a]	C^+	$(CO)_3$
H	C_6H_5 (IIIa)	98.3	92.8 (171.0)	97.6 (188.2)	98.3 (179.4)	100.2 (169.0)	144.5 (163.5)	214.2
CH_3	C_2H_5 (IIIb)	97.8		92.2	99.3		193.1	214.9
CH_3	C_6H_5 (IIIc)	98.3	93.3	94.6	98.3	99.4	184.2	215.4
C_6H_5	C_6H_5 (IIId)	96.8		95.4 (188)	96.5 (185)		201.0	217.1
C_6H_5	p-$C_6H_4OCH_3$ (IIIe) [b]	94.8		92.8 (181.0)	94.8 (182.4)		198.5	219.4
CH_3	C_6H_5 (V) [b]	98.5	77.6 (183.8)	92.6 (186.6)	92.9 (186.8)		158.6	

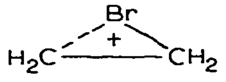
[a] Shift assignment for C(2)—C(5) have not been made. [b] The spectra of IIIe and V in CF_3COOH do not differ significantly from those in H_2SO_4. The values δ and J(CH) for anisyl ring are 132.9(—): 141.3(160.3): 117.2(169) and 173.0(—).

[23] cations, for which both experimental and calculated data [24] indicate σ-bonding of the carbenium centre with valence-nonbonded atoms in the molecule, the values of the chemical shifts for the carbenium centre are very low, δ 4.7; 57.6; 73.8 and 139.6 ppm respectively. It may therefore be assumed that in the case of metallocenylcarbenium ions with unusually low δC^+ values for the carbenium ions, direct interaction of the metal with the positively charged carbon atom takes place.

(VI)



(VII)



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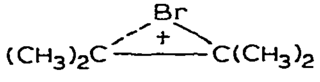


(IX)

The spin—spin coupling constant, J_{CH}, of the carbenium centre for the phenylcymantrenylmethyl carbocation IIIa, (163.5 Hz) is found in the region which is characteristic of both ferrocenyl [16—18], and alkylaryl [25] carbenium ions (160—170 Hz). On the other hand, these values correspond to the spin—spin coupling constants of the sp^2 hybridized carbon atom [25,26].

However, the value of J_{CH} evidently cannot be a reliable criterion for the hybridization state of the carbenium centre and hence of the direct participation of the metal in stabilization of the positive charge in the metallocenyl ions under consideration. Indeed, J(CH) values for carbon in the sp^2 state change considerably even in the series of related compounds carrying different charges (137—183 Hz) [27]. Further, the values of CH-constants for sp^3 hybridized carbon atoms increase sharply with a decrease in the dihedral angles and an increase in the bond tensions of these atoms [20,26]. In connection with the problem under consideration the J(CH) values for the carbenium centre in the

C_6H_5				CH_3^α	CH_3^β	CH_2	OCH_3	C_5H_5
C_{key}	C_o	C_m	C_p					
130.1	132.5 (163.2)	130.6 (161.8)	137.3 (150.0)					
				24.2	14.6	33.9		
136.4	129.9 (163.2)	129.3 (160.2)	136.6 (157.3)	27.0				
138.0	133.4 (167)	129.5 (167)	138.0 (162)					
137.3	132.7 (163.2)	128.9 (167.6)	135.3 (163.3)				57.5	
138.6	129.2 (164.7)	127.9 (158.8)	133.3 (170.5)	27.0 (129.4)				81.4 (182.4)

above-mentioned σ-bridging homocyclopropenyl (196 Hz), ethylenebromonium (185 Hz) and cyclopropylmethyl (180 Hz) cations are of particular interest. In view of the afore-mentioned it may be concluded that the values of the spin—spin coupling constants in α-ferrocenyl- and α-cymantrenyl-carbenium ions do not exclude the possibility of direct Metal → C^+ interaction.

Evidently, the absence of spin—spin coupling between iron and the carbenium centre in the methylferrocenylcarbenium ion also cannot be regarded, as pointed out in [28], as proof of the absence of such interaction. Indeed, the value of J(FeC) in ferrocene derivatives [28] lies within 2—5 Hz and in the case of $J(FeC^+)$ it may turn out to be too small for recording.

Cyclopentadienyl ring

In the ^{13}C NMR spectra of ferrocenylcarbenium ions so far described the signals due to the carbon atoms of the cyclopentadienyl rings appear downfield from the signals observed in the spectra of the initial alcohols [1,17]. A different picture is observed for cations of the cymantrenyl series (Table 4). A downfield shift takes place only for the signals of the α(2,5) and β(3,4) carbons, whereas the signal due to the key atom C(1), shifts in the opposite direction, Δδ —9.9 to —17.3 ppm. The carbon atoms of the carbonyl ligands have their signals shifted in the same direction. Consideration of the behaviour of ring carbon atoms in the formation of benzyl cations from alcohols [19] shows that it is similar to changes in the cyclopentadienyl(Cp) in the transformation of IVa—IVe into IIIa—IIIe. In both cases, as a rule, the signal due to C(1) lies between the signals from the other carbons of the ring. On the other hand, the signals due to the three carbon atoms of the cyclopropane ring in cyclopropylmethyl ions [19,20], shift downfield, which is similar to the signals due to the carbon atoms of the Cp-rings of ferrocenyl carbocations. For the two latter types of cations the characteristic value Δδ for the key atom decreases with an increase in the number, volume and donor properties of the substituents at the carbenium centre. In the case of methylphenylferrocenylcarbenium (V), this value becomes negative (—2.1 ppm).

TABLE 2

THE ^{13}C NMR SPECTRA OF CYMANTRENYLCARBINOLS IVa—IVe AND THE METHYLPHENYLFERROCENYLCARBINOL (V—OH) IN CCl_4 AND $CHCl_3$ SOLUTIONS AT 25°C (δ (ppm) FROM INTERNAL TMS)

R	R′	C(1)	C(2,5)[a]	C(3,4)[a]	COH	$(CO)_3$	C_{key}	C_o	C_m	C_p	CH_3^{α}	CH_3^{β}	CH_2	OCH_3	C_5H_5
H	C_6H_5 (IVa)	108.2	82.1	80.0	70.4	223.9	141.9	128.3	125.9	127.9					
			82.5	81.2											
CH_3	C_2H_5 (IVb)	114.1	83.3	80.7	70.2	223.7					28.6	8.4	37.4		
			82.5	78.7											
CH_3	C_6H_5 (IVc)	114.0	84.4	81.2	71.9	224.7	146.7	128.2	124.7	127.3	31.6				
			83.7	79.4											
C_6H_5	C_6H_5 (IVd)	111.5	86.9	80.0	77.2	224.3	146.4	127.9	126.9	127.6					
C_6H_5	p-$C_6H_4OCH_3$ (IVe)	112.1	89.7	80.1	76.9	224.3	146.6	127.9	126.9	127.5				55.2	
				79.9			138.9[b]	128.3	113.2[b]	158.8[b]					
CH_3	C_6H_5 (V—OH)	100.6	67.2	66.0	71.9		147.6	127.3	124.4	125.9	31.8				68.1
			67.8	66.9											

[a] Shift assignments for the ring carbons of IVb have been based upon studing the effects of adding $Eu(fod)_3$ on the signal positions. In other cases the assignment was made by analogy with Ib. [b] The values of δ for the anisyl ring.

TABLE 3

THE VALUES δ AND $\Delta\delta = \delta(\mathrm{ion}) - \delta(\mathrm{alc})$ (ppm) (IN PARENTHESES) FOR THE CARBENIUM CARBON IN THE IONS OF THE $\mathrm{A{-}C^{+}}\!\!<^{\mathrm{R'}}_{\mathrm{R}}$ type

A	R, R'				
	H, Ph	$(CH_3)_2$	CH_3, C_2H_5	CH_3, Ph	Ph_2
Ferrocenyl [a]	121.5 (49.4)	158.6 (89.9)	160.6 (90)	158.6 [b] (86.7)	
Cymantrenyl [b]	144.5 (74.1)		193.1 (122.9)	184.2 (112.3)	201.0 (123.8)
Phenyl [c]	199.7 (123.5)	253.4 (180.3)	260 (187)	228.3 (157.8)	210.9 (131.5)
Cyclo-C_3H_5 [c]	225.4 (147.7)	279.6 (210.8)		245.3 (171.3)	234.1 (157.1)

[a] From [1,16,17]. [b] The data from this study. [c] From [19,34].

On the contrary, the $\Delta\delta$ values of C(1) in the formation of cymantrenyl and benzyl ions are only small and depend indefinitely on the substituents.

As has been pointed out above, the properties of the metallocenylcarbenium ions under consideration, especially the ferrocenyl ions, differ essentially from the properties of the phenyl and cyclopropylmethyl cations. Nevertheless, the qualitative difference established by us in the behaviour of the key carbon atom of the rings suggests analogy between ferrocenyl and cyclopropylmethyl ions, and cymantrenyl and benzyl ions. Probably, this can be explained by the similarity of the mechanisms by which the adjacent carbenium centre is stabilized by cymantrenyl and phenyl radicals on the one hand, and the ferrocenyl and cyclopropyl radicals on the other. Without discussing those mechanisms by which phenyl and cyclopropyl groups delocalize the positive charge [24], we shall only point out that, in the latter case the formation of σ-bridges is essential.

It may be supposed that the $\Delta\delta$ values for the key carbon atom of the cyclopentadienyl ring in metallocenyl ions reflect direct $M \rightarrow C^+$ interaction. An increase in these values indicates an increase in the role of σ-bonding in metallocenylcarbenium ions (of structure I).

TABLE 4

THE VALUES $\Delta\delta = \delta(\mathrm{ion}) - \delta(\mathrm{alc})$ (ppm) FOR THE KEY CARBON IN THE A-RADICAL OF THE CARBENIUM IONS OF THE $\mathrm{A{-}C^{+}}\!\!<^{\mathrm{R'}}_{\mathrm{R}}$ TYPE

A	R, R'					
	H, CH_3	H, Ph	$(CH_3)_2$	CH_3, C_2H_5	CH_3, Ph	Ph_2
Ferrocenyl [a]	12.5	7.1	1.2		−2.1 [b]	
Cymantrenyl [b]		−9.9		−16.3	−15.7	−14.7
Phenyl [c]	−6.5	−10.5	−11.3		−6.4	−9.3
Cyclo-C_3H_5 [c]	45.3	24.5	36.2		21.0	17.0

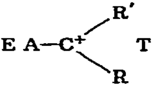
[a] From [1,17]. [b] The data from this study. [c] From [19].

An upfield shift of the signal due to the key atom C(1) and a simultaneous increase in the values of chemical shifts of C(2)—C(5) bring about a sharp decrease in the value of the range of chemical shifts for carbon atoms of the cyclopentadienyl ring in the cations IIIa—IIIe as compared to the corresponding values in the carbinol precursors IVa—IVe. As can be seen from Table 4, this range, for ferrocenyl- and cymantrenyl-carbenium ions and for the carbon atoms of the benzene ring in benzyl cations, decreases when going to more stable cations. However, the range of values of the chemical shifts for the carbon atoms of benzene rings associated with the carbenium centre in cymantrenyl- and ferrocenyl-carbenium ions was found to increase unexpectedly with an increase in their stability. In other words, with an increasing stability of phenyl-substituted metallocenyl carbocations the extent to which phenyl radicals participate in stabilizing the positive charge increases. Evidence in support of this can be found in the behaviour of the δ and $\Delta\delta$ values for carbon in the *p*-position of phenyl radicals in benzyl, ferrocenyl and cymantrenylmethyl ions *. In the first case the δ and $\Delta\delta$ values systematically decrease, while in the last two cases they only change a little and even grow with an increase in the stability of the cations (Table 5).

The observed diastereotropism for the pairs of carbon atoms in positions 2 and 5 (as well as 3 and 4) of the Cp-ring in the unsymmetrically substituted ions, IIIa and IIIc, is indicative of hindered rotation about the C(1)—C$^+$ bond. A similar phenomenon was also shown to take place in the series of ferrocenylmethyl [1,16—18] and benzyl [19,21(b),29] cations, though for the latter type

TABLE 5

THE RANGE OF CHEMICAL SHIFTS (ppm) FOR CARBON ATOMS OF CYCLOPENTADIENYL (Cp) AND BENZENE (C_6H_5) RINGS AND δC_p AND $\Delta\delta C_p$ (IN PARENTHESES) VALUES FOR THE CARBENIUM IONS OF THE



$\text{A—C}^+(\text{R})(\text{R}')$

TYPE

A	R, R'	Range of Cp-ring	Range of C_6H_5-ring	δC_p	$(\Delta\delta C_p)$
Ferrocenyl [a]	$(CH_3)_2$	22.5			
Ferrocenyl	CH_3, C_2H_5	21.9			
Ferrocenyl	H, Ph	21.7	3.5	133.4	(6.0)
Ferrocenyl	CH_3, Ph [b]	20.9	10.7	133.3	(7.4)
Cymantrenyl [b]	CH_3, C_2H_5	7.1			
Cymantrenyl	H, Ph	7.4	7.2	137.3	(9.4)
Cymantrenyl	CH_3, Ph	6.1	7.3	136.6	(9.3)
Cymantrenyl	Ph_2	1.4	9.5	138.0	(10.3)
Phenyl [c]	$(CH_3)_2$		22.6	155.0	(27.7)
Phenyl	H, Ph		17.2	150.0	(21.8)
Phenyl	CH_3, Ph		16.6	147.2	(19.4)
Phenyl	Ph_2		12.8	143.1	(15.4)

[a] From [1,16,17]. [b] The data from this study. [c] From [19].

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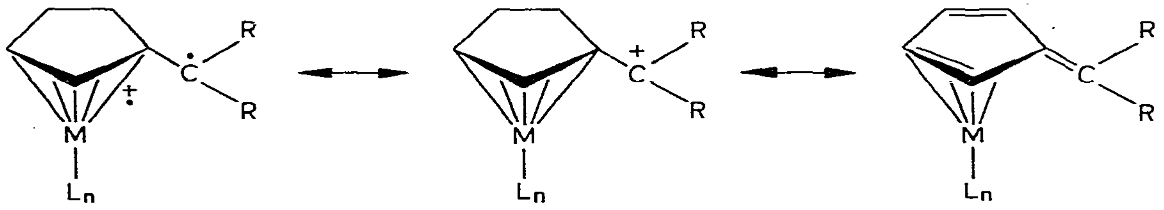
* As shown in [21(b)], the δ value for C_p is in good correlation with the full and π-charge density on this atom, obtained by the CNDO/2 method. With an increasing stability of the cation, the δ value for C_p and the charge density on C_p diminish.

of ions, this phenomenon is observed at substantially lower temperatures. Moreover, at low temperatures magnetic nonequivalence is observed for symmetrical carbenium ions as well: the benzhydryl [19], diphenylcyclopropyl- [19] and diferrocenylmethyl [30] ions. From these data it follows that the observed diastereotropism in metallocenyl ions rules out a choice between structures with direct metal—carbenium centre interaction and those without it. Nevertheless, there data are indicative of a greater hindrance to rotation about the exocyclic bond in metallocenylcarbenium ions.

Stabilization mechanism

Proceeding from the data reported here and taking into account the results obtained in numerous investigations on metallocenyl carbocations (see the references cited in [2,3,31]), we put forward the following concept of the mechanism by which metallocenyl radicals stabilize the adjacent carbenium centre.

The ground state of α-metallocenylcarbenium ions can be described by structures X, XI and XII, with the exocyclic bond inclined towards the metal atom. The contribution of these structures to that of a particular ion is dependent on a number of factors; on the nature of the metal, its ligands and the number, volume and donor properties of substituents in the ring and at the C$^+$ atom. When the carbenium centre approaches the plane of the cyclopentadienyl ring, the contribution made by structure X with the direct metal—carbenium centre interaction diminishes and the contribution made by structures XI and XII increases.



(X)
(singlet state)

(XI)

(XII)

In particular, an increase in the δ and $\Delta\delta$ values for C$^+$, up to these observed in benzyl ions, when going from primary to secondary and tertiary metallocenylcarbenium ions can be explained by an increase in steric interactions. The result of this increase is that a smaller contribution is made by structure X and, consequently, a greater similarity between the stabilization mechanisms in metallocenyl- and benzyl-carbenium ions exists.

The change in the contribution made by structures X, XI and XII in the ground state of the different ions is, evidently, one of the reasons why the influence of substituents at the C$^+$ atom on the thermodynamic stability of metallocenyl ions is small (see Introduction). An increase in the number of donor substituents at the carbenium centre leads, because of steric hindrance phenomena, to a decrease in the effective stabilization of the ion by the $M \rightarrow C^+$ interaction.

The fact that the $\Delta\delta$ value for the key carbon atom of the Cp-ring, when going from ferrocenyl- to cymantrenyl-carbeniums having a similar structure, approximates the $\Delta\delta$ values in benzyl cations, shows that the replacement of the group FeC_5H_5 by a weaker donor group $Mn(CO)_3$ also leads to an increase in the contribution made by structures XI and XII. Evidently, as follows from the data reported in [32,33], in ruthenocenyl- and osmocenyl-carbenium ions direct $M \rightarrow C^+$ interaction is of greater importance than in ferrocene derivatives.

Our concept of the stabilization mechanism is confirmed not only by the data mentioned above, but also by data obtained in the X-ray investigations of the diferrocenylmethyl [30] and diphenylferrocenylcyclopropenyl [34] cations. The data from such investigations indicate a noticeable departure of the carbenium centre from the plane of the associated cyclopentadienyl ring. For the first cation, the angle of inclination of C^+ to iron and the length of the $Fe{-}C^+$ bond are 19.9° and 2.71 Å for one radical and 17.7° and 2.85 Å for the other. In the second cation, evidently because of considerable steric hindrance phenomena between the cyclo-C_3Ph_2 fragment and the ferrocenyl radical, the observed distortion of the exocyclic bond is smaller, 5° and 2.96 Å *.

The proposed mechanism offers a good explanation of the facts relating to the properties of metallocenylcarbenium ions described in the literature. In particular;

(a) In the series of methylalkylferrocenylcarbenium ions $Fc{-}\overset{+}{C}(R)CH_3$, introduction of more bulky R substituents, must increase, because of steric hindrance phenomena, the contribution of structures XI and XII and weaken the $Fe \rightarrow C^+$ interaction (X), i.e. increase the positive charge on the C^+ atom. Indeed [1,16], the δ value for C^+, which is associated with the empirical value of the charge on the C^+ atom by the relation $q = 1 - (\delta + 135)/160$ [35], increases sharply in the series CH_3 (δ 158.6) $<$ C_2H_5 (δ 160.6) $<$ iso-C_3H_7 (δ 178.0) $<$ t-C_4H_9 (δ 195.6 ppm). At the same time, only small downfield shifts are observed for the key carbon atom of the Cp-rings (C(1) $\Delta\delta$ 2—0.8 ppm). For similar benzyl cations [36] the δ values for C^+ increase in the same series. However, the value of these changes is only δ 19 ppm, whereas in the case of ferrocenyl ions it is equal to δ 40 ppm.

(b) The data concerning the rotational barrier about the exocyclic bond in ferrocenylcarbenium ions indicate that the degree of double bonding in it is small. The value of the rotational barrier ($H^{\neq}$) for the tertiary cation proves to be 15—20 kJ/mol less than for secondary ions [32]. These data are indicative of a decrease in the distortion of the exocyclic bond (because of steric factors) and, as a consequence, of a decrease in the $Fe \rightarrow C^+$ interaction as compared with the secondary ions. Indeed, if in these ferrocenyl ions distortion of the exocyclic bond were absent, then the rotational barrier in the case of tertiary ions would have become the same as or even greater than for the secondary ions [37,38].

(c) In the polarographic reduction of benzyl cations [39] the value $E_{1/2}$ monotonically decreases with an increase in the thermodynamic stability of the cations. A different picture is observed in the case of carbenium ions of the type $Fc{-}\overset{+}{C}H(R)$ [40], whose polarographic behaviour is similar to that of benzyl

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[*] These parameters are calculated by us from the data reported in [34]. In the original, the value of 14.6° given for this angle is, evidently, erroneous. This value is equal to that of the dihedral twist angle.

cations. With an increase in the stability of the cations the reduction potential value (v) changes non-monotonically: R(v): H (—0.85); CH_3 (—1.06); Ph (—0.69); Fc (—1.0). Such a change of $E_{1/2}$ is probably also associated with smaller distortion of the C(1)—C^+ bond in the ions Fc—$\overset{+}{C}$H(R) where R = Ph and Fc and with an increase in the contribution made by structures XI and XII in these ions as compared with the first two ions.

Experimental

The synthesis and porperties of the alcohol precursors IVa—IVe and V—OH are described in [4]. Carbenium ions were generated by adding a corresponding alcohol sample to cooled concentrated H_2SO_4 (or CF_3COOH) while stirring in an argon atmosphere. ^{13}C NMR spectra were recorded on a Brucker HX-90 spectrometer.

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