Journal of Organometallic Chemistry, 121 (1976) 381—389

METALLOCENYL CATIONS

III *. CYMANTRENYL CARBENIUM IONS CONTAINING ONE PHOSPHINE LIGAND

A.G. GINZBURG *, V.N. SETKINA, P.V. PETROVSKII, Sh.G. KASUMOV, G.A. PANOSYAN and D.N. KURSANOV

Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow, 117813, Vavilova 28 (U.S.S.R.)

(Received May 11th, 1976)

Summary

A number of carbinols, cyclopentadienylmanganese tricarbonyl derivatives of general formula $(CO)_2LMnC_5H_4C(OH)RR'$ (I) (L = PPh_3 or $P(isoC_3H_7)_3$, R and R' = H, Me, Et, Ph) have been synthesised. In solution, in the presence of CF_3COOH they form stable secondary and tertiary carbenium ions, stabilised by the $(CO)_2LMnC_5H_4$ group. IR spectra and ^1H and ^{13}C NMR spectra of the carbenium ions were recorded. Substitution of a tertiary phosphine for a carbonyl group sharply increased the stability of the α-cymantrenylcarbenium ions.

Introduction

The unusually high stability of α-ferrocenylcarbenium ions has been studied previously, however metallocenylcarbenium ions stabilised by other metallocenyl groups have received comparitively less attention. It is only recently that a systematic investigation of cations containing cymantrene [1—3] and benzenechromium tricarbonyl [4,5] units has begun. It is evident that comparison of the properties of cations stabilised by metallocenyl units containing different central atoms and ligands, should clarify the nature of stabilisation of the cation centre in metallocenyl carbenium ions. Previously we have reported the formation of stable carbenium ions containing cymantrene units in solution [1]. In the present work, which is part of a systematic study of the effect of ligand substitution on the properties and reactivity of manganese π-cyclo-

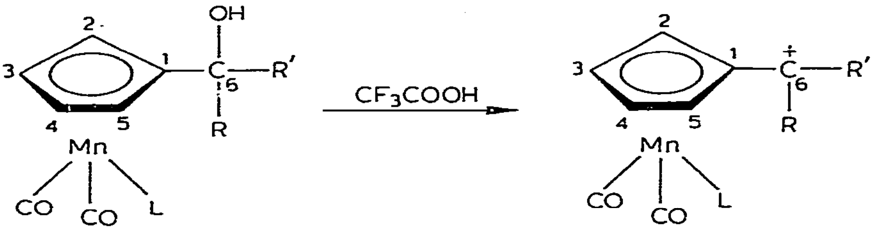
---

[*] Parts I and II, see ref. 1, 2.

pentadienyl complexes we investigated the preparation and properties of carbenium ions stabilised by $(CO)_2LMnC_5H_4$.

Results and discussion

Dissolution of carbinols Ia—Ig with various R and R′ radicals in CF_3COOH/CH_2Cl_2 mixtures leads to the formation of stable (in air), dark-red (with the exception of dark-green IIf) solutions of the corresponding cymantrenyl-carbenium ions IIa—IIg. Carbinol conversion to carbenium ions is accompanied by distinct and sharp changes in IR and NMR spectra.



(I) (II)

IR spectra

In accordance with local C_s symmetry, the $Mn(CO)_2L$ group gives two absorption bands in the $\nu(CO)$ region for all carbinols Ia—Ig. Formation of the carbenium ion shifts both $\nu(CO)$ bands by 70—90 cm^{-1} to higher wave numbers (Table 1). The considerable shift of $\nu(CO)$ frequencies shows that the positive charge in carbenium ions effectively delocalises via the cyclopentadienyl ring and the metal atom, producing a noticeable weakening of the dative contribution to the Mn—CO bond, with an increase in the contribution of structure B, as compared to the initial carbinols:

$$\underset{(A)}{Mn{=}C{=}O} \leftrightarrow \underset{(B)}{Mn^{-}{-}C{\equiv}O^{+}}$$

The frequency shift $\Delta\nu$, caused by the formation of type II carbenium ions is smaller than shifts in the same direction caused by protonation of the central manganese atom in neutral $C_5H_5Mn(CO)_2PR_3$ complexes ($\Delta\nu$ 100—130 cm^{-1}) [6,7]. Since for protonation, the reactive site (i.e. the central manganese atom), is nearer the Mn—CO bonds than the carbenium centre in the α-position of the side chain, the increase in contribution of structure B is evidently greater for protonation.

Formation of type II cations from their carbinol precursors is a reversible reaction and the equilibrium is highly sensitive to the nature of R and R′ radicals and the acidity of the medium. For example, carbinol Ia is in equilibrium with cation IIa in 100% CF_3COOH (bands of both forms are present in the $\nu(CO)$ region although the equilibrium is considerably shifted towards the cation). Carbinols Ib—Ie and Ig are practically completely converted into the

TABLE 1

THE IR SPECTRA OF CARBINOLS Ia—Ig AND THE CORRESPONDING CYMANTRENYLCARBENIUM IONS IIa—IIg

Compound	R, R'	ν(CO) frequencies (cm^{-1})								
		In CH_2Cl_2 carbinol		In CF_3COOH/CH_2Cl_2 mixture (v/v)	carbinol		cation		$\Delta\nu$(CO)	
		ν(as)	ν(s)		ν(as)	ν(s)	ν(as)	ν(s)		
Ia, IIa	H, Me	1865	1932	1 : 4	1878	1940	1975	2022	98	80
				1 : 1	1880	1945	1978	2025		
				CF_3COOH	[a]	1950	1980	2030		
Ib, IIb	Me, Me	1865	1932	1 : 20	1872	1935	1962	2008	90	73
				1 : 10			1963	2010		
Ic, IIc	Et, Et	1860	1930	1 : 20	1865	1931	1960	2005	95	74
				1 : 10			1960	2006		
Id, IId	H, Ph	1868	1932	1 : 50	1872	1940	1972	2017	100	77
				1 : 10			1972	2018		
Ie, IIe	Me, Ph	1865	1932	1 : 100	1870	1934	1960	2005	90	71
				1 : 10			1961	2007		
If, IIf	Ph, Ph	1870	1935	1 : 100			1967	2010	97	75
							1950 sh	1988	80	53
				1 : 10			1967	2010		
							1950 sh	1988		
Ig, IIg L = P-(iso-$C_3H_7)_3$	Me, Me	1850	1920	1 : 100	1855	1922	1952 br	1998	97	
								2040		
				1 ;10			1955 br	1998		
								2040		

[a] ν(asymm) CO band is distorted by CF_3COOH absorption; sh - shoulder; br - broad; all other bands are *narrow and very intense.*

corresponding cations at CF_3COOH/CH_2Cl_2 ratios in 1 : 10. According to IR spectral data, equilibrium between I and II in this case is observed at ratios of 1 : 20—1 : 50. Cation IIf (R = R' = Ph) is thermodynamically the most stable and is the most easily formed. Ionization of carbinol If is practically complete even at a CF_3COOH/CH_2Cl_2 ratio of I : 100.

IR spectra of the carbenium ions IIf and IIg have more than two bands in the region of ν(CO) frequencies: four bands for IIf; one wide (1952 cm^{-1}) and two narrow absorption bands for IIg (see Fig. 1). The position of one pair of IIf bands (1967, 2100 cm^{-1}) is similar to that of cations IIa—IIe, while the other pair (1950 sh and 1988 cm^{-1}) is shifted by 20 cm^{-1}. Apparently the bulky L groups hinder free rotation of the positively charged —CR_2^+ substituents in relation to the phosphine ligand in these cations and consequently two or more conformers with different energies and ν(CO) frequencies may be formed. In the IIa—IIf sequence (L = PPh_3), free rotation is hindered only for IIf, where R = R' = Ph; in IIe, (R = Me, R' = Ph) rotation is unhindered. For the P(iso-$C_3H_7)_3$ ligand which is sterically more hindered than PPh_3, steric effects are observed in the IIg cation, where R = R' = Me. Rotation in the initial carbinols

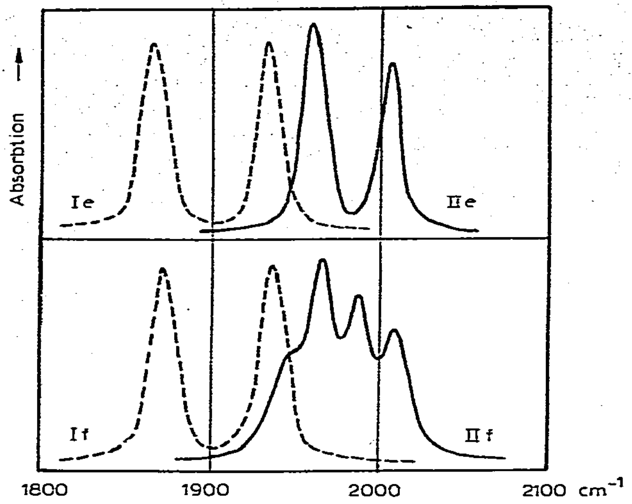


Fig. 1. IR spectra in CO stretching frequencies region of the carbinols (dotted line) and carbenium ions (full line); upper spectra, Ie and IIe; lower spectra, If and IIf.

is free and in all cases only two ν(CO) frequencies are observed. The fact that hindered rotation is only observed in the cations indicates an increase in steric barriers in passing from carbinol to cation and may be considered as an argument in favour of Gleiter's model [8], according to which, in metallocenylcarbenium ions the charged substituent is displaced from the plane of the cyclopentadienyl ring towards the metal atom.

The strong stabilising effect of donor ligands such as PPh_3 and other tertiary phosphines on the carbenium centre in the side chain is shown by the fact that carbinols Ia—Ig form carbenium ions considerably more easily and at lower acidity than their unstubstituted tricarbonyl analogues. For instance, carbinol $(CO)_3MnC_5H_4C(OH)(H)Me$ practically does not form the corresponding secondary carbenium ion in pure CF_3COOH whereas carbinol Ia with the same R and R' but with the $(CO)_2PPh_3MnC_5H_4$ group, according to IR data, is ionized to a degree of 80—90%.

PMR spectra

PMR spectra of Ib—If carbinols (Table 2) show an OH proton signal in the region of δ 2—3 ppm and two multiplets corresponding to α- and β-protons of the cyclopentadienyl ring with chemical shifts of δ 3.7—3.9 and 4.5—4.7 ppm. Multiplicity of the signals is due to spin—spin coupling of α- and β-protons with each other and with ^{31}P, the values of $J[H(\alpha)—H(\beta)]$ and $J(^{31}P—^1H)$ constants are close and do not exceed 1.5—2 Hz. For carbinols Id and Ie which have a chiral centre at the carbon atom in the side chain, α- and β-protons are not equivalent and the spectra has one two-proton signal (in high field) and two one-proton multiplets (in low field). For Ia carbinol diastereotopic nonequivalence is practically absent in the PMR spectra.

With formation of carbenium ions the OH signal disappears and the α- and β-proton multiplets and signals from the alkyl groups are shifted downfield as should be expected with the appearance of a positive charge. A slight

TABLE 2

THE PMR SPECTRA OF CARBINOLS Ib—If AND CYMANTRENYLCARBENIUM IONS IIb—IIf (δ, ppm)

Compound	R and R'	OH carbinol in $CHCl_3$	Cyclopentadienyl ring			Alkyl groups		
			carbinol	cation	Δδ ppm	carbinol	cation	Δδ ppm
Ib, IIb	Me, Me	2.05	3.80 4.57	5.00 6.26	1.2 0.69	1.53	2.28	0.75
Ic, IIc	Et, Et	~2	3.86 4.69	5.22 5.52	1.36 0.83	1.69 (CH_2) 0.84 (CH_3)	2.37 1.1	0.68 0.26
Id, IId	H, Ph	2.32	3.75 4.11 4.50	5.00 5.45 5.82	[a]	5.15 (CH)	—	—
Ie, IIe	Me, Ph	2.25	3.75 4.57 [b]	5.07 5.36 [b]	1.38 0.79	1.87	2.55	0.68
If, IIf	Ph, Ph	3.12	3.73 4.49	5.22 [c]	1.50 0.73	—	—	—

[a] Assignment of α- and β-proton signals was not carried out. [b] Average values from 4.65 and 4.50; 5.18 and 5.54. [c] α- and β-protons exhibit only one signal.

broadening of lines is observed in the spectra of cations, which is probably connected with the appearance of small quantities of paramagnetic Mn^{2+} derivatives. Shifts of α- and β-protons of the Cp-ring differ and are 1.2—1.3 ppm for the signal in the high field and 0.7 ppm in the low field. The shift of the α- and β-proton signals in cations II have the same direction and are close in value to the corresponding shifts in ferrocenyl cations. Chirality is retained in the corresponding cations as three separate Cp-ring proton signals are observed in the spectra.

In $^{13}C\{^1H\}$NMR spectra (Table 3) the cyclopentadienyl fragment with the CRR' substituent is characterised by the following set of signals: C(2—5) in achiral carbinols give two signals due to C(2,5) and C(3,4) equivalence while in chiral carbinols diastereotopy results in a separate signal for each C(2—5) carbon. The spectra also includes separate signals of C(1), C(6)—OH, alkyl and CO carbons.

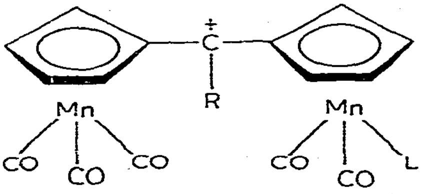
Formation of type II carbenium ions is accompanied by a downfield shift of C(2—5) and $C^+(6)$ signals (Δδ $^{13}C(6)$ +50 ppm for II a and IId secondary cations and ~ +90 ± 5 ppm for the tertiary cations). The signals of all other nuclei directly linked to the carbenium centre including resonance of C(1), methyl groups at $C(6)^+$, the key carbon of C_6H_5—$C(6)^+$ and the carbons of the Mn—CO groups are shifted upfield. The values and directions of shifts in the ^{13}C NMR spectra of cymantrenylcarbenium ions studied in the present work are in complete agreement with data obtained for a series of binuclear carbenium ions (III) [2] and for a series of the corresponding tricarbonyl cations (IV) [3].

TABLE 3

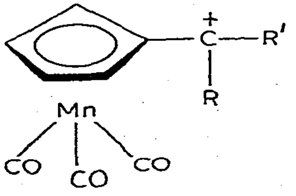
THE ^{13}C NMR SPECTRA OF CARBINOLS Ia—Ig AND THE CORRESPONDING CARBENIUM IONS IIa—IIg. CHEMICAL SHIFTS IN δ (ppm) FROM TMS [a]

Compound	R and R′	State	Cyclopentadienyl ring C (2–5)		C(1)	C(6)	Mn—CO	CH_3	Key atom of C_6H_5
Ia, IIa	H, Me	carbinol	84.1 83.6	80.6 80.0	108.2	64.6	232.9	24.2	—
		cation	104.9 103.9	95.0 93.1	99.8	115.8	223.0	18.5	
		Δδ			—8.4	+51.2	—9.9	—5.7	
Ib, IIb	Me, Me	carbinol	83.7	80.9	112.9	68.8	233.3	31.5	—
		cation	103.9	90.9	95.7	155.6	224.4	26.6	
		Δδ	20.2	10.0	17.2	+86.4	—8.9	—4.9	
Ic, IIc	Et, Et	carbinol	83.4	82.0	111.9	83.2	233.4	32.7 (CH_2)	8.0 (CH_3)
		cation	103.8	90.5	95.4	171.8	223.8	29.9	14.7
		Δδ	20.4	8.5	—16.5	+98.5	—9.4	—2.8	+6.7
Id, IId	H, Ph	carbinol	84.9 83.1	81.2 80.0	107.0	71.2	232.7	—	143.6
		cation	103.9 103.6	96.3 92.3	96.6	121.2	222.7		134.3
		Δδ			—11.4	+50.0	—10.0		—9.3
Ie, IIe	Me, Ph	carbinol	85.2 [a] 82.8	81.5 [a] 82.8	112.6	72.5	232.8	31.4	148.0
		cation	104.2 103.4	92.1 91.6	96.2	157.0	223.5	27.2	138.0
		Δδ			—16.4	+84.5	—9.3	—4.2	10.0
If, IIf	Ph, Ph	carbinol	84.8	84.1	110.2	77.7	231.9	—	147.0
		cation	102.0	93.1	100.0	168.8	224.3		138.4
		Δδ	17.2	9.0	10.2	+91.1	—7.6		—8.6
Ig, IIg	Me, Me	carbinol	81.3	78.8	112.2	68.9	235.0	31.3	—
		cation	99.1	89.6	95.5	155.1	225.8	26.6	
		Δδ	17.8	10.8	—16.7	+86.2	—9.2	—5.0	

[a] Spectra of carbinols were obtained in CH_2Cl_2: of cations in CF_3COOH/CH_2Cl_2 mixture (1 : 10), except for cation IIa which was obtained in a 1 : 1 mixture. Carbon signals of phosphine ligands are not included.
[b] Two of the four signals coincide.



(III)



(IV)

L = CO, PPh_3

^{13}C NMR spectra for various metallocenyl carbenium ions stabilised by ferrocene [9—11], cymantrene [2,3 and the present work], cyclobutadieniron tricarbonyl fragments [12] and with the cluster cobalt-containing $(CO)_9Co_3C$ fragment [13] have been reported. Despite considerable variation in the structure of metallocenyl units, ^{13}C NMR spectra of these cations have much in common: (1) the signal of the C^+ nucleus always shifts downfield and $\Delta\delta$ (cation)—(carbinol) increases in the sequence primary < secondary < tertiary cation and is considerably smaller than for purely organic carbenium ions; (2) signals of the cyclic π-ligand carbons are shifted downfield, $\Delta\delta$ 10—30 ppm; (3) alkyl and key phenyl carbon at C^+ are shifted upfield by δ 2—6 ppm for alkyl groups and δ 8—10 ppm for C_6H_5; (4) signals of the carbonyl M—CO [groups are shifted upfield by δ 7—11 ppm. These common features indicate similarity in the character of distribution of the positive charge between the —C^+RR' substituent and the metallocenyl groups. Variation of the shielding effect of the key C(1) atom is of great interest on account of the important role assigned to this atom in various models describing the nature of bonding in metallocenyl carbenium ions (see references in [14]). These models assume significant change in the geometry of the cyclic π-ligand and/or of the exocyclic C_5H_4—C^+ bond. Evidently, the shift observed with formation of cations is an overall value that includes change of both electronic and geometry factors (variation of hybridisation and of valence angles at C(1)). In iron-containing cations (ferrocenyl cations and cations of cyclobutadieniron tricarbonyl) C(1) shielding decreases and C(1) signals are shifted downfield ($\Delta\delta$ from δ 0.8—12 ppm [9—12]). At the same time, in cations of the cymantrene series C(1) signals are shifted in the opposite direction (from —8 to —20 ppm [2,3]). So far no satisfactory explanation of this difference in the direction of shift has been proposed.

Comparison of the ^{13}C NMR spectra of cations II and of their tricarbonyl analogues IV [3] shows that substitution of PPh_3 for CO does not lead to sharp qualitative changes in the distribution of positive charge, the direction and values of shifts are similar for similar nuclei. For cations with the $Mn(CO)_3$ unit, $\Delta\delta$ of $^{13}C(6)^+$ is slightly higher than for cations with $Mn(CO)_2PPh_3$ groups studied in the present work: R = H, R' = Ph, δ +74.1 and +50.0; R = Me, R' = Ph +112.3 and +84.0; R = Ph, R' = Ph +123 and +91 ppm (the first value corresponds to data for $Mn(CO)_3$ obtained in [3]). This may be explained by the fact that the more donor $Mn(CO)_2PPh_3$ group is capable of delocalising a larger part of the positive charge than $Mn(CO)_3$.

Conclusions

The data obtained show that cymantrenylcarbenium ions with the $Mn(CO)_2$-PPh_3 group are very stable and exist even at low acidity. Substitution of a CO group for a tertiary phosphine considerably increases stability of cymantrenylcarbenium ions. As in other metallocenyl cations, the positive charge in cymantrenyl cations is extensively delocalised throughout the system including cyclopentadienyl rings and carbonyl groups (data from IR spectra and shifts of ^{13}C NMR signals). The carbinol $\rightleftharpoons$ cation equilibrium can be studied using IR spectrscopy by observing the ν(CO) shifts.

Experimental

Synthesis of carbinols I

Secondary and tertiary $(CO)_3MnC_5H_4C(OH)RR'$ carbinols were prepared from acetyl-, propionyl- or benzoyl-cymantrene by reduction with $LiAlH_4$ in ether or by reaction with R'MgX. For photochemical substitution of CO 3 mmol of the corresponding carbinol and 3 mmol of L in 50—60 ml of benzene were irradiated by UV at boiling or room temperature for 4—12 h. IR spectra were recorded during the reaction. After completion, the red solution was filtered through a fine filter and solvent was evaporated in vacuum. The remaining dark-red oil was triturated with 5 ml portions of hexane until the hexane extract was no longer tinted red. Yellow crystals formed and were recrystallized from a benzene/hexane (1 : 3) mixture in an argon atmosphere, the hot solution was filtered and left to crystallize at 0° C. The yield of carbinols were 50—60%. Satisfactory analytical data were obtained and molecular masses (mass-spectroscopic data) were deteremined for all compounds. The following metling points were obtained: Ia, 90—92° C; Ib, 140—142° C; Ic, 146—148° C; Id, 148—150° C; Ie, 162—164° C; If, 195—196° C.

Spectral data

IR spectra were recorded on a Zeiss UR-20 spectrophotometer with a LiF prism in 0.1 mm NaCl cells. PMR spectra were obtained on a Perkin—Elmer R-20 spectrometer (60 MHz). To record the cation spectra the necessary amount of CF_3COOH was added to a NMR ampoule containing a solution of the corresponding carbinol in $CHCl_3$ with cyclohexane as internal standard. $^{13}C\{^1H\}$ NMR spectra were obtained in the pulsed Fourier transform mode utilizing a Bruker HX-90 spectrometer. To obtain cation spectra the necessary amount of CF_3COOH was added to the ampoule with the carbinol solution in CH_2Cl_2; ^{13}C chemical shifts were referenced to tetramethylsilane. Assignment of C(1) and C(6) signals of secondary carbinols and carbenium ions was based on comparison with $^{13}C—^1H$ coupled and decoupled spectra. The $C^+(6)$ signal is split into a doublet with ($^{13}C—^1H$) 169—170 Hz. The spectra of Ia, Ib and Ig obtained in the presence of acid contain, in addition to the set of signals produced by the cations IIa, IIb and IIg, other signals appearing after several hours. These probably correspond to products of fragmentation and further conversion of cations (II), formed in small quantities. Formation of carbenium ions (II) is reversible and decomposition of their solutions with water leads to formation of the initial carbinols (I), and/or the corresponding olefines.

References

1 A.G. Ginzburg, V.N. Setkina and D.N. Kursanov, J. Organometal. Chem., 77 (1974) C27.
2 A.G. Ginzburg, V.N. Setkina, Sh.G. Kasumov, P.V. Petrovskii, G.A. Panosyan and D.N. Kursanov, Dokl. Acad. Nauk, USSR, 228 (1976) 1386.
3 N.M. Loim, P.V. Petrovskii, V.I. Robas, Z.N. Parnes and D.N. Kursanov, J. Organometal. Chem., 117 (1976) 265.
4 D.Seyferth and C.S. Eschbach, J. Organometal. Chem., 94 (1975) C5.
5 M. Acampora, A. Cesson and M. Dal Farra, J. Chem. Soc., Chem. Commun., (1975) 871.
6 N.V. Lokshin, A.G. Ginzburg, V.N. Setkina, D.N. Kursanov and I.B. Nemirovskaya, J. Organometal. Chem., 37 (1972) 347.

7 A.G. Ginzburg, P.O. Okulevich, V.N. Setkina, G.A. Panosyan and D.N. Kursanov, J. Organometal. Chem., 81 (1974) 201.
8 R. Gleiter and R. Seeger, Helv. Chim. Acta, 54 (1971) 1217.
9 G.H. Williams, D.D. Traficante and D. Seyferth, J. Organometal. Chem., 60 (1973) C53.
10 S. Braun and W.E. Watts, J. Organometal. Chem., 84 (1975) C33.
11 G.A. Olah and G. Liang, J. Org. Chem., 40 (1975) 1849.
12 C.S. Eschbach, D. Seyferth and P.S. Reeves, J. Organometal. Chem., 104 (1976) 363.
13 D. Seyferth, G.H. Williams and D.D. Traficante, J. Amer. Chem. Soc., 96 (1974) 604.
14 A.A. Koridze, P.V. Petrovskii, S.P. Gubin and E.I. Fedin, J. Organometal. Chem., 93 (1975) C26.