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METALLOCENYL CATIONS

IV *. CYMANTRENYL CARBENIUM IONS CONTAINING TWO PHOSPHINE LIGANDS

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Summary

Cymantrene carbinols (I) with two phosphine ligands (PP) have been synthesized. Carbinols I (where PP is the chelate diphosphine $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2CH_2CH_2PPh_2$) form the corresponding carbenium ions (II), stabilized by manganese, in the presence of CF_3COOH. The phosphorus atoms of the chelate diphosphine ligands become non-equivalent in the carbenium ions. IR spectra and ^{31}P and ^{13}C NMR spectra have been recorded, and the nature of the non-equivalence and of the structure of cymantrenyl carbenium ions are discussed. In the presence of CF_3COOH carbinols I (where PP = $2PMe_2(C_6H_4CH_3\text{-}p)$ or $2PPh_2Me$) are protonated at the metal atom.

Introduction

Stabilization of the cationic center by the ferrocene moiety and the structure of ferrocenylcarbenium ions is still receiving considerable attention. Recently we began a study of carbenium ions containing metallocenyl groups other than ferrocenyl [1—3] and so, together with other authors [4], we are carrying out a systematic investigation of carbenium ions stabilized by cymantrene units.

The stability of cymantrenylcarbenium ions is considerably affected by the ligand environment of the manganese atom, e.g. replacement of one CO group by a phosphine ligand substantially increases their stability [3]. In the present work we synthesized cymantrenylcarbenium ions containing two phosphine ligands and studied their properties by NMR and IR spectroscopy.

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* Part III, see ref. 3.

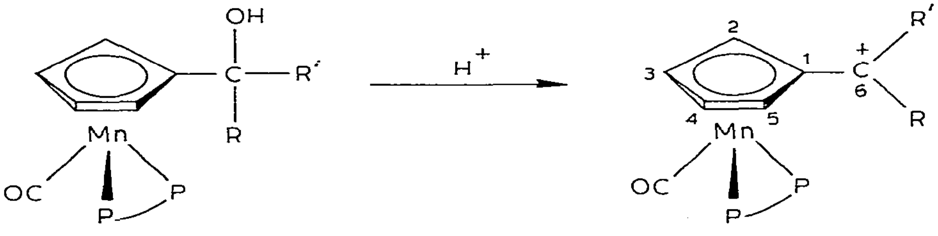
TABLE 1

^{31}P NMR CHEMICAL SHIFTS AND $\nu(CO)$ FREQUENCIES OF CARBINOLS I (IN CH_2Cl_2) AND CARBENIUMS IONS II (IN CF_3COOH/CH_2Cl_2)

Compound No.	R, R'	Melting point of carbinol (°C)	^{31}P NMR chemical shifts (downfield from 85% H_3PO_4) (ppm)				$J(P-P)$ (Hz)		$\nu(CO)$ frequencies (cm^{-1})	
			Carbinol	Carbenium ion		$\Delta\delta(P_1-P_2)$	Carbinol	Cation	Carbinol	Cation
				P_1	P_2					
			$(PP) = Ph_2PCH_2CH_2PPh_2$							
1	Me, Me	134–136	114.0	105.2	88.8	16.4		26.5	1833	1935
2	Et, Et	128–132	113.5	104.3	86.9	17.4		27	1830	1920
3	Ph, Ph	175–177	112.5	103.6	80.0	23.6		17	1830	1910
4	H, Me	170–172	114.1	98.2	90.5	7.7		35	1825	1935
5	H, Ph	174–176	115.0	98.0	87.0	11.0		39	1825	1940
			113.9							
6	Me, Ph	163–165	114.5	105.3	86.5	18.8	19.6	24	1825	1925
			111.9	103.9	86.0	17.9		27		
7	Et, Ph	98–100	115.6	105.7	88.1	17.6	20	27	1835	1930
			114.6	107.4	88.9	18.5		24.5		
8	CH_2Ph, Ph	165–168	114.5	103.3	85.3	18.0	20	27	1825	1925
			111.4	104.6	85.7	18.9		27		
			$(PP) = Ph_2PCH_2CH_2CH_2PPh_2$							
9	H, Me	160–163	79.3	58.1	48.6	9.5		68	1820	1920
10	Et, Et	173–174	77.7	68.2	43.1	25.1		68	1810	1905
11	Ph, Ph	182–185	81.0	70.5	35.0	35.5		80.5	1810	1890
12	Me, Ph	185–188	81.6	68.4	35.5	32.9		78	1825	1915
13	Et, Ph	155–160	76.3	67.2	34.5	32.7		88	1810	1895

Results and discussion

Dissolution of carbinols I (where PP is the chelate diphosphine ligand $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2CH_2CH_2PPh_2$) in CF_3COOH/CH_2Cl_2 mixtures leads to the formation of cymantrenylcarbenium ions II. Cations II containing two phosphine ligands are much more stable than the monophosphine cations: according to IR data, all carbinols I, including the carbinol with R = H and R′ = Me, are completely ionized at a CF_3COOH/CH_2Cl_2 ratio of 1/100, whereas carbinol $(CO)_2PPh_3MnC_5H_4CH(OH)Me$ is not fully ionized even at much higher acidity (1/4 ratio) [3].



(I) (II)

The stability of cations II also depends on the nature of the substituents at the carbenium center. Quenching of solutions of cations II, where R and R′ = H or alkyl, or where R or R′ = Ph, with water immediately leads to the formation of the initial carbinols I or of their mixture with the corresponding olefins (if R or R′ is alkyl). The only exceptions are cations II where R = R′ = Ph. These cations are the most stable of those studied and their solutions in CF_3COOH/CH_2Cl_2 are only slowly decomposed by water (10—20 h). Therefore the presence of two donor phosphine ligands and two Ph substituents considerably increases the stability of the cations.

Conversion of carbinols I into cations II is accompanied by a 80—110 cm^{-1} shift of the $\nu(CO)$ bands to higher frequencies in the IR spectra, indicating the appearance of a positive charge and weakening of the dative contribution to the Mn—CO bond. However, the IR spectra of diphosphine complexes are less informative than those of monophosphine complexes [3] since there is only one $\nu(CO)$ band, which is rather broad in CH_2Cl_2 solutions ($\Delta\nu_{1/2}$ 50—60 cm^{-1}). For these cases the ^{31}P and ^{13}C NMR spectra are of more interest.

In the ^{31}P NMR spectra of the initial carbinols the two phosphorus atoms of the $Ph_2PCH_2CH_2PPh_2$ ligand are either equivalent (when R = R′ = Me, Et, Ph) and exhibit one signal, or form an AB spin system, when R ≠ R′ and there is a chiral center in the side chain of the carbinol. For carbinols containing the $Ph_2PCH_2CH_2CH_2PPh_2$ ligand the phosphorus atoms, independently of R and R′, give one singlet (at temperatures up to —60 to —70°C). On addition of trifluoroacetic acid to the solutions of the carbinols in CH_2Cl_2 the pattern of the ^{31}P spectra changes sharply. The signals are shifted upfield and the phosphorus nuclei become non-equivalent. For compounds **1**—**3** (Table 1) when R = R′ the ^{31}P NMR spectra of cations have one multiplet, typical of an AX spin pattern. When R ≠ R′ (compounds **6**—**8**) the spectra display two multiplets, typical of two AX spin systems (Fig. 1). The presence of two AX systems in the spectra

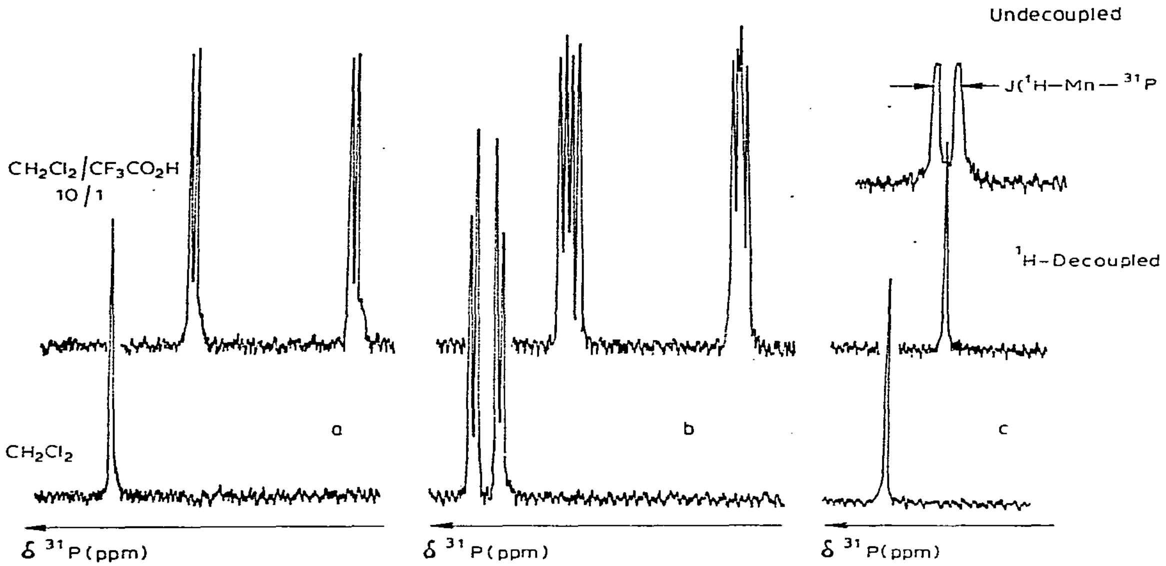
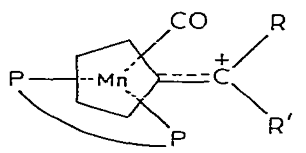
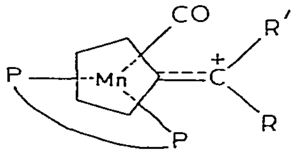


Fig. 1. ^{31}P NMR spectra of carbinols/carbenium ions (a) compounds 1—4 and 9—13, and (b) compounds 6—8; and carbinols and their protonated forms (c) compounds 14—21. Lower traces show the initial compounds in CH_2Cl_2, the upper traces were measured in CF_3COOH/CH_2Cl_2.

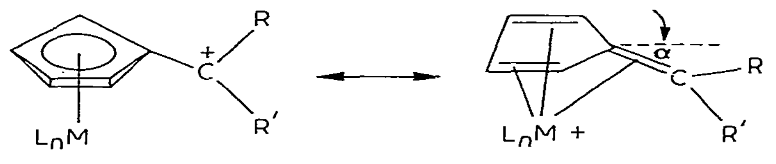
of cations 6—8 corresponds to the formation of two isomeric forms of carbenium ions when R ≠ R′. The isomers differ in the orientation of substituents R and R′, and their mutual transfer, determined by the rotation barrier about the exocyclic bond, is slow on the ^{31}P NMR time-scale for the $Ph_2PCH_2CH_2$-PPh_2 ligand (at —30 to —40°C).





For compounds 4 and 5, where R or R′ = H, and for compounds 9—13 with the ligand $Ph_2PCH_2CH_2PPh_2$, spectra of the cations exhibit only one AX multiplet. The absence of two AX spin systems may be explained by the fact that mutual transfer between isomers is fast for these compounds at —30 to —40°C.

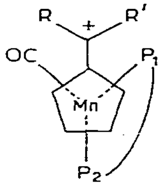
The presence in the initial carbinols of only one singlet from both phosphorus atoms indicates their equivalence. Consequently the substituent —C(OH)-RR′ does not hinder rotation of the metal—carbonyl fragment Mn(CO)(PP) about the axis passing through the Mn atom and the center of the cyclopentadienyl (Cp)ring. It is now accepted that the structure of metallocenyl carbenium ions may be described, within the framework of the resonance theory, by the two principal limiting structures III and IV (see refs. 4—6 and references therein):



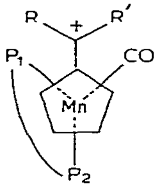
(III) (IV)

Structure III is similar to an organic carbenium ion: in the fulvene structure IV the =CRR′ substituents is tilted away from the cyclopentadienyl plane and is displaced towards the metal atom. Evidently the contribution of each structure depends on the nature of R and R′, on the presence or absence of substituents in the Cp ring and on the nature of the central atom and its ligand environment. (An assumption of direct interaction of atom M with the carbenium center has been criticised recently [5]*.) Quantum mechanical calculations on the unsubstituted ferrocenyl cation [7] and recent calculation on $(CO)_3CrC_6H_5$-CH_2^+[8] agree with the proposed models: in both cases calculations show that the minimum energy corresponds to structures with noticeable tilting of the exocyclic bond towards the iron or chromium atom (by an angle α of ~40°).

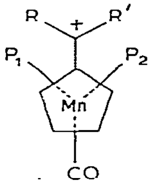
The most probable explanation of the observed non-equivalence of the phosphorus atoms in cymantrenyl cations with two phosphine ligands is that during formation of the cations the geometry of the system alters with the charged substituent C^+RR' being displaced from the Cp plane towards the manganese atom (considerable contribution of the fulvene structure IV). In cymantrenylcarbenium ions with chelate diphosphine ligands such tilting is accompanied by the appearance of a barrier to rotation of the metal/carbonyl moiety Mn(CO)(PP) with respect to the substituent in the side chain C^+RR', and at least four conformers may be formed with different arrangements of the phosphorus atoms P_1 and P_2 (conformers a, b, c, d):



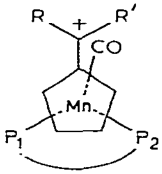
(a)



(b)

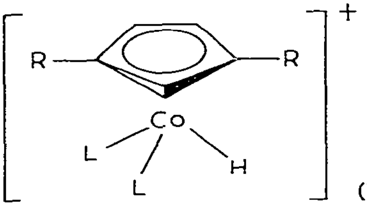


(c)

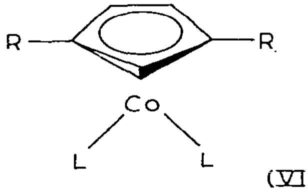


(d)

In conformers a and b P_1 and P_2 are non-equivalent. In monocyclopentadienyl complexes such non-equivalence may be caused by steric effects alone. Thus in both charged and neutral cyclopentadienylcobalt complexes with two phosphine ligands, V and VI, rotation of the fragment $Co(PMe_3)_2$ depends strongly on the type of substituents R in the Cp ring [9]:



(V)



(VI)

(L = PMe_3)

For R = $CH(Me)_2$ rotation is unhindered and the phosphorus atoms are equivalent but for R = CMe_3 rotations is hindered even at +100°C, and the phospho-

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* *Note added in proof.* However, in later work [15] authors come to the conclusion, on the basis of detailed analysis of ^{13}C and ^{57}Fe NMR data, that in ferrocenylcarbenium ions a weak bonding between iron and C^+ should exist.

rus atoms are non-equivalent (at —60° C an AB spin system is observed in the ^{31}P NMR spectrum) [9].

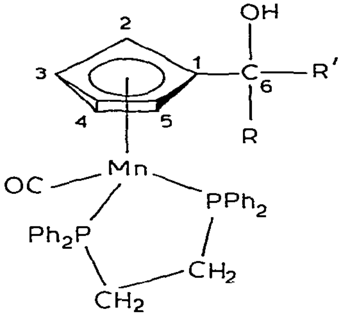
The nonequivalence of phosphorus nuclei in cymantrenyl cations **1—13** is presumably caused by steric effects connected with alteration of the geometry of the system during carbinol cation conversion, and not by the appearance of the positive charge. This is confirmed by the equivalent phosphorus nuclei in the ^{31}P spectrum of the model compound cation $[EtC_5H_4Mn(NO)(Ph_2PCH_2CH_2PPh_2)]PF_6$ (a narrow singlet is displayed with δ 92.3 ppm from 85% H_3PO_4). Another factor which may enhance steric hindrance in the cations is the increase of the $R—C^+—R'$ angle from tetrahedral (about 109°) in carbinols I to ~120° for the sp^2-hybridized C^+ atom in cations II. This factor however can hardly create a rotation barrier on its own without displacement of the charged substituent from the Cp plane since non-equivalence of phosphorus nuclei has also been observed for small substituents (R = H, R' = Me).

^{13}C NMR spectral data of cations with the $Ph_2PCH_2CH_2PPh_2$ ligand (Table 2) also support the non-equivalence of phosphorus nuclei in cations II. Formation of cations is accompanied by a downfield shift of C(2—5) signals while the C(1) signal is shifted upfield. The direction and value of the ^{13}C shifts for cations of the cymantrene series with two phosphine ligands coincide with shifts in monophosphine cations [3]. However, there is a distinct and characteristic difference between the ^{13}C spectra of cations **1** (R = R' = Me) and **2** (R = R' = Et) (this work) and the spectra of monophosphine cations with R = R' (ref. 3). In carbinols **1** and **2**, the four nuclei C(2,5) and C(3,4) are pair-wise equivalent and exhibit two singlets, as in the case of the monophosphine analogues: whereas in cations **1** and **2**, despite the absence of a chiral center (R = R'), all four C(2—5) nuclei become non-equivalent and display four separate signals in the ^{13}C spectra, while in the spectra of the monophosphine analogs these nuclei retain their pair-wise equivalence. The non-equivalence of carbon nuclei of the Cp ligand in ^{13}C spectra is in complete agreement with their non-equivalence in the ^{31}P spectra. The ^{13}C spectrum of cation **4** displays six separate signals which conforms with the presence of only one AX multiplet in the ^{31}P spectrum of this cation. Of particular interest is the ^{13}C spectrum of compound **6** (R = Me, R' = Ph). There are six separate signals from C(1—6) nuclei in the spectrum of carbinol **6** (C(2—5) nuclei are nonequivalent because a chiral center is present) and one signal from the methyl carbon. The ^{13}C spectrum of cation **6** exhibits a double set of signals due to the C(1—6) nuclei and two separate signals from the methyl carbons, which is connected with formation of two isomers of the carbenium ion. This is in excellent agreement with the presence of two AX spin systems in the ^{31}P NMR spectrum of this cation.

Let us now examine the changes in the ^{31}P NMR spectra for compounds containing two $PMe_2(C_6H_4Me)$ ligands with non-bonded phosphorus atoms (compounds **14—18**, Table 3). In this case the phosphorus nuclei are equivalent in the initial carbinols and give a single narrow signal which is independent of R and R'. On addition of CF_3COOH the signal is shifted upfield by ~4—8 ppm, the singlet structure and equivalence being retained. In the absence of $^{31}P\{^1H\}$ spin—spin decoupling the signal is split into a doublet with $J(^{31}P—Mn—^1H)$ 56—74 Hz. Exactly the same changes occur in the spectrum of the model compound, η^5-$C_5H_5Mn(CO)L_2$ (L = $PMe_2(C_6H_4Me$-$p)$), where there is no side chain

TABLE 2

^{13}C NMR CHEMICAL SHIFTS OF CARBINOLS I (IN CH_2Cl_2), AND CARBENIUM ION II (IN CH_2Cl_2/CF_3COOH)



Compound	R, R'	Solvent	^{13}C NMR chemical shifts [a], ppm downfield from TMS					
			C(1)	C(2—5)		C(6)	R	
1	Me, Me	CH_2Cl_2	109.5	78.7	77.7	69.1	CH_3	31.5
		CH_2Cl_2/CF_3COOH	98.8	103.6	88.0	148.2		25.3
				94.1	80.1			
		Δδ	—10.7	[b]	[b]	+79.1		—6.2
2	Et, Et						CH_2	CH_3
		CH_2Cl_2	108.4	79.0	78.1	73.5	31.1	8.1
		CH_2Cl_2/CF_3COOH	103.9	99.3	88.1	165.1	30.2	12.6
				93.1	79.5			
		Δδ	—4.5	[b]	[b]	+91.6	—1.9	+4.5
4	H, Me	CH_2Cl_2	103.0	78.1 [c]	77.7	65.3	CH_3	24.5
				78.1	76.8			
		CH_2Cl_2/CF_3COOH	100.2	105.0	87.5	109.5		16.2
				96.8	84.6			
		Δδ	—2.8	[b]	[b]	+44.2		—8.3
6	Me, Ph	CH_2Cl_2	108.1	79.1 [c]	78.4	72.3	CH_3	31.1
				79.1	78.1			
		CH_2Cl_2/CF_3COOH	101.6	104.5	98.3	151.0		25.1
			100.1	104.2	94.4	149.0		26.3
				88.4	81.0			
				87.9	81.0			
		Δδ	—6.5	[b]	[b]	+78.7		—4.8
			—7.0			+76.7		—6.0

[a] Signals of Ph_2PCH_2 carbon atoms are not included. [b] Shifts assignments for C(2—5) carbons have not been made. [c] Two signals coinside.

and protonation is only possible at the manganese atom. Therefore on addition of the acid to carbinols η^5-[$C_5H_4C(OH)RR'$]Mn(CO)L_2, where L = $PMe_2(C_6H_4$-Me-p), the proton attack is directed at the metal atom with formation of the protonated form. This is also true for R = R' = Ph, i.e. when the most stable of the carbenium ions studied should be formed. Consequently introduction of two strong donor phosphine ligands increases the basicity of the Mn atom to such an extent that, independent of the nature of R and R', the metal-protonated form is the more stable and not the carbenium ion.

A similar examination of the ^{31}P spectra of diphosphine complexes with the less basic PPh_2Me ligand of general formula [η^5-$C_5H_4C(OH)RR'$]Mn(CO)(PPh_2-

Me)$_2$ (compounds **19**—**21**, Table 3) show that for R = R′ = Et or R = Ph and R′ = CH$_2$Ph protonation also occurs at the metal in the presence of CF$_3$COOH, because the pattern of changes in the ^{31}P spectrum coincides with changes occurring during protonation of the model compound η^5-C$_5$H$_5$Mn(CO)(PPh$_2$-Me)$_2$, which does not have a side chain.

Unfortunately, due to poor solubility, we were unable to obtain satisfactory ^{31}P NMR spectra of the compound [η^5-C$_5$H$_4$C(OH)Ph$_2$]Mn(CO)(PPh$_2$Me)$_2$: however, changes in the ^{31}P spectra of its more soluble analog containing the PPh$_2$H ligand, [η^5-C$_5$H$_4$C(OH)Ph$_2$]Mn(CO)(PPh$_2$H)$_2$, shows that proton attack results in the formation of a carbenium ion in this case. In the presence of CF$_3$COOH the singlet of the initial carbinol (δ 116.5 ppm) disappears and an AX multiplet typical of carbenium ions is displayed to stronger field. (δ(P$_1$)-103.5, δ(P$_2$) 80.6, $\Delta\delta$ 22.9 ppm; J(P—P) 29 Hz).

Therefore in the presence of two ligands PPh$_2$Me and PPh$_2$H the basicity of the central Mn atom and of the hydroxyl oxygen are apparently quite close. In this case the direction of proton attack is determined by the capacity of substituents R and R′ to stabilize the cationic center. The Mn-stabilized carbenium ion is more stable only for R = R′ = Ph: when one or both R and R′ are alkyls the metal-protonated form is more stable.

On the basis of the data obtained in this work and that obtained earlier [3], the main factors determining formation and stability of carbenium ions stabilized by cymantrenyl substituents with phosphine ligands are as follows.

(1) The nature of radicals R and R′ (usual order of cation stability Ph >> alkyl > H).

(2) Electron-donor properties of the metallocenyl substituent (the greater they are the more stable should be the cation).

(3) The nature of the diphosphine ligand (whether the phosphorus atoms are

TABLE 3

^{31}P NMR CHEMICAL SHIFTS AND ν(CO) FREQUENCIES OF CARBINOLS η^5-C$_5$H$_4$C(OH)RR′Mn(CO)L$_2$ UNSUBSTITUTED η^5-C$_5$H$_5$Mn(CO)L$_2$ (IN CH$_2$Cl$_2$) AND CORRESPONDING PROTONATED FORMS (IN CF$_3$COOH/CH$_2$Cl$_2$)

Compound No.	R, R′	^{31}P chemical shifts (ppm downfield from 85% H$_3$PO$_4$)		$\Delta\delta^{31}$P (ppm)	J(H—P) (Hz)	ν(CO) frequencies	
		In CH$_2$Cl$_2$	In CF$_3$COOH/CH$_2$Cl$_2$			In CH$_2$Cl$_2$	In CF$_3$COOH CH$_2$Cl$_2$
		L = PMe$_2$(C$_6$H$_4$CH$_3$-p)					
14	Et, Et	59.0	53.4	—5.6	73	1820	1930
15	Ph, Ph	56.0	51.5	—4.5	75	1800	1935
16	Et, Ph	56.0	50.1	—5.9	63	1800	1920
17	Me, Ph	58.4	53.2	—5.2	[a]	1805	1923
18	Without side chain	57.0	50.7	—6.3	54	1815	1917
		L = PPh$_2$Me					
19	Et, Et	70.2	63.7	—6.5	78	1800	1915
20	Ph, CH$_2$Ph	70.0	63.7	—6.3	63.5	1800	1935
21	Without side chain	73.7	64.4	—9.7	76	1820	1940

[a] Not measured.

bonded or non-bonded into a chelate metallocycle). In the case of cymantrene carbinols with two phosphine ligands the proton may attack either the side chain with formation of a carbenium ion, or the central Mn atom, the basicity of which is considerably increased. Protonation at the central atom should be accompanied by decrease of bond angles at the metal atom from 90—100° (OC—Mn—CO, P—Mn—CO and P—Mn—P angles in pseudo-octahedral complexes $C_5H_5Mn(CO)_2PPh_3$ [10] and $C_5H_5Mn(CO)(PPh_3)_2$ [11] to 77—80° (angles at the Mn atom in the square pyramidal complex of 7-coordinated Mn [12]. Such deformation should occur more readily when the two phosphorus atoms are non-bonded and should be more difficult when they are bonded by a polymethylene chain. Consequently, for similar or identical electron-donor properties of the phosphine ligands, formation of carbenium ions is more favorable in the case of chelate diphosphines, whereas protonation at the metal atom is more probable when the phosphorus atoms are not bonded.

(4) Substantial increase of the electron-donor capacity of the phosphines (dialkylarylphosphines) leads to a sharp increase in the basicity of the central atom, and protonation at the metal becomes more favorable.

Shifts of the ν(CO) bands and of ^{31}P NMR signals indicate that in Mn-containing diphosphine cations, as in all previously studied metallocenylcarbenium ions, the positive charge is extensively delocalized throughout the system. The appearance of non-equivalent phosphorus atoms in the spectra of the cations is associated with hindered rotation in the cations in contrast with the initial carbinols where rotation is free. It should be noted that the appearance of steric hindrance has been observed in the PMR spectra of ferrocenylcarbenium ions with t-butyl substituents [6]. Recently we established that conversion of carbinols η^5-$C_5H_4C(OH)Ph_2Mn(CO)_2L$ (where L = PPh_3 or other tertiary phosphines) into cations is also accompanied by formation of a mixture of conformers, which exhibit different ν(CO) bands for each carbonyl group (IR spectra of carbinols have two ν(CO) bands while the IR spectra of the corresponding carbenium ions with R = R′ = Ph display four ν(CO) bands) [13]. The appearance of rotation barriers and the formation of conformers as manifest in the NMR and IR spectra of the cymantrenylcarbenium ion is a convincing argument in favour of the displacement of the charged substituent towards the metal atom.

Experimental

Synthesis of diphosphine complexes

Carbinols η^5-$C_5H_4C(OH)RR'Mn(CO)L_2$ were obtained by photochemical substitution of two CO groups in the corresponding tricarbonyl precursors η^5-$C_5H_4C(OH)RR'Mn(CO)_3$. The latter were prepared by treating acetyl- or benzoylcymantrene with Grignard reagents according to ref. 14 or by reduction with $LiAlH_4$ when R = H. For photochemical substitution of ligands 2 mmol of the carbinol and 5 mmol of the monodentate phosphine L or 2.25 mmol of chelate diphosphine L_2 (a slight excess of L of L_2 is required for complete substitution) in 100—120 ml of benzene were irradiated with UV light (mercury PRK-2M lamp, 400 W) while boiling in an argon atmosphere. The course of ligand substitution was monitored by IR spectroscopy. When two CO groups had been substituted the $Mn(CO)_3$ bands at 1930—1940 cm^{-1} (broad) and at 2025 cm^{-1} disappeared and a new broad ν(CO) band of carbinols I appeared at 1800—1835 cm^{-1}. After completion of the reaction the cooled solution was filtered to remove decomposition products and excess benzene was evaporated under vacuum. The red oil residue in the case of chelate L_2 (compounds **1—13**) crystallized after it was washed several times with small portions of hexane. Recrystallization from heptane or heptane/CH_2Cl_2 mixtures yielded an orange or red crystalline substance which was characterized by IR spectra in the ν(CO) and ν(OH) (one broad line at 3590—3600 cm^{-1}) region, by satisfactory elemental analyses (C, H, Mn, P) and by PMR spectra in CS_2 or $CHCl_3$. Yields of I 50—70%.

In the case of carbinols with $PMe_2(C_6H_4Me\text{-}p)$ ligand, the residue, after benzene had been removed from the irradiated solution, was a viscous red oil which did not crystallize. It was repeatedly washed with hexane and excess free L was evaporated under oil-pump vacuum. In order to record ^{31}P and ^{13}C NMR spectra on the solution of the carbinol I in CH_2Cl_2, an equivalent quantity or a 1.5-fold excess of CF_3COOH was added to it in an NMR ampoule at —30 to —40° C. On conversion of the carbinols into carbenium ions the reaction mixture immediately changed colour. Cations with R = R′ = alkyl or R = alkyl and R′ = Ph are dark cherry or violet in colour, for R = R′ = Ph they are green or blue. Solutions of metal-protonated forms are light red.

Spectral data

^{31}P and ^{13}C NMR spectra at —30 to —40° C (compounds **6—8** at —60 to —70° C) were obtained in the pulsed Fourier transform mode utilizing a Bruker HX-90 spectrometer with ^1H-decoupling. At room temperature the signals are considerably broadened and the fine structure collapses. In attempts to record the PMR spectra of cations II (in $CHCl_3$ at —20 to —30° C) addition of CF_3-COOH leads to downfield shifts of all signals and strong broadening, caused by the appearance of paramagnetic Mn^{2+} compounds.

IR spectra of carbinols were obtained in CH_2Cl_2 solutions, of cations in CF_3-COOH/CH_2Cl_2 mixtures (1/100 or 1/200), on a UR-20 spectrophotometer with a LiF prism in 0.1 mm NaCl cells.

Decomposition of cation II solutions with water leads to formation of the initial carbinols or of their mixture with the corresponding olefins (if one of the radicals R = alkyl). The olefins were isolated and their structure was confirmed by PMR spectroscopy.

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