

Carbon-13 Nuclear Magnetic Resonance Spectra of 1-*p*-Tolyloethyl- and Di-*p*-tolylmethyl-tricarbonylchromium Cations

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The ^{13}C n.m.r. spectra of 1-*p*-tolylethyl- and di-*p*-tolylmethyl-tricarbonylchromium cations and of the analogous complexed alcohols have been obtained. The chemical shifts compared with those of the corresponding uncomplexed cations are explicable in terms of structures in which the positive charge is localized on the tricarbonylchromium system to a great extent. From an analysis of the behaviour upon variations of temperature of the non-equivalent splittings of the *ortho*- and *meta*-carbons as well as of the carbonyl resonance one can deduce that two motions, around the aryl-methyl and the metal-ring bonds, characterize the dynamics of the ions.

KINETIC studies of ionization reactions¹⁻³ and pK_a measurements^{4,5} of arene- π -tricarbonylchromium derivatives have shown the great stability of alkylaryl carbenium ions complexed to tricarbonylchromium. The recent isolation of a stable hexafluorophosphate salt of the diphenylmethylbis(π -tricarbonylchromium) carbenium ion⁶ represents the first successful attempt to isolate these ions which appear to be considerably more reactive than diferrocenylmethyl carbenium ions.⁷ Attempts to produce these complexed ions in acidic media from alcoholic or chloride precursors failed (except for very dilute solutions in H_2SO_4)⁴ since rapid decomposition occurred with evolution of carbon monoxide.^{1,4,6} Thus, no direct n.m.r. spectroscopic evidence has been obtained which could provide a better understanding of the structure of the complexed ions by analogy with the extensive research in the ferrocenylalkylium ion series.⁸ We have been able to produce stable solutions of 1-*p*-tolylethyl- and di-*p*-tolylmethyl-tricarbonylchromium cations starting from the corresponding complexed alcohols in HSO_3F at -50° .

The results of a ^1H n.m.r. investigation of these cations have been reported in a preliminary communication.⁹ In this paper we give the results of a ^{13}C n.m.r. study carried out on the same cations. The n.m.r. technique provides, on the one hand, a clear understanding of the distribution of the positive charge in the organic residue, and, on the other, may give information about the stereodynamics of the molecule. For accurate comparison we have taken the ^{13}C n.m.r. spectra of the corresponding free ligand ions under the same experimental conditions, when possible.

EXPERIMENTAL

General.—All reactions were carried out under pure, dry nitrogen. M.p.s are uncorrected. Microanalyses were carried out by Mr. Turiaco, Istituto di Chimica Analitica, Università di Padova. I.r. and ^1H and ^{13}C n.m.r. analyses were performed using a Beckman IR-9 and Bruker HFX-90

¹ J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometallic Chem.*, 1965, **4**, 324.

² A. Cecon, *J. Organometallic Chem.*, 1971, **29**, C19.

³ R. S. Bly and R. L. Veazey, *J. Amer. Chem. Soc.*, 1969, **91**, 4221; R. S. Bly, R. C. Strickland, R. T. Swindell, and R. L. Veazey, *J. Amer. Chem. Soc.*, 1970, **92**, 3722.

⁴ W. S. Trahanovsky and D. K. Wells, *J. Amer. Chem. Soc.*, 1969, **91**, 5870, 5871.

⁵ M. Acampora, A. Cecon, and A. Gobbo, unpublished results.

⁶ D. Seyferth and C. S. Eschbach, *J. Organometallic Chem.*, 1975, **94**, C5.

and WH-90 (pulse Fourier transform) spectrometers. 1-*p*-Tolyloethanol and *p*-methylacetophenone were redistilled commercial materials. 4,4'-Dimethylbenzophenone was obtained from toluene and CCl_4 by a Friedel-Crafts reaction.

Tricarbonyl(1-*p*-tolylethanol)chromium.—The complex was made by heating $\text{Cr}(\text{CO})_6$ with 1-*p*-tolylethanol in diglyme. After cooling, the solvent and the residual alcohol were distilled out under reduced pressure (0.05 mmHg). The residue was purified by column chromatography (silica gel; ethyl ether-light petroleum) and the oil crystallized from ethyl ether-hexane (yield 30%), m.p. $56.5-57^\circ$ (Found: C, 52.9; H, 4.35. Calc. for $\text{C}_{12}\text{H}_{12}\text{CrO}_4$: C, 52.95; H, 4.45%). $[1-^2\text{H}]1-*p*-Tolyloethanol$, obtained by reduction of *p*-methylacetophenone with LiAlD_4 in ether, was complexed with the same procedure. I.r. and n.m.r. analyses were consistent with the structure of the two compounds.

Tricarbonyl(4,4'-dimethylbenzophenone)chromium obtained from 4,4'-dimethylbenzophenone and $\text{Cr}(\text{CO})_6$ as described by Pettit,¹ had m.p. $118-119^\circ$ (Found: C, 62.25; H, 3.95. Calc. for $\text{C}_{18}\text{H}_{14}\text{CrO}_4$: C, 62.35; H, 4.05%). I.r. and n.m.r. analyses were consistent with the structure.

Tricarbonyl(di-*p*-tolylmethanol)chromium.—The alcohol was obtained by reduction of the complexed ketone with NaBH_4 in methanol. The $[1-^2\text{H}]$ di-*p*-tolylmethanol derivative was obtained by reduction with LiAlD_4 in ether. The extent of deuteration determined by n.m.r. was >99 atom % D, m.p. $102.5-103.5^\circ$ (Found: C, 61.25; H, 4.65. Calc. for $\text{C}_{18}\text{H}_{16}\text{CrO}_4$: C, 62.05; H, 4.6%).

Preparation of Ions.—The procedure for preparation of solution of ions described below was shown to be essential to obtain stable solutions. Attempts to obtain solutions of ion (I_a^+) in $\text{SO}_2\text{-HSO}_3\text{F-SbF}_5$ at -70° failed since rapid decomposition of the substrate occurred. Preliminary experiments carried out on substrates of different structure, *i.e.* primary benzylic alcohols and bis-*p*-methoxyphenylmethanol were unsuccessful and work is in progress to obtain stable solutions of these cations.

RESULTS AND DISCUSSION

The required secondary complexed alcohol precursors were prepared according to reported methods.¹⁰ Cations

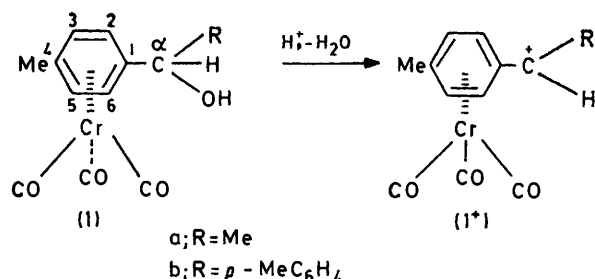
⁷ S. Lupan, M. Kapon, M. Cais, and F. H. Herbstein, *Angew. Chem.*, 1972, **84**, 1104.

⁸ For n.m.r. data see (a) J. J. Dannenberg, M. K. Levenberg, and J. H. Richards, *Tetrahedron*, 1973, **29**, 1575; (b) T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 177; S. Braun, T. S. Ahrm, and W. E. Watts, *J. Organometallic Chem.*, 1975, **97**, 429; (c) G. H. Williams, D. D. Traficante, and D. Seyferth, *J. Organometallic Chem.*, 1973, **60**, C53; (d) G. A. Olah and G. Liang, *J. Org. Chem.*, 1975, **40**, 1849.

⁹ M. Acampora, A. Cecon, M. Dal Farra, and G. Giacometti, *J.C.S. Chem. Comm.*, 1975, 871.

¹⁰ B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 1959, 551.

(1a⁺) and (1b⁺) were formed by ionization of the corresponding alcohols (1a) and (1b) in HSO₃F at -50°. To



obtain stable solutions of the ions the alcohols were dissolved in methylene chloride and the yellow solution was frozen at liquid nitrogen temperature. Fluoro-sulphonic acid was then added and solidified. By raising the temperature at -70° the two distinct solid phases began to dissolve so that the alcohol was slowly extracted by the acid from the organic layer. The acid solution immediately became red-violet. The solution of (1a⁺) was quite stable for several hours at -50°, that of (1b⁺) remained unchanged up to -20°. Carbon

TABLE 1

Carbon-13 n.m.r. data for complexed alcohols and derived ions^a

Compound	Carbon ^b	Alcohol ^c	Ion ^d	Δδ ^e	
(1a)	C _α	67.5	126.6	59.1	
	α-Me	24.9	19.6	-5.3	
	1	114.6	106.3	-8.3	
	2, 6	92.1, 92.8	103.2, 106.7	(~12.5)	
	3, 5	92.5	101.1, 101.8	(~9)	
	4	109.5	115.4	5.9	
	<i>p</i> -Me	20.3	15.2	-6.1	
	CO	233.4	226, 226.5, 227.3	(~-7)	
	(1b)	C _α	73.6	137.9	64.3
		1	113.3	102.1	-11.2
2, 6		92.3, 94.3	101.3, 106.7	(~10.7)	
3, 5		93.3	100.2, 101.0	(~7.3)	
4		110.9	115.0	4.1	
<i>p</i> -Me		20.7	19.4	-1.3	
CO		234.3	226.5, 227.3, 229.4	(~-6)	
1'		139.5	127.1	-12.4	
2', 6'		129.6	132.5	2.9	
3', 5'		126.5	130.9	4.4	
4'	138.7	148.3	9.4		
<i>p</i> '-Me	21.4	20.7	-0.7		

^a Carbon shifts are in p.p.m. from Me₄Si; the data in acidic media were converted to the Me₄Si scale assuming an internal CH₂Cl₂ signal at 54.85 p.p.m. ^b Primed numbers refer to the uncomplexed ring carbons. ^c Recorded in CDCl₃ solution at 25°. The spectra were recorded also in CH₂Cl₂ at -80° and shown to be practically identical. ^d In HSO₃F at -50°. ^e Δδ = δ_{ion} - δ_{alcohol}.

shifts of complexed alcohols and ions are summarized in Table 1; those of the analogous uncomplexed alcohols (2) and ions (2⁺) are given in Table 2. The assignments

¹¹ J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972.

of the resonances for the alcohols are based on standard ¹³C n.m.r. correlations¹¹ and on decoupled spectra. Specific peak assignments in the ion spectra were aided by deuteration of the methine C-H; the C-4 resonance has been assigned on the assumption that it appeared downfield of peaks for the *ortho*-, *meta*-, and junction positions, by analogy with the results for the phenyl carbenium ions investigated by Olah and his co-workers.¹² No effort has been made to assign in detail the *ortho*- and *meta*-phenyl resonances. The assignment given in the

TABLE 2

Carbon-13 n.m.r. data for uncomplexed alcohols and derived ions^a

Compound	Carbon	Alcohol ^b	Ion ^c	Δδ ^d	
<i>p</i> -MeC ₆ H ₄ C(OH)HMe (2a)	C _α	70.4	218.0	147.6	
	α-Me	25.2	25.4	0.2	
	1	143.2	139.2	-4.0	
	2, 6	129.3	142.0, 152.9	12.7, 23.6	
	3, 5	125.3	133.8, 134.5	8.3, 9.0	
	4	137.2	181.0	43.8	
	<i>p</i> -Me	21.2	24.7	3.5	
	<i>p</i> (-MeC ₆ H ₄) ₂ CHOH (2b)	C _α	75.9	191.6	115.7
		1	141.1	134.2	-6.9
		2, 6	129.1	140.0, 146.5	10.9, 17.4
3, 5		126.5	132.8, 133.5	6.3, 7.0	
4		137.1	164.7	27.6	
<i>p</i> -Me		21.1	23.1	2.0	

^a Carbon shifts are in p.p.m. from Me₄Si. ^b Recorded in CDCl₃ solution at 25°. ^c Spectrum of (2a⁺) recorded in SbF₅-HSO₃F-SO₂ at -50°, (2b⁺) in HSO₃F at -50°. ^d Δδ = δ_{ion} - δ_{alcohol}.

Tables seems to us the most reasonable although the discussion which follows would not be greatly affected by a different choice. Interesting features of the ion spectra are the enhanced non-equivalence of the *ortho*-phenyl resonances with respect to those of the alcohols and the appearance of such non-equivalence in the *ortho*- and *meta*-phenyl resonances of all cases except of the uncomplexed ring of (1b⁺). Both for the di-*p*-tolyl-methyl ion (2b⁺) and the complexed analogue (1b⁺), spectra at different temperatures in the interval -60 to -20° could be obtained. It was observed that the *ortho*- and *meta*-phenyl splittings of (2b⁺) collapse at ca. -30° and an approximate value of 41 kJ mol⁻¹ could be obtained for the activation energy of the process. In contrast, the *ortho*- and *meta*-splittings of the complexed ring of (1b⁺) did not collapse over the same temperature interval, the shifts values and line shapes remaining unchanged. Also, the three carbonyl resonances of both (1a⁺) and (1b⁺) show complete non-equivalence at -50°. This non-equivalence as well as that of the *ortho*-carbons are due to mutually hindered rotations of different portions of the molecules. The carbonyl non-equivalence is temperature dependent, the collapse occurring at ca. -40° for (1b⁺); however it was not possible to estimate the activation energy of the process.

¹² G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Amer. Chem. Soc.*, 1975, **97**, 3419.

It is generally accepted that chemical shifts of α -carbon atoms in ions, since they are correlated with the electronic density on the atom, are indicative of the amount of charge delocalization, hence of the ion stability. The intervention of the metal in stabilizing the α -positive charge can be estimated from comparison of the chemical shifts of the complexed ions relative to those of the free ions. For example, in the case of ferrocenylmethyl carbenium ions α -carbon chemical shifts are taken as a manifestation of their unusual stabilities^{8c} as the change in chemical shifts of the carbonyl carbon observed on conversion of the respective alcohol into the ion is relatively small if compared with

the change in systems such as $\text{Me}_2\text{CHOH}-\text{Me}_2\text{CH}^+$. Also in our case the values of $\Delta\delta = \delta_{\text{ion}} - \delta_{\text{alcohol}}$ for C_α are much smaller in the complexed [59 and 64 p.p.m. for (1a) and (1b), respectively] than in the free systems (147 and 115 p.p.m.). Moreover, C_α in the $\text{Cr}(\text{CO})_3$ ions appears to resonate at approximately the same frequency as the cationic centre of α -ferrocenyl carbenium ions. In fact, the $^{13}\text{C}_\alpha$ resonance of the secondary ion 1-ferrocenylethyl cation occurs at 117.9 p.p.m. from tetramethylsilane^{8d} in sulphuric acid solution and that of (1a⁺) at 126.6 p.p.m. We note, however, that arguments based on $\Delta\delta$ is even more adequate in the tricarbonylchromium substrates for which the free ligands constitute a valid reference, while in the ferrocenyl there is no uncomplexed system to which one can refer as a standard in order better to evaluate the intervention of the metal. Thus, from the C_α chemical shifts it appears that tricarbonylchromium carbenium ions are much more stable than the corresponding uncomplexed ions and as stable as the ferrocenyl carbenium ions. Secondly, the replacement of a methyl by a *p*-tolyl group at the cationic centre has a shielding effect in the free ions (32 p.p.m.) but a small deshielding effect in the complexed ions (5 p.p.m.), indicating that phenyl has a larger capacity than methyl to delocalize the charge in the uncomplexed ions in agreement with results of other workers,^{12,13} but approximately the same effect in the $\text{Cr}(\text{CO})_3$ co-ordinated ions. This lower charge dispersal ability of the phenyl group is connected with the different localization of the charge in the rest of the molecule as appears clearly from the following. Recently, by examining a large number of phenyl carbenium ions, Olah *et al.*¹² showed that the shifts of C-4 are linearly correlated with charge much better than the shifts of C-1 and of *ortho*- and *meta*-carbon atoms. In addition to the charge effect through space contributions can affect the shifts of the latter carbon atoms. Thus, if $^{13}\text{C}_\alpha$ and $^{13}\text{C-4}$ shifts are correlated with the fraction of positive charge at C_α and the ring respectively, from the comparison of free and complexed ions one can estimate that *ca.* 70 and 60% of the total charge is delocalized in the inorganic residue in (1a⁺) and (1b⁺), respectively. Consequently C_α and the phenyl ring which support the total charge in

free ions are greatly deprived of it in the complexed ones. Because of this positive 'sink' effect of the $\text{Cr}(\text{CO})_3$ system, the resonance stabilizing capacity of an α -ring substituent is much diminished. The preceding discussion should be regarded with some caution because the correlation between charge density and chemical shift may vary from series to series but we feel that from a qualitative point of view the arguments and the conclusions remain valid.

The third important feature of the spectroscopic data is the non-equivalence in some cases of the *ortho*- and *meta*-carbon atoms. The presence of a chiral centre in the alcohols results in diastereotopy of the *ortho*- and *meta*-ring carbons and protons on complexation with $\text{Cr}(\text{CO})_3$. A chemical shift difference is detectable, however, only for the diastereotopic *ortho*-carbons while it was observable also for the *meta*-position in the case of protons.⁹

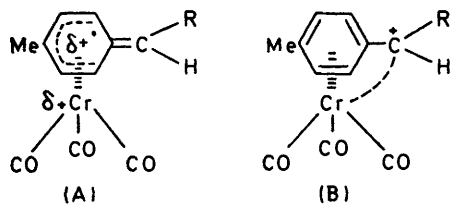
The non-equivalence of the *ortho*- and *meta*-carbons in the uncomplexed ions (2a⁺) (10.9 and 0.7 p.p.m., respectively) and (2b⁺) (6.5 and 0.7 p.p.m.) is caused, on the other hand, by the greater difficulty of rotation about the C-1- C_α bond. Aryl rings can, in fact, delocalize the charge by resonance through significant contributions from structures having C-1- C_α double bonds.



Since the α -carbon is asymmetrically substituted, the *ortho*- and *meta*-carbons do not experience the same magnetic environment. From the variable temperature experiments the magnitude of the torsional barrier amounts to *ca.* 41 kJ mol⁻¹. In the complexed ions the non-equivalence of the *ortho*- and *meta*-carbon atoms still persists in the complexed rings but it is not observed for the carbons of the uncomplexed ring of (1b⁺). This relief of magnetic non-equivalence is a clear confirmation that double bonded resonance structures are less important in the stabilization of the charge which is now localized on the metal to a great extent. Free rotation around the uncomplexed ring-methyl bond is then feasible and *ortho*- and *meta*-carbons become magnetically equivalent. As far as the non-equivalence of the complexed ring *ortho*-carbons is concerned, one can observe that it persists in (1b⁺) (5.4 p.p.m.) at temperatures higher than that for the collapse of the resonance of the ring carbons in the uncomplexed ion. In the frozen spectrum of uncomplexed (2b⁺), on the other hand, the difference in the *ortho*-carbon atom shifts is 6.5 p.p.m. Since the differences in the two cases are fairly close, this is an indication that the degree of freezing to rotation about the C_α -C-1 (complexed ring) bond must be greater than that occurring around the same bond in the uncomplexed ion. The reasons for an increased rigidity of this part of the molecule may be both an increasing importance of resonance structures (A) (resonance model), or a direct intervention of the metal at the cationic centre (anchimeric assistance) (B).

¹³ G. A. Olah and P. W. Westerman, *J. Amer. Chem. Soc.*, 1973, **95**, 7530.

In structures of type (A) chromium is bonded only to five carbons of the quinonoid system with the positive charge distributed over the remainder of the system except the methylene carbon and C-1. We believe structures (A) be the less favoured. In fact, despite the availability of two electrons of the exocyclic bond the

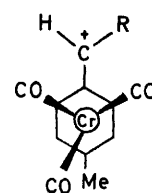


metal should co-ordinate only 16 rather than the 18 electrons needed to attain the krypton configuration. Alternatively, co-ordination of the metal with the methylene double bond and the diene system of the ring would predict a greater amount of positive charge on the *ortho*- and *para*-carbons. In contrast, the $\Delta\delta$ of C-4 are significantly smaller in the complexed than in the free ions as we have discussed above, indicating that charge density is diminished also in the complexed ring. Therefore, we conclude that resonance structures are less important and direct participation of the metal should be invoked. Finally, the situation of the metal-ring bond can be inferred by inspecting the ^{13}C chemical shifts of the carbonyl group. The three carbonyls show magnetic equivalence in the alcohols even at very low temperature (-80°). Conversely, in the ions, the three carbonyls are no longer equivalent at -50° . This splitting is clear evidence that rotation around the metal-ring bond is slow on the n.m.r. time scale with the consequence that the three carbonyls experience different magnetic environments. The eclipsed conformer shown

¹⁴ O. L. Carter, A. T. McPhail, and G. A. Sim, *Chem. Comm.*, 1966, 212; *J. Chem. Soc. (A)*, 1966, 822; 1967, 220; R. V. Emanuel and E. W. Randall, *ibid.*, 1969, 3002.

in the Figure seems the more likely on the basis that in monosubstituted benzenes groups with a $+M$ effect prefer conformations where the carbonyl is eclipsed with the group, while groups with a $-M$ effect prefer the conformation where the carbonyls are staggered to the group.¹⁴

Unfortunately, the small temperature interval where the complexed ions are stable prevented an accurate study of the temperature behaviour of these species. Nevertheless, from the fact that at -20° a splitting of *ca.* 1 p.p.m. is observed for the *meta*-carbons of the complexed ring of (1b⁺) and that the carbonyl resonances coalesce at -40° (while they spread over 3 p.p.m. in the frozen spectrum) one can infer that the motions producing the collapse of the two sets of resonances have different rates. This agrees with the interpretation which sees



FIGURE

the motion averaging the phenyl resonances as a rotation of the ring around the $\text{C}_\alpha\text{-C-1}$ bond and the one averaging the carbonyl resonances as an independent rotation of the $\text{Cr}(\text{CO})_3$ groups around the metal-ring bond. Similar uncorrelated averaging motions have been described by us already in the case of tricarbonyl(cyclo-octatetraene)-iron.¹⁵

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¹⁵ G. Rigatti, G. Boccalon, A. Ceccon, and G. Giacometti, *J.C.S. Chem. Comm.*, 1972, 1165.