^{1}H Nuclear Magnetic Resonance Spectra of 1-(*p*-Tolyl)ethyl- and Di-(*p*-tolyl)methyl-tricarbonylchromium Cations

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Summary The ^{1}H n.m.r. spectra of alkylarylcarbenium ions complexed to tricarbonylchromium are reported and the charge distribution compared with that in the corresponding free ligand ions.

Much evidence has accumulated on α-ferrocenyl-carbonium ions which are formed through solvolysis reactions[1] or from the alcoholic precursors in highly acidic media.[2] Direct ^{1}H n.m.r. observations allowed the structure of these exceptionally stable species to be formulated in detail, and a number of different metal–ligand bonding arrangements have been suggested.[3] Although it has been postulated that benzyl- and diphenylmethyl-tricarbonylchromium cations are very stable on the basis of kinetic[4] and thermodynamic data[5] to our knowledge direct ^{1}H n.m.r. spectroscopic observation of these ions has not been reported to date. We now report the ^{1}H n.m.r. spectra of the cations (I)$^+$ and (II)$^+$ in HSO_3F acid at −50 °C.

Table 1 shows the ^{1}H n.m.r. band positions and assignments for the complexed and uncomplexed ions, (I)$^+$—(IV)$^+$, and Table 2 shows the n.m.r. parameters for the corresponding alcohols (I)—(IV). The spectra of the ions (I)$^+$ and (II)$^+$ are shown in the Figure; they give quite sharp signals and appear free from impurities.

The presence of a chiral centre in the alcohols (I)—(III) results in diastereotopy of the *ortho*- and *meta*-ring protons. A chemical shift difference is detectable, however, only in favourable situations. In our case a difference in chemical shifts for the diastereotopic protons is shown in the complexed rings for the *ortho*, as well as for the *meta*-protons.

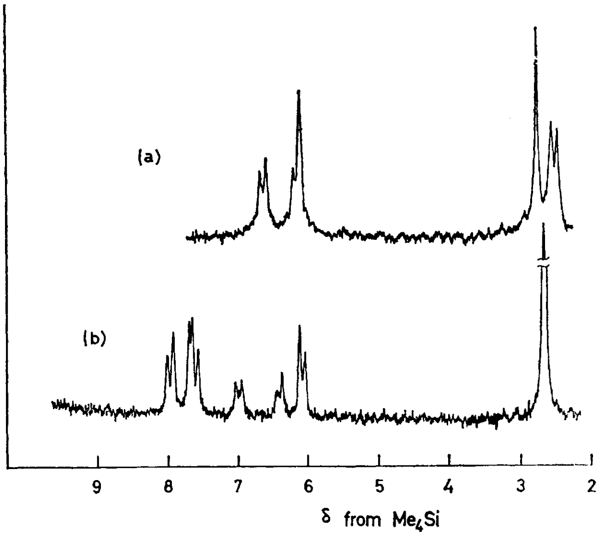

Figure. ^{1}H N.m.r. spectra of: (a) 1-(*p*-tolyl)ethyltricarbonylchromium; and (b) di-(*p*-tolyl)methyltricarbonylchromium cations. For the complexed ring the more deshielded peaks were assigned to the *ortho*-protons, assuming that an ionic carbon behaves like an electron-withdrawing substituent.

Table 1. ^{1}H N.m.r. data for the complexed and uncomplexed cations.[a]

Compound		α-H	α-Me	Complexed ring protons H_o	H_m	*p*-Me	Uncomplexed ring protons H_o	H_m	*p*-Me
$p\text{-MeC}_6\text{H}_4\overset{+}{\text{C}}\text{HMeCr(CO)}_3$[b]	(I)$^+$	6·64	2·48	6·64 6·17	6·12	2·74			
$(p\text{-MeC}_6\text{H}_4)_2\overset{+}{\text{C}}\text{HCr(CO)}_3$[b]	(II)$^+$	7·70		7·01 6·44	6·11	2·67	8·01	7·68	2·67
$p\text{-MeC}_6\text{H}_4\overset{+}{\text{C}}\text{HMe}$[c]	(III)$^+$	10·07	3·61				9·12 8·70	8·25	3·25
$(p\text{-MeC}_6\text{H}_4)_2\overset{+}{\text{C}}\text{H}$[b]	(IV)$^+$	9·53					8·39	7·84	2·80

[a] δ Values from external Me_4Si. [b] In HSO_3F at −50 °C. [c] In SbF_5–SO_2ClF (from G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Amer. Chem. Soc.*, 1971, **94**, 464).

TABLE 2. ^{1}H n.m.r. parameters of complexed and uncomplexed alcohols.[a]

Compound		α-H	α-Me	Complexed ring protons H_o	Complexed ring protons H_m	Complexed ring protons p-Me	Uncomplexed ring protons H_o	Uncomplexed ring protons H_m	Uncomplexed ring protons p-Me
$p\text{-MeC}_6\text{H}_4\text{CH(OH)MeCr(CO)}_3$	(I)	4·51	1·46	5·63 5·42	5·21 5·16	2·18			
$(p\text{-MeC}_6\text{H}_4)_2\text{CHOHCr(CO)}_3$	(II)	5·32		5·69 5·30	5·12 5·04	2·12	7·27	7·14	2·32
$p\text{-MeC}_6\text{H}_4\text{CH(OH)Me}$	(III)	4·66	1·33				7·11	6·99	2·30
$(p\text{-MeC}_6\text{H}_4)_2\text{CHOH}$	(IV)	5·69					7·22	7·08	2·30

[a] δ Values relative to Me_4Si for CDCl_3 solutions.

The spectrum of (I)$^+$ shows sharp, substantially deshielded peaks, which were assigned from their positions and areas. In the aromatic region the spectrum shows one 2H and one 3H multiplet; when the downfield multiplet was irradiated, the α-methyl doublet at δ 2·48 changed into a sharp singlet, showing that the methine resonance is overlapped by one of the *ortho* resonances. Deuteriation of the methine CH confirmed the assignment of the styryl methine proton. The position of the CH resonance for the diphenylmethyl case was determined similarly.

The spectrum of (I)$^+$ also shows inequivalence of the two *ortho*-protons, and the inequivalence of the *meta*-protons can be inferred. This behaviour, observed also for the corresponding free ligand ion, is caused by the lack of free rotation about the exocyclic bond.

For (II)$^+$ a lack of inequivalence of the *ortho*- (and *meta*-) protons in the uncomplexed ring is observed just as in the free cation (III)$^+$. The equivalence of the *ortho*- and the *meta*-protons in diphenylmethyl as well as in triphenylmethyl ions arises from the particular 'propeller like' conformation of the molecule (owing to steric hindrance of the *endo-ortho* hydrogens),[6] in which different environments are averaged by fast twisting of the two rings.

The persistence of the inequivalence in the complexed ring (II)$^+$ is an extremely clear indication of the preferential charge migration to the metal, with freezing of the rotation around the ring–carbon bond. The steric requirements for the *endo-ortho* hydrogens are met, in this case, by twisting of only the uncomplexed ring.

Charge migration toward the metal is also shown clearly by the downfield shifts of all peaks, in passing from the alcohol to the ion, which are much smaller for the complexed than for the uncomplexed system. In fact, the well known correlation of the proton chemical shift with the charge density on the adjacent carbon points to the conclusion that a considerable part of the charge is transferred to the metal, which therefore participates directly in the mechanism of stabilisation of these ions, in the same way as was suggested (on a different basis[2]) for the α-ferrocenyl-carbonium ions.

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