

## METAL-STABILIZED CARBANIONS

### V \*. A $^1\text{H}$ NMR STUDY OF THE STRUCTURES OF DI- AND TRI-PHENYLMETHYL ANIONS IN BENZYLIDENE- $\eta^5$ -TRICARBONYL-(CYCLOHEXADIENYL)CHROMIUM(0)

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#### Summary

The anions of di- and tri-phenylmethane complexed with the tricarbonylchromium group have been produced by  $\alpha$ -hydrogen abstraction and their  $^1\text{H}$  NMR spectra recorded. The spectral data suggest that the negative charge density is substantially withdrawn from the uncoordinated ring(s) and delocalized into the complexed moiety, for which a planar  $\eta^5$ -cyclohexadienyl structure bearing an exocyclic double bond is proposed.

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#### Introduction

The formation of  $\eta^5$ -tricarbonyl(cyclohexadienyl)chromium(0) anions by nucleophilic addition of carbon bases to arenes coordinated with the  $\text{Cr}(\text{CO})_3$  group, (TCC), is well known [1]. The carbon subjected to nucleophilic attack changes its hybridization from  $sp^2$  to  $sp^3$  and it is bent out of the aryl plane, as shown by  $^1\text{H}$  NMR evidence [2]. This reaction path is the preferred one even when TCC derivatives of arylmethyl hydrocarbons, for example toluene, and di- or triphenylmethane, react with *n*-butyllithium, there being no or very little side-chain proton abstraction to produce benzyl anions [3].

On the other hand, the coordination with TCC activates the benzylic protons

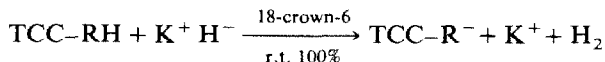
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\* For part IV, see *J. Chem. Soc., Chem. Commun.*, (1982) 907.

towards H,D isotopic exchange in basic media [4]. Moreover, the temporary introduction of TCC into an organic substrate in order to increase its susceptibility to  $\alpha$ -proton abstraction is of considerable synthetic interest and TCC-coordinated benzyl anions have been suggested as transient intermediates in many reactions [5]. Despite these facts, to our knowledge no direct spectroscopic observation of simple TCC-benzyl anions has been reported to date, and the only related ion is the bis-TCC-diphenylmethyl carbanion [6]. We describe below the easy generation of TCC-complexed di- and triphenylmethyl carbanions as stable solutions in THF and a detailed analysis of their  $^1\text{H}$  NMR spectra.

## Results and discussion

Tricarbonylchromium di-, (TCC-DPM) and tri-phenylmethane (TCC-TPM) were converted into the corresponding potassium salts by treating their THF solutions with excess KH in the presence of 18-crown-6 ether [7]. The yellow solutions of the complexed hydrocarbons quickly turned red brown, and quantitative evolution of hydrogen gas occurred according to:



Treatment of these solutions with aqueous, oxygen-free THF under argon immediately restored the yellow colour, and the TCC-di and -tri-phenylmethane were recovered unchanged in high yield.

The anion solutions are stable for several hours at room temperature and satisfactory NMR spectra could be recorded. The same metallation was checked also for TCC-toluene, and quantitative generation of hydrogen gas was observed. Unfortunately, when the excess KH was removed the solution was very unstable even at low temperature, and the NMR spectrum could not be recorded. However, the formation of the TCC-benzyl anion was confirmed beyond doubt by quenching experiments with  $\text{D}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{CH}_3\text{I}$  to give TCC-toluene- $\alpha$ -*d*, TCC-phenylacetic acid and TCC-ethylbenzene, respectively.

The spectrum of the TCC-TPM $^-$  anion consists of two AA'BB'C spin systems in the ranges  $\delta$  7.3–6.6 and 4.9–4.3 ppm, integrating in the ratio 2/1, which are attributable to the free and complexed ring protons, respectively. The uncomplexed ring protons of TCC-DPM $^-$  anion still exhibit an AA'BB'C pattern in the range  $\delta$  7.1–6.2 ppm, while an ABCDE spectrum at  $\delta$  5.2–3.7 ppm was found for the complexed ring protons. An additional single line at  $\delta$  4.29 is attributed to the methine proton. The  $^1\text{H}$  NMR parameters which well reproduce the experimental spectra by computer simulation [8] are listed in Table 1. Owing to the significant linewidth (ca. 2.5 Hz), a complete iterative analysis of the spectra was not possible, but despite this a good fit between experimental and computer simulated spectra was found, as it can be seen for the TCC-DPM $^-$  anion in Fig. 1.

For comparison, previously reported  $^1\text{H}$  NMR data for uncoordinated DPM $^-$  and TPM $^-$  anions [9] are included in Table 1.

At  $-20$  to  $+30^\circ\text{C}$  the spectrum of TCC-DPM $^-$  shows non-equivalence of the *ortho*- and *meta*-proton resonances of the complexed ring, while a complete equivalence of the corresponding positions of the uncoordinated ring is found. The same equivalence is shown by the *o*- and *m*-protons of the uncoordinated DPM $^-$ . This

TABLE 1  
<sup>1</sup>H NMR DATA <sup>a</sup> OF FREE AND Cr(CO)<sub>3</sub>-COMPLEXED DI- AND TRI-PHENYLMETHYL CARBANIONS

	$\delta_1$	$\delta_2$	$\delta_3$	$\delta_4$	$\delta_5$	$\delta_a$	$^3J_{1,2}$	$^4J_{1,3}$	$^5J_{1,4}$	$^4J_{1,5}$	$^3J_{2,3}$	$^4J_{2,4}$	$^5J_{2,5}$	$^3J_{3,4}$	$^4J_{3,5}$	$^3J_{4,5}$	$\Delta(^3J)^b$
DPM <sup>-c</sup>	6.51	6.54	5.65	6.54	6.51	4.22	8.2	1.3	0.5	2.0	6.9	2.0	0.5	6.9	1.2	8.2	1.3
Free	6.94	6.89	6.46	6.89	6.94	4.29	7.5	1.1	0.3	1.8	7.1	1.4	0.3	7.1	1.1	7.5	0.4
Complx.	4.59	4.85	4.49	4.99	3.98		7.7	0.8	0.2	1.6	5.6	1.3	0.1	5.7	0.9	7.4	2.1
TPM <sup>-d</sup>	7.229	6.598	6.048	6.598	7.229	-	8.18	1.18	0.46	2.25	6.95	1.68	0.46	6.95	1.18	8.18	1.23
Free	7.17	7.01	6.73	7.01	7.17	-	7.7	1.0	0.3	1.6	7.0	1.3	0.3	7.0	1.0	7.7	0.7
Complx.	4.41	4.84	4.53	4.84	4.41	-	7.6	0.5	0.1	1.0	5.3	1.0	0.1	5.3	0.5	7.6	2.3

<sup>a</sup> Solvent THF-*d*<sub>6</sub>;  $\delta$ (ppm) from internal TMS; *J* in Hz; *T* 307 K; for protons labeling see Text. <sup>b</sup>  $\Delta^3J = ^3J_{1,2} - ^3J_{2,3}$  (Hz). <sup>c</sup> Data from ref. 9a. <sup>d</sup> Data from ref. 9b.

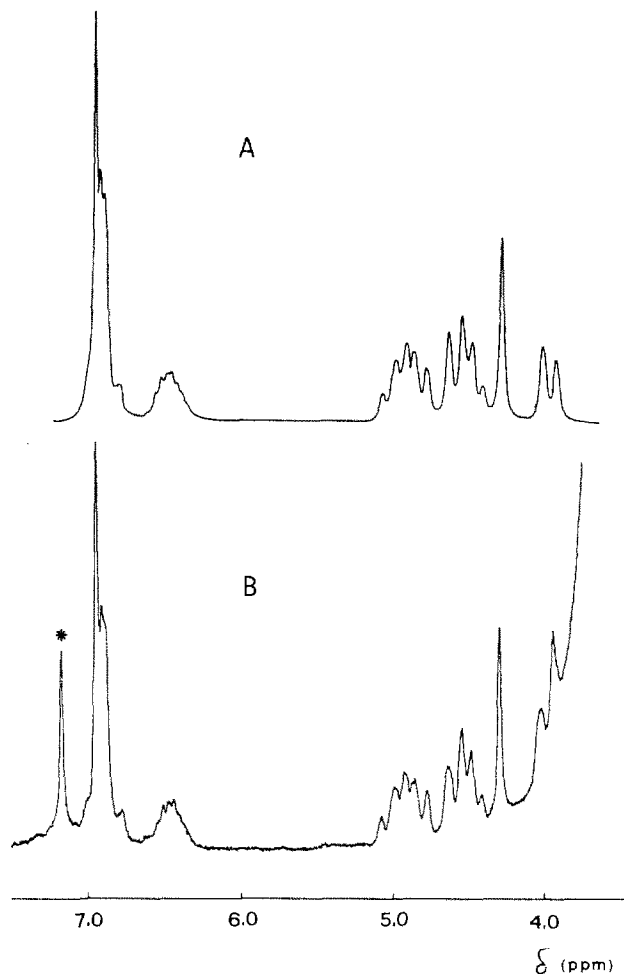
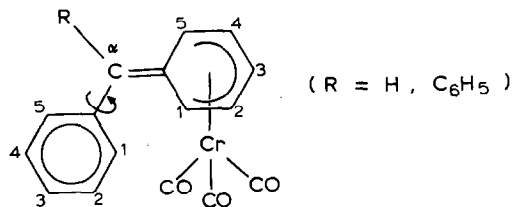


Fig. 1. (A) Computer simulated spectrum of TCC-DPM<sup>-</sup>. (B) <sup>1</sup>H NMR spectrum (in THF-*d*<sub>8</sub> at 307 K) of TCC-DPM<sup>-</sup>: asterisk indicates an impurity; the large signal at the right of the spectrum is from the 18-crown-6.

may indicate that, whereas the uncomplexed ring is free to rotate around its bond to the  $\alpha$ -carbon atom [9a,10], there must be a substantial freezing of the free rotation around the bond between the complexed ring and the exocyclic carbon. This non-equivalence caused by different environments around the complexed ring protons of TCC-DPM<sup>-</sup> is obviously lost in the case of TCC-TPM<sup>-</sup> because of the molecular symmetry (the *o*- and *m*-proton resonances of the complexed ring of neutral TCC-DPM display complete equivalence in the same solvent and the same temperature interval [11]). On the other hand, the lowering of the molecular symmetry due to complexation of TPM<sup>-</sup> does not induce magnetic non-equivalence in the uncomplexed rings, which therefore must be relatively free to rotate around their bonds with the exocyclic carbon.

Another general feature of the spectra of the complexed anions is the downfield

shifts experienced by the uncoordinated ring proton resonances upon complexation (the only exception being the *ortho*-protons of the free ring of TCC-TPM<sup>-</sup>, see Table 1). This is a clear evidence for the lowering of the negative charge on the uncoordinated ring(s), the effect being in line with the well-known electron-withdrawing power of the TCC group. On the basis of the above observations we propose the following structure for the complexed arylmethyl carbanions



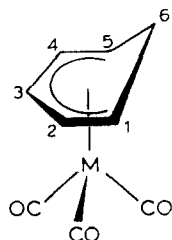
These structures represent the ions as benzylidene and benzhydrylidene- $\eta^5$ -tricarbonyl(cyclohexadienyl)chromium(0) anions, for R = H and C<sub>6</sub>H<sub>5</sub>, respectively.

Further evidence for the importance of such a structure is provided by the relationship between the *ortho*-<sup>3</sup>J(H,H) coupling constant value and the  $\pi$ -bond order both for the free [12] and TCC-complexed substrates [13]. The very small value of  $\Delta(^3J)$  (last column of Table 1), i.e. the difference between <sup>3</sup>J<sub>1,2</sub> and <sup>3</sup>J<sub>2,3</sub> (0.4, 0.7 Hz) observed in the free ring(s) of the complexed anions indicates that the  $\pi$ -bond orders between neighbouring carbon atoms are very similar and, interestingly, close to those found both in the free and complexed rings of the neutral TCC-complexed di- and triphenylmethane [11]. In contrast, the large  $\Delta^3J$ (H,H) values (2.1, 2.3 Hz) observed in the complexed ring of the anions suggest that in this ring there must be substantial double bond fixation between the C(1)-C(2) and C(4)-C(5) positions. These results, when compared also with the intermediate  $\Delta(^3J)$  values shown by the uncomplexed di- and triphenylmethide anions (1.3 and 1.23 Hz), are interpreted as strong evidence in favour of the electronic structure proposed above in which the free ring delocalizes little, if any, of the negative charge, which resides quite entirely in the complexed moiety, partly in the ring and partly in the Cr(CO)<sub>3</sub> unit.

Such a  $\pi$ -electron distribution implies interruption of the aromatic ring current in the complexed ring and therefore a decrease of its downfield contribution to the proton chemical shifts. The average values of the chemical shifts of the complexed ring of TCC-DPM<sup>-</sup> and TCC-TPM<sup>-</sup> anions ( $\delta_{av}$ , 4.58 and 4.61 ppm, respectively) do in fact appear significantly upfield with respect to the corresponding value observed for the complexed ring of  $\eta^6$ -TCC-fluorenyl anion ( $\delta$  5.73 ppm) where the complexation does not break the aromatic  $\pi$ -electron circulation [14].

The electronic structure proposed for the complexed ions implies that their stability is largely governed by the TCC-phenyl substituent and very little influenced by the presence of phenyl substituents at the exocyclic carbon. Measurements of the rate of metallation support this view, since the rate constants for TCC-toluene and TCC-DPM are almost equal and are only 1.7 times lower than that for TCC-TPM [11].

Finally, the relative values of the chemical shifts provide information about the geometric arrangement of the TCC-coordinated ring. In all known organometallic cyclohexadienyl structures of type



the six-membered organic ring is highly nonplanar, with a dihedral angle of 40–45° [15]. The  $^1\text{H}$  NMR spectrum of these molecules is characterized by a spread of 2–3 ppm for the ring proton resonances [2,16]. Even when substitution at C(6) implies a methylene group, a bent structure would still be expected [17]. In the case of  $\text{CpFe}^{\text{II}}$ -triphenylmethanide for example, an exocyclic double bond is present, and a spread of 1.85 ppm is displayed by the ring proton resonances. The extended spread of the resonances is due to the high field shifts of the 1,5-protons as a result of rehybridization of the carbons [18]. In contrast, in our TCC-complexed anions, the 1,5-protons resonate at relatively low fields and close to the 2,3- and 4-protons, so that the spread of the  $\delta$  values is much reduced. Thus, in these systems the complexed ring does not show the characteristic NMR pattern displayed by the cyclohexadienylmetal complexes, and its configuration seems to be planar even though definitive evidence can be provided only by an X-ray structure determination.

In conclusion, it has been established that in the tricarbonylchromium complexes the simple arylmethyl anions preferentially assume a planar cyclohexadienyl structure, while the  $\eta^6$ -TCC-fluorenyl anion prefers a structure in which the negative charge is mainly localized at C(9) and the aromatic characteristics of the two external rings are little modified [14]. The same problem of bonding representation has been amply discussed for the isoelectronic  $\pi$ -arene- $\pi$ -cyclopentadienyliron(II) cations [18] and the conclusion from  $^1\text{H}$  NMR and X-ray data was that the extent to which the zwitterionic (fluorenyl ligand) [19] or the methylene cyclohexadienyl (triphenyl-methanide) forms contribute to the structure of a given molecule changes on changing the molecular geometry of the organic ligand, and in particular with the extent to which the junction carbon of the complexed ring and the exocyclic carbon deviate from the plane of the remaining carbon atoms. In the  $\text{Cr}(\text{CO})_3$  series electronic rather than geometric factors seem to be important in determining the structure of the coordinated ring.

## Experimental

$^1\text{H}$  NMR spectra were recorded at 307 K on a Bruker WP-80 SY at 80.13 MHz with TMS as internal standard. HPLC analyses were performed by means of a Perkin-Elmer Series 3 liquid chromatograph equipped with a Perkin-Elmer  $5\mu$ -reversed phase C-18 column, a Perkin-Elmer LC-75 UV Detector and a Perkin-Elmer LC-75 Autocontrol Unity; a methanol/water mixture (50/50 v/v) was used as eluent. The synthesis of TCC-toluene, diphenylmethane and triphenylmethane were carried out by published methods [20,21,3].

For the NMR measurements,  $5 \times 10^{-2}$  M solutions of the anions in  $\text{THF}-d_8$  were

prepared at room temperature as previously described [14], except that two equivalents of 18-crown-6 were added.

The H<sub>2</sub> gas evolution was monitored with a standard gas burette. The products of the quenching of the anion solutions with nucleophiles (see results) were purified by column chromatography on silica gel under nitrogen, diethyl ether/hexane mixtures (50/50 v/v) being used as eluent.

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