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DETERMINATION OF THE π BARRIER TO ROTATION OF THE CARBONYL GROUP IN *para*-DIMETHYLAMINO-π-(TRICARBONYLCHROMIUM) BENZALDEHYDE BY ^{13}C NMR SPECTROSCOPY

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Summary

The barrier to rotation around the bond between the formyl group and the complexed ring in *para*-dimethylamino-π-(tricarbonylchromium) benzaldehyde (I) was determined by ^{13}C NMR spectroscopy at variable temperature and complete line shape analysis. The $\Delta G^{\neq}$ value for the interconversion in I (8.6 kcal mol^{-1}) is smaller than the corresponding value for the free arene(II) (10.2 kcal mol^{-1}). This decrease can be attributed to a loss of conjugation in the complex and/or to an interaction between the formyl group and the $Cr(CO)_3$ moiety in the transition state.

Introduction

MO calculations [1,2], physicochemical measurements [3—6] and chemical reactivity studies [7,8] with π-(tricarbonylchromium) arenes have demonstrated the electron-withdrawing effect of the $Cr(CO)_3$ moiety. On the other hand, it seems that there are no significant changes in the transmission of substituent effcts in the complexed rings [8—11].

The apparent discrepancy between these results can be interpreted in terms of the involvement of both σ and π orbitals of the arenes in the complexes [12]. Recently the use of ^{13}C NMR spectroscopy in determination of low rotational barriers of aromatic aldehydes has been demonstrated [13,14], and we have now measured the barrier to rotation about the carbonyl C(1) bond (Fig. 1) in *para*-dimethylamino-π-(tricarbonylchromium) benzaldehyde (I) by ^{13}C NMR in order to estimate the changes in conjugation between the ring and the aldehydic carbonyl group upon complexation.

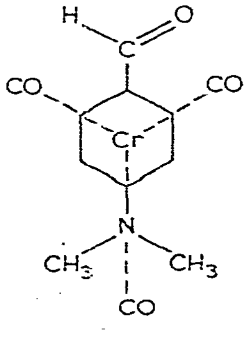
Experimental

Complex I was prepared from chromium hexacarbonyl and purified *para*-dimethylaminobenzaldehyde (II) [15]. The ^{13}C NMR spectra were recorded in the FT mode on a Varian XL 100 spectrometer operating at 25.15 MHz and equipped with a variable temperature accessory. The spectra were obtained with ca. 0.5 *M* solutions of I and II in hexadeuterioacetone in a temperature range of 20 to —103°C. The temperatures were measured by Combrisson's technique [16]. The activation parameters wer obtained by complete lineshape analysis on the *ortho*- and *meta*-carbons respectively.

Results and discussion

The spectra of *para*-dimethylamino-π-(tricarbonylchromium) benzaldehyde (I) at +20 and —103°C are shown in Fig. 1. Because of the decrease of the exchange rate, the signals of the C(2) and C(3) carbons appear as two doublets at low temperature. The coalescence temperatures and the activation parameters obtained for I and II under similar conditions are listed in Table 1. The values obtained for II are close to those measured by Drakenberg [14] with Freon as solvent. A significant decrease of ca. 1.5 kcal mol^{-1} is observed for $\Delta G^{\neq}$ (T_c) under complexation and this effect is mainly explained by a lower value of $\Delta H^{\neq}$ in complex I.

Several explanations may be advanced for these results. For example the bulky $Cr(CO)_3$ moiety could slightly bend the CHO group out of the aromatic plane away from the metal. The distance between the carbon of the aldehyde group and C(2) would then be longer in accordance with the lower $\Delta\nu$(C(2)) in I compared to II. The deviation from planarity would lead to a loss of conjugation and consequently to a decrease of $\Delta G^{\neq}(T_c)$ in the complex. However, X-ray diffraction studies on related compounds have revealed no deviation of the carbonyl substituents from the arene plane [17]. Mereover, because of the conjugation of the substituent effects, the orientation of the $Cr(CO)_3$ group with respect to the arene ring in I favours the eclipsed conformation Ia [18]. Consequently this explanation can be rejected.



(Ia)

In (1'-*t*-butyl-2' 2'-dimethylpropyl)-π-(tricarbonylchromium)benzene, the decrease of the rotational barrier about the bond between the alkyl group and the ring has been attributed to additional steric strain between the alkyl and

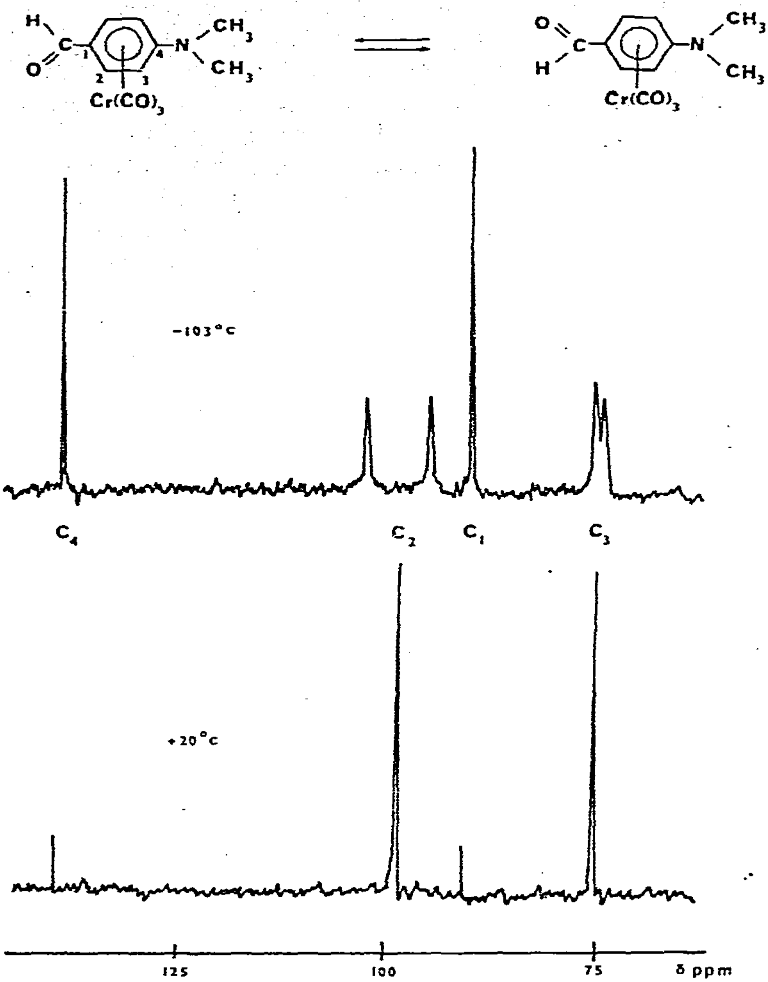


Fig. 1. Aromatic portion of the ^{13}C NMR spectra of *para*-dimethylamino-π-(tricarbonylchromium) benzaldehyde (I) at −103° C and +20° C in CD_3COCD_3. The chemical shifts are in ppm downfield from the TMS resonance as internal reference.

TABLE 1

COALESCENCE TEMPERATURES' FREQUENCY DIFFERENCES AND ACTIVATION PARAMETERS FOR I AND II

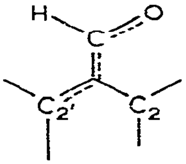
	T_c (C(2)) (°C)	$\Delta\nu$(C(2)) (Hz)	$\Delta G^{\ddagger}(T_c)$ (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} deg^{-1})
I	−82	188	8.6 ± 0.2	8.2 ± 0.2	−2.2 ± 2
II	−50	220	10.2 ± 0.2	11.5 ± 0.2	+6.0 ± 2
III			10.6 [14] [a]	11.0 [14] [a]	+1.7 [14] [a]

[a] In $CHCl_2F + CCl_2F$ [14].

the $Cr(CO)_3$ groups in the complex [19]. In I and II the CHO groups are coplanar with the rings, and it can be assumed that the ground states have similar energies in the free and complexed molecules. However, in I the transition state could be stabilized by an interaction between the negative oxygen of the formyl group and the chromium tricarbonyl moiety. The changes of sign in the $\Delta S^{\neq}$ term for I compared with those for II could be related to a loss of rotational freedom in the transition state in accordance with the above hypothesis.

On the other hand the electron-withdrawing effect of the $Cr(CO)_3$ moiety could explain the decrease of the rotational barrier. Drakenberg et al. [14] found a good correlation between $\Delta G^{\neq}(T_c)$ and Brown σ^+ constants for a series of *para*-substituted benzaldehydes. The $\Delta G^{\neq}(T_c)$ of complex I would correspond to an electron-withdrawing effect of the $Cr(CO)_3$ moiety larger than that of a *para*-nitro group. Similar electronic effects for $Cr(CO)_3$ and NO_2 groups have been proposed from chemical studies [20]. The large decrease in the rotational barrier necessarily implies the modification of the π-electron system upon complexation as a result of the electron-withdrawal by the $Cr(CO)_3$ group.

The frequency difference $\Delta\nu_{C(2)}$ depends on two opposing effects: a carbonyl compression shielding effect on C(2) and a decrease of the electron density on C(2') in the most conjugated *trans* form [21]. This latter effect could be perturbed by a change in the π-electron distribution between I and II leading to a smaller $\Delta\nu$ in the complex. However, this explanation is in conflict with several recent studies showing that the transmission of π-substituent effects is not significantly perturbed by complexation. Thus, we have shown previously that there is a good correlation between the carbon chemical shift of the *para*-carbon and the σ^+ constant in a series of free and complexed monosubstituted benzenes and the slopes of the correlations are similar in the two series [13]. Similar results were also obtained by Bodner [11].



O–C(2') *trans* form

To obtain more information on the electron distribution, it would be of interest to determine the barriers in a series of *para*-substituted π-(tricarbonylchromium) benzaldehydes. However, except for II very low temperatures are needed for determination of the thermodynamic parameters in the free benzaldehydes [14], and in the case of the complexes it would be very difficult to measure the parameters with a conventional probe.

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