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^{13}C NMR LOW TEMPERATURE STUDY OF THE ROTATION AROUND THE CHROMIUM—ARENE BOND*

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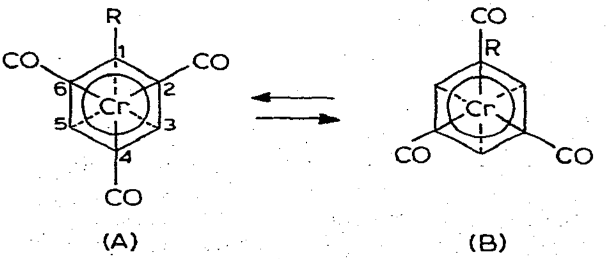
Summary

A fast equilibrium between two conformations is studied by variable temperature ^{13}C NMR for five monosubstituted benzene $Cr(CO)_3$ complexes. It is shown that the complexation does not significantly change the transmission of electronic substituent effects to the *para* position.

Introduction

On the basis of low temperature PMR studies, a rapid exchange between conformers A and B has been suggested for some substituted benzene—$Cr(CO)_3$ complexes [1—5]. However, the data do not provide an unambiguous answer to the problem. We decided therefore to reexamine the equilibrium with the aid of ^{13}C NMR, which, because of the sensitivity of the chemical shift to minor conformational changes and the simplicity of the spectra, is potentially a more suitable tool than PMR.



I, R = H
II, R = CH_3
III, R = C_2H_5
IV, R = OCH_3
V, R = $C(CH_3)_3$
VI, R = $COCH_3$

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Experimental

The ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer, operating at 25.2 MHz in the pulsed mode. The sample concentration was approximately 10% (w/v) in deuteroacetone. Chemical shifts are relative to internal TMS. Chemical shift and temperature accuracy are 0.05 ppm and ± 2°C, respectively.

Results and discussion

The ring carbon chemical shifts for compounds III, V and VI are plotted as a function of temperature in Fig. 1. While the resonances for carbons 2, 4 and 6 in II, III and IV are shifted upfield, those for carbons 3 and 5 are shifted downfield with decreasing temperature. The opposite behaviour, i.e. shielding for carbons 3 and 5, and deshielding for carbons 2, 4 and 6 is observed in VI. In the case of t-butyl substitution in V, no significant shift occurs. This divergence of ^{13}C shieldings can only be interpreted in terms of a temperature dependent equilibrium between A and B.

The upfield shift of the carbon bonded to the metal atom is as generally observed in transition metal π complexes [6,7]. Consequently, in II, III, IV (R electron-releasing), the upfield shift for carbons 2, 4 and 6 with decreasing temperature is in accordance with an increased contribution of B. The opposite behaviour is observed for VI (R electron-withdrawing). The absence of any variation in V is attributed to the existence of a single conformer, A, independent of temperature, in agreement with previous PMR studies [5].

The equilibria are governed by two competing effects: an electronic factor favouring bonding to the carbons with large electron density (A for R electron-

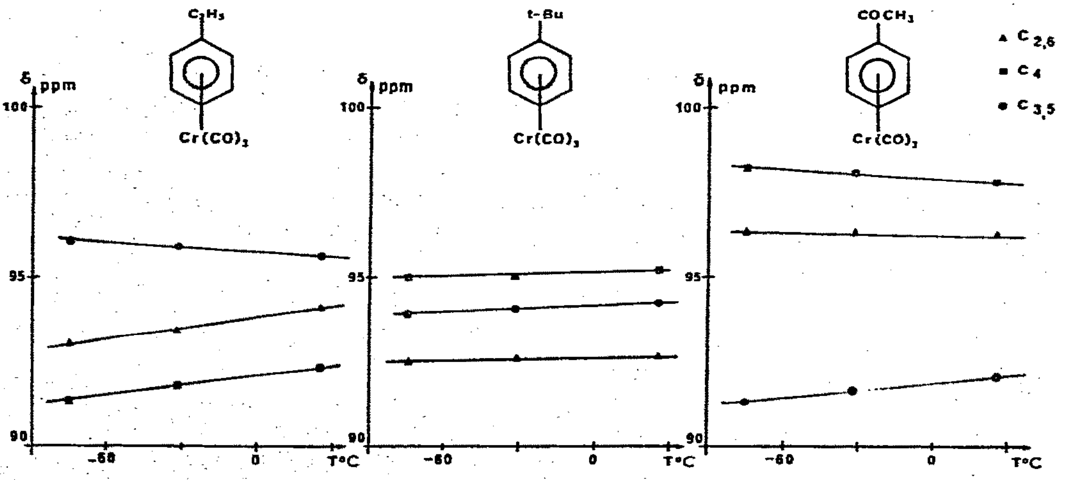

Fig. 1. Plot of ring carbon chemical shifts vs. temperature for ethylbenzene-, t-butylbenzene- and acetophenonechromium tricarbonyl complexes. (The δ values have been corrected for the slight downfield shift which occurs with the parent compound I, as the temperature is lowered.)

TABLE 1

SUBSTITUENT EFFECT ON *para* CARBON CHEMICAL SHIFTS IN FREE AND COMPLEXED BENZENES

Compound	R	$\Delta(R_{free})$ (ppm)	$\Delta(R_{compl.})$ (ppm)
IV	OCH_3	−7.90	−8.56
V	$C(CH_3)_3$	−3.05	−0.54
II	CH_3	−3.02	−4.25
III	C_2H_5	−2.74	−3.38
I	H	0	0
VI	$COCH_3$	+4.50	+2.09

withdrawing, B for R electron-releasing); and a steric effect arising from the interaction between the ring substituent R and the carbonyls. This is supported by X-ray crystallography [8,9].

Thermodynamic data were derived from the chemical shifts of the *para* ring carbon, on the following assumptions: (i) The process converting A into B is fast on the NMR time scale; (ii) The electronic effect of the substituent on $\delta(^{13}C_{para})$ is similar in free and complexed benzenes, as confirmed by the correlation of $\delta(^{13}C_{para})$ vs. Hammett σ^+ constants for both free and complexed benzenes (Table 1, Fig. 2). For the free molecules there is a good linear correlation (Fig. 2a), as shown by Nelson and co-workers [10]. For the complexes there is more scatter, but the general trend is similar except for V (R = t-Bu).

The poor correlation of $\delta(C_{para})$ vs. σ^+ (Fig. 2b) in the complexes may be due to different populations of the conformers in various derivatives. In accordance with this interpretation, a better correlation is found between σ^+ and $\delta(C_{para})$ values of complexes II, III, IV and VI at −76°C (Fig. 2c). The slope of this straight line is similar to that obtained for the free benzenes at ambient temperature. This shows that the transmission of the electronic effect of R on

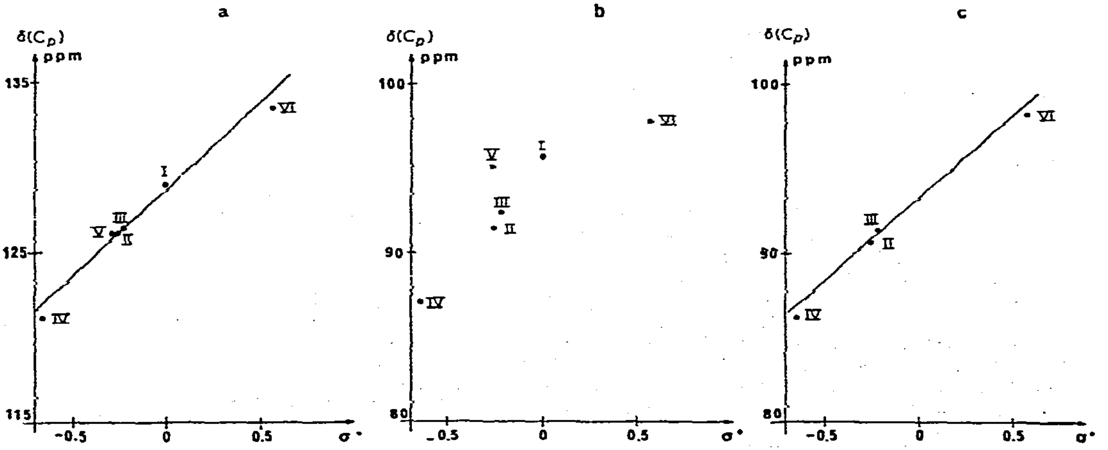

Fig. 2. Plot of $\delta(C_{para})$ vs. σ^+ for (a) free derivatives at 25°C, (b) complexed derivatives at 25°C, and (c) complexed derivatives at −76°C.

TABLE 2

THERMODYNAMIC PARAMETERS

Compound	R	P_B (%) at 25°C	P_B (%) at −32°C	P_B (%) at −76°C	ΔH^* (kcal mole^{-1})	ΔS^* (cal mole^{-1} degree^{-1})
II	CH_3	60.5	68.3	74.3	−0.85	−2.00
III	C_2H_5	51.0	60.2	67.2	−0.78	−2.53
IV	OCH_3	51.3	60.5	66.2	−0.72	−2.32
VI	$COCH_3$	79.6	75.2	73.0	+0.40	+4.00

C_{para} is almost unaltered in the complexes, and that the ratio of conformers A/B at low temperature must be of the same order for II, III, IV and VI. This assumption is confirmed by the subsequent data (vide infra).

The observed chemical shift, $\delta(C)_{obs}$, can be expressed by the following simple equation: $\delta(C)_{obs} = \delta(C)_{pIc} + \Delta(R_{free}) + \theta$ where $\delta(C)_{pIc}$ is the carbon chemical shift in benzene—Cr(CO)$_3$ (I), $\Delta(R_{free})$ is the substituent parameter obtained from the data of Table 1, and θ represents a term to take account of the localization of the C—Cr bonds. For I, in which no localization occurs, $\theta = 0$. In V, existing only in form A, one obtains $\theta = 3.09$ ppm. Consequently, the difference of $\delta(^{13}C_{para})$ between A and B is $\theta_{max} = 6.18$ ppm.

With $P_A + P_B = 100$, one obtains for the relative amount of conformer B in %:

$$P_B = 100\,(\theta_{max}/2 - \theta)/\theta_{max}$$

From the temperature dependence of the equilibrium constant $K = P_B/P_A$, the thermodynamic parameters ΔH^* and ΔS^* can be derived. These are listed in Table 2. As expected, P_B increases with decreasing temperature for II, III and IV while it decreases for VI. The ΔH^* values (difference of enthalpy between A and B) show the variation in the electronic stability of one conformer relative to that of the other as the ring substituent is changed. The ΔS^* values (difference of entropy between A and B) measure the loss of rotational freedom of R due to interactions with the CO groups. For VI the result indicates the importance of this latter effect in A, which is rather unexpected.

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