Internal Rotation in Tricarbonyl(arene)chromium Compounds

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Summary The n.m.r. spectra (−46°—+52°) of tricarbonyl-(*p*-methoxyisopropylbenzene)chromium and tricarbonyl-(*p*-methoxy-t-butylbenzene)chromium show that in these molecules the rotation of the $Cr(CO)_3$ group relative to the arene ring is fast on the n.m.r. time scale.

THE problem of internal rotation of the chromium–arene bond in tricarbonyl(arene)chromium complexes has recently been considered.[1,2] The rotation of the $Cr(CO)_3$ group relative to the arene ring seems to be fast, on the n.m.r. scale, in methyl substituted arenechromium tricarbonyls,[1] while severely restricted rotation is apparently present in tricarbonyl-(t-butylbenzene)chromium and less severely restricted rotation in tricarbonyl(isopropylbenzene)chromium.[2] These conclusions for the latter compounds were reached through the analysis of their n.m.r. spectra which show a temperature dependence for tricarbonyl(isopropylbenzene)chromium in the range −40°—+30°, while in the case of tricarbonyl-(t-butylbenzene)chromium no temperature dependence is observed for the well resolved ring-proton resonances.

We have now investigated the corresponding *p*-methoxy-derivatives, (I) and (II).† Their n.m.r. spectra, recorded in deuteriochloroform, show for the four ring protons an

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† The compounds were prepared according to known methods.[3] Compound (I) m.p. 50—52°, and compound (II) m.p. 48—50°, gave satisfactory analyses. Spectra were recorded at 60 MHz on a JEOL instrument in $CDCl_3$ solution.

AA′BB′ multiplet over the whole temperature range examined (−46°—+52°). Some results relative to the n.m.r. spectra are reported in the Table, where the values are given for the two extremes of temperature examined. Only a small variation of chemical shift is observed on changing the temperature. This is also observed in the corresponding free ligands, which were examined under the same conditions for comparison. Our results seem to indicate that the internal rotation of the chromium–arene bond is fast in the compounds here examined. This is also likely to be the case in the corresponding monosubstituted compounds, reported in ref. 2, where the complexity of the spectrum does not allow one to follow (especially for the isopropyl derivative) the variations of chemical shift of each ring proton at different sample temperatures. On the other hand, small variations of ring-proton chemical shifts due to different intermolecular interactions in tricarbonyl (isopropylbenzene)chromium should be responsible for the temperature dependence of the spectrum. It has in fact been observed that ^{1}H n.m.r. spectra of arenechromium tricarbonyls are strongly solvent dependent,[3,4] since the protons in these molecules seem to be more acidic than those of the corresponding free ligands.[3]

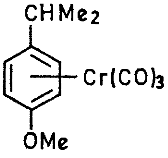
^{1}H *n.m.r. parameters for compounds* (I) *and* (II) *at different temperatures*

Compounds	$T°$	τ_o[a]	τ_m[a]	J_{om}(Hz)	τ(OMe)	τ(CH)	τ(CH$_3$)	J(CH–CH$_3$) (Hz)
(I)	52	4·89	4·48	7·3	6·27	7·46	8·77	6·7
	−46	4·89	4·41	7·3	6·23	7·46	8·77	6·7
(II)	52	4·96	4·32	7·1	6·27	—	8·72	—
	−46	4·92	4·24	7·2	6·22	—	8·71	—

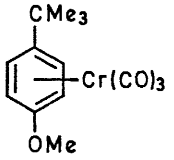
[a] τ_o and τ_m refer to the methoxy-substituent.

The results here reported could be also interpreted on the basis of severely restricted rotation in compounds (I) and (II) at +52°, but we discard this hypothesis for the following reason. If severely restricted rotation occurs and the molecules remain in one preferred conformation, which should be that represented by (III),[2] we must also accept that the shielding due to the CO groups affects the ring-protons differently,[2] and the symmetry of the AA′BB′ group would be destroyed.

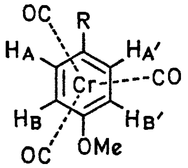
Toluenechromium tricarbonyl shows for the ring-protons, at room temperature, a complex partially well resolved multiplet, which has been analysed,[3] and not a single line as found for tricarbonyl(isopropylbenzene)chromium.[2]



(I)



(II)



(III)

It thus seems to us that changes in the shape of the spectrum of tricarbonyl(alkylbenzene)chromium derivatives which occur at different temperatures—at least in the temperature range examined up till now—can hardly be attributed to restriction of the internal rotation of the Cr(CO)$_3$ group relative to the arene ring, which on the basis of our results should be fast.

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[2] D. E. F. Gracey, W. R. Jackson, W. B. Jennings, S. C. Renninson, and R. Spratt, *Chem. Comm.*, 1966, 231; W. R. Jackson, W. B. Jennings, S. C. Rennison, and R. Spratt, *J. Chem. Soc.* (*B*), 1969, 1214. In the latter paper, Jackson *et al.* examined deuteriated compounds; however, a symmetrical trideuteriated derivative is more appropriate for the demonstration of restricted rotation.

[3] A. Mangini and F. Taddei, *Inorg. Chim. Acta*, 1968, **2**, 8.

[4] H. P. Fritz and C. G. Kreiter, *J. Organometall. Chem.*, 1967, **7**, 427.