Restricted Rotation in Tricarbonyl(arene)chromiums

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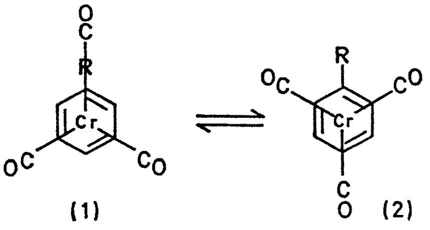
Summary The variable-temperature n.m.r. spectra of some tricarbonyl(arene)chromium compounds can be explained in terms of varying conformer populations *i.e.* in the terminology of Mislow and Raban, "thermodynamic restriction of rotation" occurs: no evidence can be found for "kinetic restriction" even for spectra of tricarbonyl-(1,4-di-t-butyl-2,5-dimethoxybenzene)chromium at −80°.

A RECENT communication[1] has criticised our interpretation of the variable-temperature n.m.r. spectra of some tricarbonyl(arene)chromium compounds.[2,3] Our results showed quite clearly that the variable-temperature spectra *e.g.* of tricarbonyl(isopropylbenzene)chromium, were due to the temperature-dependence of a conformational equilibrium about the ring–metal bond. The exchange could be described as a two component equilibrium between conformers (1) and (2); $R = Pr^i$. Electronic effects of the electron-releasing alkyl groups favoured (1) but unfavourable steric interactions favoured (2). When $R = Bu^t$, the adverse steric interactions became dominant and the equilibrium lies heavily in favour of (2). Thus in the terminology of Mislow and Raban[4] we may speak of "thermodynamic restriction of rotation." Conversely, when R = OMe or Me, the electronic term dominates and the equilibrium strongly favours conformer (1). A quantitative theory was developed for tricarbonyl(alkylbenzene)chromiums.[2] At all times rotation around the metal–ring bond was considered to be fast on the n.m.r. time-scale. Barbieri and Taddei[1] surprisingly ignore our detailed thermodynamic treatment and discuss both our results and their own in terms of "kinetically restricted rotation." In kinetically restricted rotation for tricarbonyl(arene)chromiums with bulky groups, the conformation (2) becomes the transition



(1) (2)
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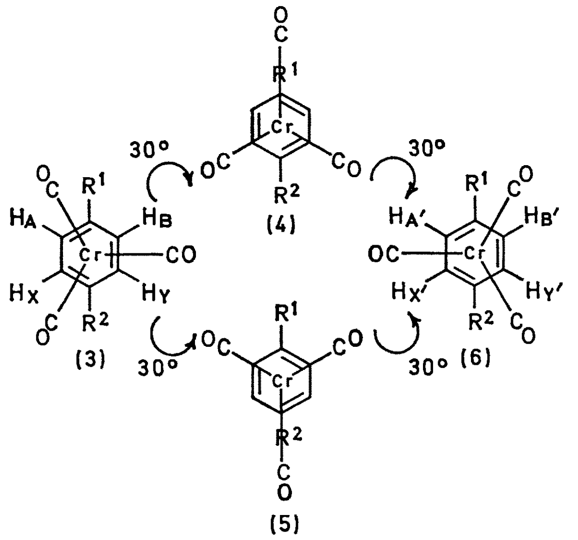
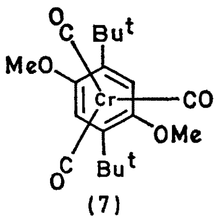
state and rotation about the ring–metal bond becomes slow on an n.m.r. time-scale. Obviously, no information about such a process could be obtained from monosubstituted alkylbenzene complexes. Barbieri and Taddei dismiss our experiments with the isopropyl compound as being too complex to follow, ignoring the work on the deuteriated compound. They ascribe any spectral changes to changes in intermolecular interactions without quoting any evidence and ignoring the fact that similar spectral changes were observed in three solvents, CS_2, $CDCl_3$, and decalin.[2]

Information about kinetically restricted rotation using the dynamic n.m.r. method[5] can be obtained for *p*-disubstituted benzene complexes provided that the preferred ground-state geometry is that in (3) or (6) and that *both* the transition states (4) and (5) for the conformational exchange are >8 kcal/mole less stable than the ground states. When these conditions are satisfied and $R^1 \neq R^2$ the aromatic protons will be divided into two intrinsically diastereotopic[6] pairs (A and B; X and Y) which may exhibit chemical-shift nonequivalence.†



Barbieri and Taddei chose to study the tricarbonylchromium compounds of *p*-isopropylanisole ($R^1 = Pr^i$, $R^2 = OMe$) and *p*-t-butylanisole ($R^1 = Bu^t$, $R^2 = OMe$). These compounds fit *neither* of the necessary conditions for observing diastereotopic nuclei. Firstly the preferred ground-state conformation is almost certainly (5; $R^1 = Pr^i$ or Bu^t, $R^2 = OMe$). This follows from our previous work,[2] the closely related investigations of Emanuel and Randall,[7] and from the *X*-ray studies of Sim *et al.*[8] Even if (3) or (6) were the ground-state conformations they could readily exchange *via* the "transition state" (5) which could be stabilised by the methoxy-group for the previously given reasons. Additionally, a bulky group R^1, *e.g.* t-butyl, which could raise the energy of (4) relative to (3) and (6) would be expected to destabilise (3) and (6) relative to (5), thus leading to steric acceleration of conformational interchange. For these reasons it is not surprising that Barbieri and Taddei failed to observe slow rotation in tricarbonyl-(*p*-t-butyl- and *p*-isopropyl-anisole)chromiums.

In order to observe kinetic restriction it is obviously necessary to destabilise the eclipsed conformations (4) and (5) by choosing a compound where *both* R^1 and R^2 are large. We have examined the n.m.r. spectra‡ of tricarbonyl-(2,5-dimethoxy-1,4-di-t-butylbenzene)chromium (7) in $[^2H_6]$-acetone in the temperature range +30 to −55° and in dichlorofluoromethane in the temperature range +30 to −75°. The potentially diastereotopic aromatic protons and methoxy-protons absorbed as sharp singlets throughout the temperature range studied. Similarly the four aromatic protons of tricarbonyl-(1,4-di-t-butylbenzene)chromium (8) remained a sharp singlet over the temperature range +30 to −70° in $[^2H_6]$acetone.



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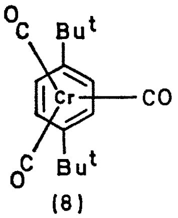

(8)

The failure to obtain any evidence of slow rotation on the n.m.r. time-scale in (7) and (8) is not surprising in view of our earlier equilibrium studies which indicated that the adverse steric interactions of a t-butyl group with a superimposed Cr–CO bond were probably < 2 kcal/mole. Additionally, the most probable ground-state conformation of (7) and (8) (as shown) also probably contains adverse steric interactions as this conformation differs from the eclipsed transition state by a torsion angle of only 30°.

Finally, the spectra of *m*-di-isopropylbenzene in deuteriochloroform solution have been examined over the temperature range +30 to −50°. No significant changes were recorded, and the *meta*-protons remained unresolved from the other aromatic signals. In this temperature range the spectra of the corresponding tricarbonylchromium compound change drastically,[2] thus negating the implication that any changes in the spectra of tricarbonylchromium compounds also occurred in the parent ligand spectra.[1]

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† Since the groups are *intrinsically* diastereotopic the magnitude of the chemical shift nonequivalence might be expected to be small, see G. Binsch, *J. Amer. Chem. Soc.*, 1969, **91**, 3999.

‡ Spectra were recorded at 100 MHz.

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