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DIRECT OBSERVATION OF THE RING CURRENT IN A π-ARENETRICARBONYL CHROMIUM (0) COMPLEX

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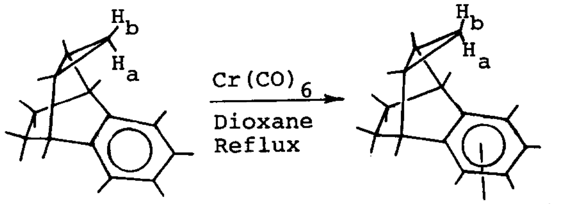
The origin of the unusual 2.0-2.5 ppm upfield chemical shift of the aromatic protons in the nmr spectra of η^6-arenechromium (0) complexes has been the subject of considerable speculation in recent years.[1] One of the more obvious explanations for this upfield shift is a decrease in the ring current as a result of complexation of the arene ring with the metal.[1b-e,2] There has been no experimental evidence, however, which attempts to observe directly the ring current in such systems and thereby confirm or rule out his most plausible hypothesis.

In order to test experimentally the ring current disruption hypothesis, a system was chosen which could serve to probe the magnitude of the ring current in both an uncomplexed and the corresponding complexed system. The η^6-arenechromium tricarbonyl complex II was therefore synthesized,[3,4] and its ^{1}H-nmr spectrum[5] was analyzed and compared to the corresponding spectrum of the free arene I.[6] The presence of substantial shielding of cyclopropyl proton H_a in arene I indicates that it is oriented above the aromatic ring and is influenced to a significant extent by its ring current.[7] A comparison, therefore, of the chemical shifts of these protons with those of the corresponding protons in complex II can serve as a direct measure of the magnitude of the ring current in each system. In addition, the remote position of these protons relative to the $Cr(CO)_3$ moiety should hopefully minimize any variations in chemical shift which may be due to electronic or magnetic effects derived from direct interaction with the metal atom or the carbonyl ligands.



I II

The pertinent chemical shift data are given in Table I. As expected, an upfield shift of 1.99 ppm in the positions of the aromatic protons does occur in going from the uncomplexed to the complexed system. However, a similar comparison of the chemical shifts of H_a and H_b in both systems shows virtually no change in the chemical shifts of these protons in the two molecules.

TABLE I. - Chemical Shifts (ppm δ)[4]

		Free Arene I	Complex II	Δδ
Aromatic Protons		7.20	5.21	1.99
Cyclopropyl Protons	H_a	-0.93	-0.88	0.05
	H_b	-0.03	-0.01	0.02

The data reported here therefore demonstrate that complexation with chromium (0) does not disrupt the aromatic ring current of the arene ligand and therefore rules out this explanation as the origin of the upfield shift of the aromatic protons in such systems.[8]

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3. Complex II was prepared by allowing arene I to react with an excess of chromium hexacarbonyl in boiling dioxane for 21 hr under nitrogen followed by chromatography on Florisil and recrystallization from acetone-hexane.

4. ^{1}H-NMR, IR, low resolution mass spectral data, and satisfactory combustion analysis were obtained for this compound.

5. ^{1}H-NMR spectra were recorded on a Varian EM-390 spectrometer. Deuterochloroform was used as the solvent; chemical shifts are reported in δ values in ppm relative to internal TMS.

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7. Construction of a Dreiding model and careful measurement of the position of H_a places it 1.95Å from the plane of the aromatic ring and 1.35Å from its center. This corresponds to an angle of 55° from the plane of the aromatic ring. Significant shielding is therefore predicted[9] and indeed found.

8. For discussions of alternative explanations to this phenomenon see refs 1,2.

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