

Preliminary communication

BARRIERS TO $\text{Fe}(\text{CO})_3$ ROTATION IN SUBSTITUTED CYCLOHEXA-DIENYL COMPLEXES

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(Received October 25th, 1983)

Summary

Rotational barriers have been determined from an analysis of exchange-broadened line-shapes in ^{13}C NMR spectra of substituted tricarbonyl(cyclohexadienyl)iron(I+) salts.

Although the barriers to rotation of the metal-carbonyl groups of a variety of transition-metal complexes have been determined [1], no such measurements have been reported for tricarbonyl(cyclohexadienyl)iron(I+) salts, which are available [2] in a wide variety of substituted forms and are of growing importance [3] in organic synthesis. In such complexes the interaction between organic substituents and the complexed olefin is not understood in detail, and yet is of practical importance since the degree of regiocontrol in alkylation reactions of unsymmetrically substituted complexes is dependent [4] on the type of substituent. In this paper we report the result of an analysis of exchange-broadened ^{13}C NMR line-shapes in spectra of complexes of type 1 which was undertaken to identify the effects of substitution on barriers to rotation of the tricarbonyliron group. The rotational barriers of a range of η^3 to η^6 complexes have previously been related [5] to the nature of the metal—ligand bonding and the effects of substituents are believed [5] to have a pronounced influence on expected rotational barriers of (arene) $\text{Cr}(\text{CO})_3$ complexes.

For this study, NMR spectra were recorded at 15.04 MHz at temperatures between 40 and -60°C in CD_3CN for high temperature measurements and liquid SO_2 for low temperature measurements. Intermediate values were recorded in both solvents and consistent linear plots were obtained over the entire temperature range. Line-shape analysis was performed by computer simulation of spectra

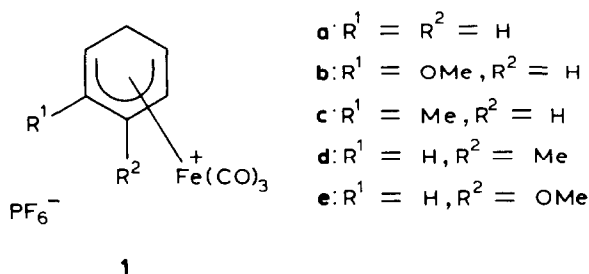
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TABLE 1

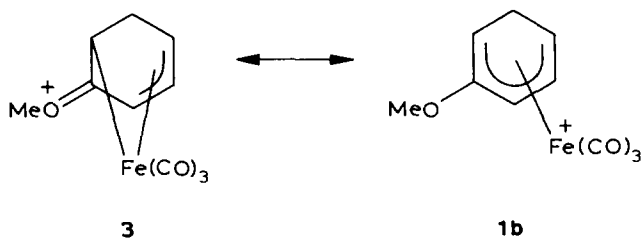
Cation	Structure	E_A (kcal mol $^{-1}$)
(Cyclohexadienyl)Fe(CO) $_3^+$	1a	10.7 \pm 0.2
(2-Methoxycyclohexadienyl)Fe(CO) $_3^+$	1b	11.4 \pm 0.5
(2-Methylcyclohexadienyl)Fe(CO) $_3^+$	1c	12.6 \pm 0.4

on the basis of simple rotation of the Fe(CO) $_3$ group. The results are indicated in Table 1.

Complexes **1d** and **1e**, with 3-methyl and 3-methoxy substituents, were also examined, but low temperature limiting spectra could not be obtained for these compounds. The former showed a single broad resonance at -60°C at 15.04 MHz but observation at 50.3 MHz revealed two overlapping peaks at 199.2 and 204.4 ppm. The 3-methoxy complex **1e** showed only a sharp singlet at all temperatures between 23 and -62°C . This is consistent with a lower barrier to rotation in **1e** than in **1d**, although a smaller separation of the chemical shifts of the carbonyl groups could also account for this observation.



The order of rotational barriers in the sequence $R^1 = \text{H} < R^1 = \text{OMe} < R^1 = \text{Me}$ for 2-substituted complexes, can be explained on steric grounds by the smaller bulk of the methoxy group compared to that of the methyl group. The interaction of a lone pair on the oxygen of the methyl ether with the η^5 -cationic complex, which can be envisaged as a contribution by the tautomer **3** to the bonding in complex **1b**, does not appear to have a pronounced effect on the barrier to rotation. In other respects, methoxy substitution is highly significant. The rates of alkylation of **1b** and **1e** differ greatly from that of **1a** and depend [6] critically on the site of substitution, and methoxy substituents have been found [5,7] to be more effective than alkyl groups in directing the position of alkylation of unsymmetrical complexes. A recent report [8], however, indicates that steric blocking of the preferred site can overcome this directing influence.



The similarity between the value for E_A obtained for complex 1a and the theoretical value calculated [9] for the acyclic cation 2 is noteworthy. Apparently the interaction [10] of the C-6 methylene group, in the cyclic ligands, with the metal—ligand bonding, has little effect on the rotation of the $\text{Fe}(\text{CO})_3$ group. Indeed, the observed [9] barrier for the acyclic complex is actually higher than those observed for the cyclohexadienyl complexes.

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