

Preliminary communication

MEASUREMENT OF BARRIERS TO ARYL ROTATION IN $\text{Cp}(\text{CO})_2\text{Fe}=\text{CHC}_6\text{H}_5^+$ AND $\text{Cp}(\text{CO})_2\text{Fe}=\text{CH}(p\text{-CH}_3\text{C}_6\text{H}_4)^+$

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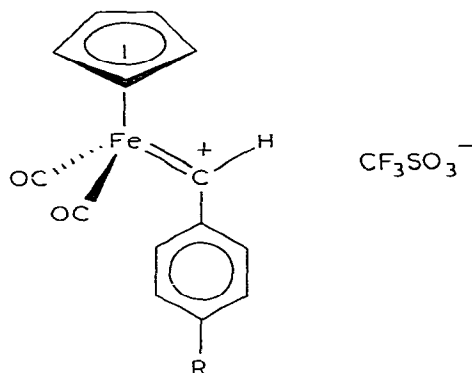
Summary

The first observation of barriers to rotation about the $\text{C}_{\text{aryl}}-\text{C}_{\text{carbene}}$ bonds in aryl-substituted metal carbene complexes is reported. Using variable temperature ^1H NMR, barriers of 9.1 and 10.4 kcal/mol have been determined for $\text{Cp}(\text{CO})_2\text{Fe}=\text{CHC}_6\text{H}_5^+$ and $\text{Cp}(\text{CO})_2\text{Fe}=\text{CH}(p\text{-CH}_3\text{C}_6\text{H}_4)^+$, respectively. The data clearly indicate a geometry of the complex in which the aryl ring lies coplanar with the $\text{Fe}-\text{C}_{\text{carbene}}-\text{C}_{\text{ipso}}$ plane.

Electron donation from carbene substituents is clearly important in the stabilization of electrophilic transition metal-carbene complexes. Heteroatom or aryl substituents are present in the majority of isolable species [1]. In the case of the heteroatom-stabilized carbenes, one indication of strong π -interaction is the existence of a substantial barrier to rotation about the heteroatom-carbene carbon bond. For example, α -amino-carbene complexes can exist as stable, isolable, *cis-trans* isomers [2] while a barrier of 12.4 kcal/mol has been observed for carbon-oxygen bond rotation in pentacarbonyl[(methoxy)(methyl)carbene]chromium(0) [3]. Analogous barriers have not been reported for aryl-substituted species. X-ray structural data for several such complexes suggests remarkably varied degrees of conjugative interaction between the aryl group and the carbene carbon. For example, in the heteroatom-substituted complex $(\text{CO})_5\text{Cr}[\text{C}(\text{OCH}_3)(\text{C}_6\text{H}_5)]$ where π -electron donation from methoxyl provides the major mode of stabilization, the twist angle of 90° between the $\text{Cr}-\text{C}_{\text{carb}}-\text{C}_{\text{ipso}}$ and aryl planes precludes conjugative interaction [4]. In contrast, twist angles observed in $(\text{CO})_5\text{W}[\text{C}(\text{C}_6\text{H}_5)_2]$, (42°) [5]; $(\text{CO})_5\text{W}[\text{C}(2\text{-thienyl})(2\text{-furyl})]$ (35° , 15°) [6] and $\text{Cp}(\text{CO})_2\text{Mn}[\text{C}(\text{C}_6\text{H}_5)(\text{COC}_6\text{H}_5)]$, ($\sim 0^\circ$) [7] are similar to, or less than those in the trityl ion (32°) [8] and clearly permit substantial interaction. No structural data are available for the $(\text{CO})_5\text{WCHC}_6\text{H}_5$ complex [9]

where the interaction would be expected to be strong. The ^1H NMR data indicates rapid aryl rotation even at -80°C [9].

The highly electrophilic cationic iron carbene complexes of general structure I have been under extensive study in this laboratory [10]. Based on ^1H and ^{13}C NMR data, we have postulated extensive π -interaction between the aryl substituent and the carbene carbon atom with substantial positive charge delocalization into the aryl ring [10]. For such interaction, the aryl ring was proposed to



(Ia, R = H;
Ib, R = CH₃)

lie coplanar with the Fe—C_{carb}—C_{ipso} plane. In this communication we report variable temperature ^1H NMR studies of Ia and Ib which have provided the first direct observation of a barrier to rotation of the aryl substituent.

The benzylidene and xylylidene complexes were generated in situ in CD_2Cl_2 by elimination of methoxide from the ether precursors [10]. 100 MHz ^1H NMR spectra were recorded at intervals of 5° from -100°C to -10°C . All observed spectral changes are reversible. Decomposition of the carbene salts are not appreciable until $+20^\circ\text{C}$.

The general spectrum of the *p*-xylylidene complex is characterized as follows: $\delta(\text{H}_{\text{carb}})$ 16.5 ppm; $\delta(\text{H}_{\text{Cp}})$ 5.87 ppm; $\delta(\text{CH}_3)$ 2.40 ppm; $\delta(\text{H}_{\text{ortho}})$, $\delta(\text{H}_{\text{meta}})$ 7.5–8.2 ppm (see below). All signals are temperature invariant except for the aryl resonances as shown in Fig. 1. At -75°C the aryl resonances appear as two bands at δ 8.23 (1H, doublet 8Hz) and δ 7.55 (3H) ppm. Clearly the two *ortho* signals are distinct with one overlapping the *meta* resonances at δ 7.55 ppm. As the temperature is raised, the low field *ortho*-doublet averages with the *ortho* proton resonance at δ 7.55 ppm. Coalescence is observed at -56°C . Above -56°C the *ortho* resonances continue to sharpen, eventually yielding two well-defined doublets $\delta(\text{H}_{\text{ortho}})$ 7.97, $\delta(\text{H}_{\text{meta}})$ 7.55 ($J = 8$ Hz) ppm. Line shape analysis* [11], of these spectra yields a first-order rate constant for site ex-

*The simple coalescence formula [1a, b] has been applied to determine rate constants at the coalescence temperature. Although this equation is strictly applicable to the averaging of single lines of equal population, negligible errors will result when applied to coupled lines if J is much less than $\Delta\nu$ as applies here ($J/\Delta\nu$ ca. 0.1) [11c]. Furthermore, any small errors introduced will be systematic ones and should not affect differences in ΔG^\ddagger 's. Conservatively, we have assigned our error limits as $T_c \pm 3^\circ\text{C}$ and $\Delta\nu \pm 16$ Hz (the entire width of the band at δ 7.55!) which leads to ΔG^\ddagger of ± 0.3 kcal/mol. A more realistic expectation in limits ($T_c \pm 2^\circ\text{C}$, $\Delta\nu \pm 6$ Hz) results in ± 0.15 kcal/mol variation in ΔG^\ddagger .

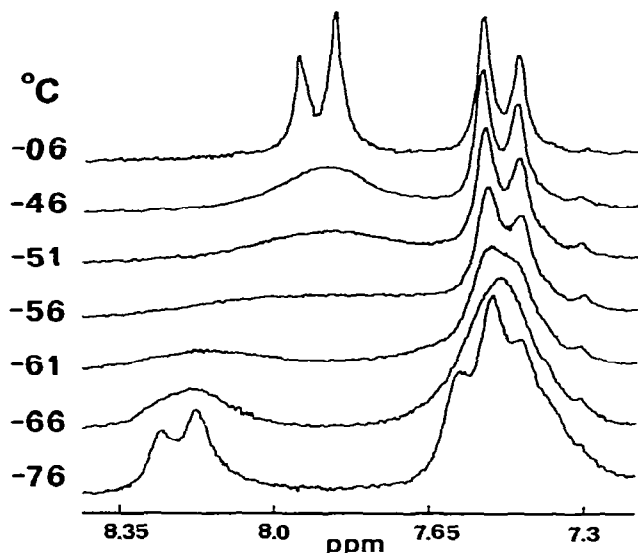


Fig. 1. Variable Temperature ^1H NMR Spectrum of Ib.

change, $k = 160 \text{ sec}^{-1}$ (-56°C), corresponding to a free energy of activation, ΔG^\ddagger , of $10.4 \pm 0.3 \text{ kcal/mol}$ for the barrier to rotation about the xyllyl axis.

In the case of the benzylidene system, Ia, similar behavior is observed but the additional *para* resonance now overlaps the single *ortho* and two *meta* resonances at δ 7.55 ppm. At -100°C the two distinct *ortho* resonances appear at δ 8.41 ppm and ca. δ 7.55 ppm (overlapped by H_{para} , H_{meta}). These bands exhibit a coalescence temperature of -80°C and average at higher temperatures. At T_c , (-80°), $k_{\text{site-exchange}} = 191 \text{ sec}^{-1}$, corresponding to ΔG^\ddagger for bond rotation of $9.1 \pm 0.3 \text{ kcal/mol}$.

These results clearly confirm coplanarity of the aryl ring in I with the $\text{Fe}-\text{C}_{\text{carb}}-\text{C}_{\text{ipso}}$ plane and a strong conjugative interaction between the aryl group and the carbene carbon atom. Additionally, the difference in the aryl rotational barriers of Ia and Ib (1.3 kcal/mol) suggests the barrier is largely electronic in nature and not of steric origin. All these factors point to high electrophilicity of the carbene center, as does the observation that Ia and Ib react rapidly with olefins at low temperatures to yield cyclopropanes [12].

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