Restricted Rotation of the Arene Ring in $(p\text{-Bu}^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$

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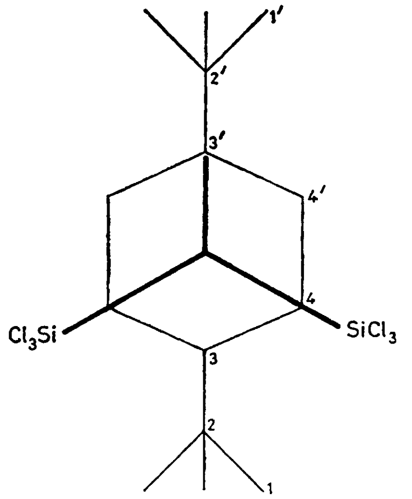
Summary The ^1H and ^{13}C n.m.r. spectra of $[(p\text{-Bu}^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2]$ indicate a restricted rotation of the arene ring about the ruthenium atom, with an estimated barrier to rotation of 51 kJ mol^{-1}.

WE have synthesized a number of derivatives of the type $(C_6H_{6-n}R_n)Ru(CO)(SiCl_3)_2$ (R = Me, n = 1—4, 6; R = Bu^t, n = 1, 2; R = Cl, n = 1), by heating *cis*- or *trans*-$Ru(CO)_4(SiCl_3)_2$ [1] with the appropriate arene at temperatures above 120 °C; an inert solvent was used in cases where the arene was a solid. As in the structure established for $(C_6H_6)Ru(CO)(GeCl_3)_2$ [2] these derivatives are believed to adopt a 'piano stool' arrangement of ligands. Of particular interest is the *p*-di-(t-butyl)benzene derivative, $(p\text{-}Bu^t_2C_6H_4)Ru(CO)(SiCl_3)_2$ (**1**), the ^1H and ^{13}C n.m.r. spectra of which are consistent with a restricted rotation of the arene ring about the ruthenium atom on the n.m.r. time scale. We believe that this is the first time such a restricted rotation has been observed using this method.



(1)

The carbonyl-group is omitted for clarity.

The ^1H n.m.r. spectrum (Figure 1) of (**1**) in the aromatic region exhibits a single signal (δ 6·61) in CD_2Cl_2 at room temperature. However, at −25 °C the signal broadens and at −60 °C it is resolved into an aa′bb′ pattern typical of aromatic systems of the type $(X)C_6H_4(Y)$. Similarly, the ^{13}C n.m.r. spectrum† at 20 °C (Figure 2) shows four resonances: δ (CD_2Cl_2; Me_4Si) 31·0 (CH_3), 35·8 [C–$(CH_3)_3$], 103·4 (ArCH), and 134·6 p.p.m. (ArC–Bu^t). Each of these resonances is split into a doublet at −60 °C, whereas the carbonyl resonance (at δ 195·5 p.p.m.) remains sharp at this temperature. That each arene carbon resonance is split into two, and only two, signals is consistent with the conformation of the rigid form of (**1**) as shown. From the collapse temperature and the chemical shift difference (in the rigid form) of pairs of signals it is possible[4] to estimate an approximate free energy of activation of 51 kJ mol^{-1} for the rotation. (A complete line-shape analysis of the spectra is planned.)

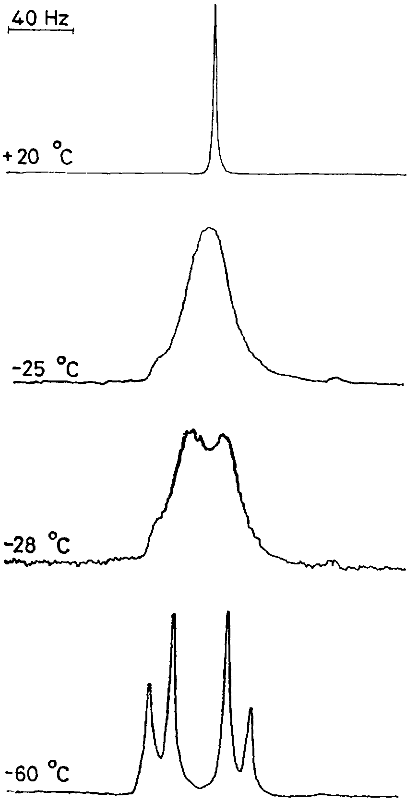


FIGURE 1. 100 MHz ^1H N.m.r. spectra (aromatic region) of (**1**) in CD_2Cl_2 solution.

The ^{13}C n.m.r. spectra of the mesitylene and *p*-xylene analogues of (**1**), at −90 °C, indicate a rapid rotation of the arene ring in these molecules. Since the electronic effects exerted by *p*-xylene and *p*-di-(t-butyl)benzene when bonded to ruthenium are not expected to be very different, it is reasonable to assume that the barrier to rotation in (**1**) is mainly due to the steric interaction between the bulky t-butyl and trichlorosilicon groups. The eclipsed conformation shown minimizes these interactions. It should be noted that an eclipsed configuration was found for $(C_6H_6)Ru(CO)(GeCl_3)_2$ in the solid state.[2]

Also of interest is the fact that the t-butyl signal at δ 1·31 in the ^1H n.m.r. spectrum (100 MHz) remained a single peak at −60 °C. As can be seen in Figure 2 the methyl ^{13}C resonance of the t-butyl groups is barely resolved at −60 °C. This very small difference (δ 0·2 p.p.m.) in the chemical shifts of the two t-butyl environments may indicate that for this molecule through-space effects on the chemical shift are small. The t-butyl signal in the ^1H n.m.r. spectrum did show a significant broadening at −90 °C (the peak width at half height was 17·5 Hz compared to 2·75 Hz for the Me_4Si signal). It is not thought that this broadening is due to the hindered rotation of the arene ring; it may indicate the onset of a restricted rotation of the butyl-groups.

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† The conditions used to obtain the ^{13}C n.m.r. spectra were similar to those given in ref. 3.

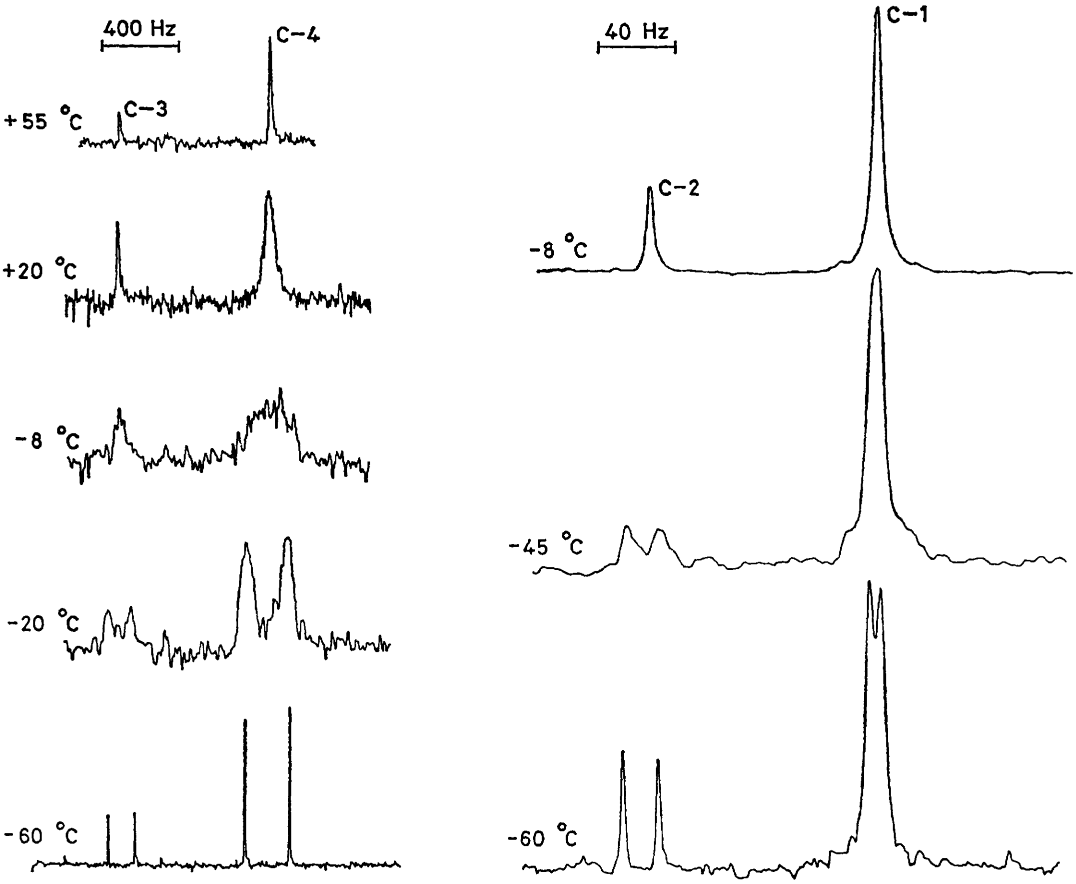

FIGURE 2. 25·2 MHz ^{13}C N.m.r. spectra of (**1**) (left: aromatic carbons; right: t-butyl carbons). In CD_2Cl_2 solution, except the spectrum at 55 °C ($CDCl_3$ solution). Tris(acetylacetonato)chromium was used as a relaxing agent in obtaining the spectrum at −60 and +55 °C.

Although many conformational studies have been carried out on arene derivatives of the Group-6 carbonyls[5] and also on some arene-ruthenium compounds,[6] in all cases rotation around the ring–metal bond was fast on the n.m.r. time scale. Using mechanical spectroscopy Shaver and his co-workers have found barriers of between 20—25 kJ mol^{-1} for the rotation of the cyclopentadienyl ring in some cyclopentadienylplatinum derivatives.[7] Also, Mislow has estimated a barrier of *ca.* 11 kJ mol^{-1} for the rotation of the arene ring in $(C_6Et_6)Cr(CO)_3$.[8]

We are grateful to the N.S.E.R.C., Canada and to the Simon Fraser University for financial support.

(*Received*, 1*st April* 1980; *Com.* 348.)

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