Preliminary communication

A variable temperature NMR study of carbonyldiphenylacetylene tris(π-cyclopentadieny1rhodium) and its bis(pentafluorophenyl) derivative

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SUMMARY

The temperature-dependent $^1$H and $^{13}$C NMR spectra of $(h^5$-$C_5H_5)_3Rh_3$(CO)C$_6$H$_5C$=$C$C$_6$H$_5$ support the view that this molecule is fluxional in solution at room temperature but is in a frozen conformation at $-88^\circ$; NMR data of $(h^2$-$C_5H_5)_3Rh_3$(CO)C$_6$F$_5C$=$C$C$_6$F$_5$ indicate that this molecule appears to be static at room temperature and fluxional at elevated temperatures. The NMR data are consistent with structures, which have been determined by X-ray methods.

It has been known for some time that some polynuclear metal carbonyl complexes are fluxional in solution, e.g., $[\{h^5$-$C_5H_5\}Fe(CO)$_2$]_2$1 $Rh_4(CO)$_{12}$2 and $[h^5$-$C_5H_5]_2$-Rh$_2$(CO)$_3$3. We have studied the PMR and C NMR spectra of $(h^5$-$C_5H_5)_3Rh_3$(CO)C$_6$H$_5C$=$C$C$_6$H$_5$ (I)$^4,6$ and $(h^5$-$C_5H_5)_3Rh_3$(CO)C$_6$F$_5C$=$C$C$_6$F$_5$(II)$^5,6$ and the results of these studies are reported here**.

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** The C NMR spectra were obtained with a Varian XL-100-15 spectrometer operating in the pulsed Fourier Transform mode at 25.1 MHz or with a Fourier transform pulsed NMR spectrometer operating at 15.08 MHz as described previously7. The proton NMR spectra were measured with a Varian HA-100 spectrometer. The $^{13}$C chemical shifts were measured relative to an internal solvent reference and then reported relative to a tetramethylsilane (TMS) standard. The chemical shift conversion factors used in this study are $\delta$(TMS) = $\delta$(CH$_3$Cl)$_2$ + 53.89 ppm and $\delta$(TMS) = $\delta$(CS$_2$) + 192.44 ppm. TMS was used as the standard for the proton NMR spectra as well. Tris(acetylacetonato)chromium(III) (0.03 to 0.1M) was added to C NMR samples to reduce $t_1$ relaxation times8. The infrared spectra were measured using a Perkin–Elmer model 137 or 137G spectrometer.
**Fig. 1.** The structure of \((h^5-C_5H_5)Rh_3\) \((CO)C_6H_5C\equiv CC_6H_5\) obtained from X-ray crystal study.

The room temperature PMR spectrum (CD$_2$Cl$_2$ solvent) of \((h^5-C_5H_5)Rh_3\) \((CO)C_6H_5C\equiv CC_6H_5\) (I) consisted of a complex multiplet centered at about 7.1 ppm due to the phenyl groups and a singlet at 5.32 ppm due to the pentahapto-cyclopentadienyl groups. When the solution was cooled to $-88^\circ$, two singlets appeared in the cyclopentadienyl region of the spectrum at 5.53 and 5.32 ppm with the intensity ratio 1/2, respectively. A single crystal X-ray diffraction study of I has yielded the structure shown in Fig. 1. The solid state structure indicates that there are two stereochemically nonequivalent types of cyclopentadienyl groups in the molecule. This information suggests that at room temperature I is fluxional in solution but is in a static conformation at $-88^\circ$.

**TABLE 1**

$^{13}$C NMR DATA OF \((h^5-C_5H_5)Rh_3\) \((CO)C_6H_5C\equiv CC_6H_5\)

<table>
<thead>
<tr>
<th>Chemical shift (ppm)$^{a,b,c}$</th>
<th>$J_{103Rh-13C}'(Hz)$</th>
<th>Chemical shift$^{b,d}$</th>
<th>$J_{103Rh-13C}'(Hz)$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>236.0</td>
<td>38.7 (quartet)</td>
<td>241.6</td>
<td>43.7 (triplet)</td>
<td>CO</td>
</tr>
<tr>
<td>128.6</td>
<td></td>
<td>128.3</td>
<td>28.4 (doublet)</td>
<td></td>
</tr>
<tr>
<td>126.8</td>
<td>weak signal</td>
<td></td>
<td></td>
<td>phenyl group</td>
</tr>
<tr>
<td>125.1</td>
<td>weak signal</td>
<td></td>
<td></td>
<td>phenyl group</td>
</tr>
<tr>
<td>89.7</td>
<td></td>
<td>89.7</td>
<td></td>
<td>(h^5-C_5H_5)</td>
</tr>
</tbody>
</table>

$^a$TMS 0 ppm. $^b$90% CH$_2$Cl$_2$, 10% Freon-11. $^c$Room temperature. $^d$90°C.

When we measured the C NMR spectrum of I with natural abundance $^{13}$C, even in the presence of 0.1M Cr(Acac)$_3$, we could not locate a signal attributable to the carbonyl carbon. A tetrahydrofuran solution of I was therefore stirred at room temperature under 90% $^{13}$C-enriched carbon monoxide (450 mm pressure) for 19 h. This gave I with its carbonyl ligand 77% labelled as measured by the relative absorbances of the $^{12}$CO band at 1847 cm$^{-1}$ and the $^{13}$CO band at 1808 cm$^{-1}$. The C NMR spectral data of $^{13}$C-enriched I is given in Table 1. In the room temperature C NMR spectrum of I, the carbonyl resonance appears as a quartet. This result suggests that at room temperature...
the carbonyl group is either (a) in symmetrical triple-bridging position and the tolane ligand is interchanging or (b) both the carbonyl and the tolane ligands are fluxional. At $-90^\circ$ the C NMR data suggest that the carbonyl group is in a static unsymmetrical triple-bridging position. The carbonyl carbon is more strongly coupled to two of the rhodium nuclei (triplet; $J^{(103\text{Rh}-^{13}\text{C})}$ 43.7 Hz) and less strongly coupled to the third rhodium nucleus (doublets; $J^{(103\text{Rh}-^{13}\text{C})}$ 28.4 Hz). These results are consistent with the unsymmetrical triple-bridging configuration of the carbonyl group found in the X-ray structure study of I (Fig. 1). The cyclopentadienyl and phenyl carbon atoms of I (measured at room temperature) have normal chemical shift values generally observed for these types of groups. A $^{13}\text{C}$ resonance for the acetylene carbon atoms of I was not located with certainty.

In contrast, the room temperature PMR spectrum (CDCl$_3$ solvent) of the related complex, ($h^5\text{-C}_5\text{H}_5$)$_3\text{Rh}_3$(CO)C$_6$F$_5$C=CC$_6$F$_5$ (II) contained two singlet resonances, which can only be attributed to the cyclopentadienyl protons, at 5.46 and 5.20 ppm with the intensity ratio of 1/2 respectively. This suggests that this molecule is static at room temperature.

Introduction of $^{13}\text{C}$-enriched carbon monoxide into II required much more forcing conditions than for I. Heating a dioxane solution of II at 95$^\circ$ for 12 h under $^{13}\text{C}$-enriched carbon monoxide gave II which was 50% labelled. The C NMR spectral data (CH$_2$Cl$_2$ solvent) of II are given in Table 2. The carbonyl carbon resonance is a triplet,

<table>
<thead>
<tr>
<th>Chemical shift$^a,b$(ppm)</th>
<th>$J^{(103\text{Rh}-^{13}\text{C})'}$(Hz)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>217.8</td>
<td>48.5 (triplet)</td>
<td>CO</td>
</tr>
<tr>
<td>89.0 (relative area two)</td>
<td></td>
<td>$h^5\text{-C}_5\text{H}_5$</td>
</tr>
<tr>
<td>84.9 (relative area one)</td>
<td></td>
<td>$h^5\text{-C}_5\text{H}_5$</td>
</tr>
</tbody>
</table>

$^a$CH$_2$Cl$_2$ solvent. $^b$Room temperature.

![Fig. 2. The structure of ($h^5\text{-C}_5\text{H}_5$)$_3\text{Rh}_3$(CO)C$_6$F$_5$C=CC$_6$F$_5$ Obtained from X-ray crystal study.](image)
suggesting that this group is bridging two rhodium atoms. A single crystal X-ray diffraction study of II has yielded the structure illustrated in Fig. 2. The most interesting feature of this structure is the location of the CO function as a bridging group between two rhodium atoms in accord with our C NMR results. Two doublet resonances in a 2/1 ratio were observed for the cyclopentadienyl carbon atoms in the single frequency off resonance decoupled C NMR spectrum of II. This adds further support to the suggestion that II is static at room temperature. The phenyl carbon resonances were not observed due probably to $^{13}$C-$^{19}$F coupling which would scatter these signals. A signal for the acetylene carbon atoms of II was not located with certainty.

We have observed with a variety of other metal-carbonyl systems that carbon monoxide exchange occurs more readily with fluxional molecules than with those that are static. We were able to achieve $^{13}$CO exchange with II only at elevated temperatures. Therefore we examined the PMR and C NMR of II at elevated temperatures. The two cyclopentadienyl resonances observed in the NMR spectra of II at room temperature were found (both in the PMR and C NMR) to collapse to a single resonance at $+87^\circ$. Further NMR studies of these interesting systems with labelled molecules are in progress.

ACKNOWLEDGEMENT

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REFERENCES