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Preliminary communication

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

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SUMMARY

The temperature-dependent ^1H and ^{13}C NMR spectra of $(h^5\text{-}C_5H_5)_3Rh_3(CO)C_6H_5C{\equiv}CC_6H_5$ support the view that this molecule is fluxional in solution at room temperature but is in a frozen conformation at −88°; NMR data of $(h^5\text{-}C_5H_5)_3Rh_3(CO)C_6F_5C{\equiv}CC_6F_5$ 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.*, $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ [1], $Rh_4(CO)_{12}$ [2] and $(h^5\text{-}C_5H_5)_2Rh_2(CO)_3$ [3]. We have studied the PMR and C NMR spectra of $(h^5\text{-}C_5H_5)_3Rh_3(CO)C_6H_5C{\equiv}CC_6H_5$ (I)[4,5] and $(h^5\text{-}C_5H_5)_3Rh_3(CO)C_6F_5C{\equiv}CC_6F_5$(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 previously[7]. 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 $\delta(TMS) = \delta(CH_2Cl_2) + 53.89$ 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 0.1*M*) was added to C NMR samples to reduce t_1 relaxation times[8]. The infrared spectra were measured using a Perkin–Elmer model 137 or 137G spectrometer.

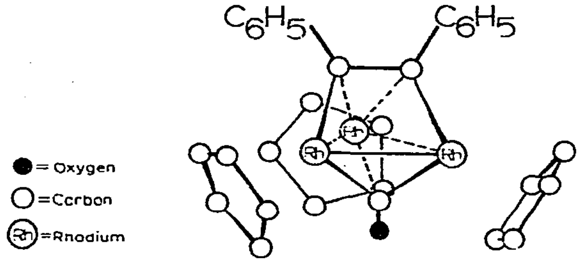

Fig. 1. The structure of $(h^5\text{-}C_5H_5)_3Rh_3(CO)C_6H_5C{\equiv}CC_6H_5$ Obtained from X-ray crystal study.

The room temperature PMR spectrum (CD_2Cl_2 solvent) of $(h^5\text{-}C_5H_5)_3Rh_3(CO)C_6H_5C{\equiv}CC_6H_5$ (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°, 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 [9]. 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°.

TABLE 1

^{13}C NMR DATA OF $(h^5\text{-}C_5H_5)_3Rh_3(CO)C_6H_5C{\equiv}CC_6H_5$

Chemical shift (ppm)^{a,b,c}	$J(^{103}Rh-^{13}C)'$ *(Hz)*	*Chemical shift*^{b,d}	$J(^{103}Rh-^{13}C)'$ *(Hz)*	*Assignment*
236.0	38.7 (quartet)	241.6	43.7 (triplet) 28.4 (doublet)	CO
128.6		128.3		phenyl group
126.8		weak signal		phenyl group
125.1		weak signal		phenyl group
89.7		89.7		$h^5\text{-}C_5H_5$

^{a}TMS 0 ppm. ^{b}90% CH_2Cl_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 0.1*M* $Cr(Acac)_3$, 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° 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; $J(^{103}Rh-^{13}C)$ 43.7 Hz) and less strongly coupled to the third rhodium nucleus (doublets; $J(^{103}Rh-^{13}C)$ 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}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, $(h^5\text{-}C_5H_5)_3Rh_3(CO)C_6F_5C{\equiv}CC_6F_5$ (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}C-enriched carbon monoxide into II required much more forcing conditions than for I. Heating a dioxane solution of II at 95° for 12 h under ^{13}C-enriched carbon monoxide gave II which was 50% labelled. The C NMR spectral data (CH_2Cl_2 solvent) of II are given in Table 2. The carbonyl carbon resonance is a triplet,

TABLE 2

^{13}C NMR DATA OF $(h^5\text{-}C_5H_5)_3Rh_3(CO)C_6F_5C{\equiv}CC_6F_5$

Chemical shift[a,b] *(ppm)*	$J(^{103}Rh-^{13}C)'$ *(Hz)*	*Assignment*
217.8	48.5 (triplet)	CO
89.0 (relative area two)		$h^5\text{-}C_5H_5$
84.9 (relative area one)		$h^5\text{-}C_5H_5$

[a] CH_2Cl_2 solvent. [b] Room temperature.

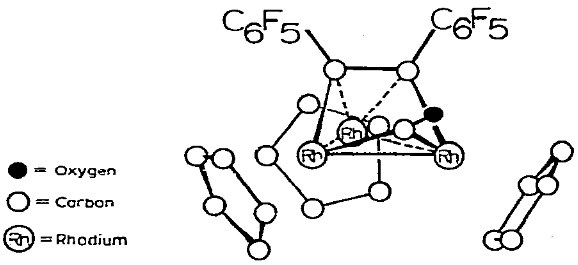

Fig. 2. The structure of $(h^5\text{-}C_5H_5)_3Rh_3(CO)C_6F_5C{\equiv}CC_6F_5$ Obtained from X-ray crystal study.

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[9]. 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[10] 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°. Further NMR studies of these interesting systems with labelled molecules are in progress.

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