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$^{13}C\{^{103}Rh\}$ NUCLEAR MAGNETIC RESONANCE OF $[Rh_7(CO)_{16}]^{3-}$

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Summary

Specific ^{103}Rh spin-decoupling has been used to make a complete assignment of the ^{13}C NMR spectrum of $[Rh_7(CO)_{16}]^{3-}$. At room temperature 3 μ_2-carbonyls exchange with 3 μ_1-carbonyls; it is shown that this carbonyl exchange occurs around the outside of the metal polyhedron rather than rotation of part of the metal skeleton within the carbonyl polyhedron. The rhodium chemical shifts show a large alternation from low to high field along the C_3-axis of the cluster.

Introduction

^{13}C NMR is of great assistance in providing structural information and in establishing carbonyl rearrangement pathways in carbonyl clusters [1,2]. Sometimes, however, ^{13}C NMR spectra alone are insufficient for structural characterisation and can lead to ambiguities (e.g. $Co_4(CO)_{12}$ [3], $[Rh_{12}(CO)_{34}]^{2-}$ [4]). As a result, we are engaged in a systematic survey of metal nuclei NMR of carbonyl clusters. In this paper we show how specific ^{103}Rh spin-decoupling of ^{13}C NMR spectra can be applied to rhodium carbonyl clusters.

Results and discussion

The structure of $[Rh_7(CO)_{16}]^{3-}$ has been reported [5] and is shown schematically in Fig. 1. At —30° C, the ^{13}C NMR spectrum (Fig. 2(4)) is entirely consistent with the solid state structure and shows resonances due to face-bridging, a, edge-bridging, b, c, and terminal, d, e, f, carbonyls in the ratio 3/3/3/3/1/3 respectively, (see experimental for data on δ and J). At room tem-

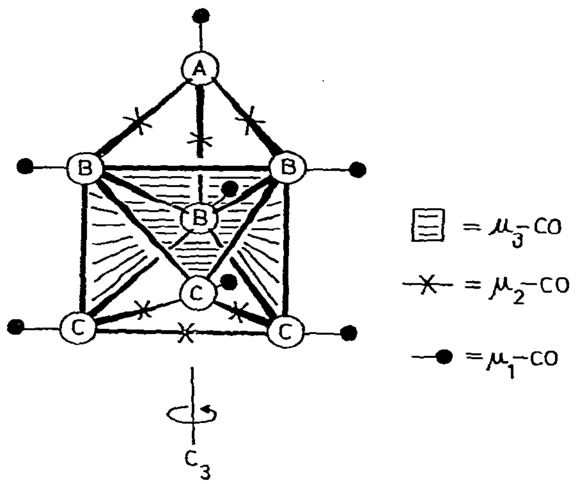

Fig. 1. Schematic structure of $[Rh_7(CO)_{16}]^{3-}$ [5].

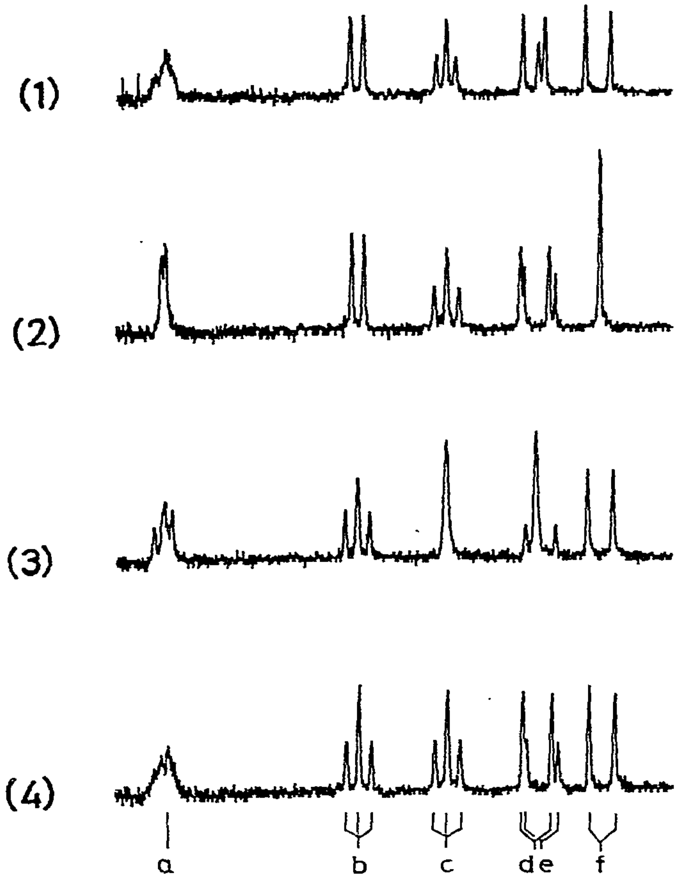

Fig. 2. Specific ^{103}Rh spin-decoupling of the ^{13}C NMR spectrum of $[Rh_7(CO)_{16}]^{3-}$ at −30°C. Decoupling at: (1) 3.161495 MHz ($\delta(Rh_A)$ +483 ppm); (2) 3.158782 MHz ($\delta(Rh_B)$ −376 ppm); (3) 3.162150 MHz ($\delta(Rh_C)$ +690 ppm); (4) no decoupling. ($Rh_{A,B,C}$ refer to Fig. 1.)

perature, resonance c coalesces with resonance d due to the onset μ_1-CO $\leftarrow$ μ_2-CO exchange [6]. From the ^{13}C NMR spectra alone, it is impossible to conclude which of the two sets of edge-bridging carbonyls are involved, although it has been suggested [6] that this exchange occurs around the triangular face incorporating the three Rh_C atoms; this has now been proved by $^{13}C\{^{103}Rh\}$ NMR (vide infra).

Whereas one group of edge-bridging carbonyls are bonded to inequivalent rhodium's (Rh_A and Rh_B), the other edge-bridging group are bonded to equivalent rhodiums (Rh_C) (Fig. 1). The ^{13}C NMR with Rh_C spin-decoupled (Fig. 2(3)) therefore results in the collapse of one triplet to a singlet, allowing resonance c to be assigned to the μ_2-carbonyls associated with Rh_C; simultaneously one doublet, d, collapses to a singlet (due to the 3 μ_1-carbonyls situated on each of the Rh_C's) and the complex resonance a, due to the μ_3-carbonyls. becomes a triplet. The carbonyls bridging the Rh_A—Rh_B edge have accidentally the same values for $^1J(Rh_A—CO)$ and $^1J(Rh_B—CO)$ which gave rise to an apparent triplet. However, irradiation at the frequency corresponding to either Rh_A or Rh_B results in the collapse of resonance b to a doublet (Fig. 2(1) and 2(2)) with concommittant changes in the remainder of the spectrum, which can be explained in a simple first order manner. It is interesting to note that the μ_3-carbonyl resonance, a, is shown clearly on spin-decoupling to consist of a doublet of triplets due to $^1J(Rh_C—CO) = 13$ and $^1J(Rh_B—CO) = 29$ Hz respectively. This suggests that the triangular face may be asymmetrically occupied but sufficiently accurate X-ray date are not presently available for this to be substantiated.

The above data confirm that at room temperature $[Rh_7(CO)_{16}]^{3-}$ undergoes μ_1-CO/μ_2-CO intra-exchange around the basal (Rh_C), triangular face with the remainder of the carbonyls remaining static on the NMR time scale. This also shows that, unlike Johnson's ideas on $Fe_3(CO)_{12}$ in solution [7], there is no rotation of the Rh_7 polyhedron within the carbonyl polyhedron. Furthermore, the ^{13}C NMR spectrum at room temperature with Rh_B spin-decoupled (Fig. 3(1)) still shows the face-bridging carbonyls as a doublet at low field. This unambiguously shows that the carbonyls are migrating around the $(Rh_C)_3$ triangular face rather than rotation of the $(Rh_C)_3$ triangle within the static carbonyl polyhedron. Moreover, around Rh_B and Rh_C there are 12 carbonyls (μ_1-CO's on Rh_B and Rh_C, μ_2-CO's on Rh_C, μ_3-CO's) distributed in an approximate hexagonal prismatic array and rearrangement, via $\mu_1 \leftrightarrow \mu_2$ carbonyl exchange around the $(Rh_C)_3$-triangular face, should involve a less sterically crowded hexagonal antiprismatic intermediate.

There is a large alternation of rhodium chemical shift * along the C_3 axis of the metal polyhedron ($\delta(Rh_A)$ +483 ppm, $\delta(Rh_B)$ —376 ppm, $\delta(Rh_C)$ +690 ppm). This variation, which is not trivially related to the number of metal—metal bonds (Rh_A, Rh_B, Rh_C have 3, 5 and 4 metal—metal bonds respectively) or to the number of carbonyls on each rhodium, may reflect a difference in charge distribution within the metal polyhedron as recent calculations suggested was the case for gold clusters [9]. Present ^{103}Rh chemical shift data [10,

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* 3.16 MHz = 0 ppm [8] at such a magnetic field that the protons in TMS resonate at exactly 100 MHz: high frequency (downfield) shifts are positive.

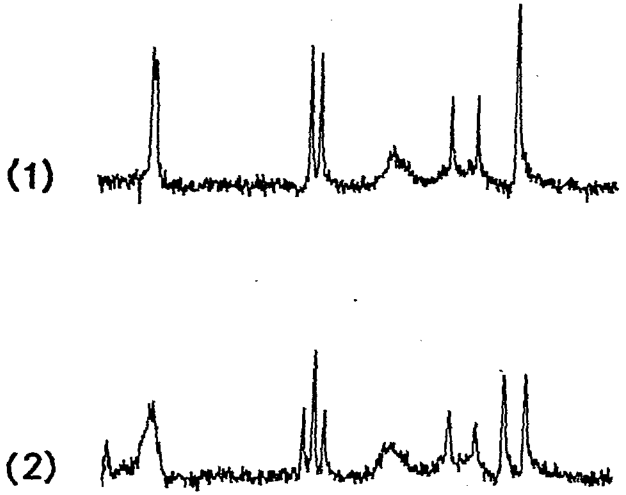


Fig. 3. Room temperature ^{13}C NMR spectrum of $[Rh_7(CO)_{16}]^{3-}$ (1) With Rh_B spin decoupled (irradiation at 3.158782 MHz); (2) no decoupling.

11] suggest that, as is found for ^{195}Pt chemical shifts [12], high oxidation states produce high frequency (low field) resonances. Further work is necessary in order to gain a better understanding of the electronic distribution within these clusters and of the factors (such as effective coordination number of the metal, charge on the clusters, etc.) which contribute to δ(Rh) and carbonyl fluxionality.

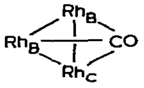
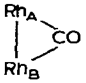
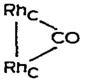
Experimental

$(NEt_4)_3[Rh_7(CO)_{16}]$ was prepared as described previously [13] and was enriched by direct exchange with ^{13}CO. A solution containing ca. 300 mg $(NEt_4)_3[Rh_7(CO)_{16}]$ (47% ^{13}CO) together with 2 mg $Cr(acac)_3$ as relaxing agent [14] was prepared in 1.2 ml CD_3CN for the NMR measurements. The chemical shifts, coupling constants and assignments for peaks a → f are shown in Table 1.

25.15 MHz $^{13}C\{^{103}Rh\}$ spectra were obtained at −30°C on a JEOL PFT-100 spectrometer modified to permit irradiation of the sample at ca. 3.16 MHz, either coherently or with noise modulation. (Full details of the modifications and experimental procedure for recording $^{13}C\{^{103}Rh\}$ NMR spectra will be published [15].) Typically 500 transients were accumulated using a 25° pulse with T_R = 2 s over a 2 KHz spectral width. 4 K data were used, giving a resolution of ca. 1 Hz. Initially high power, noise-modulated irradiation at 3.16 MHz was employed to obtain approximate values for δ(Rh). Precise values were then obtained by plotting residual ^{103}Rh—^{13}C splittings against decoupler frequency, using coherent 3.16 MHz irradiation. The zero residual splitting values so obtained are estimated to have errors of ±0.8 ppm (Fig. 4). The spectra shown in Fig. 2(1) and 2(3) were recorded using low power irradiation at the two frequencies corresponding to zero residual splittings for ^{13}C resonances (b), (e), and (d), (c) respectively of Fig. 2(4); the spectrum in Fig. 2(2) was recorded at

TABLE 1

NMR DATA AND ASSIGNMENTS OF THE SPECTRUM IN FIG. 2(4)

Resonance	δ (ppm)	J(Rh—CO) ± 2 Hz	Assignment [a]
a	254.3	$^1J(\mathrm{Rh_B—CO})$ 29 $^1J(\mathrm{Rh_C—CO})$ 13	
b	229.45	$^1J(\mathrm{Rh_A—CO})$ 39.5 $^1J(\mathrm{Rh_B—CO})$ 39.5	
c	218.05	$^1J(\mathrm{Rh_C—CO})$ 40.5	
d	206.4	$^1J(\mathrm{Rh_C—CO})$ 93	$\mathrm{Rh_C—CO}$
e	205.7	$^1J(\mathrm{Rh_A—CO})$ 103.5	$\mathrm{Rh_A—CO}$
f	198.2	$^1J(\mathrm{Rh_B—CO})$ 81	$\mathrm{Rh_B—CO}$

[a] $\mathrm{Rh_{A,B,C}}$ refer to Fig. 1.

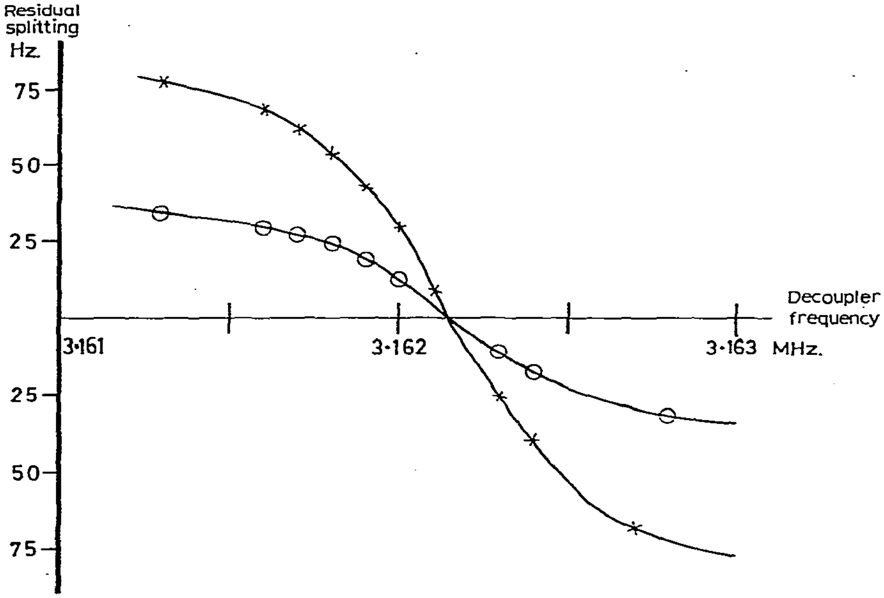


Fig. 4. Residual splitting (Hz) versus ^{103}Rh irradiation frequency for resonances c = ⊖ and d = ✱ (Fig. 2(4)). The point of intersection, 3.162150 MHz, is the resonance frequency of $\mathrm{Rh_C}$ (Fig. 1).

high power irradiation at the frequency corresponding to zero residual splitting of resonance f and b (Fig. 2(4)).

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