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^{13}C-{^{103}Rh} DOUBLE RESONANCE SPECTRA OF RHODIUM(I) AND RHODIUM(—I) CARBONYL COMPLEXES

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Summary

^{103}Rh Chemical shifts of a variety of mono- and di-nuclear rhodium carbonyl complexes are reported together with the modifications to the probe and decoupler unit of a JEOL PS-100 PFT spectrometer which enable these ^{103}Rh-decoupled ^{13}C NMR measurements to be made. These data are discussed in conjunction with ^{13}C NMR data on other rhodium carbonyls.

Introduction

Despite its favourable natural abundance (100%), ^{103}Rh is not very amenable to direct NMR observation because of its very low magnetogyric ratio. Thus, although a number of reports of direct observation of ^{103}Rh resonances in the metal have been made [1—4], to date all published ^{103}Rh chemical shift data for complexes have been obtained by the INDOR method * using CW spectrometers [5]. A range of chemical shifts ** from ca. 8000 to —800 ppm has been observed. Most of these data result from ^{1}H-{^{103}Rh}, and ^{31}P-{^{103}Rh} experiments, although ^{19}F-{^{103}Rh} spectra have also been observed, [5]. We are particularly interested in the structures and fluxional behaviour of metal carbonyl clusters in solution [6], and although ^{13}C NMR is of great assistance here, ambiguities may arise in some cases {e.g. "$[Rh_{12}(CO)_{34}]^{2-}$" [7] and $Co_4(CO)_{12}$ [8]}, when reliance is placed on ^{13}C NMR alone. In the case of platinum-containing clusters, ^{195}Pt NMR has been of considerable value [9,10] and we were anxious to extend such metal NMR studies to include rhodium.

We now report Fourier transform ^{13}C-{^{103}Rh} experiments as a means of obtaining ^{103}Rh chemical shifts, [$\delta(^{103}Rh)$], on mono- and bi-nuclear rhodium(I) complexes and the rhodium(—I) complex, $[Rh(CO)_4]^-$ together with the modifications to the spectrometer which are necessary to allow these measurements

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* Note added in proof: See, however, ref. 43.

** Shifts to high frequency of 3.16 MHz are positive.

to be made; an account of the application of this method to the solution structure and fluxional behaviour of a rhodium carbonyl cluster, $[Rh_7(CO)_{16}]^{3-}$, has already appeared [11].

Results and discussion

Good quality Fourier transform ^{13}C-$\{^{103}Rh\}$ NMR spectra (Fig. 1) have been obtained, as outlined in the experimental section. Relatively concentrated solutions (0.2 to 1.0 *M*, Table 1) of complexes prepared from ^{13}C-enriched (ca. 30—50%) CO have been used, although spectra can be obtained using more dilute, less ^{13}C-enriched samples with the normal cost in acquisition time. However, it is necessary to avoid measurements on highly ^{13}C-enriched samples since we found that complex off-resonance spectra were obtained on $[Rh(CO)_4]^-$ (87.5% ^{13}CO) and, in this case, a trial and error procedure, rather than a graphical one, had to be used to determine $\delta(^{103}Rh)$. These complications arise because of the complexity of the ^{103}Rh spectrum where the high level of enrichment gives rise to significant concentrations of the two isotopomers, $[Rh(^{13}CO)_4]^-$ and $[Rh(^{13}CO)_3(^{12}CO)]^-$, which results in the ^{103}Rh NMR spectrum consisting of a superimposed quintet and quartet in the ratio 1.75 : 1, respectively. The ^{103}Rh NMR spectrum is probably further complicated by isotope effects, in view of our previous experience with Pt-^{13}CO compounds *. As a result, it is more difficult to obtain complete low power decoupling of the rhodium resonance and this accounts for the significantly greater line width ($W_{1/2}$ 2.6 Hz) in the ^{13}C-$\{^{103}Rh\}$ spectrum of highly enriched $[Rh(CO)_4]^-$ than in the undecoupled case ($W_{1/2}$ 1.6 Hz).

Within the square-planar rhodium(I) series of complexes reported in Table 1, there is little variation in $\delta(^{103}Rh)$ on changing the substituents attached to the $Rh(CO)_2$ group, with the exception of $[Rh(acac)(CO)_2]$. This is the only complex reported above with a bidentate ligand and bond angle variations may account for this $\delta(^{103}Rh)$ being at significantly lower field since it is known that such effects are important in determining ^{13}C, ^{29}Si, ^{119}Sn and ^{195}Pt chemical shifts [12—14].

Replacement of chloride by bromide in rhodium and platinum complexes generally results in a shift of the metal resonance to high field [5,15] and this is also found for $[Rh_2X_2(CO)_4]$ (X = Cl, Br) but apparently not for $[RhX_2(CO)_2]^-$. However, in this last case the situation is complicated because at room temperature the ^{13}C resonance of $[RhCl_2(CO)_2]^-$ is broad, probably due to the exchange shown in the equation:

$$2[RhCl_2(CO)_2]^- \rightleftharpoons [Rh_2Cl_2(CO)_4] + 2\,Cl^-$$

At low temperature (—30° C), the ^{13}C resonance becomes a sharp doublet which we ascribe to $[RhCl_2(CO)_2]^-$. The ^{13}C spectrum of $[RhBr_2(CO)_2]^-$ is well resolved both at —30° C and +25° C and the decrease in shielding, 0.3 ppm/° C observed here for the ^{103}Rh resonance is similar to that observed previously [14].

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* We have observed isotope effects of —25 Hz per ^{13}C relative to the ^{12}C isotopomer in ^{195}Pt NMR studies.

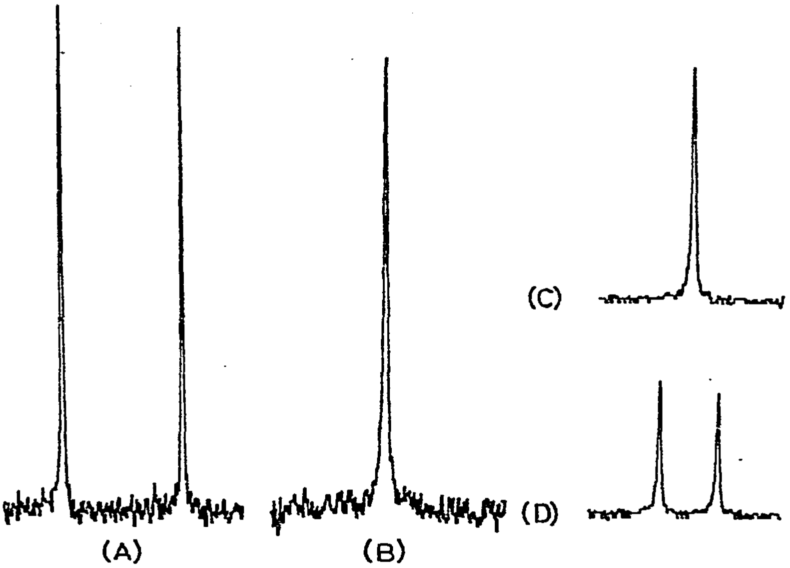

Fig. 1. ^{13}C NMR Spectra. (A) (PPN)[$Rh(CO)_4$], undecoupled; (B) (PPN)[$Rh(CO)_4$] in CD_3CN, ^{103}Rh noise-decoupled; (C) (NBu_4)[$RhBr_2(CO)_2$] in $CDCl_3$, ^{103}Rh noise-decoupled; (D) (NBu_4)[$RhBr_2(CO)_2$] in $CDCl_3$, undecoupled.

^{103}Rh chemical shifts of rhodium(I) complexes are at higher field than those of rhodium(III) complexes [5] and the very high field shift of [$Rh(CO)_4$]$^-$ is in keeping with rhodium in this anion having a formal oxidation state of —I.

It is worthwhile noting that the values of ^1J(Rh—CO) in square-planar rhodium(I) complexes and the tetrahedral rhodium(—I) anion, [$Rh(CO)_4$]$^-$, are very similar. This is consistent with the Rh—CO coupling being dominated by the Fermi-contact interaction [17] and an insignificant change in *s*-character of the metal orbital on going from *dsp*^{2} (square-planar) to *sp*^{3} (tetrahedral) hybridisation.

^{13}C chemical shifts of groups directly bonded to metals are not well understood, although previous work on olefin metal complexes [18,19] suggested an

TABLE 1

NMR DATA FOR RHODIUM (I) AND RHODIUM (—I) CARBONYL COMPLEXES.

Complex	δ(^{103}Rh) (ppm) [a]	δ(^{13}CO) (ppm) [b]	^1J(Rh—CO) (Hz)	Solvent	Molarity	Temp. (°C)
(PPN)[$Rh(CO)_4$]	—644	206.3	75.2 ± 1	CD_3CN	0.22	+25
[$Rh(CH_3CN)_2(CO)_2$]BF_4	—54	181.6	73.2 ± 2	CD_3CN	0.4	+25
[Rh(acac)$(CO)_2$]	+292	183.7	72.7 ± 1	$CDCl_3$	0.5	+60
(NBu_4)[$RhCl_2(CO)_2$]	—16.7	183.2	71.8 ± 1	$CDCl_3$	0.24	—30
[$Rh_2Cl_2(CO)_4$]	+151	180.4	76.7 ± 1	$CDCl_3$	ca. 1.0	+60
(NBu_4)[$RhBr_2(CO)_2$]	+47	181.4	71.8 ± 1	$CDCl_3$	0.27	—30
[$Rh_2Br_2(CO)_4$]	—1	179.9	74.2 ± 1	CH_2Cl_2/$CDCl_3$	ca. 0.5	+60

[a] 3.16 MHz = 0 ppm with the magnetic field such that the protons in TMS resonate exactly at 100 MHz; shifts to high frequency are positive. [b] ppm from TMS.

TABLE 2

X-RAY AND NMR DATA FOR LOW VALENT RHODIUM-CARBONYL COMPOUNDS

Compound [a]	d(Rh—CO) (Å)	δ(CO) (ppm)	Point on Fig. 3	Reference [b]
$[Rh(CO)_2(acac)]$	1.755(20)	183.7	1	20,[g]
$[Rh_2(CO)_4Cl_2]$	1.81	180.4	2	21,[g]
$[Rh_2(CO)_2Cp_2\{(CF_3)_2C_2\}]$ [c]	1.826(10)	190.8	3	22, 23
$[Rh_2(CO)_3Cp_2]$	1.867(23)	191.8	4	24, 25
	2.003(17)	231.8	5	
$[Rh_3(CO)_2Cp_3\{(C_6F_5)_2C_2\}]$	1.96(1)	217.8	6	26, 27
$[Rh_3(CO)_3Cp_3]$ [d]	2.00(2)	232.5	7	28, 29
$[Rh_6(CO)_{15}C]^{2-}$	1.89(1)	198.1	8	30, 31
	2.12(1)	225.2	9	
	2.04(1)	236.3	10	
$[Rh_6(CO)_{16}]$	1.864(15)	180.1	11	32, 33
	2.168(12)	231.5	12	
$[Rh_7(CO)_{16}]^{3-}$ [e]	2.14	254.3	13	34, 33
$[Rh_{12}(CO)_{30}]^{2-}$	1.88(3)	186.3	14	35, 36
	1.89(3)	186.1	15	
	1.82(3)	183.4	16	
	2.00(2)	211.5	17	
	2.225(25)	237.4	18	
$[Rh_{13}(CO)_{24}H_2]^{3-}$ [f]	1.99(2)	235.4	19	37, 38
$[Rh_{17}(CO)_{33}S_2]^{3-}$	1.81(2)	194.1	20	39, 39
	1.850(25)	196.8	21	
	1.99(2)	231.0	22	
	2.03(2)	252.7	23	

[a] Abbreviations: -acac = acetylacetonato, Cp = η^5-C_5H_5. [b] X-ray data first followed by reference pertaining to ^{13}C NMR data. [c] *trans*-isomer. [d] C_{3v}-isomer. [e] Data for inequivalent μ_1- and μ_2-CO's were not presented. [f] Data for static μ_2-CO on hexagonal Rh_6, plane at 25°C. [g] This work.

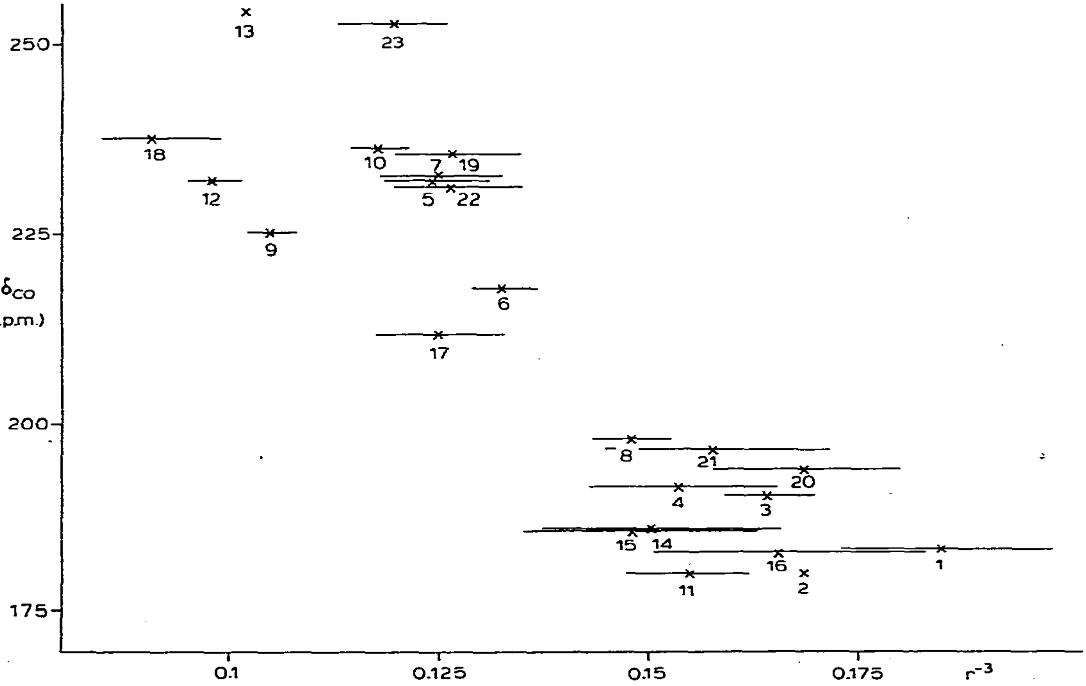

Fig. 2. Plot of $\delta(^{13}CO)$ (ppm) in a rhodium carbonyl complex vs. the reciprocal of the cube of the metal—carbon distance (Å^{-3}). The points refer to the numbers in Table 2 and error bars are 2σ on r.

approximate linear relationship of $\delta(^{13}C)$ with r^{-3} (r is the metal—carbon bond distance). Data for all presently known low valency rhodium-containing carbonyl compounds, which give ^{13}C NMR spectra consistent with their solid state structures thus allowing unambiguous assignments, are collated in Table 2. These data are plotted in Fig. 2 using the relationship previously suggested by Powell et al [18,19]. There is rather a large scatter of points, resulting probably from the various diamagnetic contributions produced in such a random selection of available structures. Nevertheless, if data from only one compound (e.g. $[Rh_{17}(CO)_{32}S_2]^{3-}$ points 20—23, or $[Rh_{12}(CO)_{30}]^{2-}$ points 14—18) are considered, then the above linear relationship is much improved and, using least squares analysis, the correlation coefficients are —0.9695 and —0.9767 respectively. Thus the longer the metal—carbonyl distance the greater the observed downfield shift and, in this context, it would be of interest to have X-ray structural data on $[Rh(CO)_4]^-$ since this has δ(CO) at considerably lower field than the other compounds shown in Table 1.

Experimental

Operational procedure and spectrometer modifications for ^{13}C-$\{^{103}Rh\}$ measurements

Spectra were obtained on a JEOL PS-100 PFT spectrometer operating at 25.15 MHz for ^{13}C and 3.16 MHz for Rh. The ^{13}C probe was modified for ^{13}C-$\{^{103}Rh\}$ experiments as outlined below. Typically 4 K data points were used over a 2 kHz spectral width, giving a ^{13}C resolution of ca. 1 Hz. The pulse width employed was usually 10 μs (ca. 23° tip angle) with a repetition time of 2 s. High-power, noise-modulated irradiation at ca. 3.16 MHz was used in the first instance to obtain approximate values of $\delta(^{103}Rh)$. Precise values were then obtained by plotting residual ^1J(Rh—CO) values for the carbonyl ^{13}C resonances against decoupler frequency, using coherent 3.16 MHz irradiation. The zero residual splitting values obtained in this way are considered to have a maximum error of ±1 ppm. In some cases, specific low-power decoupling was employed to check values obtained by the graphical procedure (Fig. 1).

Preliminary experiments using separate irradiation coils attached to the existing insert Dewar over the ^1H-irradiation coils gave unsatisfactory power levels. It was therefore decided to use the ^1H-irradiation coils which had to be retuned and matched to the ^{103}Rh frequency, ca. 3.16 MHz. In order to bring the Q of the circuit up to an acceptable level, the parallel-wound ^1H coils were reconnected in series, thus bringing up the inductance value without any need for more complex alterations to the existing insert Dewar assembly. The capacitance was increased to ca. 1500 pf, with 250 pf variable. The output from the JEOL PA-1 was matched into the decoupler transmitter as shown in Fig. 3. An SWR meter was constructed from ca. 2.0 m of Uniradio 67 Coaxial cable and calibrated with a matched dummy load and watt meter, as described by Evans and Jessop, [40]. This greatly facilitated the matching of C_1 and C_2. In more recent experiments this was more conveniently replaced by an SML SWR-25 standing wave ratio and RF power meter operating between 3.5 and 150 MHz.

The JEOL PA-1 power amplifier required some minor alteration to permit operation at 3.16 MHz, as the lowest existing operational frequency range for

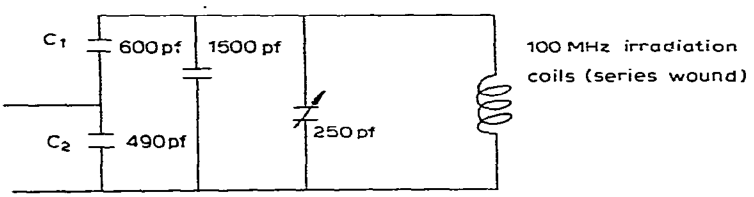

Fig. 3. Circuit diagram for $^{13}C-\{^{103}Rh\}$ double resonance experiments.

this unit is 4—5 MHz. The tuned anode load was altered by adding 60 extra turns to the first rf amplifier coil (L405) and 40 extra turns to the second rf amplifier coil (L413). The matching output was also altered by adding to the output matching coil (L421) a new 21-turn coil of the same diameter, connected in series. The existing JNM-SD-HC spin decoupler unit was also modified to include noise modulation band widths of 250, 100 and 50 Hz. This facility greatly increased our ability to obtain approximate values of $\delta(^{103}Rh)$. The 3 MHz signal was derived from a Schomandl ND-100M frequency synthesiser through the existing JNM-FA-1 F.S. connection unit.

For optimum performance it was crucial to ensure that the 25 MHz ^{13}C transmitter tuning and trap circuits were carefully adjusted. A four-turn search coil inserted in the sample region greatly aided this operation. It may be found necessary to adjust the geometry of the probe paddles to compensate for increased leakage problems. In the event, in our hands it proved possible to achieve acceptable 90° pulse widths (ca. 40 μs) using the existing paddles.

Preparation of complexes

$[Rh_2X_2(CO)_4]$ (X = Cl, Br) was prepared by reaction of carbon monoxide with $RhX_3 \cdot x\ H_2O$ at 100°C [41]. $(NBu_4)[RhX_2(CO)_2]$ (X = Cl, Br) was obtained from the reaction of $[Rh_2X_2(CO)_4]$ with NBu_4X as described previously [42]. The reaction of $[Rh_2Cl_2(CO)_4]$ with acetylacetone in basic media was used to prepare $[Rh(acac)(CO)_2]$ [16] and addition of $AgBF_4$ (2 mol) to a solution of $[Rh_2Cl_2(CO)_4]$ (1 mol) in acetonitrile solution gave $[Rh(CH_3CN)_2(CO)_2]BF_4$. PPN$[Rh(CO)_4]$ (PPN = Bis(triphenylphosphino)iminium cation) was prepared by the reaction of $[Rh_4(CO)_{12}]$ with KOH in dimethylsulphoxide solution under an atmosphere of carbon monoxide; subsequent addition of (PPN)Cl gave the desired compound. All isotopic enrichments were carried out by direct exchange with ^{13}CO.

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