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CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF RHODIUM CARBONYL COMPLEXES

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Summary

The ^{13}C NMR spectra of a series of rhodium carbonyl complexes were measured. An approximate correlation of $\delta(^{13}CO)$ chemical shifts with carbonyl group stretching frequencies $\nu(CO)$ was observed. For square planar complexes the variations in $\nu(CO)$ parallel that of the coupling constants $^1J(Rh—C)$. The oxidative addition to planar rhodium(I) complex with formation of octahedral rhodium(III) complex results in opposite trends for $\nu(CO)$ and J. The greater $\nu(CO)$ value reflects the diminished electron density on the central atom and a lower coupling constant is due to the reduced contribution of the rhodium 5*s* orbital in the Rh—CO bond.

Introduction

Recent reports [1—4] have revealed the versatility of ^{13}C NMR in bonding and structural investigations of transition metal carbonyl compounds. The ^{13}C chemical shifts and carbonyl carbon—metal coupling constants are sensitive to changes in stereochemistry of complexes and the electronic environment of the CO ligand. It was specifically demonstrated that an increased transition metal → carbonyl group π-back donation (and/or decreased carbonyl → metal σ-donation) was associated with decreased shielding of carbonyl carbon resonances.

In this paper the ^{13}C NMR spectra of a range of rhodium carbonyl complexes are presented and compared with results of other workers.

Results and discussion

The findings of this study and some data from literature sources [2,5,6] are collected in Table 1. The IR stretching frequencies, $\nu(CO)$, are listed together with ^{13}C NMR parameters. Four patterns of spectra were observed due to car-

TABLE 1

^{13}C NMR PARAMETERS AND CARBONYL STRETCHING FREQUENCIES OF RHODIUM CARBONYL COMPLEXES

No.	Compound	Solvent	δ rel. TMS (ppm)	Coupling const. (Hz)		Wavenumber [d] (cm^{-1}) $\nu(^{12}CO)$
				^1J(RhC)	^2J(RhPC)	
I	$Rh(Ph_3P)_2COCl$	$CDCl_3$	187.4	73	16	1980 ($CHCl_3$)
II [a]	$Rh(Et_2PhP)_2COCl$	$CHCl_3$	179.8	64.9	9.6	1953 (C_6H_6 [7])
III [a]	$Rh(Tol_3Sb)_2COCl$	CH_2Cl_2	185.5	68.3	—	—
IV	$[Rh(CO)_2Cl]_2$	$CDCl_3$	177.5	75	—	2089; 2035 (C_6H_{14} [8])
IV [a]	$[Rh(CO)_2Cl]_2$	C_6H_6	177.8	75.5		
V	$Ph_4P^+[Rh(CO)_2Cl_2]^-$	$CDCl_3$	181.3	72		2065. 1980 ($CHCl_3$)
VI [b]	$Pr_4N^+[Rh(CO)_2Cl_2]^-$	$(CD_3)_2CO$	183.1	72		2070; 1994 (CH_2Cl_2 [5])
VII [b]	$Pr_4N^+[Rh(CO)_2Br_2]^-$	$(CD_3)_2CO$	183.4	72		2068; 1993 ($CDCl_3$ [5])
VIII [a]	$Rh_2(Phtal)(CO)_4$	CH_2Cl_2	181.6	72.7		2094—2001 [e] (solid, [9])
IX [a]	$Rh(Py)(CO)_2Cl$	CH_2Cl_2	183.1	64.5		2075; 2010 [f] (solid, [9])
			181.2	67.3		
IX [c]	$Rh(Py)(CO)_2Cl$	$C_6H_5CH_3$	185.6	67		
			181.3	73		
X	$Rh(Acac)(CO)_2$	C_6H_5D	177.7	73		2086; 2013 ($CHCl_3$)
X [a]	$Rh(Acac)(CO)_2$	CH_2Cl_2	183.8	71.9		
XI	$Rh(Oxq)(CO)_2$	C_6H_5D	186.3	68	*trans*-N	2084; 2010 ($CHCl_3$)
			184.9	71	*trans*-O	
XII	$Rh(Acac)(Ph_3P)CO$	C_6H_5D	190.4	76	25	1984 ($CHCl_3$)
XII [a]	$Rh(Acac)(Ph_3P)CO$	CH_2Cl_2	189.5	74.8	24.8	
XIII [a]	$Rh(Acac)(Ph_3As)CO$	CH_2Cl_2	188.4	73.7		1976 [10]
XIV	$Rh(Oxq)(Ph_3P)CO$	C_6H_5D	192.0	71	21	1970 ($CHCl_3$)
XV	$Rh(Oxq)(C_8H_{14})CO$	$CDCl_3$	187.7	76		1978 ($CHCl_3$)
XVI	$Rh(Ph_3P)_2COCl \cdot TCNE$	$CDCl_3$	182.7	61	11	2071 (solid)
XVII	$Rh(Oxq)(Ph_3P)CO \cdot TCNE$	C_6H_5D	183.0	59	13	2075 (solid)
XVIII	$Rh(Ph_3P)_2COCl_3$	$CDCl_3$	175.5	58	8	2105 (solid)
XIX	$Rh(Acac)(Ph_3P)COI_2$	C_6H_5D	180.3	55	15	2094 (C_6H_6)
XX [a]	$Rh(\eta^5\text{-}C_5H_5)(CO)_2$	$CHCl_3$	190.9	83		2051; 1987 (C_6H_6 [11])

[a] ^{13}C data from review 2.

[b] Data from ref. 5.

[c] Data from ref. 6 at —60°C.

[d] Wavenumbers without references are from this study.

[e] 6 bands between reported values.

[f] Values for the two stronger bands.

bonyl carbon—rhodium coupling (^{103}Rh, $I = 1/2$, natural abundance 100%) and to additional splitting of resonance lines in the presence of phosphine ligands (^{31}P, $I = 1/2$, natural abundance 100%):

(*i*) The carbonyl carbon resonance of a monocarbonyl complex free of phosphine (XV) and of dicarbonyl complexes with equivalent carbonyl groups (IV, V, X) appeared as a doublet.

(*ii*) The spectrum of a dicarbonyl complex (XI) with non-equivalent carbonyl groups contained two doublets.

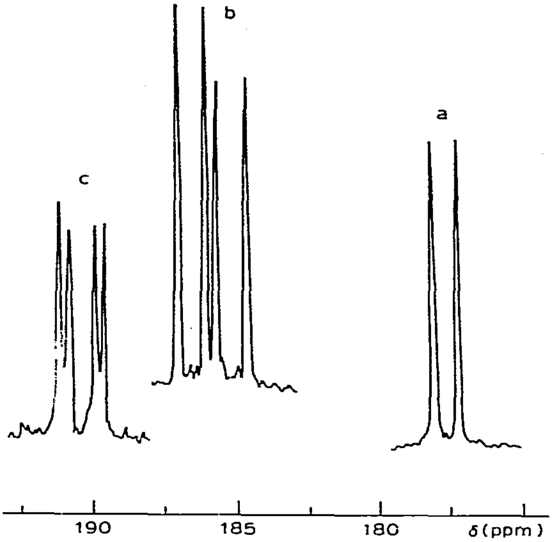

Fig. 1. The ^{13}C NMR spectra of (a) $Rh(Acac)(CO)_2$, (b) $Rh(Oxq)(CO)_2$ and (c) $Rh(Oxq)(Ph_3P)$ CO in benzene recorded at 67.88 MHz in FT mode, 1500, 2000 and 950 scans, resp., sweep width 18 000 Hz. Relaxation reagent 0.07 *M* $Cr(Acac)_3$. Chemical shifts (ppm) downfield from TMS.

(*iii*) A doublet of doublets for monophosphine complexes (XII, XIV and XIX) and
(*iv*) a doublet of triplets for bis-phosphine complexes (I, XVI and XVIII) arising from P—Rh—C coupling was observed as expected.

Representative spectra are shown in Fig. 1 and 2. The assignment of resonances in the spectrum of XI was suggested by the values of ^1J(Rh—C). The larger value is tentatively attributed to the carbonyl group *trans* to oxygen on basis of results for other complexes: ^1J(Rh—C) are in the range ca. 71—76 Hz for carbonyl groups *trans* to oxygen in XIV and XV [12,13] and also in VIII, X, XII and XIII. Applying the same reasoning to the spectrum of IX in toluene [6] means the downfield signal should be assigned to the carbonyl group *trans* to nitrogen.

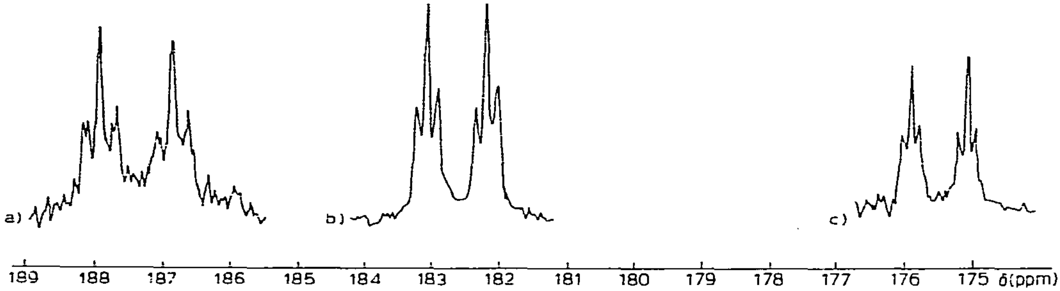

Fig. 2. The ^{13}C NMR spectra at 67.88 MHz of (a) $Rh(Ph_3P)_2COCl$, (b) $Rh(Ph_3P)_2COCl \cdot TCNE$ and (c) $Rh(Ph_3P)_2COCl_3$ in $CDCl_3$, measured under conditions of Fig. 1.

The data of Table 1 indicate that carbonyl carbon shielding is sensitive to the composition of the complex and to the oxidation state of the central atom. The carbonyl resonances of monocarbonylrhodium(I) complexes are generally at a lower field in relation to the dicarbonyl derivatives. The increase of $\delta(^{13}C)$ on successive replacement of CO by better charge donors (i.e. on enhancing the electron density on the central atom) has already been reported for carbonyl complexes of other transition metals [1—3]. A considerable upfield shift at a higher oxidation state of rhodium observed in XVIII and XIX relative to I and XII, respectively, can also be ascribed to the decrease in electron density on the rhodium atom brought about by strong acceptor ligands (axial halogen atoms). The magnitudes of $\delta(^{13}C)$ of tetracyanoethylene (TCNE) adducts XVI and XVII fall between the respective values for rhodium(I) and rhodium(III) complexes.

Plotting the data of chemical shifts against IR stretching frequencies $\nu(CO)$, gives an approximate correlation: on increasing $\nu(CO)$ the $\delta(^{13}C)$ tends to decrease (Fig. 3). The only point strongly out of line is that for complex II. Linear correlation with carbonyl group stretching parameters (frequency or force constant) is more manifest in a series of closely related carbonyl compounds [2,3,14]. These empirical trends are extensively discussed in the literature [1—3,14] leading to conflicting conclusions, since the nature of ^{13}C chemical shift is not yet clearly understood.

The variations of $^1J(Rh—C)$ and $^2J(P—Rh—C)$ essentially parallel each other, the magnitude for four-coordinate square planar complexes of rhodium(I) being higher than that of the respective TCNE adducts and octahedral rhodium(III) complexes. This is consistent with the current view [15] that the coupling constants are dominated by the Fermi contact term, since the 5*s* orbital of the rhodium atom in the square planar complex is used to form four bonds and in octahedral complex it is distributed among six bonds. (The coordination number of rhodium and its oxidation state in the TCNE adducts may be arbitrarily assigned the values of 5 and +1 or 6 and +3 respectively.)

The replacement of an olefin ligand in the square planar complex XV by the better charge donor Ph_3P results in a simultaneous decrease of $\nu(CO)$ (due to the stronger Rh → CO π-back donation) and $^1J(Rh—C)$ (arising from reduced

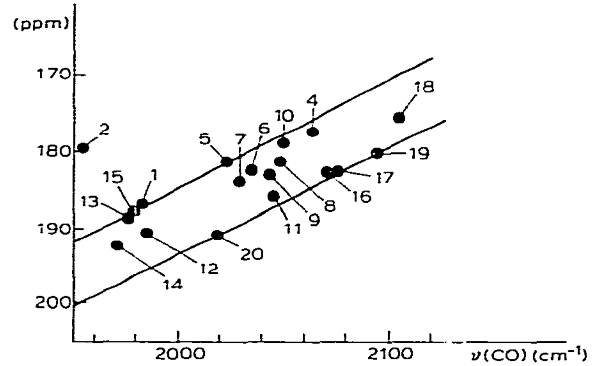

Fig. 3. Plot of the ^{13}C NMR chemical shifts (δ, ppm) for carbonyl carbon resonances in rhodium complexes vs. $\nu(CO)$ streching frequencies (arithmetic mean $\nu(CO)$ value for dicarbonyl complexes). Arabic numerals correspond to numbers of compounds in Table 1.

contribution of the rhodium acceptor 5s orbital to the Rh—C σ-bond). The smaller values of ^1J(Pt—C) for complexes containing ligand X, with stronger σ-donor properties, were already observed in the *trans*[PtXL$_2$CO]$^+$ series [4].

Our data indicate that in rhodium complexes the magnitude of ^1J(Rh—C) is sensitive to the nature of the *cis*-ligand. The ^1J(Rh—C) values of XIV and XV remained however in the range characteristic of carbonyl *trans* to oxygen, indicating the stronger influence of the *trans*-ligand [2,4]. In compound XI the lower ^1J(Rh—C) for carbonyl *trans* to nitrogen infers that the nitrogen of the heterocycle is a better σ-donor that the phenolate oxygen. On the other hand, the position of olefinic proton signals in the ^{1}H NMR spectrum of Rh(Oxq)-(Cod) (τ 5.70 ppm for HC=CH *trans* to oxygen, τ 5.12 ppm for that *trans* to nitrogen) was attributed [16] to the better π-acceptor properties of the nitrogen. The ease of substitution of carbonyl *trans* to nitrogen in XI [12,13,16] may be accounted for by both these effects associated with nitrogen which will result in weakening of σ- as well as π-bonds Rh—C.

It should be noted that in the closely related pairs XIV, XV and XII, XIV (and also in the series of platinum planar complexes *trans*(XC$_5$H$_4$N) PtCl$_2$CO [14] and PtCOX$_3^-$ [5]) the lower values of coupling constants correspond to lower ν(CO) frequencies. Unlike this the transition from I to XVI and XVIII, from XII to XIX and also from XIV to XVII is reflected in a decrease of ^1J(Rh—C) and ^2J(P—Rh—C) and in an increase of ν(CO). This observation suggests that in the latter case changes in coupling constants and in IR frequencies are accounted for by different factors: the increase of coordination number results in a decrease of J; the addition of electron acceptor ligands (TCNE, 2 Cl, 2 I) reduces the electron density at the central atom and hence increases the ν(CO). It is apparent that only in complexes of the same geometry does ν(CO) and ^1J(Rh—C) vary in the same way. In this case when the hybridization of valence shell orbitals of the central atom remains unaltered, the involvement of the metal *s* orbital in the bond with the carbonyl group is controlled predominantly by the donor properties of the other ligands.

It should be noted in conclusion that all the complexes reported in this study are static during the NMR measurement since the fine structure and the number of resonances conformed to the expected pattern of spectra. Our results indicate that although the redistribution of carbonyl groups in M(PR$_3$)$_2$-COX (M = Rh, Ir; X = Cl, Br) is complete within a few seconds [17] it is still slow on the NMR time scale. The exchange in *trans*-Rh(Ph$_3$P)$_2$COCl induced the doublet of triplets to collapse into a singlet only at 94°C [2]. The static structure ^{13}C NMR spectrum was also obtained for "Vaska compound", Ir(Ph$_3$P)$_2$COCl (badly resolved triplet, $\delta(^{13}$C) 168.5 ppm, ^2J(P—Ir—C) ca. 6 Hz).

Experimental

^{13}C-enriched complexes I, IV, X and XI were prepared by ligand exchange with 59% enriched carbon monoxide. The flasks with solutions of the complexes were connected in series and carbon monoxide was slowly bubbled through. The unlabelled Rh(Ph$_3$P)$_2$COCl (I), [Rh(CO)$_2$Cl]$_2$ (IV), Rh(Acac)-(CO)$_2$ (X) and Rh(Oxq)(CO)$_2$ (XI) were obtained by established methods [18—21]. IV and XI were treated with ^{13}CO in benzene solution, I and X in chloroform. Compounds X and XI were also prepared in the same apparatus by displacement of cyclooctene ligand with carbon monoxide in $Rh(Acac)(C_8H_{14})_2$ and $Rh(Oxq)(C_8H_{14})CO$, respectively [13]. The solvent was removed in vacuo and the complexes isolated were used for ^{13}C NMR measurements and for further synthesis of labelled substances.

The amount of ^{13}CO incorporation was estimated from IR spectra. The stretching carbonyl frequencies for labelled I, IV, X and XI are: I, 1930; IV, 2076, 2047, 2002, 1987; X, 2071, 2038, 1985, 1972; XI, 2054, 2030, 1985, 1965 cm^{-1}. The carbonyl region of ^{13}C-enriched dicarbonyl complexes contained four bands due to stretching vibrations of *cis*-dicarbonyl fragments $Rh(^{13}CO)_2$ and $Rh(^{12}CO)(^{13}CO)$.

The ^{13}CO-enriched compounds V, XII, XIII, XVI, XVII and XVIII were prepared from labelled complexes by treating them in solution with the appropriate reagent. The NMR spectra were recorded immediately after preparation without isolation of the complex.

The salt $Ph_4P^+[Rh(^{13}CO)_2Cl_2]^-$ (V) ($\nu(^{13}CO)$ in $CHCl_3$ 2050, 2018, 1960 and 1945 cm^{-1}) was obtained by chlorine bridge splitting of $[Rh(^{13}CO)_2Cl]_2$ with an equimolar amount of Ph_4PCl in chloroform solution [22]. $Rh(Acac)(Ph_3P)$-^{13}CO (XII), ($\nu(^{13}CO)$ in $CHCl_3$ 1933 cm^{-1}) was prepared by adding an equivalent quantity of Ph_3P to $Rh(Acac)(^{13}CO)_2$ in benzene [10]. Synthesized similarly was $Rh(Oxq)(Ph_3P)^{13}CO$ (XIV) ($\nu(^{13}CO)$ in $CHCl_3$ 1915 cm^{-1}) from $Rh(Oxq)(^{13}CO)_2$ [21]. I was converted into $Rh(Ph_3P)_2{}^{13}COCl_3$ (XVIII) ($\nu(^{13}CO)$ 2080 cm^{-1} (solid)) by bubbling gaseous chlorine into a benzene solution of I [23]. $Rh(Acac)(Ph_3P)^{13}COI_2$ (XIX) ($\nu(^{13}CO)$ 2056 cm^{-1} in C_6H_6) was prepared from XII by treatment with an equimolar amount of iodine in benzene solution [24].

The tetracyanoethylene (TCNE) adducts $Rh(Ph_3P)_2{}^{13}COCl \cdot TCNE$ (XVI) and $Rh(Oxq)(Ph_3P)^{13}CO \cdot TCNE$ (XVII) were obtained by adding double amounts of TCNE to I in $CHCl_3$ and XIV in benzene, respectively [25,26].

$Rh(Oxq)(C_8H_{14})CO$ (XV) was synthesized by a literature method [13].

$Ir(Ph_3P)_2{}^{13}COCl$ ($\nu(^{13}CO)$ 1909 cm^{-1} (solid)) was obtained from unlabelled complex by exchange with ^{13}CO in chloroform solution.

Instrumentation

The ^{13}C NMR spectra were recorded on a Bruker HX-270 spectrometer operating in the Fourier transform mode at 66.88 MHz. Proton-undecoupled ^{13}C spectra of the ^{13}CO enriched complexes were obtained in $CDCl_3$ or C_6H_5D with the addition of 0.07 *M* $Cr(Acac)_3$ as a relaxation agent [27]. The chemical shifts were measured relative to an internal solvent reference and then reported in ppm downfield from TMS. The chemical shift conversion factors used in this study are δ (TMS) = δ ($CHCl_3$) + 77.2 and δ (TMS) = δ (C_6H_6) + 128.6 [2]. The digital accuracy was 2.3 Hz per point.

The IR spectra were recorded on a Specord-75 IR spectrometer.

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References

1 P.S. Braterman, D.W. Milne, E.W. Randall and E. Rosenberg, J. Chem. Soc. Dalton, (1973) 1027.
2 L.J. Todd and J.R. Wilkinson, J. Organometal. Chem., 77 (1974) 1.
3 G.M. Bodner, Inorg. Chem., 14 (1975) 1932.
4 W.J. Cherwinski, B.F. Johnson, J. Lewis and J.R. Norton, J. Chem. Soc. Dalton, (1975) 1156.
5 J. Browning, P.L. Goggin, R.J. Goodfellow, M.G. Norton, A.J.M. Rattray, B.F. Taylor and J. Mink, J. Chem. Soc. Dalton, (1977) 2061.
6 A.J. Pribula and R.S. Drago. J. Amer. Chem. Soc., 98 (1976) 2784.
7 J. Chatt and B.L. Shaw, J. Chem. Soc. A, (1966) 1437.
8 C.W. Garland and J.R. Wilt, J. Chem. Phys., 36 (1962) 1094.
9 D.N. Lawson and G. Wilkinson, J. Chem. Soc., (1965) 1900.
10 F. Bonati and G. Wilkinson, J. Chem. Soc., (1964) 3156.
11 E.O. Fischer and K. Bittler, Z. Naturforsch. B, 16 (1961) 225.
12 L.G. Kuz'mina, Yu. S. Varshavsky, N.G. Boky, Yu. T. Struchkov and T.G. Cherkasova, Zh. Strukt. Khim., 12 (1971) 653.
13 Yu. S. Varshavsky, T.G. Cherkasova, N.A. Buzina and V.A. Kormer, J. Organometal. Chem., 77 (1974) 107.
14 D.G. Cooper and J. Powell, Inorg. Chem., 16 (1977) 142.
15 J.N. Murrell, Progr. NMR Spectros., 6 (1971) 1.
16 R. Ugo, G. La Monica, S. Cenini and F. Bonati, J. Organometal. Chem., 11 (1968) 159.
17 P.E. Garrou and G.E. Hartwell, Chem. Commun., (1974) 381.
18 A.A. Grinberg, M.M. Singh and Yu. S. Varshavsky, Zh. Neorg. Khim., 13 (1968) 2716.
19 K.S. Brenner, E.O. Fischer, H.P. Fritz and C.G. Kreiter, Chem. Ber., 96 (1963) 2632.
20 Yu. S. Varshavsky and T.G. Cherkasova, Zh. Neorg. Khim., 12 (1967) 1709.
21 Yu. S. Varshavsky, N.N. Knjazeva, T.G. Cherkasova, N.V. Ivannikova and T.I. Ionina, Zh. Neorg. Khim., 15 (1970) 715.
22 L. Vallarino, Inorg. Chem., 4 (1965) 161.
23 M.M. Singh and Yu. S. Varshavsky, Zh. Neorg. Khim., 14 (1969) 2434.
24 Yu. S. Varshavsky, T.G. Cherkasova and N.A. Buzina, Zh. Neorg. Khim., 17 (1972) 2208.
25 W.H. Baddley, J. Amer. Chem. Soc., 88 (1966) 4545.
26 Yu. S. Varshavsky, T.G. Cherkasova, M.M. Singh and N.A. Buzina, Zh. Neorg. Khim., 15 (1970) 2746.
27 O.A. Gansow, A.R. Burke and G.N. La Mar, J. Chem. Soc. Chem. Commun., (1972) 456.