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Preliminary communication

CARBON-13-NUCLEAR MAGNETIC RESONANCE SPECTRA OF 5-COORDINATE TRIS-OLEFIN COMPLEXES OF RHODIUM(I)

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SUMMARY

Studies of the ^{13}C N.M.R. spectra of the series $RhX[P(CH_2CH_2CH=CH_2)_3]$ and $RhX[P(CH_2CH_2CH_2CH=CH_2)_3]$ where X = Cl or Br have revealed that (a) the $J(^{103}Rh-^{13}C)$ (olefin) for the complexes studied is only $\frac{1}{2}-\frac{1}{3}$ that found for square-planar complexes, and (b) the fluxional character in the olefinic carbons observed for the compounds $RhX[P(CH_2CH_2CH=CH_2)_3]$ is related to the partial rotation of the olefin about the rhodium-olefin bond.

Rhodium-olefin complexes are generally not very stable compounds e.g. $RhCl(C_2H_4)(PPh_3)_2$[1] decomposes in solution in the absence of ethylene as does the dimeric compound $Rh_2Cl_2(C_2H_4)_4$[2]. The stability is enhanced by using chelating diolefins e.g. $Rh_2Cl_2(C_8H_{12})_2$[3] (C_8H_{12} = cis cis 1,5-cyclooctadiene) or by using electron withdrawing groups on the olefin, e.g. $Rh(C_5H_5)(CH_2=CHF)_2$[4] or by using chelating tertiary unsaturated phosphines[5]. Since rhodium, isotope 103, occurs in 100% natural abundance with $I=\frac{1}{2}$, rhodium-olefin complexes are ideal for studying bonding effects

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TABLE 1

^{13}C Chemical Shifts[a,b,c], in the Compounds

RhX[P$(CH_2CH_2CH{=}CH_2)_3$] and

RhX[P$(CH_2CH_2CH_2CH{=}CH_2)_3$],

X=Cl or Br

Compound	C_1[d,e]	C_2	C_3	C_4	C_5
P$(CH_2CH_2CH{=}CH_2)_3$	113.2	137.7	29.8	26.1	
RhCl[P$(CH_2CH_2CH{=}CH_2)_3$]	59.4(53.8)	81.0(56.7)	26.5(3.3)	19.7(6.4)	
RhBr[P$(CH_2CH_2CH{=}CH_2)_3$]	58.9(54.3)	81.7(56.0)	26.8(3.0)	19.8(6.3)	
P$(CH_2CH_2CH_2CH{=}CH_2)_3$	113.7	136.9	35.0	26.4	25.1
RhCl[P$(CH_2CH_2CH_2CH{=}CH_2)_3$]	55.4(58.3)	78.5(58.4)	16.9(18.1)	29.5(−3.1)	22.4(2.7)
RhBr[P$(CH_2CH_2CH_2CH{=}CH_2)_3$]	54.4(59.3)	77.6(59.3)	16.7(18.3)	29.4(−3.0)	22.4(2.7)

(a) ^{13}C resonances measured at 67.89MHz in ppm relative to TMS $\delta = 0$ppm. (b) All compounds were dissolved in $CDCl_3$. (c) The values for P$(C_4H_7)_3$, P$(C_5H_9)_3$, RhX[P$(C_5H_9)_3$] were taken at ambient temperatures (∿35°C), while the values for RhX[P$(C_4H_7)_3$] are those taken at -40°C. (d) The carbon atoms are numbered from the olefinic bond. (e) Values in parentheses are the chemical shift difference between the complex and the corresponding ligand.

via ^{13}C N.M.R. Also, since rhodium(I)-olefin complexes can exist as four coordinate square-planar or as five coordinate trigonal bipyramidal complexes, changes in stereochemistry should be manifested in changes in the $^{103}Rh-^{13}C$ coupling constant. It was with this in mind that we have commenced a study of the ^{13}C chemical shifts and $^{103}Rh-^{13}C$ coupling of a series of compounds and now wish to report our initial findings on the compounds $RhX[P(CH_2CH_2CH = CH_2)_3]$ and $RhX[P(CH_2CH_2CH_2CH = CH_2)_3]$, X = Cl, Br.

It has been shown recently[6] that nonbonding paramagnetic shielding effects (σ_p) are a major contributor to the upfield shift in the chemical shift of coordinated olefins in transition metal complexes, similar to the theory proposed for the chemical shift of protons in transition metal hydride complexes.[7] The effect of olefin-π^* back bonding as envisaged in the Dewar-Chatt-Duncanson scheme[8] of metal-olefin bonding is therefore of minor importance[6] upon the chemical shift of olefin complexes, and may not even have relative importance within a defined series of complexes (e.g. a series in which a halide atom is changed - see reference 6). The complexes we have studied are five coordinate complexes[5] with a trigonal bipyramidal structure[9] (see Figure 1). Upon coordination there is an upfield shift of the olefinic carbons of between 50-60ppm (See Table 1), which is of the same order as has been found previously[10,11,12] for square-planar Rh(I) complexes. This is

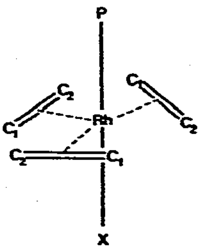

FIGURE 1 Essential features of the trigonal bipyramidal structure occurring in the complexes $RhX[P(CH_2CH_2CH=CH_2)_3]$ and $RhX[P(CH_2CH_2CH_2CH=CH_2)_3]$, X = Cl or Br.

accompanied by much smaller shifts in the methylenic carbons except for C_3 ($\Delta\delta C \sim 18$ ppm) in the $RhX[P(CH_2CH_2CH_2CH = CH_2)_3]$ compounds. Previously it has been suggested that the ligand $P(CH_2CH_2CH_2CH = CH_2)_3$ would be very bulky[5], and it seems likely that the upfield shift of C_3 in that ligand in the complexes is due to steric factors. There is no fluxional character present in the complexes $RhX[P(CH_2CH_2CH_2CH = CH_2)_3]$ up to +60°C, confirming the rigid nature of the molecule.[5] However, there is fluxional character present in the complexes $RhX[P(CH_2CH_2CH = CH_2)_3]$ as has been shown by ^1H variable temperature N.M.R. In the ^1H variable temperature N.M.R. fluxional character was shown to be present in the methylenic protons due to partial rotation about the C-C bonds; but, at the same time no fluxional character was apparently present in the olefinic protons, as there was no change in the chemical shift or ^1H-^1H coupling constants of the olefinic protons in the +60° to -60° range[5]. We have now shown by ^{13}C N.M.R. that such fluxional character is present in the olefin (see Figure 2) and this must be due to the partial rotation (albeit small) of the olefin about the rhodium-olefin bond. It is not due to an equilibrium between bonded and unbonded olefin since no uncoordinated olefin was observed in the solution infrared spectra of the compounds.[5]

Although the ^{13}C chemical shifts of coordinated olefins have little if any application in describing the bonding between the metal and olefin, the M-^{13}C coupling constant appears to have some validity in describing the bonding mode in metal olefin complexes providing the oxidation state and stereochemistry of the complex are taken into account.[13] The X-^{13}C spin-spin coupling interactions are largely dependent on the Fermi contact term which is transmitted via the S contribution to the bond and hence the degree of S character should be reflected in the size of the X-^{13}C coupling constant. The ^{103}Rh-^{13}C(olefin) spin-spin coupling constants for a number of Rh(I)-olefin four-coordinate 16é square planar complexes[10,11,12] lie in the 13-17 Hz range, whereas the ^{103}Rh-^{13}C(olefin) coupling constants for three 18é Rh(I) cyclopentadiene compounds are somewhat lower in the 10-14 Hz range.[10] the ^{103}Rh-^{13}C(olefin) coupling constant in the only

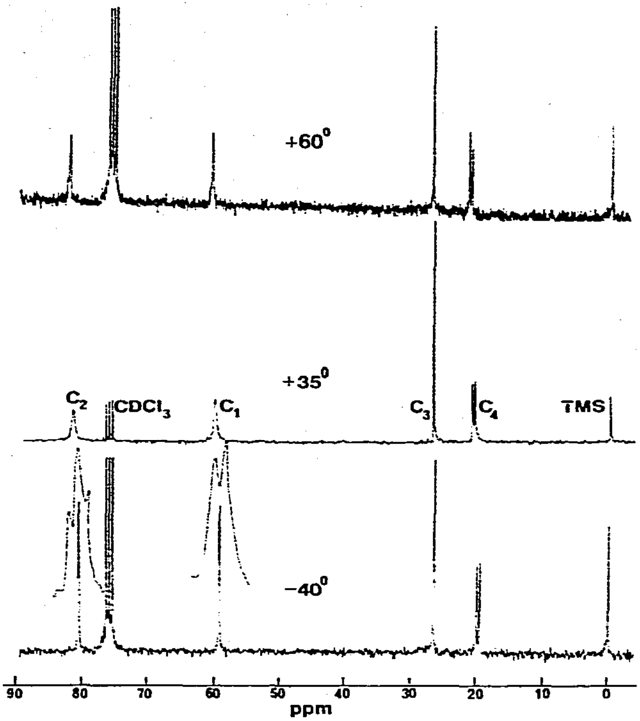

FIGURE 2 Variable temperature ^{13}C N.M.R. Spectra of $RhCl[P(CH_2CH_2CH=CH_2)_3]$; the expanded portions shown were recorded on a 500Hz sweep width compared to the normal sweep width of 7.5kHz

Rh(I) compound containing a tertiary unsaturated phosphine[12] (*viz.* $RhCl[Ph_2PCH_2CH_2CH = CHCH_2CH_2PPh_2]$ so far measured is 16.5Hz. In the five coordinate trigonal bipyramidal complexes we have studied, the $^{103}Rh-^{13}C$(olefin) coupling constants are only about 6Hz (See Table 2). If the hybridisation in the square planar and trigonal bipyramidal complexes is taken to be dsp^2 and dsp^3 respectively, then the change

TABLE 2

Coupling Constants[a,b] for the Compounds

$P(CH_2CH_2CH=CH_2)_3$

$P(CH_2CH_2CH_2CH=CH_2)_3$, $RhX[P(CH_2CH_2CH=CH_2)_3]$ and $RhX[P(CH_2CH_2CH_2CH=CH_2)_3]$

$X = Cl$ or Br

Compound	$J(^{103}Rh-^{13}C_1)$	$J(^{103}Rh-^{13}C_2)$	$J(^{31}P-^{13}C_1)$	$J(^{31}P-^{13}C_2)$	$J(^{31}P-^{13}C_3)$	$J(^{31}P-^{13}C_4)$	$J(^{31}P-^{13}C_5)$
$P(CH_2CH_2CH=CH_2)_3$			0	11.0	12.8	14.7	
$RhCl[P(CH_2CH_2CH=CH_2)_3]$	6.4	6.0	0	6.0	0	26.6	
$RhBr[P(CH_2CH_2CH=CH_2)_3]$	5.5	5.5	0	5.7	0	27.7	
$P(CH_2CH_2CH_2CH=CH_2)_3$			0	0	11.0	12.8	14.7
$RhCl[P(CH_2CH_2CH_2CH=CH_2)_3]$	5.5	5.5	0	0	0	0	33.0
$RhBr[P(CH_2CH_2CH_2CH=CH_2)_3]$	6.4	5.5	0	0	0	2.8	32.0

(a) Coupling constants measured in Hz. (b) Coupling constants accurate to ± 0.5Hz.

in J(^{103}Rh-^{13}C) to the olefinic carbons can at least be qualitatively correlated to the amount of S character in the metal-olefin δ bond. The triplet nature occurring in the C_2 resonance of the RhX[P($CH_2CH_2CH = CH_2$)$_3$] complexes (See Figure 2) is due to ^{103}Rh-^{13}C and ^{31}P-^{13}C couplings of approximately equal magnitude (ca. 6 Hz) and since the ^{31}P-^{13}C coupling is not visible in the C_1 resonance in the RhX[P($CH_2CH_2CH = CH_2$)$_3$] complexes or in either of the olefinic resonances (C_1 or C_2) in the RhX[P($CH_2CH_2CH_2CH = CH_2$)$_3$] complexes, then apparently the ^{31}P-^{13}C coupling is transmitted via the carbon chain and not via the rhodium atom. Further studies on the similar series {RhX[PhP($CH_2CH_2CH = CH_2$)$_2$]}$_2$ and RhX(CO)[PhP($CH_2CH_2CH = CH_2$)$_2$] and the analogous iridium complexes to the above series are in progress.

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