

Preliminary communication

Rapid intramolecular rearrangements in pentacoordinate transition metal compounds.

II*. Intramolecular and intermolecular exchange in some rhodium(I) complexes

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Earlier¹ we have described a series of pentacoordinate Ir^I complexes of the type, $RIr(COD)P_2$, ($R = H, CH_3$; $COD = 1,5$ -cyclooctadiene; $P =$ tertiary phosphine) in which rapid intramolecular rearrangement is found to occur. In order to obtain a more secure assignment of the ground state geometry for such complexes and to clarify the mechanism for the exchange (intra- and intermolecular) we have extended our studies to some analogous norbornadiene (NBD) complexes. The conformational stability (and the high symmetry) of norbornadiene as a ligand can provide additional information on the structure of the complexes, and may be expected to impose greater constraints on interchange processes than COD . Studies on coordinated norbornadiene have shown that the methine protons^{★★}, as well as the vinylic protons, are a sensitive probe for stereochemical assignments.

The complexes^{★★★}, $CH_3Rh(\text{diene})L_2$, ($\text{diene} = \text{NBD or } COD$; $L =$ phosphine or arsine; see Table 1) were prepared by reacting $[Rh(\text{diene})Cl]_2$ with methyl lithium in toluene in the presence of a stoichiometric amount of L . The reactions were initiated at -78° under an atmosphere of nitrogen and the yellow crystalline compounds isolated at 0° . The proton NMR spectra of these complexes (CH_2Cl_2 as solvent) were measured from -95° to $+50^\circ$ (Table 1). Above $+35^\circ$ several complexes showed irreversible changes in the NMR spectrum indicating chemical reaction to be occurring^{★★★★}.

The low temperature limiting spectra show the rhodium bound methyl as a triplet of doublets in the phosphine complexes (I–III, V, VI) indicating coupling of the methyl to ^{103}Rh and equal coupling to two ^{31}P nuclei. In addition, in the PMe_2Ph and $AsMe_2Ph$ complexes (I, IV, V, VII) two diastereotopic methyl resonances are observed. Further, the low temperature limiting spectra of all complexes show two separate vinylic resonances for the diene ligand^{★★★★★}, but, significantly, only one reasonably

★Part 1, see ref. 1.

★★We have observed that appreciable chemical shift separations (30–60 Hz) are found for chemically non-equivalent methine protons^{2a}; see also ref. 2b.

★★★Satisfactory analyses were obtained for all complexes.

★★★★These reactions are currently being investigated but it may be noted that NMR studies indicate that methane is evolved during decomposition³.

★★★★★Unfortunately, as yet, we have been unable to observe ^{103}Rh coupling to the vinyl protons in any of these complexes. The methine protons, which must be decoupled, lie too close to the observed resonances for satisfactory data to be obtained (cf. ref. 4).

sharp* resonance for the methine protons in the NBD complexes. This data identifies the trigonal bipyramid (TBP) structure (Fig. 2) rather than a square pyramidal (SP) structure¹ as the idealized ground state geometry for such complexes.

On raising the temperature; the proton NMR indicates two different types of behavior are occurring. In compounds I, II and IV a gradual coalescence of the vinyl resonances to their mean is observed with no concomitant loss of coupling of the methyl on rhodium to the ³¹P nuclei (Fig. 1). Further in I and IV the diastereotopic methyl groups

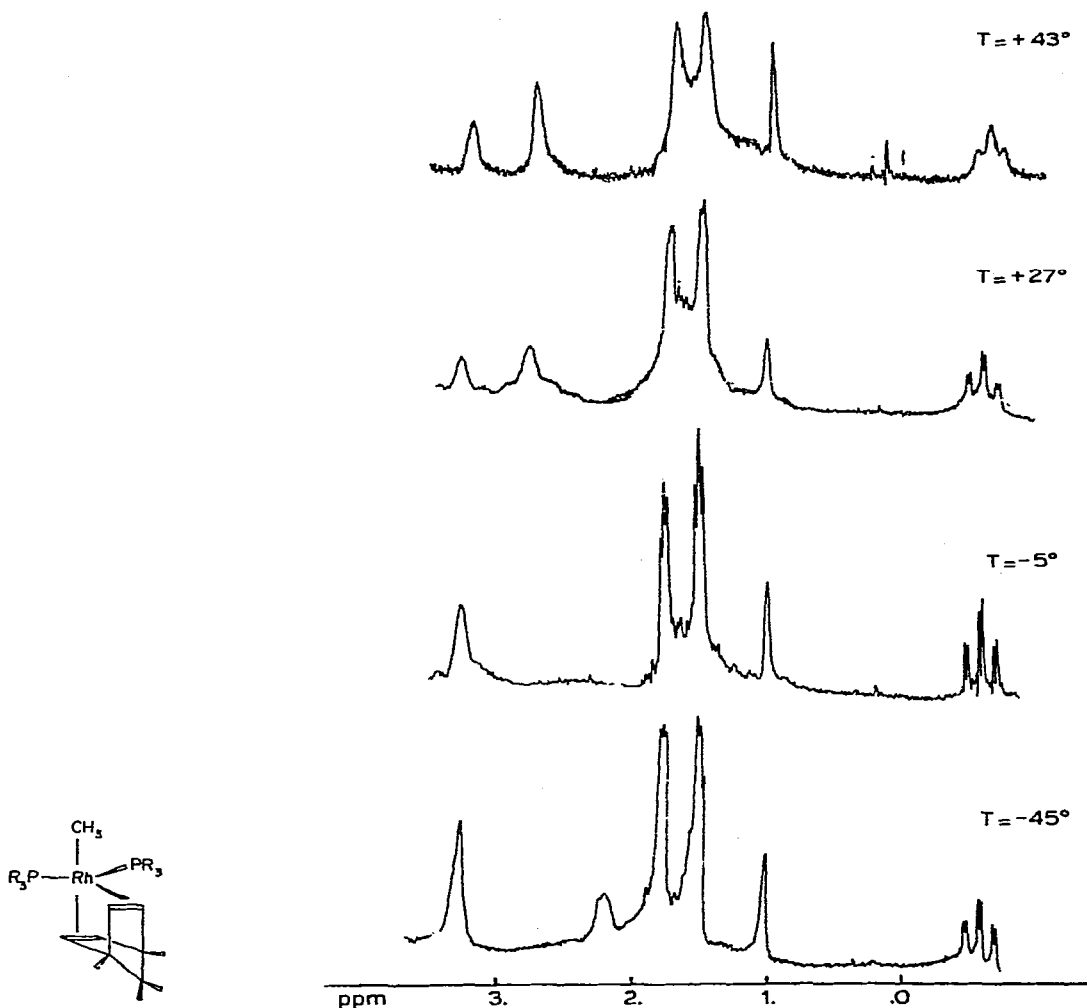


Fig.1.

Fig.2. Proton NMR spectra of $\text{CH}_3\text{Rh}(\text{NBD})(\text{PMe}_2\text{Ph})_2$ over the temperature range -45° to $+43^\circ$.

*Observed line widths (7–9 Hz) are in accord with those found for NBD complexes with chemically equivalent methine protons, *e.g.*, as in Fig. 3. For I (Fig. 2) the methine protons overlap one of the vinyl sets in the limiting spectrum, but the total line width is only 8 Hz.

TABLE I
NMR DATA (CHEMICAL SHIFTS δ SCALE)

Complex	Vinylc	Methine	Methylene	Methyl-Rh	Methyl-P(As)	T ^a
I RhCH ₃ (NBD)(PMe ₂ Ph) ₂	3.11/2.04	3.14	0.91	-0.68	1.41/1.66	+27
II RhCH ₃ (NBD)(PMePh ₂) ₂	3.35/2.17	2.92	0.82	-0.78	1.66	-20
III RhCH ₃ (NBD)(PPh ₃) ₂	3.72/2.67	2.78	0.93	-0.57		-35
IV RhCH ₃ (NBD)(AsMe ₂ Ph) ₂	3.51/2.46	3.35	1.08	-0.69	1.32/1.45	
V RhCH ₃ (COD)(PMe ₂ Ph) ₂	3.63/2.38		1.8-2.2	-0.42	1.46/1.63	-17
VI RhCH ₃ (COD)(PMePh ₂) ₂	3.0/2.03		1.8-2.2	-0.16	1.77	-31
VII RhCH ₃ (COD)(AsMe ₂ Ph) ₂	3.75/2.43		1.74-2.3	-0.71	1.17/1.32	

^aT = temperature at which rhodium bound methyl is broadened by 1 Hz due to intermolecular phosphine exchange (loss of ³¹P coupling).

are also not equilibrated during this process. This behavior is entirely analogous to that observed in the Ir^{I} complexes undergoing rapid intramolecular rearrangement¹ and needs no further comment here. However, in III, V, VI and VII no coalescence of the vinyl groups occurs on raising the temperature (see Fig. 3). This is observed even when in III, V and VI the methyl on rhodium resonance collapses to a doublet ($J(\text{Rh}-\text{CH}_3) = 1-2 \text{ Hz}$) indicating loss of phosphine coupling from the onset of rapid intermolecular phosphine exchange. In VII the intermolecular arsine exchange was indicated by coalescence of the diastereotopic methyl resonances which was shown to be caused by intermolecular exchange since addition of free arsine yielded only one averaged resonance.

The results indicate that for these pentacoordinate complexes with this idealized molecular geometry, the intra- and intermolecular exchange processes are entirely independent. This may be contrasted with the results of studies⁵ on the exchange of phosphine on four coordinate diene complexes of Rh^{I} and Ir^{I} , where five-coordinate species similar to the complexes studied in this paper are proposed as intermediates. Furthermore, it was assumed that the observed

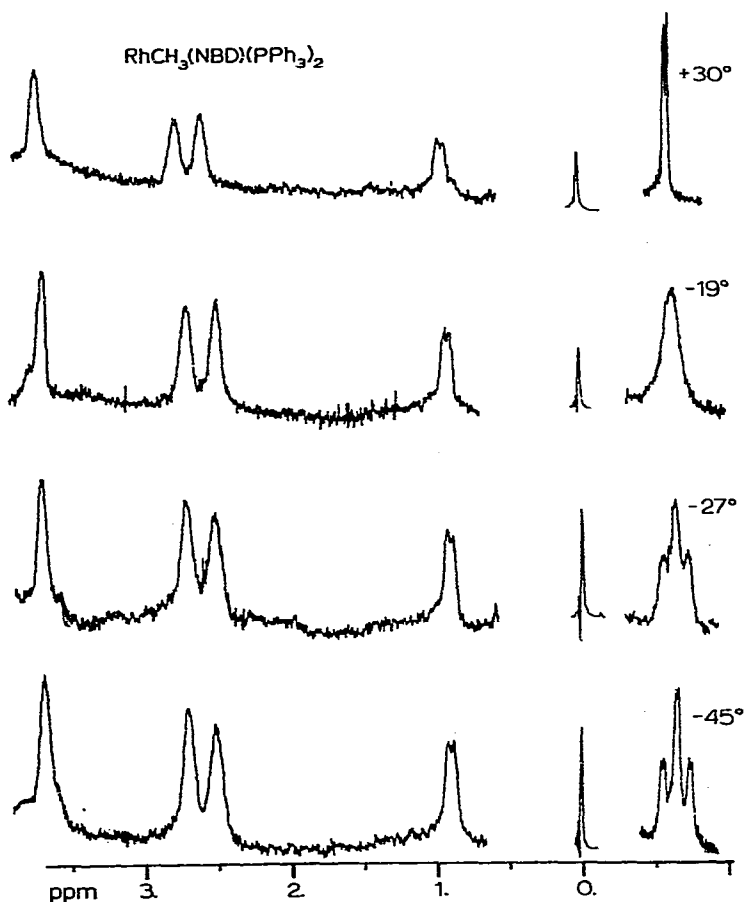


Fig.3. Proton NMR spectra of $\text{CH}_3\text{Rh}(\text{NBD})(\text{PPh}_3)_2$ over the temperature range -45° to $+30^\circ$.

coalescence of the vinyl protons was a direct measure of the rate of intermolecular phosphine exchange. It is clear, however, from our results that, in certain cases, rapid intermolecular exchange may occur without interchange (and, hence coalescence) of the vinyl protons. A full discussion of these observations and their mechanistic implications will be presented elsewhere. It may also be noted that intramolecular exchange in these rhodium(I) complexes occurs more readily with NBD than with COD as ligand whereas in the intermolecular exchange process the reverse holds (*cf.* observations in ref. 5b). Further, comparison of these results with those on Ir^I complexes¹, would indicate that the phosphines are more labile in the pentacoordinate Rh^I than in Ir^I complexes.

In complexes (III, V, VI, VII) where no intramolecular exchange is observed the observation of separate vinylic resonances throughout the intermolecular exchange indicates that the four-coordinate intermediate preserves magnetic non-equivalence of the vinyl sets. A square, but not a tetrahedral, idealized geometry can be accommodated as such an intermediate. This is, of course, entirely in accord with the square planar TBP mechanism generally proposed for d^8 square planar substitution processes⁶.

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