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π-ALLYLIC COMPLEXES OF RHODIUM(III) AND PLATINUM(II)
II. INTRAMOLECULAR REARRANGEMENT OF THE ALLYL LIGAND AS INFLUENCED BY GROUP V DONOR LIGANDS

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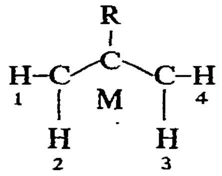
INTRODUCTION

In a preliminary communication[1] we reported on the synthesis and the NMR spectra of $(Ph_3P)_2Cl_2Rh(\pi\text{-}C_4H_7)$ and of $[(Ph_3P)_2Pt(\pi\text{-}C_3H_5)]Cl$. The methylene protons 1, 2, 3 and 4 of the allyl group were found to be magnetically equivalent at temperatures above −20° and −10° for the rhodium and platinum complexes, respectively; the NMR spectrum is thus characteristic of the so-called dynamic allyl form. The allyl group remains bonded to the same metal atom, as is evidenced by the coupling of the nuclear spin of the metal atom with protons of the allyl ligand in the whole temperature range studied. It was suggested that the interchange of protons 1 and 2 (and thus of 3 and 4), which causes the magnetic equivalence, proceeds via a short-lived σ-allyl intermediate.



In order to assess the effect of the electron donor and acceptor properties of ligands on the π-allyl–metal bonding a kinetic investigation of the interchange process* was carried out in the iso-structural series $L_2RhCl_2(\pi\text{-}C_4H_7)$, L being a Group V donor ligand. The syntheses and structures of these complexes were described in Part I[2]. In addition, our views on the nature of the dynamic form, which has been discussed before[3,4], are treated more extensively.

EXPERIMENTAL

The rhodium and platinum compounds were prepared according to methods given in Part I[2].

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* Kinetic studies of the monomolecular interconversion of the *syn*- and *anti*-protons have recently been reported for $Zr(\pi\text{-}C_3H_5)_4$[5,6] and $Th(\pi\text{-}C_3H_5)_4$[6]. The activation energies are about 10 and 15 kcal/mole, respectively. No entropy values were given.

The NMR spectra were determined with a Varian HA 100 spectrometer; low temperatures were obtained with Varian variable dewar inserts, TMS (tetramethylsilane) being used as an internal reference, $CDCl_3$ or CH_2Cl_2 as solvents.

The lifetimes τ of the protons were calculated with formulas appropriate for the slow[7,8], intermediate[7,8,9] and fast exchange[7,8] cases. The observed line-widths were corrected—with respect to the widths in the absence of exchange—by the natural line-width of the CH_3 group (corrected for the coupling with the Rh-spin). This natural line-width correction varied between 1.5 and 2.5 c/s.

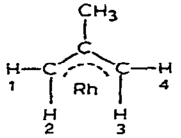
RESULTS

The NMR spectra of the rhodium compounds $L_2Cl_2Rh(C_4H_7)$ were examined as a function of the temperature $\{L = Ph_3P, Ph_3As, [p\text{-}(CH_3)_2NC_6H_4]_3As, Ph_3Sb\}$. Only the methallyl complexes were investigated, since the corresponding allyl complexes were much less stable in $CDCl_3$.

Table 1 gives the chemical shifts of protons 1, 2, 3 and 4 and of the methyl protons at various temperatures.

TABLE 1

CHEMICAL SHIFTS OF PROTONS 1 TO 4 AND OF THE CH_3 GROUP IN PPM FROM TMS (δ) OF THE $L_2Cl_2Rh(\pi\text{-}C_4H_7)$ IN $CDCl_3$ AS A FUNCTION OF L AND TEMPERATURE T (AT 100 Mc)



L	*Temp.* (°*C*)	*Protons* (1,4)	(2,3)	*Temp.* (°*C*)	*Protons* (1,2,3,4)	*Methyl protons*
Ph_3P	−80	3.84[a]	3.60[a] 3.50[a]	+20	3.75 (3.73[a])[d]	1.82 (four peaks)[e]
				+60	3.75 (singlet)	1.82 (doublet)[f]
Ph_3As[b]	−60	4.15	3.74	+60	3.95	1.80 (doublet)[g]
	+20	4.12	3.76			
$\{p\text{-}(CH_3)_2NC_6H_4\}_3As$	−50	4.08	3.70	+40	3.90	1.85 (doublet)[g]
	+20	4.06	3.73			
Ph_3Sb[c]	−50	4.39	3.15			
	+80	4.23	3.17			

[a] Measured in CH_2Cl_2. [b] The chemical shifts of the (1,4) and (2,3) signals are 4.19 and 3.72 ppm, respectively in CH_2Cl_2, at +20°. [c] No broadening was observed for the (1,4) and (2,3) peaks in the temperature range measured. [d] Triplet; $J[(1,2,3,4)\text{-}P] = 2.0$ c/s. [e] $J(CH_3\text{-}P) = 1.2$ c/s; $J(CH_3\text{-}Rh) = 1.4$ c/s. [f] $J(CH_3\text{-}Rh) = 1.4$ c/s. [g] $J(CH_3\text{-}Rh) = 1.6$ c/s.

A. Complex $(Ph_3P)_2Cl_2Rh(\pi\text{-}C_4H_7)$

The NMR spectrum of the allyl group of the phosphine compound in CH_2Cl_2 from −80 to −50° shows four signals at 3.84, 3.60, 3.50 and 1.82 ppm(δ), respectively, in the intensity ratio 2:1:1:3, which were assigned[2] to protons (1,4), 2, 3, (or 3,2) and the CH_3 group (see Fig. 1a). The inequivalence of protons 2 and 3 was ascribed to a small asymmetry in the compound[2] at low temperature. Between −50 and −20° the signals due to protons 1 to 4 broaden and eventually they coalesce to form one signal at 3.73 ppm (3.75 ppm in $CDCl_3$), which value agrees well with the weighted mean of 3.70 ppm of the chemical shifts of the three original absorptions (see Fig. 1b).

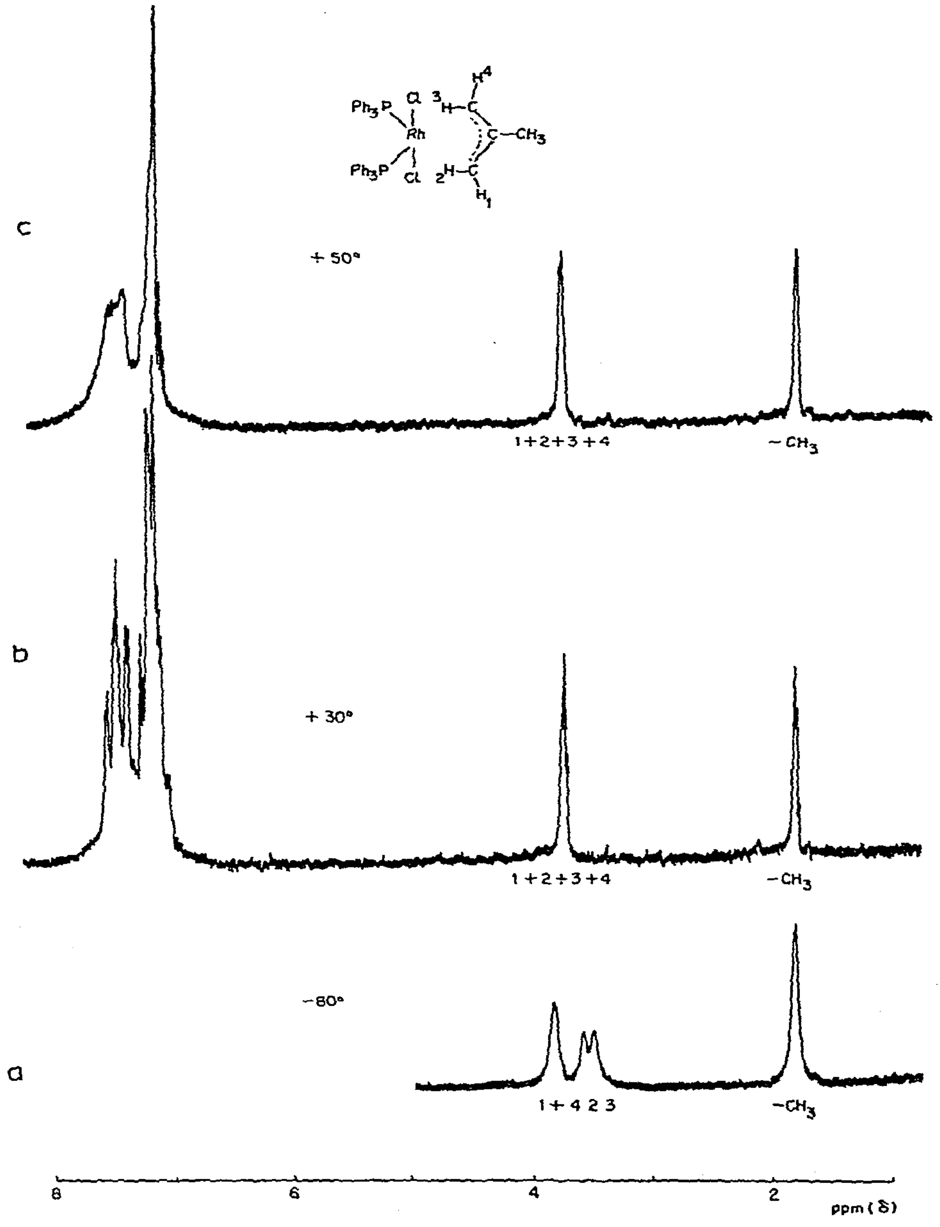


Fig. 1. Temperature dependence of the NMR spectrum of $(Ph_3P)_2Cl_2Rh(\pi\text{-}C_4H_7)$ (at 100 Mc).

By measuring the line broadening of the signal at 3.84 ppm we were able to determine the activation parameters of the interchange of the *syn*- and *anti*-protons (see Table 2 and Fig. 5).

A further increase in temperature from −20 to +30° led to sharpening of the absorption at 3.73 ppm. Because of the sharpness of this signal a small coupling could be observed of the methylene protons (1,2,3,4) with the two equivalent P-nuclei

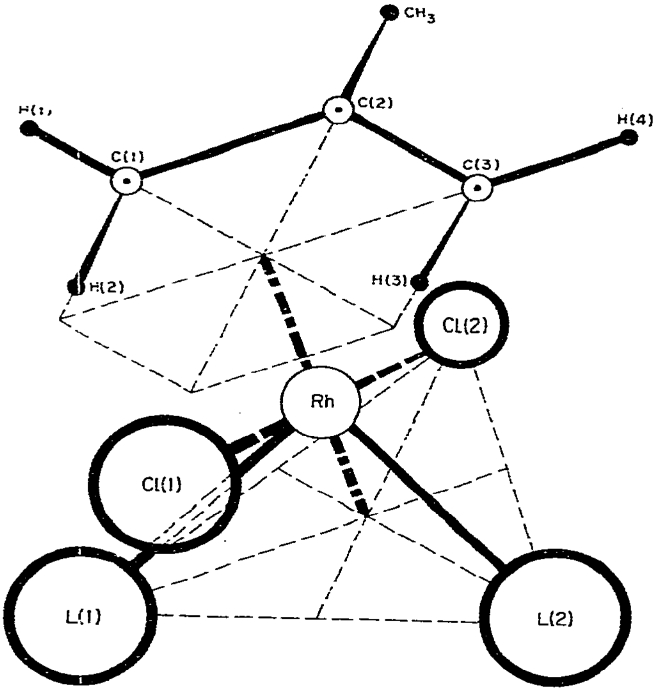


Fig. 2. Idealized structure for compounds $L_2Cl_2Rh(\pi\text{-}C_4H_7)$.

(spin $\frac{1}{2}$), which gave a triplet in the intensity ratio 1:2:1 (see Table 2). The methyl absorption is composed of four signals, due to a combination of a coupling with the ^{103}Rh-atom (spin $\frac{1}{2}$) and the two P-atoms (Table 1 and Fig. 1b).

Above +30° the Ph_3P ligands begin to exchange (in $CDCl_3$ and CH_2Cl_2), as is concluded from the broadening of the phenyl absorptions of the triphenylphosphine ligands and from the disappearance of the phosphorus coupling with the methylene and methyl protons, (see Fig. 1c and Table 1); the triplet at 3.75 ppm has become a singlet and the four signals centred at 1.82 ppm have changed into a doublet [$J(Rh\text{-}CH_3) = 1.4$ c/s].

B. Complexes $L_2Cl_2Rh(\pi\text{-}C_4H_7)$ {$L = Ph_3As$, $[p\text{-}(CH_3)_2NC_6H_4]_3As$ and Ph_3Sb}

The NMR spectra of these compounds in $CDCl_3$ at −60° are characteristic of π-methallyl complexes. Three signals are present in the intensity ratio 2:2:3, due to protons (1,4), (2,3) and the CH_3 protons. From −60 to 0° the three signals sharpen up*, which is very probably due to a decreasing viscosity of the solution.

Above room temperature the signals due to protons (1,4) and (2,3) of the triphenylarsine complex begin to broaden and coalesce to one peak (see Fig. 3). The same phenomenon has also been observed for the $[(CH_3)_2NC_6H_4]_3As$ complex.

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* This sharpening may be due to a rotation of the π-methallyl group in its own plane analogous to the rotation in the species (π-allyl)$PdClL_2$[3,4]. One would then have to assume that protons 1 and 4 (and 2 and 3) have slightly different chemical shifts at low temperature (~0.03 ppm). This rotation, however, seems very unlikely, because of the expected steric hindrance by the Cl (1) atom (see Fig. 2).

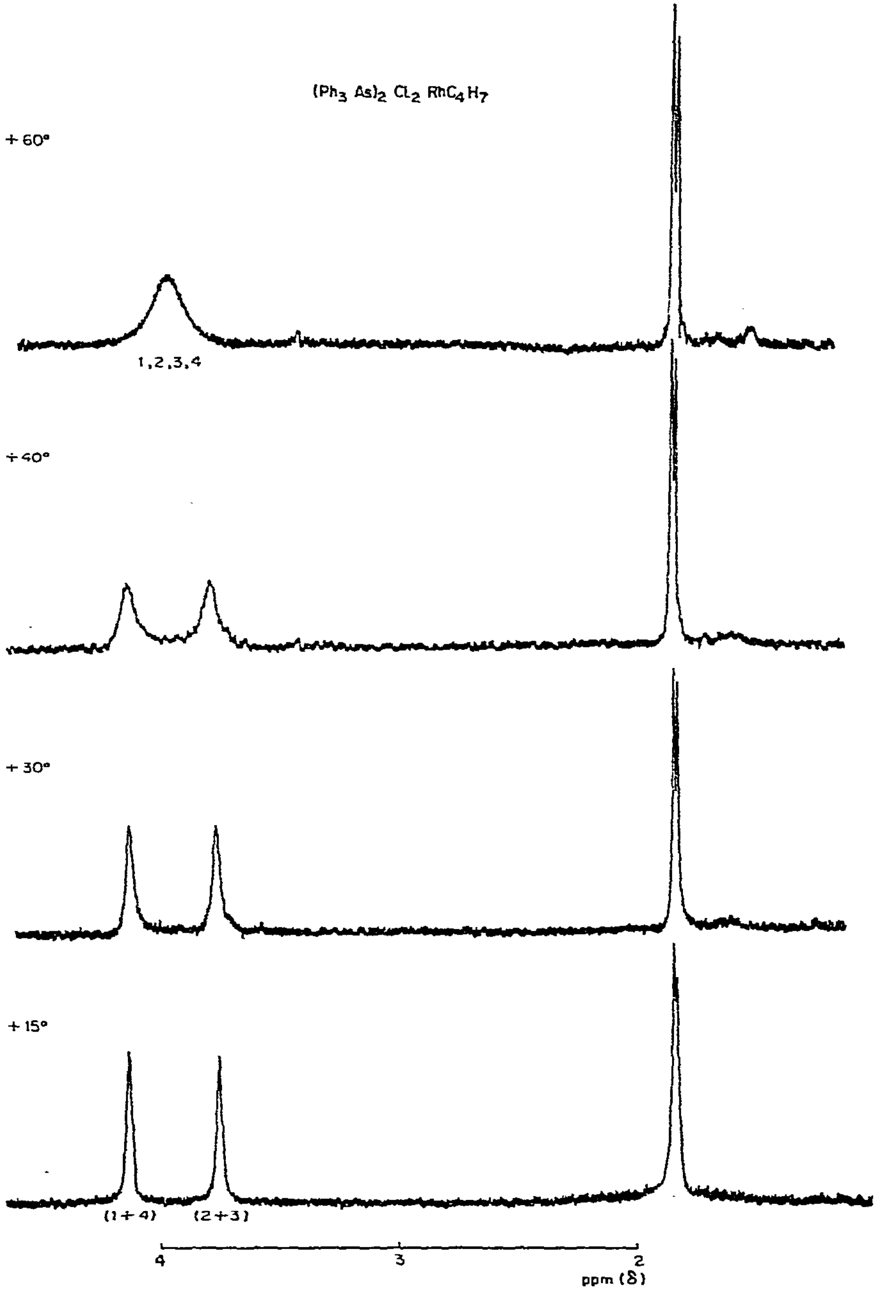

Fig. 3. Temperature dependence of the NMR spectrum of $(Ph_3As)_2Cl_2Rh(\pi\text{-}C_4H_7)$ (at 100 Mc).

We have calculated the kinetic parameters for the arsine compounds for the interconversion (see Table 2). Fig. 4 gives plots which describe the dependence of the reaction velocity $1/\tau$ (τ is the lifetime of the protons concerned) for the arsine complexes on the reciprocal of the temperature T.

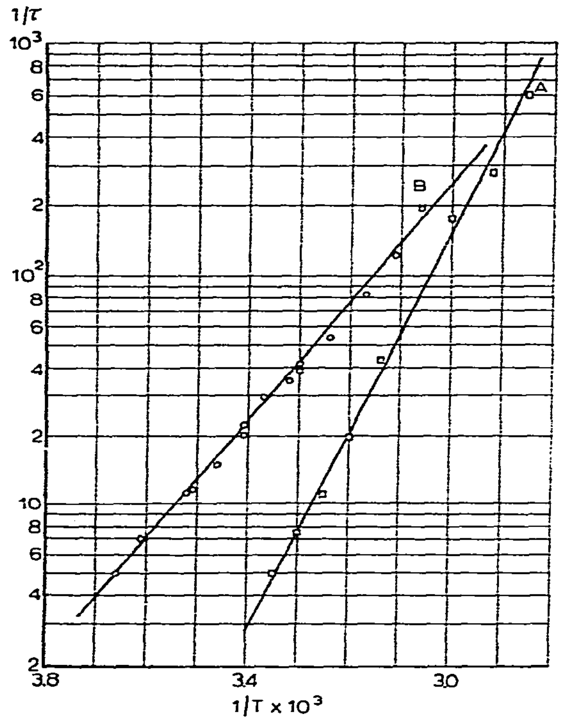

Fig. 4. Dependence of $1/\tau[L_2Cl_2Rh(\pi\text{-}C_4H_7)]$ on $1/T$ of the *syn*- and *anti*-protons for A, L = Ph_3As; B, L = $[p\text{-}(CH_3)_2NC_6H_4]_3As$ (at 100 Mc). Calculated in slow, intermediate and fast exchange limit.

TABLE 2

ARRHENIUS AND TRANSITION STATE THEORY PARAMETERS[a] FOR THE KINETIC PROCESS INVOLVING THE COALESCENCE OF THE SIGNALS DUE TO PROTONS (1,4) AND (2,3) FOR $L_2Cl_2Rh(\pi\text{-}C_4H_7)$

L	E_A (*kcal/mole*)	*A* (s^{-1})	$\Delta H^{\neq}$ (*kcal/mole*)	$\Delta S^{\neq}$ (*e.u.*)
Ph_3Sb	>20.0			
Ph_3As[b]	18.0 ± 1.0	10^{13}	17.3 ± 1.0	$+3 \pm 3$
$\{p\text{-}(CH_3)_2NC_6H_4\}_3As$	11.8 ± 1.0	10^{10}	11.3 ± 1.0	-14 ± 3
Ph_3P	9.2 ± 1.0	10^{10}	8.5 ± 1.0	-15 ± 3

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[a] E_A and A are defined[22] by the equation $k = A \cdot \exp(-E_A/RT)$, while $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are defined by

$$k = (k_B T/h) \cdot \exp(-\Delta S^{\neq}/R) \cdot \exp(-\Delta H^{\neq}/RT) \quad \text{with } \Delta H = E_A - RT.$$

[b] The same activation parameters were found for the arsine complex in CH_2Cl_2, although the chemical shifts of the methylene protons were different from the values observed in $CDCl_3$.

The kinetic processes are fairly slow; for example, at +20° the reaction rate constant k ($= 1/\tau$ for a monomolecular process) is about 3 and 20 s^{-1} for the triphenylarsine and the substituted arsine compound, respectively.

From Table 2 we can conclude that the activation energy decreases with increasing electron donor capability of the ligands L. In the case of the stibine compound we believe that the activation energy is higher than for the arsine compound, since even at +80° no broadening of the signals of protons (1,4) and 2,3) could be observed for the first complex.

An interesting phenomenon is that the Rh-spin couples with the methyl protons, but not with the methylene protons of the methallyl ligand.

C. Spectra of the ligand L in $L_2Cl_2Rh(\pi\text{-}C_4H_7)$

The phenyl proton absorptions of the ligands L (L = Ph_3P, Ph_3As and Ph_3Sb) in the complexes $L_2Cl_2Rh(\pi\text{-}C_4H_7)$ lie between 7 and 7.5 ppm from TMS. The patterns are quite complicated, as is shown in Fig. 1b for the phosphine compound, and have not been interpreted. Above +30°, as has been mentioned before, the phenyl proton absorptions broaden, which is probably due to dissociation of the phosphine molecules*, *e.g.*

$$(Ph_3P)_2Cl_2Rh(C_4H_7) \underset{\Delta}{\leftrightarrows} (Ph_3P)Cl_2Rh(C_4H_7) + Ph_3P$$

No broadening at all was observed for the arsine and antimony complexes in the temperature range from −60° to +80°.

Addition of excess ligand to $CDCl_3$ solutions of the compound had no effect in the case of the arsine and antimony complexes, while unidentified products were formed with the phosphine complex. Addition of free triphenylphosphine to the arsine and antimony compound in $CDCl_3$ led to quantitative formation of the phosphine compound.

It is therefore concluded that the phosphine complex is thermodynamically the most stable of the series, but kinetically the most labile with respect to the ligand L.

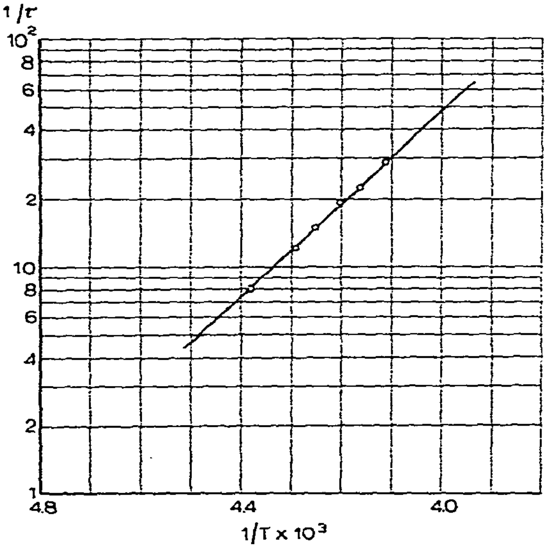

Fig. 5. Dependence of $1/\tau[(Ph_3P)_2Cl_2Rh(\pi\text{-}C_4H_7)]$ on $1/T$ of the protons (1,4) (at 100 Mc). Calculated in slow exchange limit.

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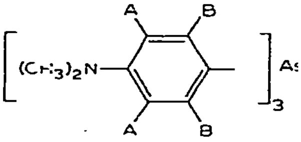
* It should be noted that Ph_3P may exchange also below +30°. In that case, however, the exchange is too slow to be observed by NMR, as is evidenced by the coupling of P with the allylic protons below +30° (see Table 1 and Fig. 1). It is clear that the exchange rate of the π–σ reaction (Fig. 5) is then very much faster than the phosphine exchange.

The spectrum of the ligand $[p\text{-}(CH_3)_2NC_6H_4]_3As$ bonded in the rhodium compound is much simpler and may be compared with the NMR spectrum of the free ligand. Table 3 lists the chemical shifts of the various proton species.

TABLE 3

CHEMICAL SHIFTS (δ) OF THE PROTONS IN PPM FROM TMS OF THE FREE LIGAND L AND OF THE LIGAND L BONDED IN $L_2Cl_2Rh(C_4H_7)$ FOR $L = [p\text{-}(CH_3)_2NC_6H_4]_3As$ IN $CDCl_3$ AT ROOM TEMPERATURE (AT 100 Mc)



Species	*Proton A* (*ppm*)	*Proton B* (*ppm*)	J_{AB} (*c/s*)	$\delta_A - \delta_B$ (*ppm*)	$(CH_3)_2N$ (*ppm*)
L	7.18 (doublet)	6.63 (doublet)	8.9	0.55	2.86
$L_2Cl_2Rh(C_4H_7)$	7.28 (doublet)	6.46 (doublet)	8.9	0.82	2.85

From this table it can be concluded that the arsine atom is co-ordinated to the Rh-atom and not to the N-atom, since the chemical shift of the $(CH_3)_2N$ group is the same for the free ligand and for the ligand bonded in the complex.

It is further of interest to point out that the difference in chemical shift $\delta_A - \delta_B$ is larger for the bonded ligand, which is in general an indication[10] that an electron drift has taken place from the phenyl group to—in this case—the arsine atom.

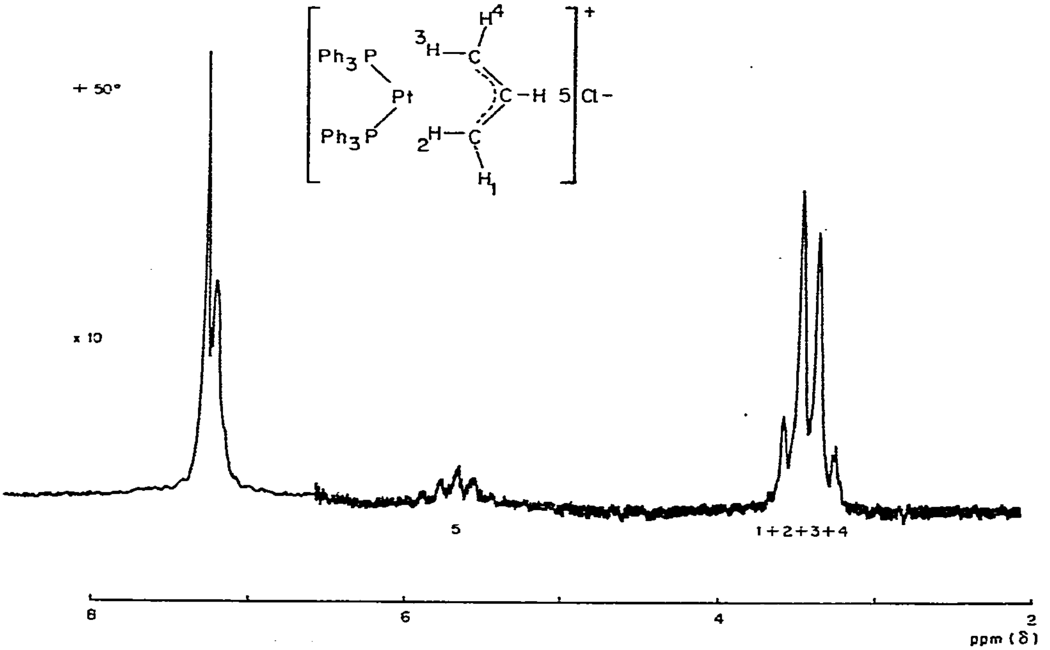


Fig. 6. NMR spectrum of $[(Ph_3P)_2Pt(\pi\text{-}C_3H_5)]^+Cl^-$ (at 100 Mc).

D. *Influence of excess halide ions on the spectra of* $L_2Cl_2Rh(\pi\text{-}C_4H_7)$

Addition of Cl^- ions in the form of a solution of LiCl in acetone to $CDCl_3$ solutions of the complexes $L_2Cl_2Rh(\pi\text{-}C_4H_7)$ had no measurable effect on either the phenyl or the allylic proton absorptions*. This does not mean that no exchange of chloride ions can occur, since the exchange may be independent of the concentration of the attacking halide ion, as has been observed for many octahedral compounds[11].

E. *Complexes* $[(Ph_3P)_2Pt(\pi\text{-}C_3H_5)]X$ $(X = Cl, Br)$

From −70 to about −10° the spectrum of the complex $[(Ph_3P)_2Pt(C_3H_5)]Cl$** consists of the phenyl proton absorptions (7.0–7.5 ppm from TMS) and of three absorptions originating from the *meso*-proton (5), protons (1,4) and (2,3), respectively. From +20 to +50° the bands of protons (1,4) and (2,3) have collapsed to one absorption, which occurs as four signals in the approximate intensity ratio of 8:42:42:8, because of the combination of the coupling of protons (1,2,3,4) with proton 5 {J-[(1,2,3,4)-5] = 11 c/s} and with the ^{195}Pt-isotope (spin $\frac{1}{2}$) {J[(1,2,3,4)-Pt] = 22 c/s}. This isotope occurs in 33% natural abundance (see Fig. 6). Absence of phosphorus coupling and the shape of the phenyl absorptions, which is similar to that of Ph_3P itself[12], show that the phosphine exchanges in solution.

The interchange of proton 1 with 2 (and 3 with 4) is caused not only by a monomolecular process, but also by an attack of free phosphine on the Pt-complex, analogous to the Pd-case[3,4]. The influence of phosphine, however, could not be determined, since excess PPh_3 yields the complex $Pt(PPh_3)_n$, as was discussed in Part I[2].

BONDING CHARACTERISTICS OF THE Rh–ALLYL AND Pt–ALLYL COMPLEXES

Since the detailed structures of the Rh– and Pt–π-allyl compounds are not yet known, we have drawn in Fig. 2 an idealized structure for the compounds $L_2Cl_2Rh(\pi\text{-}C_4H_7)$, analogous to the idealized structure of one half of the dimer $[(\pi\text{-}C_3H_5)PdCl]_2$[3]. The chloride ions have been placed on the positive and negative X-axes. The idealized structure of the complex cation $[(Ph_3P)_3Pt(\pi\text{-}C_3H_5)]^+$ may be derived from Fig. 2 by removing the two Cl-atoms.

The plane of the allyl ligand makes an angle of 125° with the RhP(1)P(2) plane, which seems reasonable in view of the actual values in $(\pi\text{-}C_4H_7)PdCl(Ph_3P)$ (119°)[13], in $[(\pi\text{-}C_3H_5)PdCl]_2$ (112° at −140° [14] and 108° at room temperature[15]) and in $[(\pi\text{-}C_3H_5)Pd(OAc)]_2$ (110° and 125°)[16].

In the idealized structure the two P-atoms and Cl(2) occupy the corners of the lower triangle of an octahedron, while the plane of the allyl ligand*** runs parallel to this triangle. The complex thus has a plane of symmetry through the ZX-

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* Also, addition of the organic salt benzylhexadecyldimethylammonium chloride had no observable effect on the exchange rates.

** The spectrum of the disubstituted complex $\{(Ph_3P)_2Pt[\pi\text{-}(CH_3)_2C{=}CH{=}CH_2]\}Cl$ could not be measured accurately, because of decomposition in solution, but an interconversion of the type mentioned above seems to occur also in this case.

*** For the sake of convenience the CH_3 group in Fig. 2 has been drawn in the C(1)C(2)C(3) plane. It must be understood, however, that the C(2)–CH_3 bond may be tilted about 20° away from the C(1)C(2)C(3) plane[13].

plane, as required by the NMR data. It seems likely that in the real structure the actual dihedral angle will be nearer to 90°, because of possible steric hindrance of the Cl(1) atom with protons 2 and 3 (*see* Fig. 2). The deviation from the ideal angle, however, will make no essential difference for the discussion. (For a more complete description of the bonding, see ref. 3). It may be deduced that the bonding situation in $[(Ph_3P)_2Pt(C_3H_5)]^+$ is similar to that in analogous palladium compounds[3,4,15], since both have the same spin-paired d^8-electron configuration and similar stereochemistries. The energy diagrams will only differ in the relative position of the energies of the metal atom orbitals and the energies of the allyl orbitals.

The situation is different for the compounds $L_2Cl_2Rh(\pi\text{-}C_4H_7)$ in that Rh(III) has a spin-paired d^6-electron configuration, while the metal atom has acquired a six-coordinate stereochemistry through the addition of two Cl^- ions on the X-axis. Furthermore the energy of the 4*d*-orbitals for Rh(III) will differ in value from that for Pd(II).

The effect of the two Cl^- ions on the MO diagram, when compared with the situation for $[(\pi\text{-}C_3H_5)PdCl]_2$[3], will be a rise in $d_{x^2-y^2}$ orbital energy relative to the energy of the other *d*-orbitals. The $d_{x^2-y^2}$ orbital is filled in Pd(II) ($4d^8$ configuration); however, for Rh(III) ($4d^6$ configuration) it is empty.

The average energy of the five *d*-orbitals of Rh(III) in compounds is not known. It is expected, however, that it will be lower than the analogous energy for Pd(II).

DISCUSSION

The NMR spectra of the compounds $L_2Cl_2Rh(\pi\text{-}C_4H_7)$ have shown that for L is R_3As or R_3P the allyl protons 1 and 2 (and thus also 3 and 4) may interchange their positions. At sufficiently high temperatures this process results in the magnetic

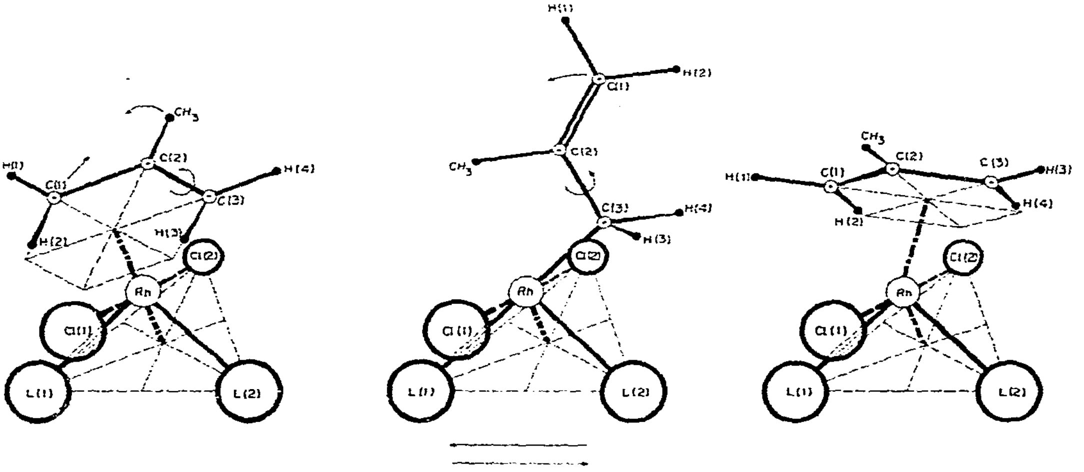

Fig. 7. Interconversion of the *syn*- and *anti*-proton at C(3) via a σ-allyl form (either transition state or intermediate). Obviously, the same process occurs also at C(*1*).

equivalence of the four allyl protons (see Fig. 1 and 3). It has been suggested before[1,3,17,18,19,20,23], that this type of interchange proceeds via a short-lived σ-allyl species. It should be noted, however, that a one-step process, in which the transition state resembles a σ-allyl intermediate, cannot be ruled out. In both cases, however, the rearrangements necessary are a rotation around the C(1)–C(2) bond, by which protons 1 and 2 interchange, and one around the C(2)–C(3) bond, by which protons 3 and 4 become magnetically equivalent*. The latter process** is drawn in Fig. 7.

An alternative mechanism has been suggested by Becconsall and O'Brien for $Zr(\pi\text{-}C_3H_5)_4$ and π-allyl palladium compounds[5]. It involves the rotation of the methylene groups around the C(1)–C(2) and C(2)–C(3) ones, while the allyl group stays in the π-allyl configuration. A model, however, shows that rotations around the C(1)–C(2) and C(2)–C(3) bonds are sterically hindered to a considerable extent. Moreover, the experimental activation energies for the interchange process for $Zr(\pi\text{-}C_3H_5)_4$[5,6] ($\sim$10 kcal/mole), $Th(\pi\text{-}C_3H_5)_4$[6] ($\sim$15 kcal/mole), $(\pi\text{-}C_4H_7)PdCl(Ph_3As)$[4] ($\sim$ 7 kcal/mole) and the rhodium compounds studied here (see Table 2) are rather low.

Table 2 contains data on the influence of the ligand L upon the rate of the monomolecular exchange process in $L_2Cl_2Rh(\pi\text{-}C_4H_7)$. It should be noted that both ligands L are each situated *trans* to one side of the π-allyl group[2] (see Fig. 2). The activation parameters shown in Table 2 (see also Fig. 4 and 5), as well as preliminary data for Ph_2MeAs*** and $(p\text{-}Br\text{-}C_6H_4)Ph_2P$†, clearly indicate that the activation energy decreases with an increase in total electron donor capacity of the ligand L.

This result is in accordance with the qualitative discussion on the bonding in (π-allyl)PdCl(L)[3,4], where it was pointed out that ligands with a large total electron donor capacity increase the electron density on the metal, thus causing a rise in energy of the metal *d*-orbitals. As a result, the π-allyl group may acquire also a more negative charge, which leads to a destabilization of the π-allyl mode of bonding in favour of the σ-allyl form. This may be understood if it is realized that in the σ-allyl form a five-coordinate metal atom is present, in which at the metal centre two electrons less have to be stored than with the six-coordinate π-allyl form. In this connection we suggest that there may be a relation between the above series and the "*trans*-effect" series, which is defined as the effect of a coordinated group L upon the rate of substitution of ligands X opposite (*trans*) to it. According to Basolo and Pearson[11] the ligand L may either destabilize the initial state (which is reflected in a lengthening and weakening of the metal–X bond) or to a stabilization of the transition state (in general we will have a combination of both effects). It is expected that the initial state is mainly determined by the electron donor capacity of the ligand L and occurs in particular in octahedral complexes[21]. Hence the *trans*-effect is expected to decrease

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* These rotations may be combined with rotations around the Rh–C(1) and Rh–C(3) axes.

** It is relevant to note that in the drawing on the left-hand side of Fig. 7 the pseudo-trigonal axis (-----) perpendicular to the allyl plane goes through the midpoint of the L(1)L(2)Cl(2) triangle, whereas in the right-hand drawing where 3 and 4 have changed places, the trigonal axis perpendicular to the allyl plane goes through the midpoint of the L(1)L(2)Cl(1) triangle. There is of course no difference between the two structures.

*** $\Delta H^{\neq} = 13.2$ kcal/mole; $\Delta S^{\neq}$ -14 e.u.

† $\Delta H^{\neq} = 9.8$ kcal/mole; $\Delta S^{\neq}$ -12 e.u.

in the order P > As > Sb, which is similar to that found in our series. The fact that preparation of π-allyl rhodium compounds with more powerful electron donor ligands than Ph_3P, *e.g.* $PhEt_2P$, failed—$(PhEt_2P)_3RhCl_3$ is formed instead—may be due to kinetic reasons, or to their intrinsic instability.

The activation entropies for the interconversion processes are in general negative with the exception of the complex $(Ph_3As)_2Cl_2Rh(\pi\text{-}C_4H_7)$, although one would expect positive values, since it seems likely that the motion in the transition state is less restricted than in the initial state. Similar low values have been observed for Pd-systems[4]; they are not yet understood.

SUMMARY

A proton magnetic resonance investigation of the temperature dependence of the allyl ligand behaviour in the complexes $L_2Cl_2Rh(\pi\text{-}C_4H_7)$ and $[(Ph_3P)_2Pt\text{-}(\pi\text{-}C_3H_5)]Cl$ (L is a group V donor ligand) has shown that the *syn*- and *anti*-protons of the allyl ligand may become magnetically equivalent owing to the occurrence of a σ-allyl form.

The kinetic parameters of this interconversion process were determined for various ligands L. It appears that the increase in total electron donor capacity of L (in the order $Ph_3Sb < Ph_3As < \{p\text{-}(CH_3)_2NC_6H_4\}_3As < Ph_3P$) decreases the activation energy.

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