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INFLUENCE OF THE PHOSPHINE LIGANDS IN THE ^{1}H AND ^{31}P NMR BEHAVIOUR OF [(η^3-ALLYL)Pt(PHOSPHINE)Cl] COMPLEXES

G. CARTURAN, A. SCRIVANTI,
Centro di Chimica e Tecnologia dei Composti Metallorganici del CNR, c/o Istituto di Chimica Industriale, Via Marzolo 9, Padova (Italy)

B. LONGATO and F. MORANDINI
Centro di Stabilità e Reattività dei Composti di Coordinazione del CNR, Via Marzolo 1, Padova (Italy)

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Summary

The ^{1}H and ^{31}P NMR spectra of [(η^3-allyl)Pt(PR_3)Cl] (PR_3 = PMe_3, PCy_3, P-t-Bu_3, P-n-Bu_3, PPh_3, PPh_2Me, $PPhMe_2$ and P(p-Tol)$_3$) complexes in chloroform have been studied. The results suggest that there is bonding interaction between the phosphine and the allyl group via central metal atom.

Introduction

It has recently been observed that the reactivity of η^3-allylpalladium(II) complexes towards H_2 is strongly affected by the nature of the allyl moiety and of the ancillary ligands [1]. The products of the reaction of η^3-allylpalladium(II) complexes with conjugated dienes were also shown to vary with the nature of the allyl group [2], and insertion of butadienes into the Pd—allyl bond is known to occur only in the case of [Pd(allyl)Cl]$_2$ derivatives [3]. Furthermore, the cooligomerization of butadiene and butadiene—CO_2 catalyzed by Ni or Pd species via allyl intermediates was found to be strongly influenced by the nature of the phosphines in the starting complex [4—6], and very different products can be obtained by changing the nature of the phosphine.

These facts underline the great importance of the coordinated ligands in promoting the reactivity of η^3-allyl complexes. With the aim of studying the effects of the metal—phosphine bond on the metal—allyl interactions we examined the ^{1}H and ^{31}P NMR spectra of platinum(II) complexes of the type [(η^3-allyl)Pt(PR_3)Cl]. With platinum(II) complexes the possibility of observing the J(Pt—P) and J(Pt—H) coupling constants constitutes a definitive advantage, since these parameters may be related to the nature of the corresponding bonds.

In addition, systematic studies have been made of the steric and electronic influences of PR$_3$ ligands [7,8].

Results and discussion

The compounds of the type [(η^3-allyl)Pt(PR$_3$)Cl] (eq. 1) were prepared analogously to the complex [(η^3-allyl)Pt(PPh$_3$)Cl] [9] by treating [Pt(C$_3$H$_5$)Cl]$_4$ with the stoichiometric amount of phosphine in CH$_2$Cl$_2$:

$$[\mathrm{Pt(C_3H_5)Cl}]_4 + 4\ \mathrm{PR_3} \rightarrow 4[(\eta^3\text{-allyl})\mathrm{Pt(PR_3)Cl}] \qquad (1)$$

(I)

(PR$_3$ = PEt$_3$, PCy$_3$, P-t-Bu$_3$, P-n-Bu$_3$, PPh$_3$, PMePh$_2$, PMe$_2$Ph and P(p-Tol)$_3$)

The PMe$_3$ analog of I was prepared by treating [Pt(C$_3$H$_5$)Cl]$_4$ with AgI · 0.5 PMe$_3$ [10] in C$_2$H$_4$Cl$_2$ solution. Some analytical and IR data for the new complexes are listed in Table 1.

The ν(Pt—Cl) bonds were observed as single peaks in the region 305—285 cm^{-1}, in agreement with terminal Pt—Cl stretching vibrations. Chloroform solutions of compounds I are non-conducting ($\Lambda \leqslant 3$ mol^{-1} cm^2 Ω^{-1}). Molecular weight determinations carried for some of these complexes confirm the monomeric formulation I.

The ^{1}H NMR data for these complexes are listed in Table 2. The compounds exhibit the expected approximately first order patterns for the allylic protons, in agreement with a static and asymmetric allyl configuration. The assignments of protons 1, 2, 3, 4 and 5 were based on the values of J(P—H(2)) ≈ 9 Hz [12],

TABLE 1

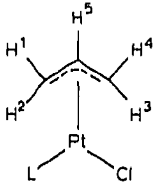
ANALYTICAL DATA, MELTING POINTS, MOLECULAR WEIGHT AND ν(Pt—Cl) FOR THE NEW COMPLEXES OF THE TYPE [(η^3-allyl)PtLCl] (L = tertiary phosphine)

L	Analysis (Found (calcd.) (%))			M.p. (°C)	Mol. wt. [a]	ν(Pt—Cl) [b] (cm^{-1})
	C	H	Cl			
PMe$_3$	21.3	3.9	10.8	102—105		290
	(20.72)	(4.05)	(10.19)			
PCy$_3$	45.9	7.1	6.3	187	560	295
	(45.69)	(6.93)	(6.42)		(552)	
P-n-Bu$_3$ [c]	38.3	7.1	7.7			305
	(38.00)	(6.80)	(7.48)			
PEt$_3$ [c]	28.3	5.4	9.4			301
	(27.72)	(5.17)	(9.09)			
P(p-Tol)$_3$	49.9	4.5	6.2	175—177	543	300
	(50.04)	(4.55)	(6.16)		(575)	
PMe$_2$Ph	31.9	3.8	8.2	83—85		296
	(32.23)	(3.93)	(8.16)			
PMePh$_2$	40.7	3.8	7.6	142—145	480	300
	(40.71)	(3.84)	(7.51)		(472)	
P-t-Bu$_3$	37.7	7.0	7.3	138—140	475	288
	(38.00)	(6.80)	(7.48)		(474)	

[a] Determined in CHCl$_3$. [b] Nujol mull. [c] Isolated as oil.

TABLE 2

^{1}H NMR DATA (τ, ppm) FOR [(η^3-allyl)PtLCl] COMPLEXES [a]



L	τ_1	τ_2	τ_3	τ_4	τ_5	τ_4—τ_2	PR_3 protons resonances (τ)
PPh_3 [b]	5.67 J_5 8 J(P) 4.5	6.97 J_5 11.4 J(P) 9	7.76 J_5 12 J(Pt) 84	7.20 J_5 8 J(Pt) 20	5.06	0.23	2.2—2.8 phenyl protons
P(p-Tol)$_3$	5.65 J_5 8 J(P) 4	7.00 J_5 12.5 J(P) 9	7.75 J_5 12 J(Pt) 82	7.17 J_5 8	5.00	0.17	2.4—2.8 phenyl protons 7.64 CH_3 protons
PMe_3	5.80 J_5 7.8 J(P) 4	7.21 J_5 13.2 J(P) 9.2	7.93 J_5 11.8 J(Pt) 81	6.78 J_5 8.8 J(Pt) 23	5.35 J(Pt) 65	−0.43	8.45 CH_3 protons ^2J(P—H) 13.5; ^3J(Pt) 39.0
$PMePh_2$	5.65 J_5 8.3 J(P) 4.2	7.18 J_5 12.5 J(P) 9.3	7.80 J_5 12 J(Pt) 82	7.10 J_5 7.8 J(Pt) 25	5.23 J(Pt) 70	−0.08	2.1—2.7 phenyl protons 7.92 CH_3 protons ^2J(P—H) 9.0; ^3J(Pt) 36.1
PMe_2Ph	5.73 J_5 8.4 J(P) 4.2	7.15 J_5 12 J(P) 9.3	7.90 J_5 12 J(Pt) 78	6.90 J_5 9 J(Pt) 24	5.25 J(Pt) 66	−0.25	2.8—2.5 phenyl protons Two unequivalent CH_3 protons at 7.95 and 8.00; ^2J(P—H) 11.5; ^3J(Pt) 36.0
P-t-Bu_3 [c]	5.71 J_5 8.2 J(P) 4	6.62 J_5 12.6 J(P) 8.1	7.85 J_5 12.1 J(Pt) 85	6.22 J_5 8.2 J(Pt) 24	5.25 J(Pt) 67	−0.40	8.41 butyl protons ^3J(P—H) 12.8
PCy_3 [d]	5.81 J_5 8.2 J(P) 4.5	7.22 J_5 13 J(P) 9.0		6.86 J_5 7.5	5.32	−0.36	7.5—9.2 cyclohexyl protons
P-n-Bu_3 [d]	5.75 J_5 8.2 J(P) 4.5	7.18 J_5 12.5 J(P) 9.0		6.75 J_5 7.3 J(Pt) 26	5.30 J(Pt) 64	−0.43	7.8—8.8, 9.0—9.2 butyl protons
PEt_3 [d]	5.80 J_5 8.1 J(P) 4.8	7.22 J_5 11.1 J(P) 9.4		6.83 J_5 7.4	5.33	−0.39	9.18 CH_3 protons; J(H—H) 6.7; ^3J(P—H) 17 8.3 CH_2 protons (complex multiplet)

[a] Measured in $CDCl_3$ at 35°C, J values in Hz. [b] Quoted also in ref. 9. [c] Quoted also in ref. 11 and registered at −40°C. [d] Partially covered by phosphine protons resonances.

TABLE 3

^{31}P NMR DATA FOR $[(\eta^3\text{-}C_3H_5)PtLCl]$ COMPLEXES [a]

L	Coordinated [b] (ppm)	Δ_{cs} [c] ppm	J(Pt—P) (Hz)
P-t-Bu_3 [d]	80.54	17.2	4548
PCy_3	35.44	24.1	4277
PPh_3	22.926	28.7	4453
PPh_2Me	10.55	38.5	4354
$PPhMe_2$	—2.79	44.2	4299
PMe_3	—11.61	51.7	4238
P(p-Tol)$_3$	21.11	28.8	4453
PEt_3	21.42	42.4	4255
PBu_3	13.50	46.8	4240

[a] Spectra registered at 35°C in $CDCl_3$. [b] IUPAC recommended sign convention [15]. [c] $\Delta_{cs} = \delta(^{31}P_{complex}) - \delta(^{31}P_{free\ ligand})$; $\delta(^{31}P_{free\ ligand})$ taken from ref. 16 and 17. [d] Quoted also in ref. 11.

J(Pt—H(3)) ≈ 80 Hz [9, 11, 13] and on the magnitude of the couplings of protons 1, 2, 3 and 4 with 5 [14]. Except for the P-t-Bu_3 complex, the spectra were temperature independent in the range —40 — +35°C, and there were substantial parallels in the pattern of J(P—H), J(Pt—H) and J(H—H) coupling constants. The most significant feature is the variation of the chemical shifts of the allylic protons. These values are considerably affected by the nature of the PR_3 ligands, which must modify substantially the electronic charge distribution among the allylic carbons. In general, on going from the P(aryl)$_3$ to the P(alkyl)$_3$ complexes the shifts increase with the exception of τ_4 which is shifted to lower values. Therefore in P(aryl)$_3$ complexes the sequence is $\tau_1 < \tau_2 < \tau_4 < \tau_3$ whereas in P(alkyl)$_3$ complexes is $\tau_1 < \tau_4 < \tau_2 < \tau_3$. On this basis the difference $\tau_4 - \tau_2$, listed in Table 2, may be chosen as the parameter which best reflects the effect of the phosphine nature on the ^1H NMR behaviour of these complexes.

The ^{31}P NMR spectra of compounds I (Table 3) were recorded at —30 — +40°C, the spectra (single ^{31}P signal flanked by the satellites arising from coupling with ^{195}Pt) were independent of the temperature, indicating that the phosphine ligand was not involved in dissociation and/or exchange equilibria. While the chemical shifts are strongly affected by the type of phosphine, the values of J(Pt—P) fall in a relatively narrow interval (4240—4550 Hz).

A plot of the values of ^{31}P chemical shift of the free phosphine vs. the coordination chemical shift Δ_{cs} ($\Delta_{cs} = \delta(^{31}P_{complex}) - \delta(^{31}P_{free\ ligand})$) gives a straight line. Such behaviour is well known for recognized phosphino complexes [18] and parallels the trend observed in the case of *trans*-[Rh(CO)L_2Cl) compounds [19], where it was interpreted in terms of modification of the R—P—R angles on coordination [7,19]. The coordination chemical shift is large in the case of phosphines bearing small alkyl groups and small in the case of phosphine bearing bulky substituents, in agreement with the fact that the R—P—P angles are in the latter little changed on coordination. A plot of Δ_{cs} values vs. the cone cone angle, θ, of the phosphine giving the straight line shown in Fig. 1, was

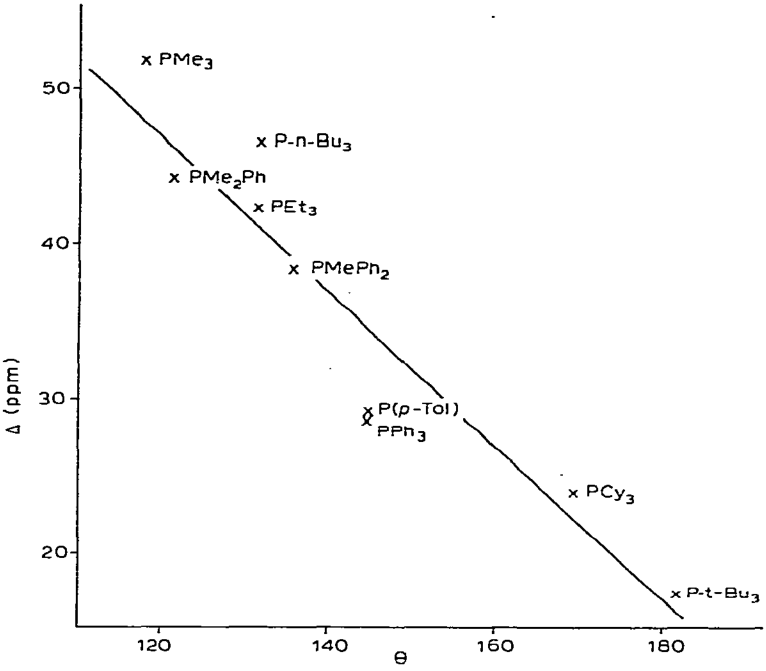


Fig. 1. Plot of the coordination chemical shift, Δ_{cs}, vs. the cone angle, θ, of the phosphine.

obtained *. This confirms that steric hindrance is dominant in determining the chemical shift [7]. The line of Fig. 2 is defined by

$$\delta(^{31}P_{complex}) = 107(9) - 0.50(6).\ \theta + \delta(^{31}P_{free\ ligand}) \qquad (2)$$

The values of J(Pt—P) fall in a fairly narrow range, which is ≈7% of the average of the J(Pt—P) values, i.e. the variation is much smaller than for some other of J(M—P) couplings [21—23]. In the case of the P-t-Bu_3 complex, J(Pt—P) is larger than for the other $P(alkyl)_3$ derivatives, nevertheless this compound, in contrast to the other η^3-allyl complexes, shows a dynamic ^1H NMR spectrum at room temperature, and so must be regarded as a special case. Changes in J(Pt—P) could be related to changes in the *s* character of the Pt orbital used for bond formation with phosphorus. These arguments have been used [24] to define a *trans* influence sequence for various X ligands *trans* to P groups in X—Pt—P type complexes, based on J(Pt—P) values. Conversely in our case, since only the phosphine is changed, while the allyl group remains the same, small variations in J(Pt—P) are to be expected. However a clear linear relationship if found between J(Pt—P) vs. τ_4—τ_2 (Fig. 2), and this represents a direct evidence for interaction between Pt—P and Pt—allyl bonds. Whether this is due to steric or electronic effects, or both, of the phosphine substitutents, is not yet clear. Relevant evidence will probably arise from X-ray structural determinations now in progress [11,25].

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* We used the cone angle measured on models instead of the θ_n values calculated from crystal structure data [20] because the latter must be strongly influenced by crystal forces.

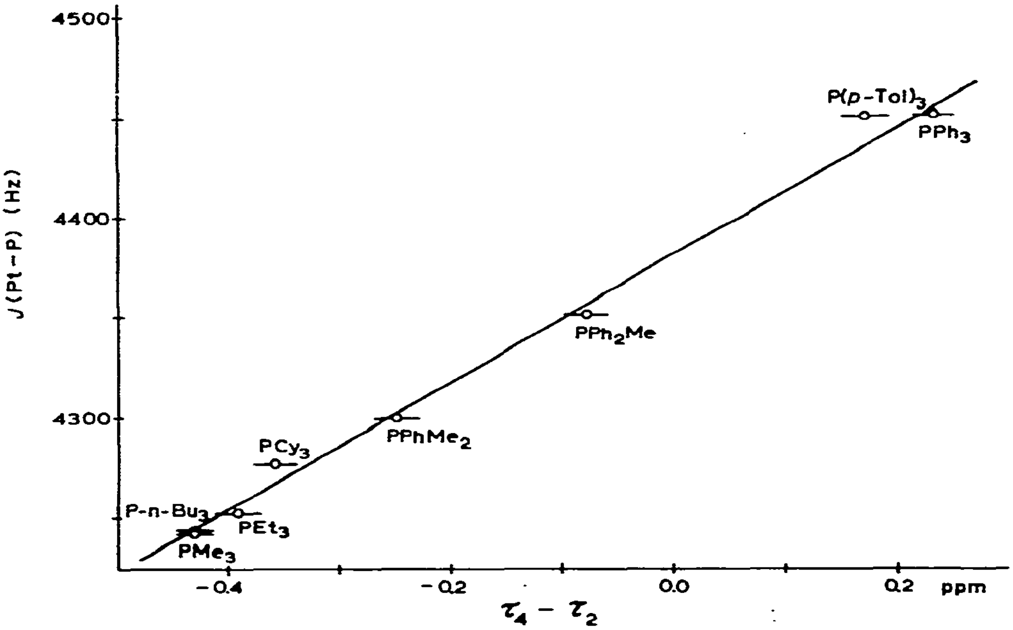

Fig. 2. Direct relationship between J(Pt—P) and τ_4—τ_2 values (±0.04 ppm).

Experimental

Physical measurements. ^{1}H NMR spectra were recorded with a 90 MHz Varian or with a Bruker 270 MHz instrument. ^{31}P NMR spectra were recorded on a Bruker WP-60 spectrometer at 24.28 MHz in the Fourier transform mode with ^{1}H complete decoupling. IR spectra were obtained with a Perkin—Elmer 457 spectrophotometer in Nujol mulls. Molecular weights were measured with a Knauer Osmometer in $C_2H_4Cl_2$.

Materials. AgI · 0.5 PMe_3 [10], P-t-Bu_3 [26], $[Pt(C_3H_5)Cl]_4$ [27] and [Pt(allyl)—PPh_3Cl] [9] were prepared by published procedures. Other materials were commercially available in reagent grade quality and were used without further purification.

Preparation of [(η^3-allyl)Pt(PR_3)Cl] complexes (PR_3 = PCy_3, P-t-Bu_3, P-n-Bu_3, PEt_3, PMe_2Ph, $PMePh_2$ and P(p-Tol)$_3$). These compounds were obtained similarly to the PPh_3 analogue [9]. To a stirred suspension of $[Pt(allyl)Cl]_4$ in CH_2Cl_2 kept at —10°C a stoichiometric amount of the appropriate phosphine in CH_2Cl_2 solution (Pt/PR_3 1) was added dropwise with stirring. The suspension was set aside until complete dissolution had occurred, and concentrated under reduced pressure. Treatment with ethyl ether and cooling to —20°C usually gave the products as white crystals. In the case of the P-n-Bu_3 and PEt_3 compounds oils were obtained and these were washed with petroleum ether and dried under vacuum.

Preparation of [(η^3-allyl)Pt(PMe_3)Cl]. A stirred suspension of $[Pt(C_3H_5)Cl]_4$ (542 mg, 0.5 mmol) in 70 ml of $C_2H_4Cl_2$ was treated under nitrogen at room temperature with AgI · 0.5 PMe_3 (1092 mg, 4 mmol). After 24 h AgI was filtered off and the solution was evaporated to dryness. The white solid was dissolved in n-hexane, and cooling to —30°C gave the product as white crystals.

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