Palladium(II) Complexes with Aminophosphonates
I. K_2PdCl_4 Coordination to Aminophosphonic Acid Analogues of Glycine and α-Alanine

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Abstract

^{31}P, ^{1}H and ^{13}C NMR spectroscopy is applied to study the reactions of K_2PdCl_4 with 1-aminomethanephosphonic acid (GlyP), 1-amino-1-phenylmethanephosphonic acid (PhGlyP), 1-aminoethanephosphonic acid (α-AlaP) and 1-(n-propylamino)-ethanephosphonic acid (α-(NH-nPr)AlaP) in a wide pD range.

The ligands examined easily form PdL_2 and $PdLX_2$ ($X = Cl^-$, H_2O, OH^-) chelate {N, O} species. In strongly basic solutions monodentate complexes are formed with coordination through the amino nitrogen only, except for α-(NH-nPr)AlaP which forms exclusively PdL_2 and $PdLX_2$ chelates.

No complexes with the ligand bonded only through the phosphonate oxygen are observed.

The forming of diastereoisomeric complexes in Pd(II): racemic ligand systems is discussed.

Introduction

The aminophosphonic acids, as analogues of amino acids in which the COOH group is replaced by the phosphonyl one ($PO(OH)_2$), are of considerable interest due to their biological properties and their chelating abilities. Metal complexes of aminophosphonic acids have been studied both in the solid state and in solution. Due to the fact that up to now crystallization was performed only from low pH solutions the X-ray data are limited almost entirely to the polymeric species with metal ions linked through single or double phosphonate bridges. This type of coordination was shown for the Cu(II) and UO_2^{2+} complexes with simple methylphosphonic [1] and hydroxymethylphosphonic [2] acids, respectively, as well as for the transition metal complexes of the aminomethylphosphonic [3, 4] and aminomethyl(methyl)phosphinic acids [5]. The last ligand forms monomeric $MnCl_2(AMPh)_2(H_2O)_2$ with phosphonate coordination only [6]. It also creates the only chelate complex with Cu(II) described so far [7].

The studies in solution of the aminophosphonic acids complexation properties concern mainly potentiometric examination of the labile metal ions coordination [8–11]. The most important issue is that at high pH the aminophosphonic ligands easily form stable ML_n chelate species. In acidic solution MeHL species are formed which involve only phosphonate coordination. This coordination mode is not observed when labile metal ions coordinate to the aminocarboxylates because of the lower basicity of the carboxylate group. However, carboxyl coordination was proposed for the Co(III) complexes with some amino acids [12] and O-bonded intermediate species were detected when *cis*-$Pt(NH_3)_2^{2+}$ reacted with glycine [13].

Although, palladium and platinum coordination to amino acids has been extensively investigated [14, 15], only a few examples of phosphate and phosphonate ligand coordination to Pt(II) ions are reported in the literature [16–18]. Appleton and co-workers in their studies of the reactions of *cis*-$Pt(NH_3)_2^{2+}$ with simple phosphonic ligands [18] revealed the formation of both monodentate 'metastable' O-bonded complexes and chelate species. To extend the study on platinum group metal coordination towards phosphonates we present ^{31}P results supported by ^{13}C and ^{1}H NMR studies of complexation of phosphonic analogues of glycine (GlyP, PhGlyP) and α-alanine (α-AlaP, α-(NH-nPr)-AlaP) with K_2PdCl_4 in a wide pD range.

Experimental

Phosphonic ligands of general formula $R^1CH(PO_3H_2)(NH_2^+R^2)$ were obtained by the method described in ref. 19. All ligands containing asymmetric carbon were used as racemates. A small amount of (–)PhGlyP prepared according to ref. 20 was used in an additional experiment.

K_2PdCl_4 was obtained by crystallization of KCl and the $PdCl_2$ solution containing HCl.

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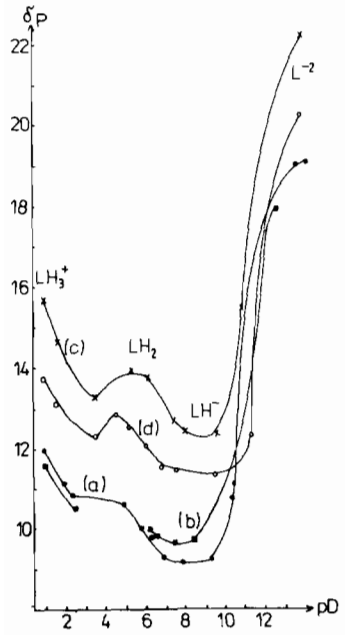


Fig. 1. Variation of δ_P with pD for solutions of GlyP (a), PhGlyP (b), α-AlaP (c) and α-(NH-NPr)AlaP (d) phosphonic acids.

Samples for obtaining the NMR spectra were prepared at 0.1 (^{31}P) and 0.3–0.5 (^{1}H, ^{13}C) mol dm^{-3} ligand concentrations. Solutions in D_2O with Pd(II) to ligand molar ratios of 1:1, 1:2 and 1:5 were employed.

pH measurements were made with the use of a Mera-Elmat N-517 pH meter. pD values in D_2O were obtained by application of the correction pD = meter reading + 0.40 [21].

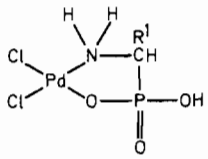
^{31}P spectra were recorded on a JEOL PS 100 FT NMR system at 40.48 HMz in the FT mode. The number of scans varied from 200–600 with a repetition time of 3 s. H_3PO_4 was used as an external standard.

^{1}H (100 MHz) and ^{13}C (25.14 MHz) NMR spectra were recorded on a Tesla BS 567 A spectrometer with t-butanol and dioxane, respectively, as internal standards. The ^{1}H chemical shifts were converted to the DSS by adding 1.23 ppm, whereas the ^{13}C chemical shifts were converted to the TMS by adding 67.73 ppm.

All NMR spectra were measured at room temperature. Figure 1 presents the pD effect on the ligands ^{31}P spectra which is needed to identify signals due to the free ligand in the examined samples.

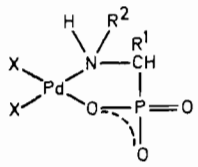
Results and Discussion

The examined ligands coordinate Pd(II) ions at the pD of *c.* 3.8. As a result the shifted ^{31}P signals due to phosphorus incorporation into the five-membered {N, O} chelate ring are observed [22]. Equimolar $PdLHCl_2$ species **(I)** appearing in this



I $PdLHCl_2$
R^1 = H, CH_3, C_6H_5

pD region gradually lose the acid proton (Fig. 2) finally giving $PdLCl_2$ complexes **(IIa)** where the phosphonate group is completely deprotonated at pD *c.* 5.



II-a,b,c $PdLX_2$
R^1 = H, CH_3, C_6H_5 ; R^2 = H
R^1 = CH_3; R^2 = $(CH_2)_2CH_3$
a X = Cl^-
b X = H_2O
c X = OH^-

Figure 3 presents the ^{31}P data for the Pd(II):GlyP 1:1, 1:2 and 1:5 solutions. Raising of the pD implies a deprotonation of $PdLHCl_2$ (δ_P = 39.78 ppm) towards $PdLCl_2$ (δ_P = 37.55 ppm). A new PdL_2 complex **(III)** (δ_P = 34.10 ppm) with two bidentately

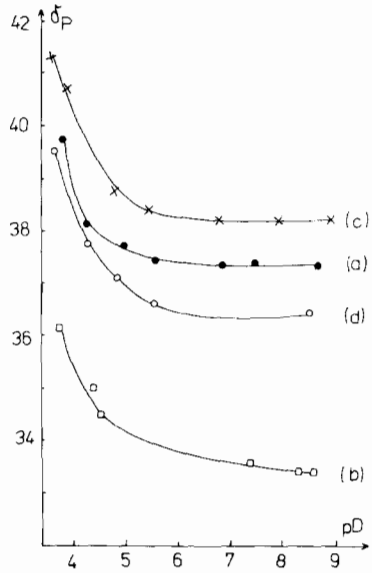


Fig. 2. Effect of pD on ^{31}P NMR chemical shifts of the $PdLHCl_2$ complex in equimolar solutions of K_2PdCl_4 with GlyP (a), PhGlyP (b), α-AlaP (c) and α-(NH-nPr)AlaP (d) phosphonic acids.

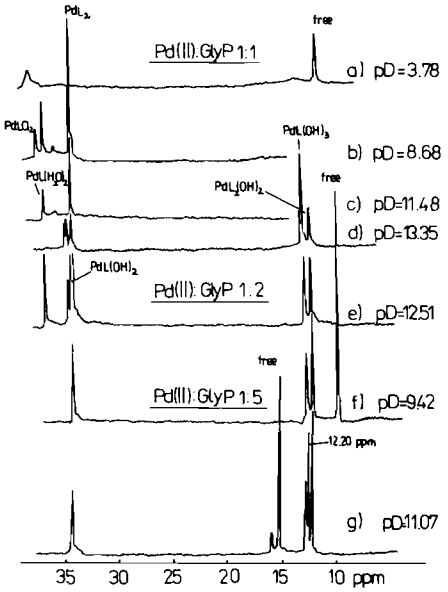
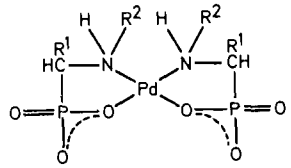


Fig. 3. ^{31}P NMR spectra of Pd(II):GlyP 1:1 (a, b, c, d). 1:2 (e) and 1:5 (f, g) solutions.

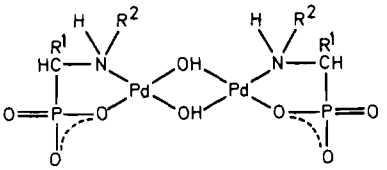
{N, O} coordinated ligand molecules is formed at a pD of *c.* 5. This undoubtedly most stable species is the major form in both 1:1 and 1:2 solutions in



III PdL_2
$R^1 = H, CH_3, C_6H_5$; $R^2 = H$
$R^1 = CH_3$; $R^2 = (CH_2)_2CH_3$

the pD range of about 6.5–11.5 and the only chelate species in solutions with an excess of ligand (Fig. 3 (f), (g)). The presence of only one signal corresponding to the PdL_2 complex evidently shows that only one geometrical isomer (*trans* or *cis*) is preferred in solution.

Raising of the pD implies a stepwise hydrolysis of the equimolar $PdLCl_2$ complex. The equilibrium between chloro and aquo (**IIb**) (δ_P = 36.68 ppm) species is observed in the pD range of *c.* 6–10. This pD region is considered by several authors as the area where μ-hydroxo bridged dimers are formed [18, 23–26]. Lim and Martin in their investigations on the aqueous chemistry of $Pd(dien)(H_2O)^{2+}$ and $Pden(H_2O)^{2+}$ [23] gave potentiometric evidence for the presence of μ-hydroxo and μ-dihydroxo bridged complexes. The kinetic studies of Erickson and Erickson [26] also supported the formation of the dimeric $Pt(dien)(H_2O)^{2+}$ species in concentrated ($c_{Pt} > 0.003$ mol dm^{-3}) solutions. Dimeric complexes with platinum atoms bridged by phosphonate and hydroxo groups were also detected by Appleton and co-workers in reactions of *cis*-$Pt(NH_3)_2^{2+}$ with GlyP and α-AlaP [18]. According to the above results the existence of the $[PdLOH]_2$ dimeric species (**IV**) in solution instead of $PdL(H_2O)_2$ could not definitely be excluded.

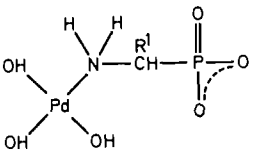


IV $[PdLOH]_2$
$R^1 = H, CH_3, C_6H_5$; $R^2 = H$
$R^1 = CH_3$, $R^2 = (CH_2)_2CH_3$

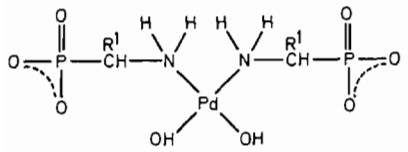
Similarly, in the low pD region the uncoordinated $PdCl_4^{2-}$ ions undergo acid hydrolysis preferring the *cis*-$PdCl_2(H_2O)_2$ species due to the greater *trans* effect of the chlorine ions compared to the water [27]. In the pD region 6–10 soluble $\{PdCl_2(\mu\text{-}OH)\}_n^{n+}$ (n = 2, 3) species fairly resistant to substitution are probably formed. The formation of the similar *cis*-$[Pt(NH_3)_2(OH)]_n^{n+}$ was observed earlier [28]. Thus, the appearance of Pd(II) oligomers which are resistant to phosphonic ligand coordination and $Pd(OH)_4^{2-}$ ions which are known to be soluble at pD over *c.* 10.5 considerably decreases the amount of Pd(II) ions able to coordinate the phosphonic ligand. In fact, PdL_2 may be formed favourably even in equimolar solutions.

New resonances are observed in a strongly alkaline solution (Fig. 3(d), (e)). The signal at 34.45 ppm corresponds most likely to the monomeric $PdL(OH)_2$ (**IIc**) and the one at 35.64 ppm to the intermediate $PdL(OH)(H_2O)$ species. The peaks, which are shifted upfield in relation to the chelate species, prove that some portion of the metal to ligand 1:1 and 1:2 chelates undergoes a ring opening reaction. As a result, monodentate complexes (**Va, b**) are formed with the ligand bonded only through the amino nitrogen. Reaction is facilitated in an excess of ligand (Fig. 3(f), (g)).

The additional resonance at 12.20 ppm in the solution containing excess of GlyP ligand (Fig. 3(g)) (not observed for the remaining phosphonic acids discussed below) and the appreciable shift of the



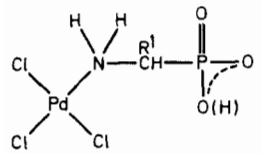
V-a $PdL(OH)_3$
$R^1 = H, CH_3, C_6H_5$



V-b $PdL_2(OH)_2$
$R^1 = H, CH_3, C_6H_5$

d–d absorption band (λ = 338 nm, pH = 12.20) suggest that a new monodentate species, with more than two ligand molecules (monodentately bonded to palladium), is formed. This kind of coordination appears to be sterically favoured in the case when the additional GlyP molecule coordinates to the *cis* monodentate $PdL_2(OH)_2$ complex rather than to the *trans*. The above statement is consistent with the results of the X-ray crystal structure determinations of Pd(II) complexes with carboxylic amino acids which issues *cis* in preference to *trans* isomers [29–31].

PhGlyP, due to the steric hindrance on the C_α carbon, forces a coordination mode of the Pd(II) ions which is different from that of GlyP (Figs. 4 and 5). Besides the chelate $PdLHCl_2$ (δ_P = 36.07 ppm), a new complex characterized by δ_P = 15.97 ppm is observed in acidic solution. It corresponds to $PdLHCl_3$ **[VIa]** with the ligand coordinated through the amino nitrogen. Monodentate phosphonate oxygen coordination was definitely excluded



VI-a $PdLHCl_3$
VI-b $PdLCl_3$
$R^1 = C_6H_5$

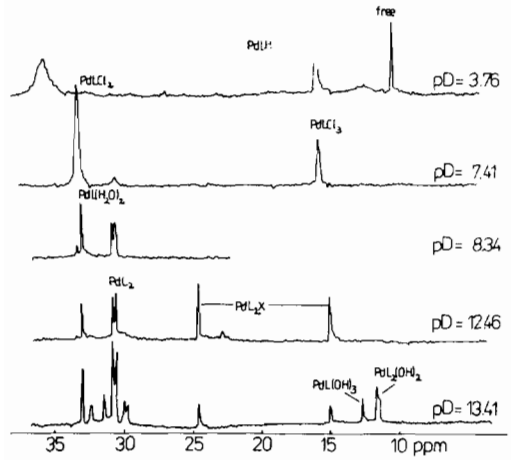


Fig. 4. ^{31}P NMR spectra of Pd(II):PhGlyP 1:1 solutions.

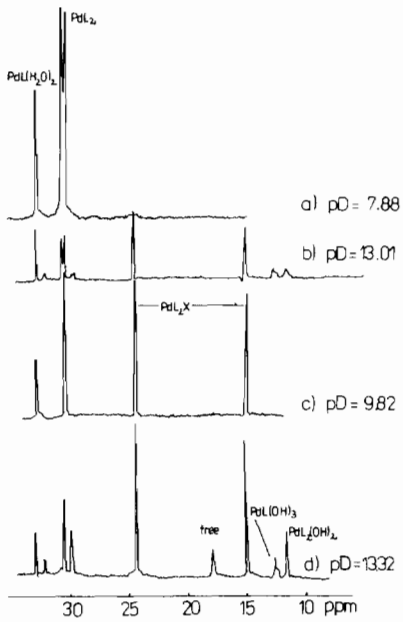


Fig. 5. ^{31}P NMR spectra of Pd(II):racemic PhGlyP (a, b) and Pd(II):(–)PhGlyP (c, d) 1:2 solutions.

by studying the 1-hydroxy-1-phenylmethanephosphonic acid coordination to palladium where no complex formation is observed up to a pD of *c.* 12.5.

Raising of the pD causes a deprotonation of both chelate and monodentate species. The signal corresponding to the monodentate complex gradually decreases due to the closure of the chelate {N, O} ring. At a pD of *c.* 7.5 only the chelate species are present in solution. (The PdL_2 complex (δ_P = 30.60 ppm) is formed at pD over 7.5 in the 1:1 solution and over 5 in the 1:2 solution, respectively).

The equilibrium between the $PdLX_2$ chloro (δ_P = 33.32 ppm), aquo (δ_P = 32.96 ppm) and monomeric hydroxo (δ_P = 31.31 ppm) complexes takes place in a similar way as in the Pd(II):GlyP system discussed above.

A further increase of pD above 9.5 leads to the appearance of a new ^{31}P signals set (at 24.42 and 14.86 ppm) with the intensity decreasing in a strongly alkaline solution (pD > 13.5). The simultaneous decrease of the PdL_2 doublet intensity (Fig. 4) suggests that the rearrangement of the chelate complexes towards monodentate species occurs more slowly than in the Pd(II):GlyP system and an intermediate PdL_2X, containing both chelated and monodentately coordinated ligand molecules, may be formed. The presence of the bulky aromatic substituent on the C_α carbon hinders the formation of the monodentate $PdL_2(OH)_2$ and $PdL(OH)_3$ species which results in the lower intensity of the corresponding ^{31}P signals in relation to those of the analogous Pd(II):GlyP solution.

A comparison between the ^{31}P spectra of the Pd(II):PhGlyP 1:2 systems containing an optically active (–) (the absolute configuration *S* [32]) or a racemic ligand is presented in Fig. 5. They clearly demonstrate that the counterparts of the doublets in the Pd(II):racemic PhGlyP system are singlets in the Pd(II):(–)PhGlyP system. The singlet resonance at 30.50 ppm corresponds to the chelate (*S,S*)-PdL_2 complex and the one at 11.43 ppm corresponds to the monodentate (*S,S*)-$PdL_2(OH)_2$ complex in which both ligands contain an *S* configuration at the asymmetric C_α centre (Fig. 5(c), (d)). Hence, in the analogous Pd(II): racemic PhGlyP system (Fig. 5(a), (b)) containing both molecules with *R* and *S* configurations at the C_α carbon the mixture of (*R,R*), (*S,S*), (*R,S*), (*S,R*) stereoisomers is expected for PdL_2 chelates and in strongly alkaline solution for $PdL_2(OH)_2$ monodentate species. Analysis of the molecular models has shown that for both the possible *cis* and *trans* geometrical isomers the (*R,R*), (*S,S*) and the (*S,R*), (*R,S*) bis-ligand palladium complexes are in pairs of enantiomers, whereas the complexes of different pairs of enantiomers e.g. (*R,R*), (*R,S*) appear to be diastereoisomers.

The obtained results demonstrate that the ^{31}P NMR method enables a direct spectroscopic observation of the diastereoisomeric species which are formed in the Pd(II):racemic ligand system. The parameter $\Delta\delta$ which describes the separation of the signals corresponding to the chiral (both ligands are *R* or *S* enantiomers) and the *meso* (*R* and *S* ligands) PdL_2 chelate and $PdL_2(OH)_2$ monodentate species is equal to 0.18 and 0.06 ppm, respectively.

The results presented above allow us to establish definitely that from the two resonances corresponding to the monodentate complexes (observed in alkaline solution) the lower field signal corresponds to equimolar $PdL(OH)_3$, whereas the higher field signal corresponds to the $PdL_2(OH)_2$ complexes.

The ^{31}P spectra recorded for the Pd(II):α-AlaP system initially did not show any doublet expected for the PdL_2 diastereoisomeric complexes. Further examination of the Pd(II):phosphonic ligand systems with R^1 substituents of different size, as well as recording the ^{31}P NMR spectra at a higher resonance frequency [33] revealed that $\Delta\delta$ increases with the magnitude increase of the R^1 substituent on the C_α carbon. For ligands containing R^1 = CH_3–, CH_3-CH_2–, $(CH_3)_2CH$–, $(CH_3)C_6H_4$– and $(CH_3O)C_6$-H_4– substituents (measured in similar conditions: 1:2 metal to ligand solution, pD of about 8.5–9) it is noted to be 0.04, 0.05, 0.09, 0.16 and 0.15 ppm for PdL_2 chelates, respectively.

The remaining data obtained for the Pd(II):α-AlaP system are similar to those discussed above. Equimolar $PdLHCl_2$ as well as $PdLX_2$ (X = Cl^-, H_2O OH^-) are also formed depending on the pD of the examined solution. No complexes with an amino coordination are observed up to pD of *c.* 12.5 in the 1:1 and 1:2 solutions. However, the monodentate species are noted when the ligand is added in excess.

TABLE 1. NMR spectra of palladium complexes with GlyP and PhGlyP phosphonic ligands[a]

Species	GlyP			PhGlyP		
	$\delta_P(^{31}P)$	$\delta_{CH_2}(^{13}C)$ (ppm)	$\delta_{CH_2}(^1H)$	$\delta_P(^{31}P)$	$\delta_{CH}(^{13}C)$ (ppm)	$\delta_{CH}(^1H)$
LH_3^+	11.90	36.69(148.4)	3.13(13.0)	11.53	54.14(142.7)	4.74(17.0)
LH_2	10.58	37.59(140.8)	3.07(12.5)			
LH^-	9.17	38.63(129.6)	2.87(12.0)	9.66	56.11(125.8)	4.27(15.0)
L^{2-}	19.06	39.87(135.2)	2.42(10.5)	17.96	56.79(129.8)	3.81(15.5)
$PdLHCl_3$				15.97		
$PdLCl_3$				15.39		
$PdLHCl_2$	39.78			36.07		
$PdLCl_2$	37.35			33.32		
$PdL(H_2O)_2$	36.68	39.46(144.6)	2.51(10.0)	32.96	56.36(139.0)	3.86(17.0)
$PdL(OH)_2$	34.45			31.31		
$PdL(H_2O)(OH)$	35.64			32.24		
PdL_2	34.10	41.10(144.6)	2.54(10.0)	30.60[b]	56.69(139.0)	3.92(17.0)
$PdL_2(OH)_2$	11.90		2.70(12.5)	11.40[c]		
			2.67(11.0)			
$PdL(OH)_3$	12.42			12.50		
PdL_2X				14.82		
X = (H_2O, OH^-)				24.44		

[a]Coupling constants values (Hz) included in parentheses. [b]$\Delta\delta$ = 0.18 ppm. [c]$\Delta\delta$ = 0.06 ppm.

TABLE 2. NMR spectra of palladium complexes with α-AlaP and α-(NH-nPr)AlaP phosphonic ligands[a]

Species	α-AlaP			α-(NH-nPr)AlaP		
	$\delta_P(^{31}P)$	$\delta_{CH}(^{13}C)$ (ppm)	$\delta_{CH_3}(^{13}C)$	$\delta_P(^{31}P)$	$\delta_{CH}(^{13}C)$ (ppm)	$\delta_{CH_3}(Ala)(^{13}C)$
LH_3^+	15.65	45.21(152.1)	14.33(3.7)	13.72	51.78(144.6)	12.90(1.9)
LH_2	13.95	46.22(142.7)	15.00	12.50	51.91(139.0)	12.47
LH^-	12.30	47.41(135.2)	15.82	11.29	53.99(131.5)	13.58
L^{2-}	22.20	47.11(135.2)	16.71	20.25	53.70(139.5)	15.67
$PdLHCl_2$	41.29			not detected		
$PdLCl_2$	38.18			36.49		
$PdL(H_2O)_2$	37.67	46.85(148.4)	17.68	34.83	52.04(146.5)	15.14
$PdL(OH)_2$	35.91			34.26		
$PdL(H_2O)(OH)$	36.79			34.69		
PdL_2	35.10[b]	48.46(146.5)	17.83	33.32[d]	52.94(142.7)	16.11
$PdL_2(OH)_2$	14.96[c]					
$PdL(OH)_3$	15.85					

[a]Coupling constants values (Hz) included in parentheses. [b]$\Delta\delta$ = 0.04 ppm (ν = 121.5 MHz). [c]$\Delta\delta$ = 0.10 ppm. [d]$\Delta\delta$ = 0.05 ppm.

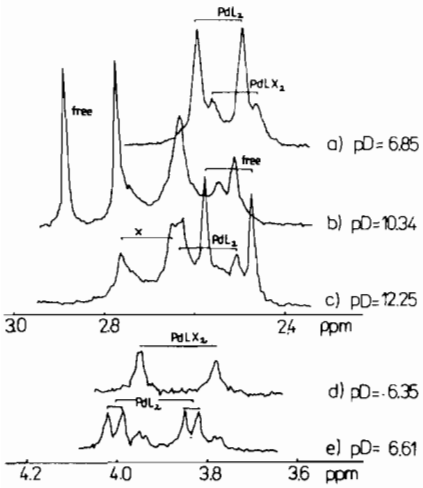


Fig. 6. ^1H NMR spectra of Pd(II):GlyP 1:2 (a), 1:5 (b, c) solutions and of Pd(II):PhGlyP 1:1 (d) and 1:2 (e) solutions (x corresponds to the monodentate N-coordinated species).

The coordination mode of the last studied α-(NH-nPr)AlaP ligand is limited only to the $PdLX_2$ (X = Cl^-, H_2O, OH^-) and PdL_2 chelate species. Furthermore, the formation of the PdL_2 complex is found to be considerably hindered. As a result, the signals corresponding to the equimolar complexes are easily observed even when a five-fold excess of the ligand is used.

^1H and ^{13}C NMR spectra appear to be less useful for the detailed analysis of the species distribution in the Pd(II):phosphonic ligand systems presented above. They are able to distinguish only the 1:1 and 1:2 chelated species. Figure 6 presents the ^1H $-CH_2(P)$ and $-CH(P)$ doublets of the Pd(II):GlyP and Pd(II):PhGlyP systems, respectively. They clearly show that adding of the second ligand molecule with the following formation of the monodentate species shifts both the ^1H signals towards the lower field. The doublet of doublets ($J_{(P-H)}$ = 17 Hz, $\Delta\delta$ = 0.03 ppm) related to the PdL_2 chelate in the Pd(II):PhGlyP system supports the formation of the diastereoisomeric complexes discussed earlier.

The ^{31}P, ^{13}C and ^1H parameters for the complexes discussed above are collected in Tables 1 and 2.

Conclusions

The results presented in this paper show that Pd(II) ions easily form chelate PdL_2 and $PdLX_2$ (X = Cl^-, H_2O, OH^-) species with simple phosphonic analogues of glycine and α-alanine. However, in a strongly alkaline solution an opening of the chelate {N, O} ring occurs and monodentate complexes are formed with coordination through the amino nitrogen. Their stability decreases as follows: GlyP > PhGlyP > AlaP. α-(NH-nPr)AlaP with a bulky substituent on the amino nitrogen forms entirely chelate equimolar and bis-ligand species with palladium.

No complexes with a purely phosphonate coordination (reported by Appleton *et al.* [18] when *cis*-$Pt(NH_3)_2^{2+}$ reacted with phosphonic acids) are observed in the examined systems. This discrepancy could originate in the greater kinetic inertness of the Pt(II) relative to the Pd(II) ions which allows the formation of both the 'metastable' O-bonded species and the products of their rearrangement, i.e. chelate complexes to be observed.

Only one geometrical isomer of the PdL_2 and $PdL_2(OH)_2$ complexes (probably *cis*) is formed in solution. Their diastereoisomers are readily distinguishable by ^{31}P NMR spectroscopy in the Pd(II):racemic phosphonic acid systems.

The preliminary results show that $\Delta\delta$ defining the separation of the signals corresponding to these diastereoisomeric complexes is strongly dependent on the size of the substituent on the C_α carbon.

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