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PYRIDINE PROMOTED *syn–syn* AND *anti–anti* PROTON EXCHANGE IN ASYMMETRIC π-ALLYLIC PALLADIUM(II) COMPLEXES

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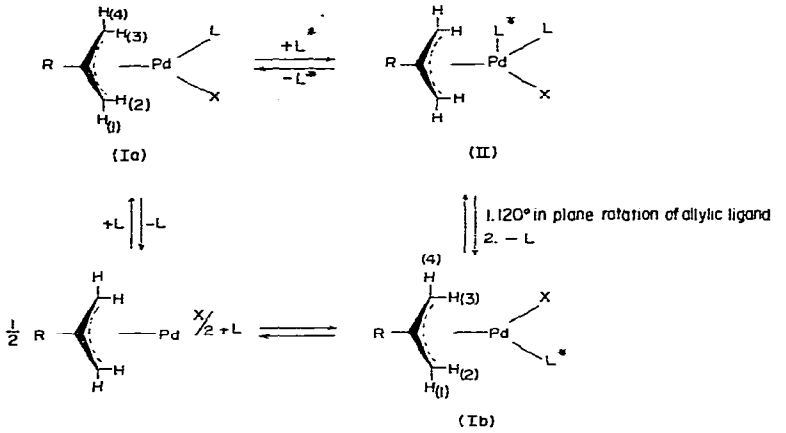
SUMMARY

A series of π-allylic palladium(II) complexes containing the anionic, asymmetrically chelating picolinate or oxinate ligands have been prepared and structurally characterised. Addition of base, such as pyridine, to the 2-substituted π-allylic complexes of the type $[(\pi\text{-2-}RC_3H_4)Pd(chelate)]$ promotes exchange of the non-identical *syn*-protons with simultaneous exchange of the *anti*-protons. The data obtained from PMR and conductivity studies support an exchange mechanism which involves partial substitution of the chelate ligand rather than rotation of the π-allylic ligand.

INTRODUCTION

Since 1965 the dynamic stereochemistry of π-allylic palladium(II) complex–ligand systems has received considerable attention[1-8]. Whilst *syn–anti* proton exchange in π-allylic complexes occurs via σ-allylic intermediates[3-8], *syn–syn* (protons 1 and 4) and *anti–anti* (protons 2 and 3) exchange in asymmetric π-allylic systems such as (Ia) may occur via a dissociative process [as has been observed in several π-allylic palladium(II) halide–amine systems[2], see Scheme 1], or via an associative, base promoted process. From variable temperature PMR studies of (2-methylallyl)-palladium chloride–tertiary phosphine (*e.g.* PPh_3) systems in $CDCl_3$ at P/Pd ratios between 1 and 1.5, Vrieze *et al.*[4] have proposed that the observed rapid exchange of *syn* protons 1 and 4 and *anti*-protons 2 and 3 in (Ia) (*e.g.* L = PPh_3) occurs via addition of L* to give a square pyramidal intermediate (II), shown in Scheme 1. A postulated "120° in plane rotation of the π-2-methylallyl group, followed by loss of the originally coordinated ligand L (PPh_3) to give (Ib) results in 1–4 and 2–3 exchange", *i.e.* according to this mechanism 1–4 and 2–3 exchange and exchange of ligand L are synonymous. All previously reported studies of base promoted 1–4 and 2–3 exchange have been carried out on systems of the type [(π-allyl)PdClL] + L and as such simultaneous exchange of ligand L, as is required by the mechanism of Vrieze *et al.* has always been possible. We report here studies of the pyridine promoted *syn–syn* and *anti–anti* proton exchange in π-allylic palladium(II) complexes of the type $[(\pi\text{-2-}RC_3H_4)Pd(O_2CC_5H_4N)]$ and $[(\pi\text{-2-}RC_3H_4)Pd(OC_9H_6N)]$ containing the chelating picolinate

SCHEME 1
Previously proposed mechanisms for 1–4 and 2–3 exchange in asymmetric π-allylic complexes[2-4].



and oxinate ligands respectively. In these systems simultaneous 1–4 and 2–3 exchange and pyridine (ligand L) exchange is not possible. A mechanism, in which the base promoted dynamic stereochemistry of these π-allylic palladium(II) picolinates and oxinates is interpreted solely in terms of S_N2 ligand substitution processes, is proposed.

RESULTS AND DISCUSSION

A. Preparation and PMR spectra of complexes

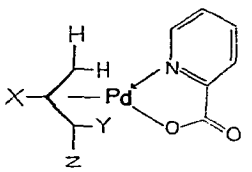
π-Allylic palladium oxinate and picolinate complexes were isolated in high yield as crystalline solids by a displacement reaction of 8-hydroxyquinoline or 2-picolinic acid with the corresponding acetate complex:

$$[\pi\text{-}C_3H_5PdOAc]_2 + 2\,[HO\widehat{\ }N] \rightarrow 2\,[\pi\text{-}C_3H_5Pd(O\widehat{\ }N)] + 2\,HOAc$$
$$(O\widehat{\ }N = C_9H_6NO,\ C_6H_4NO_2)$$

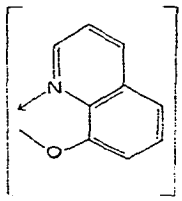
The oxinate and picolinate complexes were shown to be monomeric by osmometric molecular weight studies.

The low temperature PMR spectra of the π-allyl, π-2-methylallyl and π-2-tert-butylallyl picolinate complexes (IIIa), (IIIb) and (IIIc) and the corresponding oxinate complexes exhibited four resonances assignable to the four non-equivalent terminal protons of the allylic ligand (Table 1, protons 1–4). The assignment of *syn* and *anti* proton resonances is based on the magnitude of the spin–spin coupling constants in the π-allyl complexes [9,10] and on long range coupling between the non-identical *syn* protons 1 and 4. Conclusive assignment of the protons relative to the stereochemistry of the N and O atoms of the chelating oxinate or picolinate ligand is not possible but in view of the results obtained for unsymmetrically terminally substituted π-allylic picolinate complexes the low field *syn* and *anti*-proton resonances have been *tentatively* assigned to the protons in *trans* position to the nitrogen atom.

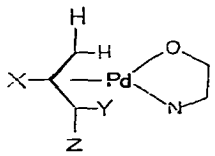
The low temperature PMR spectra of the terminally substituted *syn*-1-methylallyl and 1,1-dimethylallyl complexes show the presence of two conformational isomers in solution. Whilst the isomer ratio is approximately 1/1 for the oxinate



Picolinate
(IIIa) Y = Z = H; X = H
(IIIb) Y = Z = H; X = Me
(IIIc) Y = Z = H; X = t-Bu
(IVa) X = Y = H; Z = Me
(IVb) X = H; Y = Z = Me
(Va) X = Me; Y = H; Z = t-Bu
(Vb) X = Me; Y = t-Bu; Z = H



or oxinate



(VIa) X = Y = H; Z = Me
(VIb) X = H; Y = Z = Me
(VII) X = Me; Y = t-Bu; Z = H

complexes, isomer ratios of 10/1 or greater are observed for the picolinate complexes. From steric arguments, based on studies of molecular models, interaction between a *syn*-methyl group and an adjacent α-hydrogen of a *cis*-pyridyl ring in conformation (VIa) and (VIb) is anticipated. As such the minor allylic resonance patterns of the 1-methylallyl and 1,1-dimethylallyl picolinate complexes are tentatively assigned to the conformations (VIa) and (VIb) respectively (proton 3 and proton 4 resonances are at low field) and the major patterns to conformation (IVa) and (IVb) respectively. The PMR spectra of both the (1-tert-butyl-2-methylallyl)palladium picolinate and oxinate complexes exhibit three allylic resonance patterns of different intensities. Molecular models indicate that a *syn*-tert-butyl group adjacent a *cis*-pyridyl ring is sterically unfavourable. The major allylic pattern is assigned to the π-*syn*-1-tert-butyl-2-methylallyl complex of conformation (Va) with the *syn*-tert-butyl group *cis* to oxygen. The two minor patterns are assigned to the two possible π-*anti*-1-tert-butyl-2-methylallyl conformational isomers (Vb) and (VII). When (1-tert-butyl-2-methylallyl)palladium acetate is prepared from a ca. 1/1 mixture of *syn*- and *anti*-(1-tert-butyl-2-methylallyl)palladium chloride[11] the *syn/anti* ratio of ca 1/1 is maintained in the acetate. The ratio is also maintained at ca. 1/1 when the mixed acetate is converted into the corresponding picolinate or oxinate complexes. On standing at room temperature in chloroform solution the 1/1 *syn/anti*-(1-tert-butyl-2-methylallyl)-palladium oxinate mixture slowly equilibrates over a period of 5 days to give a *syn/anti* isomer equilibrium ratio of ca. 4.7/2.2 [(Va)/(Vb)/(VII) is ca. 4.7/1.2/1.]. The 1/1 *syn/anti* picolinate complex equilibrates over a period of 3 days and gives a *syn/anti* isomer ratio of ca. 12/1 [(Va)/(Vb)/(VII) is ca. 36/2/1]. The relative ratio of the two *anti*-tert-butyl-2-methylallyl isomers in these systems is always constant. The pure *syn*-1-tert-butyl isomer could be isolated by column chromatography of the equilibrium mixture. Again equilibration of the pure *syn* isomer occurred after several days in chloroform solution.

B. Base promoted exchange of allylic protons

Addition of pyridine or 2-picoline to $CDCl_3$ solutions of allyl-, (2-methylallyl)- or (2-tert-butylallyl)palladium picolinate in the temperature range −20° to −70° results in a rapid exchange on the PMR time scale of the *syn* protons (1–4 exchange) and also the *anti* protons (2–3 exchange) (*e.g.* for the π-2-methylallyl

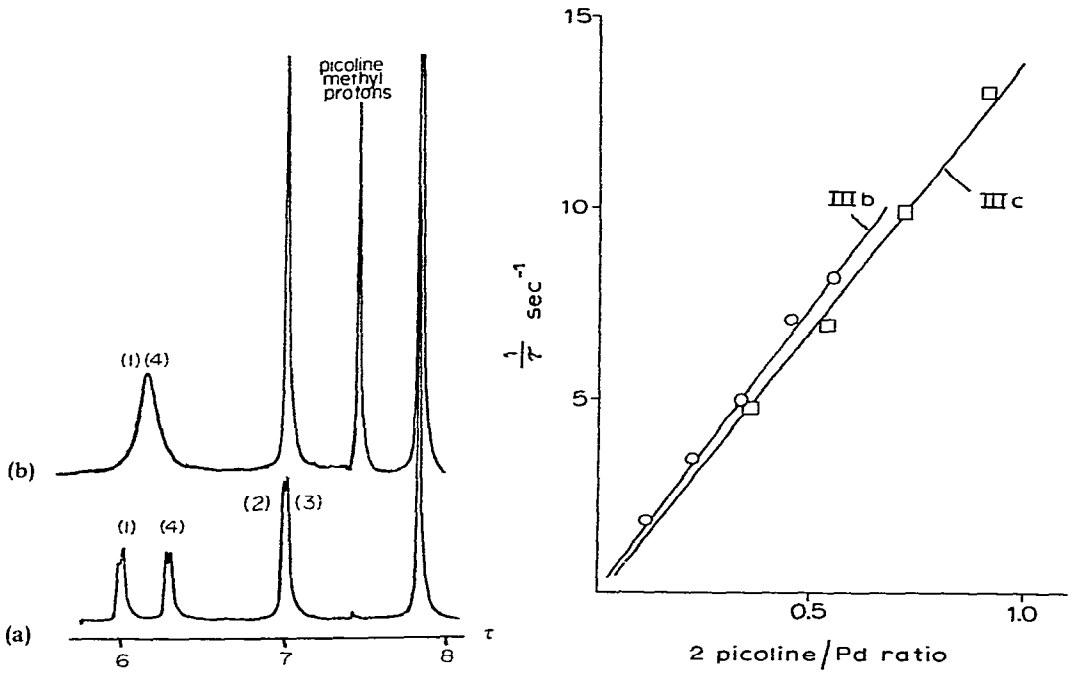
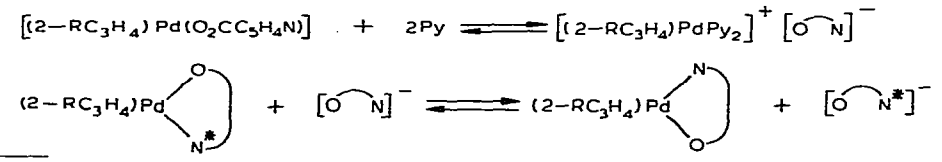


Fig. 1. The allylic PMR spectrum of a 0.37 *M* $CDCl_3$ solution of [(π-2-methylallyl)Pd($O_2CC_5H_4N$)] (a) at −20°; (b) at −20° in the presence of 0.5 molecules of 2-picoline per Pd atom. (See table for numbering of allylic protons).

Fig. 2. The rate of exchange of protons 1 and 4 in 0.37 *M* $CDCl_3$ solutions of [(π-2-RC_3H_4)Pd($O_2CC_5H_4N$)] [(IIIb), R = Me; (IIIc), R = t-Bu] at −60° as a function of added 2-picoline.

complex see Fig. 1). The chemical shifts of protons 1 and 4 in the region of fast exchange are essentially the mean value of those in the absence of exchange. Molecular weight studies of pyridine and picoline additions to chlorform solutions of (π-2-methylallyl)-palladium picolinate (IIIb) at 37° together with analysis of PMR data indicate that for most of the time the pyridine (or 2-picoline) is not co-ordinated to the palladium atom. (The chemical shifts and coupling constants of the 2-picoline protons are unaffected by addition of excess complex and the solutions still smell strongly of the free ligand.)

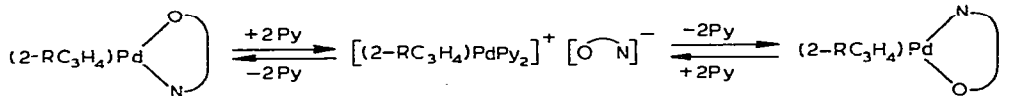
The rate of exchange at −60° of *syn*-protons 1 and 4 calculated from half height line width studies[1,2] exhibits a first order dependence on the concentration of added 2-picoline (Fig. 2). Furthermore, the rate is relatively insensitive to replacement of a 2-methylallylic substituent with a 2-tert-butylallylic substituent. A first order dependence on the concentration of added base rules out the possibility of 1–4 exchange via a rapid co-ordinated picolinate–ionic picolinate exchange of the type*:



* For footnote see page 409.

for which the rate of exchange would be second order in pyridine concentration.

Conductivity studies of pyridine and 2-picoline additions to (π-2-methylallyl)-palladium picolinate in 20% aqueous acetone showed no sign of salt formation. Since chloroform is a very poor ionizing solvent when compared with aqueous acetone, the possibility of salt formation in $CHCl_3$ is very unlikely. As such we may eliminate exchange mechanisms involving ionic intermediates including the possibility of exchange via a chelate–pyridine exchange process of the type**:



In the light of these results two alternatives for rapid 1–4 and 2–3 exchange in (III)/Py systems may be envisaged. One would involve formation of a highly fluxional five coordinate intermediate in which a pseudo rotation of the π-allylic ligand occurs via a mechanism different from that proposed by Vrieze *et al.* This seems unlikely since replacement of a 2-methyl group by a 2-tert-butyl group, which would be anticipated to increase steric strain during rearrangement of a 5 co-ordinate intermediate, has little effect on the rate of 1–4 and 2–3 exchange***. The most plausible mechanism for 1–4 and 2–3 exchange in view of the above observations is via a series of S_N2 ligand substitution processes as shown in Scheme 2 in which the intermediate species (VIII) has a four co-ordinate square planar geometry and intermediate species (IX) probably has a five co-ordinate geometry****. Ligand substitution may be considered to occur via a trigonal bipyramidal transition state in which only the incoming and leaving ligand–palladium bonds are radically perturbed, the relative stereochemistry of the three remaining ligand palladium bonds being unaffected. A sequence of S_N2 ligand substitution processes of this type as shown in Scheme 2 results in 1–4 and 2–3 exchange. Strong supporting evidence for pyridine substitution of the chelating picolinate ligand to give an intermediate such as (VIII) is provided by the addition of Me_2PhP to (π-2-methylallyl)palladium picolinate[13]. Unlike pyridine, Me_2PhP co-ordinates strongly to the palladium atom and the low temperature PMR spectrum at a P/Pd ratio of one confirms the presence in solution of the complex [(π-2-methylallyl)-

(*continued on* p. 412)

* Chelate ligand exchange of this type has been observed in other systems[13]. For example conductivity studies and low temperature PMR studies of the addition of 2-picoline to $CDCl_3$ solutions of π-allylic palladium hexafluoroacetylacetonates have shown the F_6Acac ligand to be readily displaced by two picolines to give an ionic complex (isolated as a white crystalline solid):

$$[(2\text{-}RC_3H_4)Pd(F_6Acac)] + 2\ CH_3C_5H_4N \rightarrow [(2\text{-}RC_3H_4)Pd(CH_3C_5H_4N)_2]^+[F_6Acac]^-$$

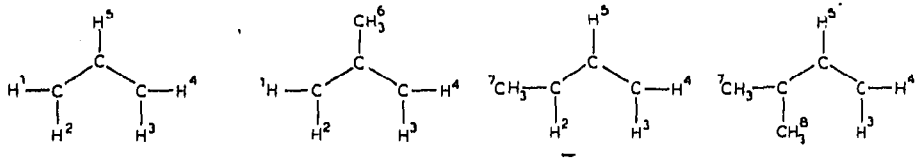
Co-ordination of the 2-picoline results in a 0.19 ppm downfield shift of the 2-picoline methyl proton resonance. A variable temperature PMR study of (2-methylallyl)palladium hexafluoroacetylacetonate–2-picoline systems at picoline/Pd ratios between 0.5 and 1.5 has shown rapid exchange of $[F_6Acac]^-$ with co-ordinated F_6Acac ligands to occur[13].

** Studies by Vrieze *et al.*[4c] have shown the formation of the ionic complex $[(2\text{-methylallyl})Pd(PPh_3)_2]^+Cl^-$ from $[(2\text{-methylallyl})PdCl(PPh_3)] + PPh_3$ in $CDCl_3$ to be a relatively slow reaction as compared to π-allylic proton exchange processes.

*** The nature of the 2-substituent on a π-allylic ligand has been shown to have a marked effect on the ease of 3–4 exchange via a σ-allylic intermediate[8].

**** The structure of the proposed intermediate (IX) is similar to the reported structure of the five co-ordinate nickel complex $[(2\text{-methylallyl})Ni(Ph_2PCH_2CH_2PPh_2)Br]$, determined by X-ray crystallography[14].

TABLE 1



100 MHz PMR FOR THE ALLYLIC PROTONS OF π-ALLYLIC PALLADIUM(II) OXINATE AND PICOLINATE COMPLEXES RECORDED IN $CDCl_3$ SOLUTION

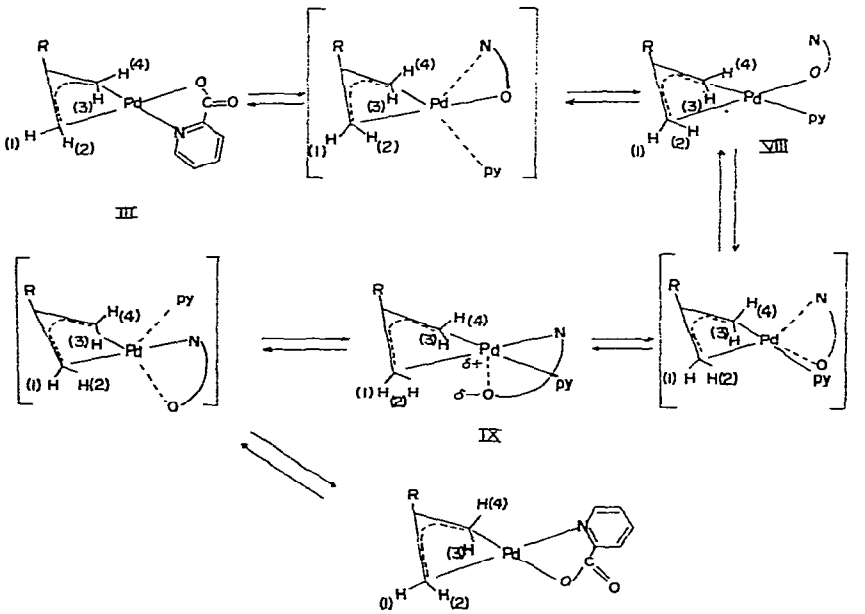
Chelate ligand	Allylic ligand	Temp. (°C)	Isomer	Chemical shift[a], τ(ppm) and spin–spin coupling constants, J_x(Hz)								Other data
				H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8	
Oxinate	Allyl	30	(IIIa)	5.98d $J_5=6$	6.95d $J_5=11$	6.95d $J_5=11$	6.30d $J_5=6$	4.42m				
Oxinate	2-Methyl-allyl	−40	(IIIb)	6.02d $J_{1,4}=2$	7.02	7.06	6.41d $J_{1,4}=2$		7.82			
Oxinate	*syn*-1-Methylallyl	−40	(IVa)		6.36m	7.15d $J_5=11$	6.46d $J_5=6$	4.6m		8.58d $J_2=6$		IVa/VIa is ca. 1/1
			(VIa)		6.10m	7.03d $J_5=11$	5.92d $J_5=6$	4.6m		8.38d $J_2=6$		
Oxinate	1,1-Dimethylallyl	−40	(IVb)			6.89d $J_5=14$	6.43d $J_5=7$	5.2m		8.38	8.76	IVb/VIb is ca 1/1
			(VIb)			6.70d $J_5=14$	5.88d $J_5=7$	5.2m		8.22	8.60	
Oxinate	1-tert-Butyl-2-methyl-allyl	−28	(Va)		6.56	7.18	6.64		7.76	(τ t-Bu=8.64)		Equil. ratio Va/Vb/VII is ca. 5/1/1
			(Vb)	5.76		6.49	6.11		7.90	(τ t-Bu=8.87)		
			(VII)	5.52		6.44	ca. 6.5[b]		7.94	(τ t-Bu=8.82)		
Picolinate	Allyl	−20	(IIIa)	5.75d $J_5=7$	6.86d $J_5=12$	6.86d $J_5=12$	6.07d $J_5=7$	4.32m				
		30[c]	(IIIa)	5.96d $J_5=7$	6.93d $J_5=12$	6.99d $J_5=12$	6.26d $J_5=7$	4.40m				

(continued)

Picolinate	2-Methylallyl	−20	(IIIb)	5.92d $J_{1,4}=2$	6.92	6.92	6.23d $J_{1,4}=2$	7.76				
Picolinate	2-tert-Butyl-allyl	−50	(IIIc)	5.85d $J_{1,4}=2$	7.07	7.13	6.09d $J_{1,4}=2$	(τ t-Bu = 8.75)				
Picolinate	*syn*-1-Methylallyl	−27	(IVa)		6.24m	7.07d $J_5=6$	6.00d $J_5=12$	4.33m		8.46d $J_2=6$		IVa/VIa is ca. 20/1
			(VIa)	[d]						8.79d $J_2=6$		
Picolinate	1,1-Dimethylallyl	−50	(IVb)			6.86d $J_5=12$	6.26d $J_5=7$	4.72m		8.30	8.64	IVb/VIb is ca. 10/1
			(VIb)			6.64d $J_5=12$	5.83d $J_5=7$	4.72m		8.32	8.74	
Picolinate	1-tert-Butyl-2-methylallyl[e]	30	(Va)		6.53	7.25	6.57		7.80	(τ t-Bu = 8.75)		Equil. ratio Va/Vb/VII is ca. 36/2/1
			(Vb)	5.71		6.52	6.16		7.98	(τ t-Bu = 8.90)		
			(VII)	5.52		6.52	6.39		7.98	(τ t-Bu = 8.90)		

[a] b = broad; d = doublet; m = multiplet. Tentative assignment of low field *syn*- and *anti*-proton resonances to protons in *trans* position to N is based on steric arguments for the terminally substituted π-allylic picolinate complexes. The H^3 and H^4 protons of the minor isomers (VI) and (VII) absorb at low field. [b] Peak obscured by resonances of other isomers. [c] In CD_2Cl_2. [d] With exception of methyl protons resonances assignable to minor isomer not observed due to very low concentration. [e] Recorded at 60 MHz.

SCHEME 2
Mechanism of pyridine promoted 1–4 and 2–3 exchange in the complexes $[(\pi\text{-2-RC}_3\text{H}_4)\text{Pd}(\text{O}_2\text{CC}_5\text{H}_4\text{N})]$.



$\text{Pd}(\text{O}_2\text{CC}_5\text{H}_4\text{N})\text{Me}_2\text{PhP}]$ *in which* the picolinate ligand occupies only one co-ordination site in the square plane and in bonded through an oxygen atom to the palladium, [*i.e.* structurally analogous to (VIII)]. The possibility of a Vrieze type pseudo-rotation of the π-allylic ligand in the intermediate (VIII) resulting in 1–4 exchange would appear unlikely in view of the first order dependence on pyridine concentration and the insensitivity of 1–4 exchange towards bulky substituents on the central allylic carbon atom.

At 30° broadening of the terminal allylic resonances due to rapid 1–4 and 2–3 exchange is observed in solutions of allyl-, (2-methylallyl)- and (2-tert-butylallyl)-palladium picolinate in the absence of pyridine. These PMR spectra exhibit a marked concentration dependence consistent with a bimolecular exchange process in which another molecule of complex acts as a base and promotes exchange in a similar manner to pyridine. Above 30° addition of pyridine results in complete PMR equivalence of the terminal allylic protons. Rapid *syn–anti* proton exchange is observed and probably occurs via a σ-allylic intermediate similar to that proposed for *syn–anti* proton exchange in $[\pi\text{-allyl Pd(OAc)PMe}_2\text{Ph}]$[8].

Addition of pyridine to π-allyl-and (π-2-methylallyl)palladium oxinate also promoted rapid *syn–syn* and *anti–anti* exchange but at a much higher temperature (30°) than is observed in π-allylpalladium picolinate (−70°). This observation is consistent with the greater stability associated with the chelating oxinate ligand *i.e.* substitution of the oxinate nitrogen group by pyridine is more difficult.

Addition of pyridine to non-equilibrium $CDCl_3$ solutions of *syn/anti*-(1-tert-butyl-2-methylallyl)palladium oxinates and picolinates [(IIIa) + (IIIb) + (V)] at 30° promoted PMR equivalence of the π-allylic patterns assigned to the two *anti*-tert-

butyl conformations (Vb) and (VII) (*i.e.* via the mechanism outlined in Scheme 2). Pyridine and trace amounts of PPh_3 also catalysed the equilibration of the *syn* and *anti* isomers presumably through a σ-allylic intermediate[11]. Addition of weak ligands such as acetic acid and dimethyl sulphoxide also promotes *syn–syn* and *anti–anti* exchange in allylpalladium picolinate and oxinate.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are corrected. Molecular weights were measured on a Mechrolab 301A Osmometer. Conductivities were measured on an Industrial Instruments Conductometer. PMR spectra were recorded on Varian HA-100 and A56/60D Spectrometers. The rates of 2-picoline induced exchange of protons 1 and 4 in the complexes [(π-$2RC_3H_4$)Pd-($O_2CC_5H_4N$)], (IIIb) and (IIIc), in the slow exchange limit were calculated from half-height line width measurements[12].

The π-allylic palladium chloride complexes were prepared by the method of Dent, Long and Wilkinson[15] with exception of (2-tert-butylallyl)palladium chloride and (1-tert-butyl-2-methylallyl)palladium chloride which were prepared by the method of Volger[11,16]. The allylic palladium acetate complexes were prepared by the method of Robinson and Shaw[17].

π-Allyloxinatopalladium(II)

8-Hydroxyquinoline (1.015 g) was added to a solution of di-μ-acetatodi-π-allyldipalladium(II) (1.436 g) in chloroform. The solution was eluted with chloroform through an alumina column and evaporated to dryness under reduced pressure. The product recrystallized from benzene/light petroleum (b.p. 30–60°) as yellow needles (1.830 g, 91%), decompn. above 150°. (Found: C, 49.17; H, 4.06. $C_{12}H_{11}NOPd$ calcd.: C, 49.42; H, 3.80%.)

The following compounds were similarly prepared from the corresponding π-allylic palladium acetates:

(2-Methylallyl)oxinatopalladium(II). Yellow prisms (81%), m.p. 170–180° from benzene/light petroleum (b.p. 30–60°). (Found: C, 51.20; H, 4.44; mol. wt. osmometrically in chloroform, 295. $C_{13}H_{13}NOPd$ calcd.: C, 51.08; H, 4.28%; mol. wt., 306.)

(1-Methylallyl)oxinatopalladium(II). Yellow prisms (67%), decompn. slowly above 120° and melted at 165–170°, from acetone/light petroleum (b.p. 30–60°). (Found: C, 50.86; H, 4.51. $C_{13}H_{13}NOPd$ calcd.: C, 51.08; H, 4.28%.)

(1,1-Dimethylallyl)oxinatopalladium(II). Yellow plates (91%), m.p. 160–175° from acetone/light petroleum (b.p. 30–60°). (Found: C, 52.40; H, 4.85. $C_{14}H_{15}NOPd$ calcd.: C, 52.60; H, 4.73%.)

(1-tert-Butyl-2-methylallyl)oxinatopalladium(II). Yellow prisms (86%), decompn. above 175° from acetone/light petroleum (b.p. 30–60°). (Found: C, 56.51; H, 6.05. $C_{17}H_{21}NOPd$ calcd.: C, 56.44; H, 5.85%.)

(π-Allyl)picolinatopalladium(II)

Picolinic acid (0.823 g) was added to a solution of di-μ-acetatodi-π-allyldipalladium(II) (1.315 g) in chloroform. The solution was filtered and the filtrate eluted

with chloroform through an alumina column. The solution was evaporated to dryness under reduced pressure to give a white solid. The product (a monohydrate) recrystallized from chloroform/ether as white microprisms (1.433 g, 79%), m.p. 170–172°. (Found: C, 37.79; H, 3.61, $C_9H_9NO_2Pd \cdot H_2O$ calcd.: C, 37.58; H, 3.86%.)

The following compounds were similarly prepared from the corresponding π-allylic palladium acetates:

(2-*Methylallyl*)*picolinatopalladium*(*II*). White prisms (70%), m.p. 128–130° from chloroform/light petroleum (b.p. 30–60°). (Found: C, 42.43; H, 4.10; mol.wt. osmometrically in a 0.15% w/v chloroform solution, 273. $C_{10}H_{11}NO_2Pd$ calcd.: C, 42.35; H, 3.91% mol.wt., 284.)

(1-*Methylallyl*)*picolinatopalladium*(*II*). White prisms (70%), decompn. above 145° from chloroform/light petroleum (b.p. 30–60°). (Found: C, 42.34; H, 3.95. $C_{10}H_{11}NO_2Pd$ calcd.: C, 42.35; H, 3.91%.)

(2-*tert-Butylallyl*)*picolinatopalladium*(*II*). White prisms (62%), m.p. 160° from chloroform/light petroleum (b.p. 30–60°). (Found: C, 47.94; H, 5.26. $C_{13}H_{17}NO_2Pd$ calcd.: C, 47.56; H, 5.48%.)

(1,1-*Dimethylallyl*)*picolinatopalladium*(*II*). White prisms (50%), decompn. above 140°, from acetone/light petroleum (b.p. 30–60°). (Found: C, 44.73; H, 4.46. $C_{11}H_{13}NO_2Pd$ calcd.: C, 44.39; H, 4.40%.)

(1-*tert-Butyl*-2-*methylallyl*)*picolinatopalladium*(*II*). White prisms (76%), decompn. above 175°, from acetone/light petroleum (b.p. 30–60°). (Found: C, 49.42; H, 5.64. $C_{14}H_{19}NO_2Pd$ calcd.: C, 49.35; H, 5.92%.)

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