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LIGAND SUBSTITUENT EFFECTS ON THE RELATIVE STABILITIES OF π-ALLYLIC AND σ-ALLYLIC COMPLEXES OF PALLADIUM(II)

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SUMMARY

The reaction of dimethylphenylphosphine with the π-allylic palladium(II) complexes [(π-All)Pd(X–Y)]. [All = allyl, 2-methylallyl, 1,1-dimethylallyl; X–Y = S_2COMe (xanthate), S_2CNMe_2 (carbamate), $O_2CC_5H_4N$ (picolinate), OC_9H_6N (oxinate) and Acac] has been investigated. Conductivity and low temperature PMR studies indicate initial formation of a non-conducting 1/1 adduct of the type [(All)Pd(X–Y)Me_2PhP]. For X–Y = S_2COMe the allylic ligand is π-bonded in the 1/1 adduct whilst the xanthate acts as a monodentate ligand. For X–Y = $O_2CC_5H_4N$ the picolinate ligand acts as a monodentate ligand in the π-2-methylallyl 1/1 adduct but in the allyl and 1,1-dimethylallyl analogues the allylic ligand is σ-bonded and the picolinate is chelated to the palladium. Addition of Me_2PhP to (π-2-methylallyl)palladium *N,N*-dimethylcarbamate gives the σ-allylic species [(CH_2=C(Me)–CH_2)Pd(S_2CNMe_2)Me_2PhP]. Variable temperature PMR studies have indicated that the chelating potential of the anionic ligand X–Y and the nature and position of allylic ligand substituents are important factors in determining the stability of σ-allylic palladium(II) complexes relative to their π-allylic analogues. Addition of two dimethylphenylphosphines to [(π-All)Pd(X–Y)] gives the ionic species [(π-All)Pd($Me_2PhP)_2]^+$[X–Y]$^-$.

INTRODUCTION

Extensive, variable temperature PMR studies of the ligand induced dynamic stereochemistry of dimeric π-allylic palladium chlorides and π-allylic palladium acetates have been reported[1-7]. Addition of ligand L to such systems gives the monomeric species [(π-All)PdXL] [L = Me_2PhP, Ph_3P, Ph_3As, Ph(Me)CHNH_2, pyridine; X = Cl, OAc; π-All = allylic ligand] which exhibit various temperature dependent allylic PMR behaviour depending on the nature of L and X and the L/Pd ratio. Recent results have indicated the participation of σ-allylic species as intermediates in ligand promoted *syn–anti* proton exchange processes[1-7]. No such studies on the ligand induced dynamic stereochemistry of monomeric π-allylic palladium(II) complexes containing anionic chelate ligands have been previously reported. Since studies of the reactions of π-allylic palladium(II) complexes containing anionic chelate ligands with unsaturated hydrocarbons suggest that such complexes may be useful for a variety of organic syntheses and as model systems for catalytic reactions[8-10], we have undertaken studies of the effect of a variety of ligands on several such complexes. In this paper we report conductivity and variable temperature PMR studies of the effect of added dimethylphenylphosphine on π-allylic palladium(II) complexes of the type [(π-All)Pd(X–Y)] [(I), X–Y = *N,N*-dimethylcarbamate (S_2CNMe_2), methylxanthate (S_2COMe), oxinate (C_9H_6NO), 2-picolinate ($O_2CC_5H_4N$), and acetylacetonate]. Dimethylphenylphosphine was chosen because of the added structural information that may be obtained from the phosphine–methyl proton spectra[3,11]. Xanthate and carbamate ligands were chosen as examples of symmetrical anionic chelate ligands as previous studies have suggested (though by no means proved) that addition of methyldiphenylphosphine to Pt^{II} and Pd^{II} carbamates and xanthates gives five co-ordinate species in solution[12]. Since five co-ordinate π-allylic palladium(II) species have been postulated by Vrieze *et al.*[2] as intermediates in which a postulated "inplane rotation of the π-allyl ligand may occur", it was of interest to see whether or not five co-ordinate π-allylic complexes could be isolated. The oxinate and picolinate ligands are examples of asymmetric chelates and as such the sites of the terminal π-allylic carbon atoms in these complexes are non-equivalent[13].

RESULTS AND DISCUSSION

Preparation of complexes

π-Allylic palladium xanthate and *N,N*-dimethylcarbamate complexes were isolated, in moderate yields, as orange or golden yellow crystals, by reaction of the corresponding chloride complex with the appropriate potassium xanthate or carbamate salt:

$$\tfrac{1}{2}[\pi\text{-}C_3H_5PdCl]_2 + S{=}C(SK)Y \longrightarrow [\pi\text{-}C_3H_5Pd(S_2CY)] + KCl \qquad (Y = OMe,\ OEt,\ NMe_2)$$

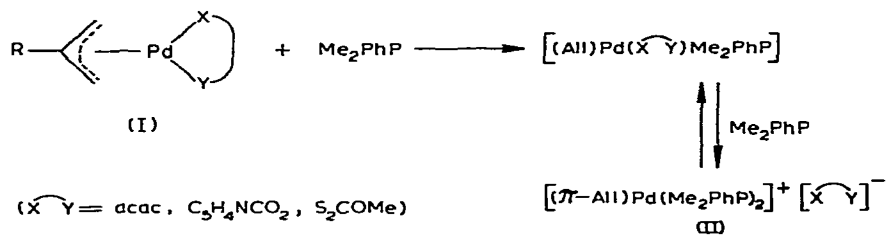
Osmometric molecular weight studies in $CHCl_3$ at 37° confirmed that the complexes are monomeric and their PMR spectra are consistent with a symmetrical, π-allylic structure. The preparations of the other π-allylic palladium chelate complexes used in this study have been previously reported[13,14].

Conductivity Studies

When tertiary phosphines are added to solutions of π-allylic palladium chloride dimers in acetone, ionic species may be formed[15]:

$$\tfrac{1}{2}[(\pi\text{-All})PdCl]_2 + PR_3 \longrightarrow [(\pi\text{-All})PdClPR_3] \xrightarrow{PR_3} [(\pi\text{-All})Pd(PR_3)_2]^+\ Cl^-$$

We have now obtained evidence for the formation of similar ionic species from conductiometric studies at 24° on the effect of added increments of Me_2PhP to 0.0011 *M* acetone solutions of several π-allylic palladium chelate complexes (see Fig. 1). For π-allylic palladium acetylacetonates, picolinates, xanthates, and acetate dimers (0.0006 *M* solution) the results are consistent with initial formation of a non-conducting 1/1 adduct at Me_2PhP/Pd ratios $\leqslant 1$ and formation of ionic species at Me_2PhP/Pd ratios >1:



The shape of the conductivity curves for Me_2PhP addition to the acetylacetonates and picolinates indicated a distinct difference in the behaviour of the analogous π-allyl and π-2-methylallyl complexes. In these systems a non-conducting 1/1 adduct is formed between Me_2PhP and the π-allyl complexes which, at Me_2PhP/Pd ratios > 1 give the ionic species (II) (see Fig. 1c and 1g). The π-2-methylallyl complexes showed a marked tendency to form ionic species even at Me_2PhP/Pd ratios < 1 (see Fig. 1b and 1d). However, the formation of a small amount of a 1/1 adduct may be inferred from the inflexion point in the conductivity plot at a Me_2PhP/Pd ratio of ca. 1. (π-1,1-Dimethylallyl)palladium picolinate exhibited a similar conductivity plot to the π-allyl complex indicating formation of a 1/1 adduct. Previous studies have shown that *anti* terminal methyl groups on the allylic ligand decreases the tendency to form ionic species such as (II)[15]. For the allylic acetylacetonato and 1,1-dimethylallyl picolinato systems at Me_2PhP/Pd ratios > 1 the conductivity plots are only approximate owing to the instability of the ionic species formed. This instability probably reflects reduc-

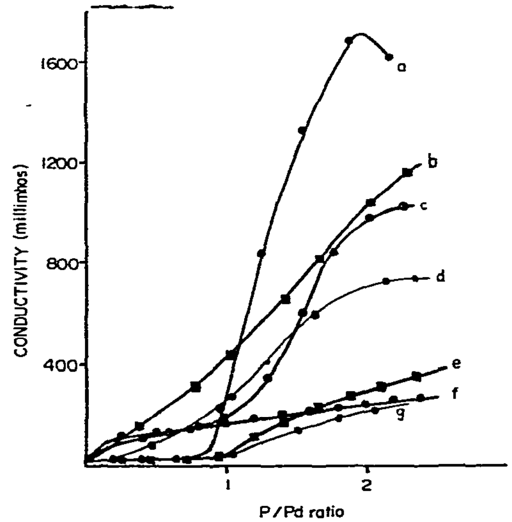


Fig. 1. Plot of conductivity measured at 24° *vs.* number of molecules of Me_2PhP per Pd atom when Me_2PhP is added in increasing amounts to 0.0011 *M* acetone solutions of (a) (2-methyllallyl)palladium acetate (0.0006 *M*); (b) (2-methylallyl)palladium picolinate; (c) allylpalladium picolinate; (d) (2-methylallyl)-palladium acetylacetonate; (e) (2-methylallyl)palladium methylxanthate; (f) (2-methylallyl)palladium *N,N*-dimethylcarbamate; (g) allylpalladium acetylacetonate.

TABLE I

100 MHz PMR DATA FOR THE COMPLEXES $[(\pi\text{-}2\text{-}RC_3H_4)Pd(X_2CY)(L)]$, (III)

Measured in $CDCl_3$ at —60° with TMS as internal standard. Coupling constants, J-values (± 0.5), measured in Hz: d = doublet; b = broad; q = quartet.

R	X_2CY	L	τ_1	τ_2	τ_3	τ_4	τ_R	J_{P-1}	J_{P-2}	$\tau(Me_2P)$	J_{P-H}	Other data
H	S_2COMe	Me_2PhP	5.32q	~5.9[a]	7.10d,b	7.10d,b	4.26	4.5	~ 9	8.19d	10	[b]
CH_3	S_2COMe	Me_2PhP	5.52d	6.60d	6.95b	6.95b	8.11	5	9	8.20d	10	[c]
CH_3	$O_2CC_5H_4N$	Me_2PhP	5.86d	6.32d	7.18	7.18	7.98	6	9	8.39d	10	[d]
CH_3	$O_2CC_5H_4N$	Ph_3P	5.86d	6.36d	7.00	7.00	7.94	6	10			[d]

$[(\pi\text{-}1,1\text{-Dimethylallyl})Pd(OAc)Me_2PhP]$ (recorded at 60 MHz), allylic protons: $\tau(\text{central-}H^5) = 4.80$; $\tau_3 = 5.74$b,d; $\tau_4 = 7.07$b,d; $\tau(syn\text{-}Me) = 8.24$d; $\tau(anti\text{-}Me) = 8.53$d; $J_{5-3} = 12$; $J_{5-4} = 6$; $J_{P-syn\text{-}Me} = 9$; $J_{P-anti\text{-}Me} = 5$ Hz. Other protons: $\tau(OAc) = 7.95$; $\tau(Me_2P) = 8.30$; $J_{P-Me} = 10$ Hz.

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[a] Resonance due to proton 2 obscured by overlap with OMe proton resonance. [b] $J_{R-1} = 6$, $J_{R-2} \approx 12$ (see also footnote [a]), $J_{R-3,4} \approx 6$ Hz; $\tau(OMe) = 5.90$. [c] $\tau(OMe) = 5.95$. [d] Picolinate protons not recorded.

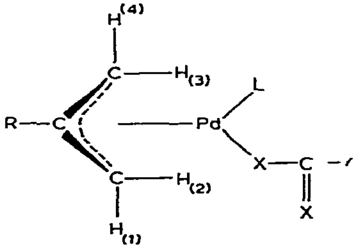
tion to palladium(0) species. The addition of excess Ph_3P to acetone solutions of these complexes results in the ready formation of $(Ph_3P)_4Pd$.

The π-allylic palladium xanthate complexes gave low and constant conductivities at Me_2PhP/Pd ratios $\leqslant 1$ and then increased slowly on further addition of Me_2PhP (*e.g.* see Fig. 1e). However, the conductivities remained relatively low even at a Me_2PhP/Pd ratio of 3 indicating a low tendency for salt formation in these xanthate complexes. The formation of a 1/1 adduct was confirmed by molecular weight studies of [(2-methylallyl)Pd(S_2COMe)] + Me_2PhP in the ratio 1/1 at 37° in $CHCl_3$. The experimentally observed molecular weight is approximately the sum of the molecular weights of the two species.

The π-allylic palladium carbamates and oxinates have low conductivities in acetone which increase slowly with increasing amounts of added Me_2PhP. The addition of Ph_3P to acetone solutions of these π-allylic palladium chelate complexes gave non-conducting or only slightly conducting solutions.

^1H *NMR studies*

Low temperature PMR studies have proven particularly useful for elucidating the structure and dynamic stereochemistry of the Me_2PhP–complex 1/1 adducts*. The low temperature PMR spectra of (π-2-methylallyl)palladium xanthate in $CDCl_3$ in the presence of one Me_2PhP molecule per Pd atom are shown in Fig. 2 and are very similar to the previously reported PMR spectra of [(2-methylallyl)$PdXPR_3$] (X = Cl, OAc; $PR_3 = PPh_3$, Me_2PhP)[1,2,5,6]. Thus the major solution species in this methylxanthate system at low temperatures is the square planar asymmetric, π-2-methylallyl species (III) (L = Me_2PhP; R = CH_3; $X_2CY = S_2COMe$). Assignment of allylic protons in (III) given in Table 1 is based on identical arguments previously used to assign the allylic PMR spectra of the related acetato and chloro complexes[1,6]. Particularly diagnostic is the magnitude of the *trans* ^{31}P nucleus coupling with protons 1 and 2 of 5 and 9 Hz, respectively. The resonances assigned to protons 3 and 4 of the xanthate complex are observed at −80° in CH_2Cl_2 as two broad singlets**. On



(III)

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* In all the studies reported here, coordination of dimethylphenylphosphine to the palladium is confirmed by the magnitude of the ^{31}P–methyl coupling constant[11]. Phosphine methyl groups in the π-allylic complexes (III) in the absence of exchange are non-equivalent[3,6].

** We have not, as yet, been able to observe the PMR spectrum of {(π-2-methylallyl)Pd[S–C(=S)OMe]-Me_2PhP} below −80° because of solubility problems and as such have not been able to completely resolve the resonances of protons 3 and 4 as exchange of these protons in still occurring at −80°.

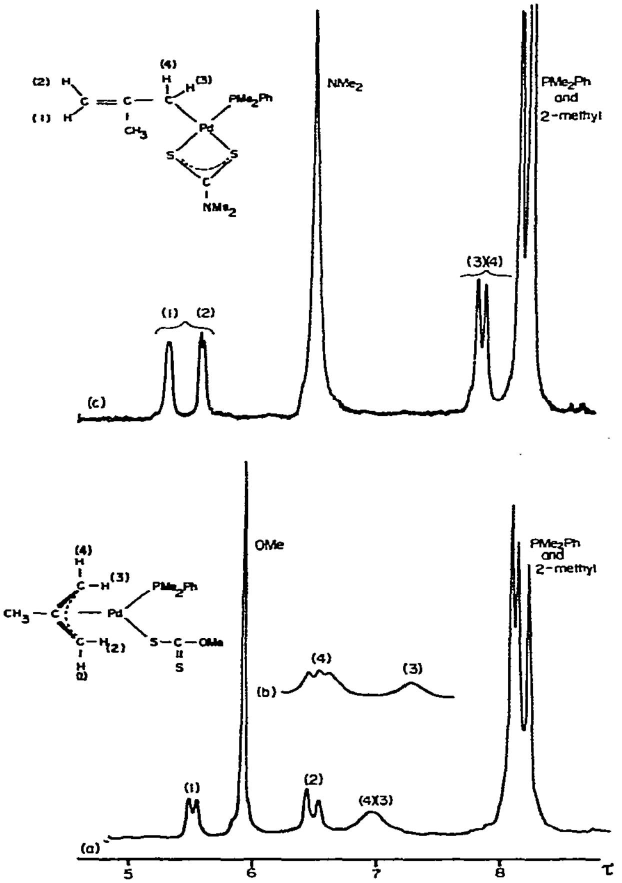
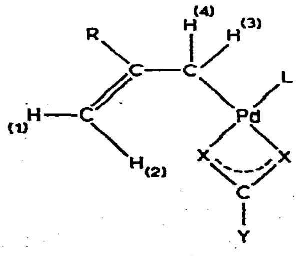


Fig. 2. PMR spectra of (a) [(2-methylallyl)Pd(S_2COMe)Me_2PhP] in $CDCl_3$ at −60°; (b) in $CH_2Cl_2/CDCl_3$ (30% by volume) at −80°; (c) [(σ-2-methylallyl)Pd(S_2CNMe_2)Me_2PhP] in $CDCl_3$ at −60°.

warming, the resonances due to protons 3 and 4 coalesce to a single peak at −60°. The rapid interchange of protons 3 and 4 is independent of concentration. Since resonances due to protons 1 and 2 remain sharp and coupled to the ^{31}P nucleus, the 3–4 exchange process is clearly intramolecular. Rapid 3–4 exchange is readily explained in terms of a $\pi \rightarrow \sigma \rightarrow \pi$ process involving a σ-allylic species such as (IV)^{5,6}. Owing to



(IV)

the much stronger *trans*-bond weakening effect of the Me_2PhP ligand relative to that of the xanthate ligand, the formation of the σ-allylic intermediate (IV) involves the breaking of the π-allyl–palladium bond in *trans*-position to Me_2PhP[1,16]. The σ-allylic species (IV) may reform a π-allylic species in one of two ways resulting in 3–4 exchange[5,6]. Recently both van Leeuwen and Praat[5], and ourselves[6] have shown that the observed PMR equivalence at room temperature of *syn* proton 4 and *anti* proton 3 in complexes such as (III) ($L = PPh_3$[6], PMe_2Ph[6]; $R = CH_3$; $X_2CY = O_2CCH_3$) likewise occurs via the intermediacy of a σ-allylic species such as (IV). The variable tem-

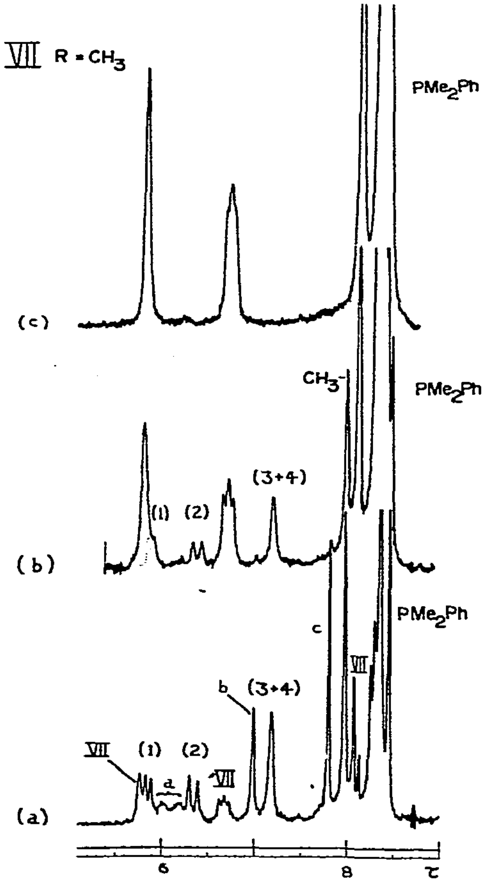


Fig. 3. The effect of increasing amounts of Me_2PhP on the 100 MHz PMR spectrum of a $CDCl_3$ solution of $[(\pi\text{-}2\text{-methylallyl})Pd(O_2CC_5H_4N)]$ recorded at −50°. (a) At a Me_2PhP/Pd ratio of one resonance patterns assignable to $[(\pi\text{-}2\text{-methylallyl})Pd(Me_2PhP)_2]^+[O_2CC_5H_4N]^-$ (VII), $[(\pi\text{-}2\text{-methylallyl})Pd(O_2CC_5H_4N)\text{-}Me_2PhP]$ (V) (see scheme) and starting material* (resonances a, b and c) are observed. (b) At a Me_2PhP/Pd ratio of 1.6 resonance patterns assignable to (V) and (VII) are observed. (Resonances of (V) are numbered.) (c) At a Me_2PhP/Pd ratio of 2 the resonance pattern is assignable to (VII).

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* A rapid exchange of the non-identical *syn*-protons (a) with simultaneous exchange of the non-identical *anti*-prtons (b) is observed for $[(\pi\text{-}2\text{-methylallyl})Pd(O_2CC_5H_4N)]$ in the presence of (V) and (VII) which is not observed at −50° for $[(\pi\text{-}2\text{-methylallyl})Pd(O_2CC_5H_4N)]$ alone[13]. This may well be due to rapid exchange of the coordinated $(O_2CC_5H_4N)$ ligand with the $[O_2CC_5H_4N]^-$ anion of (VII)[13].

perature PMR spectra of [(π-allyl)Pd(S_2COMe)] in $CDCl_3$ in the presence of one Me_2PhP per Pd atom can likewise be interpreted in terms of formation of [(π-allyl)Pd-{S–C(=S)OMe}Me_2PhP] [*i.e.* (III); R=H; X_2CY=S_2COMe see Table 1] in which rapid intramolecular exchange of protons 3 and 4 via an intermediate such as (IV) is occurring, even at −80°.

The low temperature allylic PMR of (π-2-methylallyl)palladium picolinate in $CDCl_3$ in the presence of one Me_2PhP per Pd atom is shown in Fig. 3 and is consistent with the presence in solution of [(π-2-methylallyl)Pd($O_2CC_5H_4N$)], [(π-2-methylallyl)Pd($O_2CC_5H_4N$)Me_2PhP] (V) and [(π-2-methylallyl)Pd($(PhMe_2P)_2$)]$^+$ [$O_2CC_5H_4N$]$^-$. On addition of a further mol. of Me_2PhP/Pd the low temperature allylic PMR spectrum (Fig. 3) is very similar to those previously reported for [(π-2-methylallyl)Pd($(Me_2PhP)_2$)][BPh_4][15] and [(π-2-methylallyl)Pd($Ph_2PCH_2CH_2PPh_2$)]-[PF_6][4] indicating that the solution species is the ionic complex [(π-2-methylallyl)-Pd($(Me_2PhP)_2$)]$^+$ [$O_2CC_5H_4N$]$^-$. The allylic PMR pattern for the 1/1 adduct (see Fig. 3 and Table 1) exhibits *trans* ^{31}P coupling with protons 1 and 2 of 6 and 9 Hz,

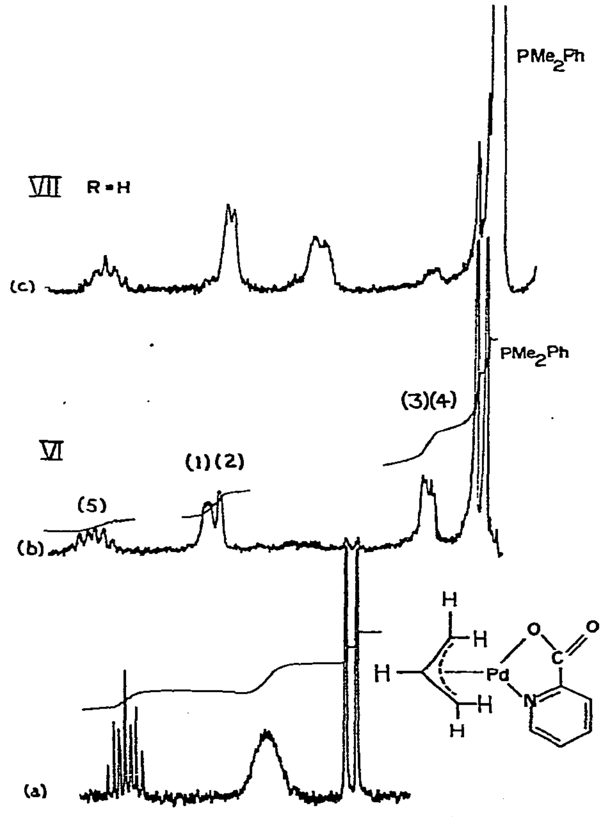

Fig. 4. The PMR spectrum of [(π-allyl)Pd($O_2CC_5H_4N$)] (a) in $CDCl_3$ at 27°. (See ref. 13 for a discussion of *syn–syn* and *anti–anti* proton exchange in this complex). (b) at −40° after addition of one Me_2PhP/Pd. *i.e.* (VI), see Scheme 1. (c) at −40° after addition of two Me_2PhP/Pd. *i.e.* (VII).

respectively consistent with the π-2-methylallyl structure (V). However, rapid exchange of protons 3 and 4 presumably via an intermediate similar to (IV) is still observed at −60°. The PMR spectrum of [(π-2-methylallyl)Pd($O_2CC_5H_4N$)] in the presence of one Ph_3P/Pd in $CDCl_3$ at −60° (see Table 1) is consistent with sole formation of [π-(2-methylallyl)Pd($O_2CC_5H_4N$)Ph_3P] similar to (V), no ionic species being observed. These results are consistent with the observed conductivity plots in acetone solution and the relative basisities of Me_2PhP and Ph_3P.

Below −20° the PMR spectrum of [(π-allyl)Pd($O_2CC_5H_4N$)] in $CDCl_3$ in the presence of one Me_2PhP per Pd atom, shown in Fig. 4, is markedly different from that of the 2-methylallyl system. The allyl protons give rise to an $ABMX_2$ pattern which may be assigned to the σ-allylic complex [(CH_2=CH–CH_2)Pd($O_2CC_5H_4N$)Me_2PhP] (VI). Protons 1 and 2 give rise to a complex pattern centred at τ 5.40 typical of vinylic protons with no sign of the large ^{31}P coupling which is observed in π-allylic complexes of type (III). Protons 3 and 4 are equivalent and give rise to a 1/1/1/1 quartet at τ 7.66 due to coupling with proton 5 and the *cis* ^{31}P nucleus ($J_{5-3,4}$ = 9; $J_{cis-P-3,4}$ = 4 Hz*; peak separations, recorded at 60 MHz and 100 MHz, independent of field strength). Proton 5 gives rise to a multiplet resonance at τ 4.14.

The PMR spectrum at −50° of [(1,1-dimethylallyl)Pd($O_2CC_5H_4N$)] in $CDCl_3$ in the presence of one Me_2PhP per Pd atom is also consistent with the formation of a σ-allylic complex [(Me_2C=CHCH_2)Pd($O_2CC_5H_4N$)Me_2PhP]. The methylene protons give rise to a broad, poorly resolved, resonance centred at τ 7.68 and the central olefinic proton gives a broad 1/2/1 triplet at τ 4.66. More diagnostic is the fact that no ^{31}P coupling with the methyl proton resonances at τ 8.58 and 8.85 of the 1,1-dimethylallyl ligand is observed. The PMR spectra of $CDCl_3$ solutions of the complex [π-(1,1-dimethylallyl)PdOAcMe_2PhP], which was studied for comparative purposes, indicated rapid exchange of the *syn* and *anti* protons (*i.e.* 3–4 exchange) without loss of the *trans* ^{31}P coupling of 9 and 5 Hz to the *syn* and *anti* methyl protons at −25°[1,6]. (See Table 1 for low temperature PMR data).

On addition of a further mol. of Me_2PhP per Pd to $CHCl_3$ solutions of (VI) at −40° the allylic PMR spectrum corresponds to formation of the symmetrical π-allylic cationic species [(π-allyl)Pd(Me_2PhP)$_2$]$^+$ [$O_2CC_5H_4N$]$^-$ (see Scheme 1).

The low temperature PMR spectrum of the (2-methylallyl)palladium *N,N*-dimethylcarbamate/PMe_2Ph system in $CDCl_3$ at a P/Pd ratio of one is shown in the Fig. 2c and is consistent with the formation of a (σ-2-methylallyl)palladium complex [(CH_2=CMe–CH_2)Pd(S_2CNMe_2)PMe_2Ph] [(IV); R = Me; X_2CY = S_2CNMe_2]. The high field resonance at τ 7.85 assigned to the methylene protons is a doublet owing to coupling with the ^{31}P nucleus of the *cis*-Me_2PhP ligand [J(P–CH_2) = 6 Hz; doublet separation independent of field strength]. The low field resonances at τ 5.32 are typical for non co-ordinated vinylic protons. Also, unlike the asymmetric complexes of type (III) where phosphorus coupling of ca. 6 and 10 Hz with the low field resonances of protons 1 and 2 is always observed and is diagnostic of a π-bonded asymmetric allyl[1] (*e.g.* Fig. 2a), no spin–spin coupling with the low field allylic resonances greater that 3 Hz is observed for [(CH_2=CMe–CH_2)Pd(S_2CNMe_2)Me_2PhP].

On warming $CDCl_3$ solutions of [(σ-allyl)Pd($O_2CC_5H_4N$)Me_2PhP] and [(σ-2-methylallyl)Pd(S_2CNMe_2)Me_2PhP] to room temperature the terminal allylic

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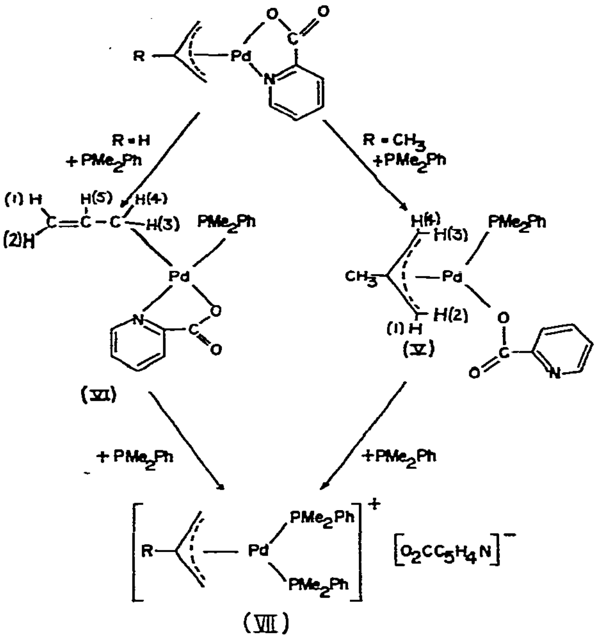
* *cis*-^{31}P coupling to the methyl protons in *trans*-[PdIMe(Ph_3P)$_2$] is 5 Hz[17].

SCHEME I



proton resonances coalesce to a single resonance consistent with a rapid $\sigma \rightarrow \pi \rightarrow \sigma$ process probably involving π-bonded intermediates similar to (V) and (III). Whilst σ-allylic species have been inferred as intermediates in a variety of dynamic allyl palladium exchange processes[1-7] this is the first reported example in which the major solution species has been shown to be a σ-allyl complex.

The relative stabilities of π-allylic complexes of type (III) relative to their σ-allylic analogues (IV) as indicated by the free energy of activation of 3–4 exchange calculated by the usual coalescence method[21] are tabulated in Table 2. Previously Van Leeuwen and Praat[3] pointed out that partial stabilization of a σ-allylic species [(σ-2-methylallyl)PdOAc(PMe_2Ph)] by a chelating acetate [*i.e.* (IV); $X_2CY = O_2CCH_3$] may occur but they did not consider that such a process was of prime importance in inducing formation of the σ-allylic intermediate.

From our studies it is clear that the chelating potential of the anionic ligand (X_2CY) is an important factor in stabilizing σ-allylic species such as (IV). The stability of the σ-allylic species (IV) relative to the π-bonded species (III) decreases in the order $X_2CY = S_2CNMe_2$ (σ-2-methylallyl) > $O_2CC_5H_4N$ [σ-allyl, (π-2-methylallyl)] > S_2COMe [π-allyl, (π-2-methylallyl), 3–4 exchange] > O_2CCH_3 (π-allylic ligands, 3–4 exchange) > Cl (π-allylic ligands, no 3–4 exchange) (see Table 2).

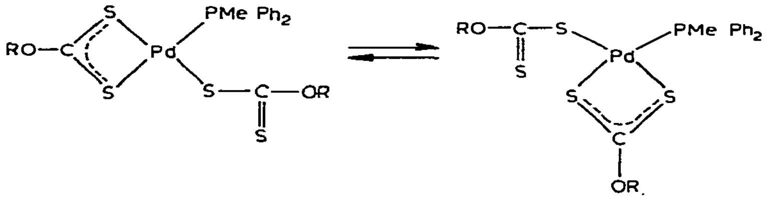
The formation of σ-allylic palladium intermediates may be considered to occur via an S_N2 ligand substitution of the π-allyl–palladium bond. Thus in [(2-methylallyl)-PdCl(Me_2PhP)] in $CDCl_3$ at 34°, where no suitable ligand is available to effect the formation of a relatively stable, co-ordinatively saturated σ-2-methylallyl intermediate, 3–4 exchange is not observed. However, when chloride bridged species are present [*e.g.* (π-2-methylallyl)palladium chloride dimer] 3–4 exchange does occur and

TABLE 2

FREE ENERGY OF ACTIVATION AND COALESCENCE TEMPERATURE DATA (T_c) FOR 3–4 EXCHANGE IN THE COMPLEXES $[(All)Pd(X_2CY)PMe_2Ph]$ OBTAINED FROM 100 MHz PMR STUDIES OF THESE COMPLEXES IN $CDCl_3$

Allylic ligand	(X_2CY)	T_c(°C)	$\Delta G^‡_{T_c}$ (±0.2 kcals/mole)
π-2-Methylallyl	Cl		
π-Allyl	O_2CCH_3	−40	11.0[6]
π-2-Methylallyl	O_2CCH_3	− 7	12.9[6]
π-2-tert-Butylallyl	O_2CCH_3	+45	14.5[6]
π-2-Neopentylallyl	O_2CCH_3	+49	15.8[6]
π-1,1-Dimethylallyl	O_2CCH_3	−33	12.0[b]
π-2-Methylallyl	S_2COMe	< -70	< 10[c]
π-Allyl	S_2COMe	< -80	< 10[c]
π-2-Methylallyl	$O_2CC_5H_4N$	< -70	< 10[c]
Allyl	$O_2CC_5H_4N$	[d]	
2-Methylallyl	S_2CNMe_2	[e]	

[a] 3–4 exchange is not observed. [b] Recorded at 60 MHz. [c] The 3–4 exchange process in these complexes could not be completely "frozen out" owing to solubility problems below −80°. Because of this and related problems we have not as yet been able to ascertain whether or not the non-bonded sulphur and nitrogen atoms are weakly co-ordinated to the palladium atom. In the absence of 3–4 exchange it is possible that two isomers may be observed if such an interaction occurs. Such an interaction is very unlikely in the analogous acetate complex. Previous PMR studies at −40° on palladium xanthate–methyldiphenylphosphine systems (P/Pd = 1) have been interpreted in terms of the formation of a five co-ordinate palladium complex[12]. However, these results may also be interpreted in terms of the formation of a square planar, four co-ordinate complex in which rapid interchange of chelating xanthate ligand and monodentate xanthate ligand via an S_N2 type process, similar to that proposed for 3–4 exchange in (III), results in PMR equivalence of the xanthate ligands, *i.e.*:



[d] Major solution species is a σ-allyl complex (VI). [e] σ-2-methylallyl species (IV).

is thought to involve a co-ordinatively saturated σ-2-methyllyl intermediate of the type (IV) [$R = CH_3$, $L = Me_2PhP$; X_2CY = "Cl_2Pd(π-2-methylallyl)"]. When the anionic ligand X_2CY is potentially a very good chelating ligand addition of Me_2PhP results in preferential substitution of the π-allylic ligand to give a stable σ-allylic complex.

The nature and position of the allylic ligand substituents also has a marked effect on the relative stabilities of the π- and σ-allylic species. From this and previous work[6,18–20] it can be concluded that the relative stability of the σ-allylic species decreases in the order 2-chloroallyl[18–20] > allyl > 2-methylallyl > 2-tert-butylallyl > 2-neopentylallyl. Furthermore, a 2-alkyl substituent, as might be anticipated from a consideration of inductive effects, stabilizes π-allylic cationic species. Steric interactions between terminal π-allylic substituents and a large bulky *cis* ligand[15] would be anticipated to decrease the relative stability of the π-allylic ligand. It seems probable that both electronic and steric factors are important in determining the relative stability of the 2-substituted σ-allylic species: electron withdrawing groups enhancing the stability and large bulky groups, which would be involved in steric repulsions with *cis* ligands in (IV), decreasing the stability of the σ-allylic species relative to the π-bonded analogue.

The low temperature PMR spectra of [(π-2-methylallyl)Pd(Acac)] and [(π-2-methylallyl)Pd(oxinate)] in the presence of one Me_2PhP per Pd atom indicated the presence of several species in solution but were too broad and complex to satisfactorily interpret.

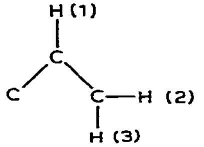
Attempts to further verify the formation of the σ-allylic complexes (VI) and (IV) ($R = CH_3$; $X_2CY = S_2CNMe_2$) from laser Raman and solution IR studies have so far proved unsuccessful owing to decomposition in the laser beam; the complexity of the infrared spectrum of (IV) in the region of C=C stretching frequencies; and fairly rapid disproportionation reactions. In particular, in the *N,N*-dimethyldithiocarbamate system [$Pd(S_2CNMe_2)_2$] commences to precipitate from room temperature $CHCl_3$ solutions after several minutes. The low temperature PMR studies of this system were carried out by adding Me_2PhP to a sample of [(π-2-methylallyl)Pd(S_2CNMe_2)] already situated in the probe and recording the spectrum immediately.

EXPERIMENTAL

Melting points were determined on a Kofler Hot Stage Apparatus and are corrected. Molecular weight determinations were carried out using a Mechrolab 301A Osmometer. PMR spectra were recorded on Varian HA-100 and A56/60D Spectrometers.

π-Allylic palladium acetates, acetylacetonates, oxinates, and picolinates were prepared by previously reported methods[13,14]. New π-allylic palladium(II) complexes and their analytical and PMR data in $CDCl_3$ are recorded below. Allylic protons are numbered as shown in (VIII). *J*-values (±0.5) measured in Hz.

All studies involving dimethylphenylphosphine were carried out under an atmosphere of nitrogen. PMR samples containing Me_2PhP were stored at $-78°$ when not in the probe.



(VIII)

(2-*Methylallyl*)(*methylxanthato*)*palladium*(*II*)

A solution of potassium methylxanthate (0.383 g) in methanol (10 ml) was added to a solution of di-μ-chlorobis(2-methylallyl)dipalladium(II) (0.516 g) in chloroform (3 ml). The solution was filtered and the orange filtrate evaporated to dryness under reduced pressure to give the required product as orange microprisms (0.48 g; 69%), m.p. 75–80°. (Found: C, 27.09; H, 3.72; mol. wt. osmometrically in 1.0% w/v chloroform solution, 251. $C_6H_{10}OPdS_2$ calcd.: C, 26.82; H, 3.75% mol.wt. 269.) $\tau_2=5.88$; $\tau_3=7.16$; τ(2-methyl)$=7.99$; τ(OMe)$=5.74$. Also prepared in this manner were:

(2-Methylallyl)(ethylxanthato)palladium(II). Yield 90%. Orange prisms, m.p. 49–52°. (Found: C, 29.68; H, 4.08, $C_7H_{12}OPdS_2$ calcd.: C, 29.74; H, 4.28%.) $\tau_2=5.97$; $\tau_3=7.20$; τ(2-methyl)$=8.00$; τ(OEt)$=5.32$ (CH_2-quartet), 8.51 (CH_3-triplet).

Allyl(methylxanthato)palladium(II). Yield 78%. Orange-brown amorphous solid m.p. 40–44°. (Found: C, 21.04; H, 2.74. $C_5H_8OPdS_2$ calcd.: C, 23.58; H, 3.16%.) $\tau_1=4.67$; $\tau_2=5.65$; $\tau_3=7.01$; $J_{1,2}=6$; $J_{1,3}=12$; τ(OMe)$=5.73$.

(2-Methylallyl)(dimethyldithiocarbamato)palladium(II).

A 50% aqueous solution of potassium dimethyldithiocarbamate (0.7 ml) was added to a solution of di-μ-chlorobis(2-methylallyl)dipalladium(II) (0.431 g) in a 1/1 mixture of chloroform and methanol (71 ml). The solution was filtered and the yellow filtrate evaporated to dryness under reduced pressure. The solid residue recrystallized from chloroform/light petroleum (b.p. 30–60°) as yellow prisms (0.366 g, 58%), m.p. 133–134° with decompn. (Found: C, 29.97; H, 4.74. $C_7H_{13}NPdS_2$ calcd.: C, 29.84; H, 4.65%.) $\tau_2=6.04$; $\tau_3=7.28$; τ(2-methyl)$=7.99$; $\tau(NMe_2)=6.53$.

Attempts to isolate the Me_2PhP–complex 1/1 adducts gave oily products which were not further characterized.

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