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π-ALLYLIC PALLADIUM SCHIFF BASE COMPLEXES

IAN D. RAE, BERNHARD E. REICHERT and BRUCE O. WEST
(*Department of Chemistry, Monash University, Clayton, Victoria, 3168 (Australia)*
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Summary

π-Allylic palladium(II) complexes with bidentate *N*-organosalicylaldimines, (All)PdSal=N—R, and also some binuclear complexes in which a tetradentate Schiff-base forms a bridge between two allylpalladium units have been synthesized. The ^{1}H NMR spectra of these complexes have enabled isomeric forms of several of the compounds to be detected as well as providing information about their dynamic stereochemistry. On the basis of these latter studies competing monomolecular and bimolecular mechanisms for end-to-end exchange of the π-allyl group are proposed, which may change in relative importance with temperature. Insertion reactions of 1,3-dienes have also been studied.

Introduction

The last decade has seen extensive investigation of π-allylic compounds of palladium [1], particularly ^{1}H NMR studies of their dynamic stereochemistry. Two basic exchange processes are known to occur, viz. a *syn—anti* exchange at one end of the allyl group, and a simultaneous *syn—syn* and *anti—anti* exchange where the two ends of the group exchange. Most of the systems studied have involved bimolecular reactions with additional donor molecules taking part.

This paper describes the synthesis and properties of a series of π-allylic palladium(II) complexes with salicylaldimine Schiff bases, some of which we have earlier reported in a preliminary communication [2]. These compounds have the basic structure shown in Fig. 1 and provide examples of π-allyl complexes where the allyl group faces an asymmetric ligand, and thus its two ends are distinguishable by NMR spectroscopy. The protons H(2) and H(3) are referred to as *syn* (this being with respect to H(1)) and H(4) and H(5) as *anti*. We have also prepared some binuclear complexes of *N,N'*-ethylenebis(salicylaldimine) ($SalenH_2$), which behaves as a bridging ligand bidentate on each of two allylpalladium units as previously proposed [2]. Some salicylaldehyde complexes of these systems which were also synthesized proved to be relatively unstable, but reacted with primary amines to give the Schiff base compounds.

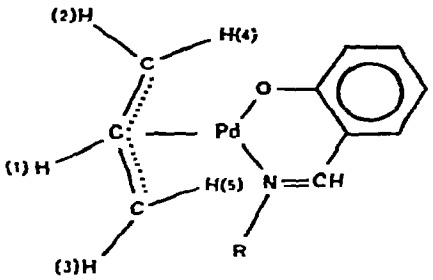

Fig. 1. Structure of (All)PdSal=N—R.

^{1}H NMR measurements on the compounds have enabled the primary exch phenomenon in non-coordinating solvents to be described as an end-to-end exchange of the *syn* protons 2 and 3 and the *anti* protons 4 and 5, as is the case in other π-allylpalladium chelate complexes [3, 4]. On the basis of the concentrati dependence of the rate of this exchange, we propose that a rotation of the π-all group about its axis to the metal, a monomolecular mechanism, is taking place in competition with a bimolecular mechanism of the type suggested for picolina complexes [3]. Some quantitative measurements of the rate of exchange have been made.

The ^{1}H NMR spectra have also enabled the detection of isomeric forms of several of the complexes.

Attempts at insertions of 1,3-dienes into the allyl—palladium bond proved successful in only one case. The ease of insertion appears to correlate with the ra of exchange above.

Results and discussion

Syntheses

The compounds (All)PdSal=N—R [(All) = π-allylic group; Sal=N—R = N—R substituted salicylaldiminato anion] were synthesized by reaction of the appropriate chloro-bridged dimer $[(All)PdCl]_2$ with TlSal=N—R in benzene. The complexes are all yellow, those of *N*-methylsalicylaldimine being much lighter in colour, and are readily soluble in most common organic solvents except alkanes. The salicylaldehyde complexes allylPdSal and 2-methylallylPdSal, made using TlSal, are much less stable and blacken within a few days at room temperature. The bridged compounds $[(All)Pd]_2$Salen were similarly prepared by reaction with Tl_2Salen in dichloromethane.

The compounds prepared, together with analytical figures and recrystallizati solvents, are shown in Table 1.

Although 2-chloroallylPdSal=N—CH_3 was readily prepared, attempts to synthesize 2-chloroallylPdSal=N—C_6H_5 resulted only in removal of the allylic group and formation of $Pd(Sal{=}N{-}C_6H_5)_2$. This lability of the 2-chloroallyl group may be related to its high reactivity in insertion reactions of dienes with π-allylpalladium compounds [5, 6], which has also been observed for the Schiff base complex 2-chloroallylPdSal=N—CH_3 (see under insertion reactions).

Schiff base complexes (All)PdSal=N—R were also obtained by reaction of

he corresponding salicylaldehyde complex with a primary amine. Another alternative method of synthesis is the reaction of the chloro-bridged dimer with the free salicylaldimine HSal=N—R in the presence of potassium hydroxide. The reaction with HSal=N—CH_3 using methylamine as base in place of potassium hydroxide gave the same product, but use of *p*-toluidine in the reaction with HSal=N—*p*-$C_6H_4CH_3$ gave only (All)Pd(*p*-toluidine)Cl. It is apparent that *p*-toluidine is not a sufficiently strong base to deprotonate the Schiff base to the necessary extent.

Mass spectra

The mass spectra of all the mononuclear complexes show the parent ion. The fragmentation pattern tends to vary but typical fragments are $[HPdSal=N—R]^+$ (presumably due to loss of an allene), $[HSal=N—R]^+$ and $[Sal=N—R]^+$. On the other hand parent ions for the bridged binuclear derivatives were not detected, but fragments such as $[PdSalen]^+$ and $[SalenH_2]^+$ were evident. The salicylaldehyde complexes do shown the parent ion, and have a more clearly defined fragmentation pattern. Main fragments are $[(All)PdOC_6H_5]^+$, $[PdO_2C_6H_4]^+$, $[PdOC_6H_5]^+$, $[(All)Pd]^+$, $[SalH]^+$ and $[Sal]^+$.

Isomerism and NMR spectra

Schiff base complexes. The compounds described here may give rise to several forms of isomerism which are illustrated in Fig. 2. The complexes with

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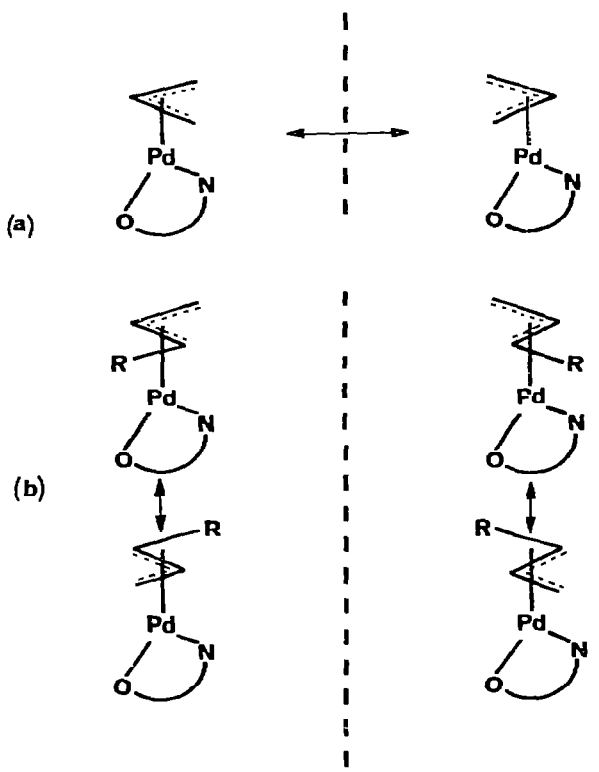

Fig. 2. Isomerism of (All)PdSal=N—R complexes. Broken line indicates relationship by a mirror plane. Double headed arrows indicate interchange by rotation of π-allyl group.

TABLE 1

COMPOUNDS PREPARED WITH ANALYTICAL DATA AND RECRYSTALLIZATION SOLVENTS

Complex	Formula	Analyses found (calcd.) (%)				Recrystallization solvent
		C	H	N	Cl	
AllylPdSal=N—R						
R = CH_3	$C_{11}H_{11}NOPd$	47.11 (46.91)	4.68 (4.65)	4.80 (4.97)		CH_2Cl_2/hexane
R = C_6H_5	$C_{16}H_{15}NOPd$	55.81 (55.91)	4.51 (4.40)	4.03 (4.08)		CH_2Cl_2/hexane
R = *p*-$C_6H_4CH_3$	$C_{17}H_{17}NOPd$	56.98 (57.08)	4.97 (4.79)	3.86 (3.92)		CH_2Cl_2/hexane
2-MethylallylPdSal=N—R						
R = CH_3	$C_{12}H_{15}NOPd$	48.82 (48.75)	5.15 (5.11)	4.71 (4.74)		Ether/hexane
R = C_6H_5	$C_{17}H_{17}NOPd$	57.38 (57.08)	4.99 (4.79)	4.08 (3.92)		CH_2Cl_2/hexane
R = *p*-$C_6H_4CH_3$	$C_{18}H_{19}NOPd$	58.05 (58.16)	5.24 (5.15)	3.77 (3.77)		CH_2Cl_2/hexane
R = *p*-C_6H_4Cl	$C_{17}H_{16}NOClPd$	52.46 (52.07)	4.42 (4.11)	3.68 (3.57)	9.1 (9.0)	CH_2Cl_2/hexane
2-ChloroallylPdSal=N—R						
R = CH_3	$C_{11}H_{12}NOClPd$	41.84 (41.80)	3.86 (3.83)	4.41 (4.43)	11.6 (11.2)	CH_2Cl_2/hexane
2,4-CyclooctadienylPdSal=N—R						
R = CH_3	$C_{16}H_{19}NOPd$	55.51 (55.27)	5.57 (5.51)	3.81 (4.03)		Ether/hexane
R = *p*-$C_6H_4CH_3$	$C_{22}H_{23}NOPd$	62.51 (62.35)	5.83 (5.47)	3.34 (3.31)		CH_2Cl_2/hexane

2,3-Dimethyl-2-butenylPdSal=N—R					
R = CH_3	$C_{14}H_{19}NOPd$	52.14	5.91	4.67	CH_2Cl_2/hexane
		(51.95)	(5.92)	(4.33)	
R = C_6H_5	$C_{19}H_{21}NOPd$	Obtained as oil only, not analysed			
4-Methoxy-2-methyl-2-butenylPdSal=N—R					
R = CH_3	$C_{14}H_{19}NO_2Pd$	49.71	5.64	4.15	CH_2Cl_2/hexane
		(49.50)	(5.64)	(4.12)	
R = C_6H_5	$C_{19}H_{21}NO_2Pd$	56.62	5.21	3.51	CH_2Cl_2/hexane
		(56.80)	(5.27)	(3.49)	
R = p-$C_6H_4CH_3$	$C_{20}H_{23}NO_2Pd$	58.55	5.70	3.20	CH_2Cl_2/hexane
		(57.77)	(5.58)	(3.37)	
$(AllylPd)_2$Salen	$C_{22}H_{24}N_2O_2Pd_2$	47.40	4.54	4.82	CH_2Cl_2/ethanol
		(47.08)	(4.31)	(4.99)	
$(2\text{-MethylallylPd})_2$Salen-$2C_6H_6$	$C_{36}H_{40}N_2O_2Pd_2$	58.06	5.61	3.74	CH_2Cl_2/benzene
		(58.00)	(5.41)	(3.76)	
$(2\text{-MethylallylPd})_2$Salen	$C_{24}H_{28}N_2O_2Pd_2$	48.76	4.81	4.94	CH_2Cl_2/hexane
		(48.92)	(4.79)	(4.75)	
$(2,4\text{-CyclooctadienylPd})_2$Salen	$C_{32}H_{36}N_2O_2Pd_2$	55.55	5.41	4.13	CH_2Cl_2/benzene
		(55.43)	(5.23)	(4.04)	
$(4\text{-Methoxy-2-methyl-2-butenylPd})_2$Salen	$C_{28}H_{36}N_2O_4Pd_2$	49.37	5.25	3.95	CH_2Cl_2/hexane
		(49.65)	(5.36)	(4.14)	
AllylPdSal	$C_{10}H_{10}O_2Pd$	44.87	3.38		CH_2Cl_2/hexane
		(44.72)	(3.75)		
2-MethylallylPdSal	$C_{11}H_{12}O_2Pd$	46.78	4.33		CH_2Cl_2/hexane
		(46.75)	(4.28)		

TABLE 2

^{1}H NMR SPECTRA OF THE BIDENTATE SCHIFF BASE COMPLEXES [a]

Complex	δ values [b]									Coupling constants (Hz)				
	CH=N [c]	Aromatic	H(1)	H(2)	H(3)	H(4)	H(5)	Other [d]		J_{12}	J_{13}	J_{14}	J_{15}	J_{23}
2-MethylallylPdSal=N—R														
R = CH_3	7.79	6.21–7.20		3.69 d	3.02 d	2.92	2.47	CH_3(1)	2.14					2.8
								N—CH_3	3.66 d [e]					
R = C_6H_5	7.93	6.26–7.35		2.70 d	2.36 d	2.89	2.42	CH_3(1)	2.09					2.7
R = p-$C_6H_4CH_3$	7.90	6.24–7.25		3.68 d	2.38 d	2.87	2.42	CH_3(1)	2.08					2.8
								C_6H_4—CH_3	2.33					
R = p-C_6H_4Cl	7.88	6.26–7.31		3.70 d	2.39 d	2.90	2.41	CH_3(1)	2.17					2.6
AllylPdSal=N—R														
R = CH_3	7.72	6.21–7.20	5.50 m	3.84 q	3.19 q	3.03 d	2.53 d	N—CH_3	3.55 d [e]	7.1	6.6	12.5	11.7	1.9
R = C_6H_5	7.93	6.26–7.34	5.47 m	3.89 q	2.67 q	3.02 d	2.46 d			6.6	(6.5) [f]	12.7	12.2	1.8
R = p-$C_6H_4CH_3$	7.90	6.15–7.25	5.46 m	3.87 q	2.58 q	3.01 d	2.40 d	C_6H_4—CH_3	2.32	6.9	6.4	12.3	11.7	1.8
2-ChloroallylPdSal=N—R														
R = CH_3	7.77	6.24–7.23		4.05 t [g]	3.39 t [h]	3.28 d [g]	2.77 d [h]	N—CH_3	3.69 d [e]					3.0
2,3-Dimethyl-2-butenylPdSal=N—R														
R = CH_3 (I)	7.76	6.16–7.17			2.99		2.70	CH_3(1)	2.03					
								CH_3(2)	1.45					
								CH_3(4)	1.26					
								N—CH_3	3.65 d [i]					
R = C_6H_5 (I)	7.86	6.20–7.33			2.44		2.68	CH_3(1)	1.97					
								CH_3(2)	1.43					
								CH_3(4)	1.23					

R = C_6H_5	(II)	7.86	6.20—7.33	3.50		2.97		CH_3(1)	2.03
								CH_3(3)	1.34
								CH_3(5)	1.15
4-Methoxy-2-methyl-2-butenylPdSal=N—R									
R = CH_3	(I)	7.73	6.18—7.19		3.03	*j*	2.47	CH_3(1)	2.09
								O—CH_3	3.34
								O—CH_2	*j*
								N—CH_3	3.62 [c]
R = C_6H_5	(I)	7.89	6.23—7.34		2.40	*j*	2.43	CH_3(1)	2.03
								O—CH_3	3.33
								O—CH_2	*j*
R = C_6H_5	(II)	7.89	6.23—7.34	*k*		2.85	*j*	CH_3(1)	2.03
								O—CH_3	3.33
								O—CH_2	*j*
R = *p*-$C_6H_4CH_3$	(I)	7.87	6.22—7.23		2.43	*j*	2.43	CH_3(1)	2.04
								O—CH_3	3.33
								O—CH_2	*j*
								$C_6H_4CH_3$	2.31
R = *p*-$C_6H_4CH_3$	(II)	7.87	6.22—7.23	*k*		2.86	*j*	CH_3(1)	2.04
								O—CH_3	3.33
								O—CH_2	*j*
								$C_6H_4CH_3$	2.31

[a] At 100 MHz in CCl_4 at 306 K. [b] Ppm downfield from internal TMS. d = doublet, t = triplet, q = quadruplet, m = higher multiplet; other peaks are singlets. [c] In cases where R = CH_3 this peak is broadened by coupling with the methyl group which gives four unresolved lines. [d] Numbering of methyl groups corresponds to the protons they replace in Fig. 1. [e] Doublet due to coupling with CH=N proton, *J* 1.2 Hz. [f] Estimated, as obscuring by H(5) makes accurate measurement impossible. [g] J_{24} 2.7 Hz. [h] J_{35} 2.8 Hz. [i] Coupling with CH=N proton, *J* 1.0 Hz. [j] Non equivalent CH_2 protons and adjacent allylic proton form complex multiplet. [k] Obscured by complex multiplet of CH_2 and adjacent allylic protons.

bidentate Schiff base ligands where the ligand is able to achieve an average plan configuration in solution, will show only one isomer where the allyl group is symmetrical (i.e., has both ends similarly substituted). Rotation of the allyl group about its bond to palladium (or, equivalently, exchange of oxygen and nitrogen donors of the Schiff base) will simply generate the other enantiomer (Fig. 2a). Where the two ends of the allyl group are different *cis* and *trans* isomers are possible (each having two enantiomers). Rotation of the allyl group will interconvert the *cis* and *trans* isomers as shown in Fig. 2b. The ^{1}H NMR spectra of the bidentate complexes are summarized in Table 2; the 2,4-cyclooctadienyl complexes have complex NMR spectra which do not show any clear features in the allylic region and are hence not included. The *cis* and *trans* isomers I and II are as shown in Fig. 3. Assignments of the allylic protons as *syn* and *anti* can be made on the basis of the *syn* protons H(2) and H(3) having higher δ values and smaller coupling with H(1) in the allyl complexes, as has be found in other examples [1]. Apart from the 2-chloroallyl complex the only sig nificant coupling between the allylic protons is that between the two *syn* protons, which is in agreement with theoretical considerations [7] and most observations in other asymmetric π-allyl systems [8, 9]. The magnitude of this coupling appears to be increased by a substituent in the 2-position. The relativel large geminal coupling constants in the 2-chloroallyl complex are slightly larger than those first found for 2-chloroallyl compounds by Lupin and Shaw [10], and recently a similar effect has been reported in a 2-phenylallylpalladium Schif base complex [11], although the values found there were somewhat smaller. It is perhaps significant that in both these examples the substituent in the 2-position is more electronegative than the hydrogen or methyl group in the other compounds. Under favourable conditions it is also possible to detect very small unresolved *syn—anti* and *anti—anti* couplings of approx. 0.3 Hz in 2-methylallyl PdSal=N—R (R = CH_3, C_6H_5) from the line shapes.

All the coupling constants have been confirmed by decoupling experiments.

The protons H(2) and H(4) which have higher δ values were initially assign to the carbon *trans* to the imine nitrogen by comparison with phosphine comple

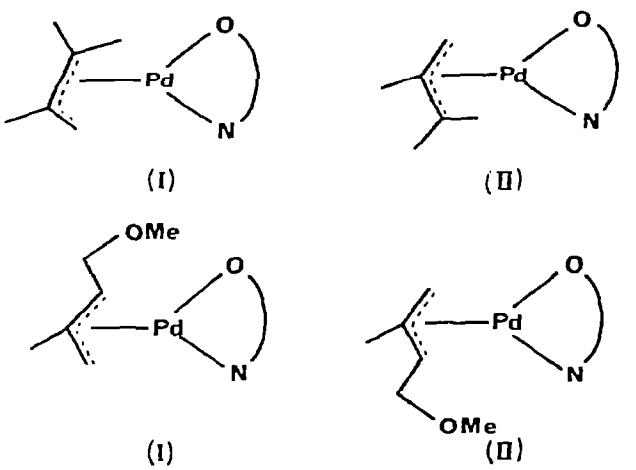

Fig. 3. *Cis* and *trans* isomers of complexes with the asymmetrical allyl ligands.

es [8, 12], on the assumption that the nitrogen and oxygen donors would parallel the phosphorus and halogen respectively. It can be noted from the spectra that H(3) undergoes a large upfield shift when *N*-methylsalicylaldimine is replaced by an *N*-arylsalicylaldimine while the other protons are essentially unaffected. This suggests a through-space shielding from the ring current of the aromatic ring, and confirms the assignment of this proton to the carbon *cis* to the nitrogen donor.

Double irradiation also provides information about the exchange processes taking place. In allylPdSal=N—CH_3 irradiation of H(2) at ambient temperature (306 K), as well as removing H(2)—H(3) coupling, causes a diminution in the signal due to H(3), while irradiation of H(5) diminishes the signal from H(4). The intensity of the other resonances remains essentially unaffected in both cases. In 2-methylallylPdSal=N—R (R = CH_3, C_6H_5) irradiation of either of the *anti* protons (singlets) reduces the intensity of the resonance of the other. This effect may be attributed to site transfer of spin saturation [13], where saturation of one site is partly transferred to another by chemical exchange, and hence diminishes the signal due to the second site. The effect has previously been noted in allylic palladium compounds [4, 14, 15] and here shows clearly that the main exchange phenomenon occurring is exchange of H(2) with H(3) and H(4) with H(5), i.e. an end-to-end exchange of the allyl group. This may be considered as a rotation of the π-allyl group about its axis to the palladium [16], although this cannot be distinguished from exchange of the oxygen and nitrogen donors of the chelating ligand [3] which produces exactly the same net result.

In the 2-chloroallyl complex the effect is particularly notable (Fig. 4), indicating a faster rate of exchange (quantitative measurements will be discussed later). Note that the geminal H(3)—H(5) coupling is removed on irradiating H(5), and the signal from H(4) greatly diminished. At 323 K irradiation of H(5) virtually destroys the resonance of H(4), and the other peaks are also reduced in size, which suggests that at this temperature there is not only rapid *syn—syn* and *anti—anti* exchange, but also slower *syn—anti* exchange becoming apparent.

Nevertheless, at 306 K at which the spectra were normally run, all the compounds undergo exchange sufficiently slowly to make all the sites clearly visible without appreciable broadening.

Both examples of asymmetric allyl groups where *cis* and *trans* isomers are possible (2,3-dimethyl-2-butenyl and 4-methoxy-2-methyl-2-butenyl) give only one isomer with *N*-methylsalicylaldimine, but with the *N*-phenyl and *N*-*p*-tolyl ligands both isomers shown in Fig. 3 are evident in the NMR spectrum. The methoxymethyl group has been assigned to the *syn* position as this is its position in the starting material [17] and there is no evidence for the *anti* isomer in any of these complexes. The resonances of positions 2, 3, 4 and 5 have been assigned by comparison with both the starting material and the corresponding 2-methylallyl complexes. As the allyl group has been shown to be capable of rotation which would interchange the *cis* and *trans* isomers, it is apparent that the presence of these isomers is thermodynamically rather than kinetically controlled. Hence in the case of the methyl Schiff base the equilibrium lies virtually entirely on the side of isomer I, while with the aryl Schiff bases appreciable quantities of isomer II are present in the equilibrium mixture. The spectra of 4-methoxy-2-methyl-2-butenylPdSal=N—R (R = C_6H_5, *p*-$C_6H_4CH_3$) in deuterochloroform show a larger

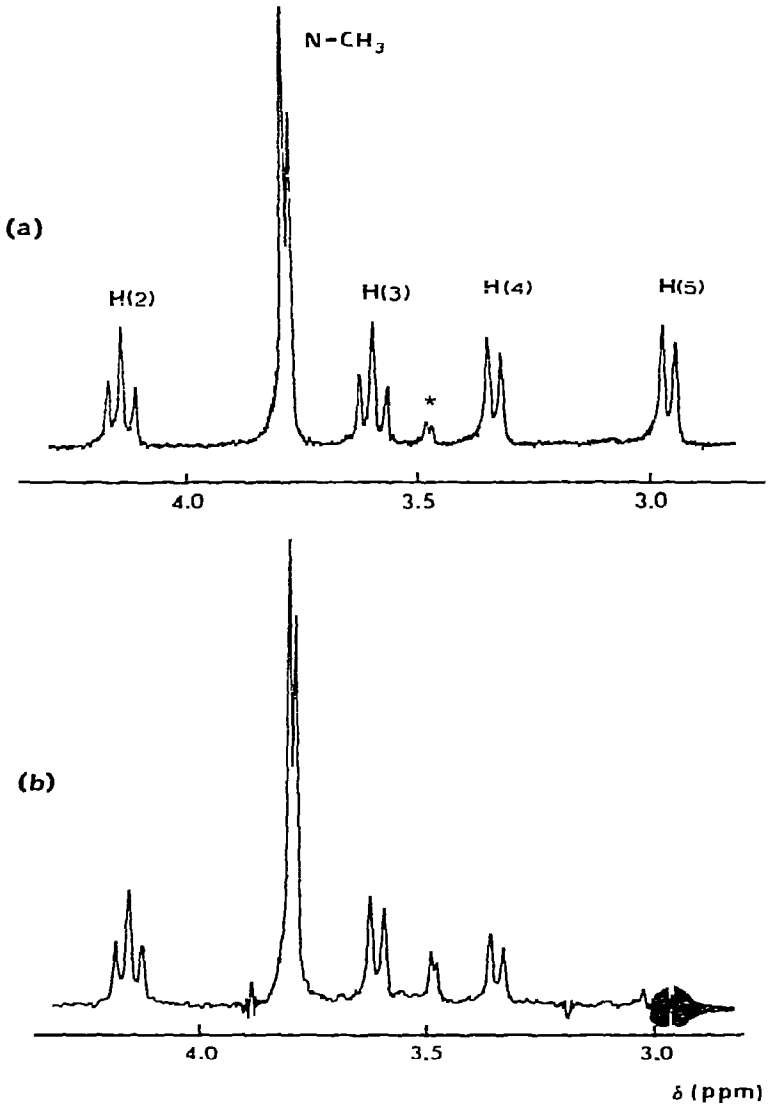

Fig. 4. ^{1}H NMR spectrum in allylic region of 2-chloroallylPdSal=N—CH_3 (in $CDCl_3$). (a) undecoupled (b) irradiated at H(5). Peak marked by * is due to Pd(Sal=N—CH_3)$_2$ formed by decomposition.

proportion of isomer II. Lowering the temperature of these solutions also increases the proportion of isomer II, which confirms the presence of an equilibrium mixture. The solvent also has an appreciable effect on the chemical shift, and the temperature may also produce small variations. Thus isomer I of the *p*-tolyl complex at 306 K shows both H(3) and H(5) at δ 2.43 ppm in CCl_4 and δ 2.55 ppm in $CDCl_3$, while at 253 K the two protons are separated to give two peaks at δ 2.44 and 2.48 (CCl_4) and δ 2.58 and 2.62 ($CDCl_3$) ppm.

Whether the greater directing effect of *N*-methylsalicylaldimine is due to electronic or steric factors cannot be definitely decided. Certainly the nitrogen donors of *N*-alkylsalicylaldimines have been shown to have a greater *trans*

influence than their aryl analogues in dimethylplatinum(IV) complexes [18, 19], and this greatly increases the difference in *trans* influence of the oxygen and nitrogen donors. On the other hand the fact that the major isomer (and for the methyl Schiff base the only isomer) is that with the substituents *trans* to the imine grouping suggests that steric effects may be involved. If the benzene ring of an *N*-arylsalicylaldimine is oriented parallel to the allyl group (as suggested by its shielding effect on H(3)) it would offer less steric repulsion than a methyl group.

The binuclear complexes containing bridging Salen have different symmetry properties and hence different NMR spectra. An X-ray determination of the structure of (2-methylallylPd)$_2$Salen [20] has shown that in the solid state the two allyl groups are fully equivalent, the molecule having a centre of symmetry bisecting the carbon—carbon bond of the ethylene bridge. The structure is shown in Fig. 5. In solution one would expect the molecule to have the same mean configuration with the allyl groups equivalent. However the chiral group (2-methylallylPdSal=N—CH_2—CH_2—) now attached to the nitrogen of the chelate ring means that when the π-allyl group is rotated through 180° around the palladium allyl axis, the resulting configuration is no longer related to the original structure by a mirror plane as drawn in Fig. 2a, but the two are now diastereomers and will be expected to have different NMR spectra. The synthesis from optically inactive starting materials means that both isomers will be present in the product, and furthermore rotation of the allyl group as in the mononuclear complexes will interchange the two in solution. That such a rotation is in fact occurring here at the temperature of the spectra (306 K) has been confirmed by spin saturation transfer in (2-methylallylPd)$_2$Salen.

The ^{1}H NMR spectra of the binuclear complexes are summarized in Table 3. The spectrum of (2-methylallylPd)$_2$Salen shows two resonances for H(3) and H(5) due to the existence of diastereomers corresponding to the two isomers indicated in Fig. 2a. These two protons are the closest allylic protons to the chiral substituent on the nitrogen and hence expected to be the most strongly affected.

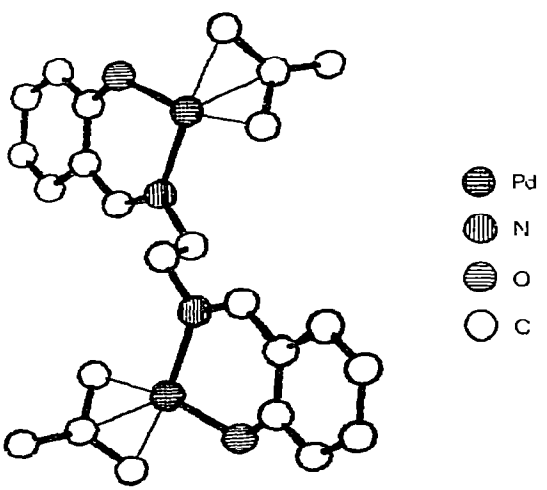

Fig. 5. X-ray structure of (2-methylallylPd)$_2$Salen.

TABLE 3

^{1}H NMR SPECTRA OF THE BINUCLEAR SALEN COMPLEXES [a]

Complex	δ values [b]									Coupling constants (Hz)				
	CH=N	Aromatic	H(1)	H(2)	H(3)	H(4)	H(5)	Other [c]		J_{12}	J_{13}	J_{14}	J_{15}	J_{23}
(2-Methylallyl)Pd)$_2$-Salen	7.83	6.28–7.29		3.77 d	3.05 d 3.07 d Δδ = 0.024	2.98 2.99 Δδ = 0.012	2.63 2.66 Δδ = 0.034	CH_3(1) N–CH_2	2.14 4.09					2.3
(Allyl)Pd)$_2$Salen	7.87	6.32–7.31	5.58 m	3.95 q	3.25 q	3.13 d 3.11 d Δδ = 0.016	2.68 d			6.8	6.9	12.6	11.8	2.0
(4-Methoxy-2-methyl-2-butenyl)Pd)$_2$-Salen	7.79	6.26–7.28			3.04 3.09 Δδ = 0.047	m [d]	2.58 2.63 Δδ = 0.047	CH_3(1) O–CH_3 O–CH_2 N–CH_2	2.12 3.43 m [d] 4.07					

[a] At 100 MHz in $CDCl_3$ at 306 K. [b] Ppm downfield from internal TMS; d = doublet, q = quadruplet, m = higher multiplet; other peaks are singlets; Δδ values are differences in δ of the given proton for the two diastereomers. Where only one δ value is given the diastereomers are not distinguishable. [c] CH_3(1) is that substituting H(1) of Fig. 1. [d] The non-equivalent O–CH_2 protons and H(4) give a complex multiplet.

For H(4) the chemical shift difference is very small and the peaks can only be resolved when broadening due to the small geminal coupling is removed by irradiation of H(2). The other protons, including the other allylic proton H(2), show only a single resonance and hence their environments must be very similar in the two isomers. Surprisingly (allylPd)$_2$Salen does not show separated resonances for H(3) and H(5), the only evidence for the two isomers being a poorly resolved splitting of H(4) giving a chemical shift difference of approx. 0.016 ppm. (4-Methoxy-2-methyl-2-butenylPd)$_2$Salen, which exists in the form with the methoxymethyl group *trans* to the nitrogen donor (Fig. 3, isomer I), shows two well separated resonances for H(3) and H(4), the only allylic protons whose signals can be seen clearly. The diastereomers of this latter compound are not being interconverted in solution by rotation of the allyl group, as this could also interchange *cis* and *trans* isomers and is hence not occurring, but are initially formed in equal amounts by the synthesis from optically inactive materials.

Salicylaldehyde complexes. The ^{1}H NMR spectra of 2-methylallylPdSal and allylPdSal have been measured in several solvents and the data are summarized in Table 4. At ambient temperature (306 K) both compounds show only single resonances (doublets due to coupling with H(1) in the allyl compound) for both the *syn* protons and the *anti* protons. This unexpected result could be explained by either chemical shift equivalence of both *syn* and both *anti* protons, or by a rapid end-to-end exchange of the allyl group at these temperatures. In $CDCl_3$ at 223 K the *anti* resonance separates into two peaks whereas the *syn* resonance is unchanged, so that if the two *anti* peaks are due to a slowing of exchange it is necessary to still postulate accidental chemical shift equivalence for the *syn* protons. At intermediate temperatures (such as 273 K) the spectrum is similar to the low temperature case, but the separation of the *anti* doublet is reduced. There is no real appearance of line broadening as expected for intermediate rates of exchange. In chlorobenzene, lowering the temperature to 253 K, produces no splitting of signals, merely some chemical shift change. Hence it is necessary to postulate either a vastly different rate of exchange or chemical shift equivalence. Although the evidence cannot be considered conclusive, it does appear that the most likely explanation of the ambient temperature spectra is chemical shift equivalence of the two ends of the allyl group, and that the splitting of the *anti* resonance at low temperature in $CDCl_3$ is due to different temperature effects on the chemical shifts of the two *anti* protons. Such a conclusion is nevertheless somewhat surprising, as the two oxygen donors of the salicylaldato anion show differing *trans* influences on methyl groups [19] although the chemical shift differences are not as pronounced as for Schiff bases.

Rates of exchange

Rate constants for the end-to-end exchange of the allyl group have been estimated from ^{1}H NMR studies for several of the compounds. Initial estimates of the rates were obtained from spin saturation transfer experiments involving the two *anti* protons in 2-methylallylPdSal=N—R (R = CH_3, C_6H_5) which give singlet peaks. (These will be referred to as sites A and B). The original method developed by Forsén and Hoffman [13] of observing the decay of signal A on saturation of signal B and recovery after removal of the saturating field was not found suitable due to very rapid decay and recovery, and very small *anti—anti* couplings which

TABLE 4

^1H NMR SPECTRA OF THE SALICYLALDEHYDE COMPLEXES [a]

Complex		δ Values and coupling constants					
		CH=O	Aromatic	H(1)	*syn*	*anti*	CH_3
2-MethylallylPdSal							
CCl_4	306 K	9.10	6.26–7.31		3.62	2.79	2.21
$CDCl_3$	313 K				3.74	2.83	
$CDCl_3$	223 K				3.81	2.86	
						2.90	
C_6H_5Cl	306 K				3.43	2.50	
AllylPdSal							
CCl_4	306 K	9.11	6.26–7.32	5.52 m	3.85 d	2.88 d	
					J_1 6.8	J_1 12.2	
$CDCl_3$	313 K			5.60 m	3.94 d	2.95 d	
					J_1 6.9	J_1 12.0	
$CDCl_3$	223 K			5.67 m	4.03 d	3.06 d	
					J_1 6.3	J_1 12.2	
						3.00 d	
						J_1 12.0	
C_6H_5Cl	306 K			5.05 m	3.54 d	2.52 d	
					J_1 6.5	J_1 11.9	

[a] Measured at 100 MHz; δ values in ppm downfield from internal TMS; d = doublet, m = higher multiplet, other peaks singlets; J_1 refers to coupling with H(1) (in Hz).

ıffected the height of peak A when site B was saturated and hence decoupled. This latter effect made signal height unsatisfactory as a measure of the magnetization. An alternative approach [21] was therefore used which employs the same equations but measures the ratio of the steady state integrated intensities of signal A with and without saturation of B, and determines the longitudinal relaxation time T_{1A} separately. The limitations of the instrumentation, particularly the difficulty of obtaining better than a rough estimate of T_1, prevented us from obtaining results which could be considered as more than similarly crude estimates of the rates of exchange. For 1 *M* solutions of the compounds in $CDCl_3$ at 306 K rate constants ($1/\tau$, where τ is the lifetime of the site) for the exchange were 0.43 s^{-1} (R = CH_3) and 0.99 s^{-1} (R = C_6H_5). These lead to values for the free energy of activation $\Delta G^{o\ddagger}$ of 75 and 77 kJ respectively. The difference between these may appear insignificant in view of the errors involved, but the difference is most clearly seen in the measured rate, where a factor of two is probably significant.

Comparison of the ^1H NMR spectra in 1,1,2,2-tetrachloroethane at temperatures near coalescence with theoretical spectra was used to obtain more accurate values. It can be qualitatively noted that the 2-methylallylPdSal=N—C_6H_5 spectrum coalesces at a lower temperature than that of 2-methylallylPdSal=N—CH_3 and allylPdSal=N—CH_3, while the spectrum of 2-chloroallylPdSal=N—CH_3 coalesces at a much lower temperature than any of the above.

Least-squares fitting of the calculated spectra with iteration of the rate gave results shown in Table 5 for 0.5 *M* solutions in 1,1,2,2-tetrachloroethane. It should be noted that the free energy values are relatively insensitive to errors in the rate determination, e.g. a three fold error in the rate produces a 5% error in $\Delta G^{o\ddagger}$ for values of the order of magnitude found here.

From these results it is apparent that there is little significant effect from replacing a 2-methylallyl group with an allyl group, but that a 2-chloroallyl group produces a much lower barrier to exchange, and replacing *N*-methylsalicylaldimine with its phenyl analogue also decreases the free energy of activation.

It should be noted that the "rate of exchange" measured here (the reciprocal of the lifetime of one of the sites) has the dimensions of $time^{-1}$ and is equal to the true rate (in terms of concentration) divided by the concentration, so is actually a first order rate constant. Where the reaction is not monomolecular and hence not first order, this will no longer be a true constant but will depend on concentration. In the case of a bimolecular reaction it will be equal to the second order rate constant times the concentration of the second molecule involved; where two molecules of the same compound are involved the measured

TABLE 5

KINETIC DATA FOR EXCHANGE FROM LINESHAPE ANALYSIS

Complex	Rate constant (s^{-1})	Temperature (K)	$\Delta G^{o\ddagger}$ (kJ)
2-MethylallylPdSal=N—C_6H_5	54.6	364	77.7
2-MethylallylPdSal=N—CH_3	48.4	385	82.7
AllylPdSal=N—CH_3	39.0	383	82.9
2-ChloroallylPdSal=N—CH_3	33.8	338	73.3

"rate constant" will therefore be directly proportional to the concentration of this species. The spectra of the compounds studied here do indicate some incre of rate with concentration, suggesting a bimolecular mechanism, but not to the extent of direct proportionality so that a bimolecular mechanism cannot be the only means of exchange. Ban, Chan and Powell [3] have proposed a bimol cular mechanism for the pyridine or 2-picoline promoted *syn—syn* and *anti—anti* exchange in allylic palladium picolinate chelate complexes which actually involves an exchange of the coordination sites of the O—N donor ligand, and have suggested a similar mechanism for the exchange in the absence of added base which occurs at higher temperature, a second molecule of the complex act as the base to form the postulated intermediates. A similar mechanism here wo account for concentration dependence, but as this is less than that required for a bimolecular mechanism it appears that a monomolecular process also takes pl probably a simple rotation of the π-allyl group about its axis to palladium in the square planar complex. For such a monomolecular reaction the entropy of activation would be expected to be very small, making the free energy barrier effectively independent of temperature, while for a bimolecular mechanism the expected negative entropy of activation will cause the free energy of activation to increase with temperature. Hence the relative importance of the monomolecular process will increase in importance at higher temperature, helping to expla its appearance in these measurements while it is not observed at the lower temperature (213 K) used for the study of the pyridine promoted exchange. Furthe in the unpromoted case the rate for the bimolecular reaction at all temperatures will be much lower than when a base is added, so it may not achieve a completel dominant role even at low temperatures, where the immeasurably slow overall rate prevents information from being obtained.

The probable temperature dependence of $\Delta G^{o\ddagger}$, as some contribution from a bimolecular mechanism is apparent, does raise questions about the validity of comparing $\Delta G^{o\ddagger}$ values at different temperatures. Moreover, the value is no long a simple free energy barrier to rotation, but a quantity derived from a resultant rate constant, $k = k_1 + k_2$ [complex] (where k_1 and k_2 are the actual rate constants for the mono- and bi-molecular reactions respectively) which has contribu tions from two different paths of exchange.

Possibly the most reliable feature from which to deduce relative ease of exchange is the fact that comparable (within a range of ± 25%) rates are obtained at quite different temperatures which puts the order of decreasing ability to und go exchange as 2-chloroallylPdSal=N—CH_3 > 2-methylallylPdSal=N—C_6H_5 > 2-methylallylPdSal=N—CH_3 ~ allylPdSal=N—CH_3. This order is also suggested by qualitative observations of coalescence temperatures. The higher lability of the 2-chloroallyl group, which was also observed from qualitative observations of spin saturation transfer where measurements were all made at the same tempe ature, supports the proposal of a monomolecular mechanism involving rotation of the allyl group rather than an exchange of O and N donors which leads to exactly the same exchange phenomenon.

The discrepancy between the values of $\Delta G^{o\ddagger}$ obtained for the 2-methylallyl complexes by the two different methods is probably attributable in the main to three factors, viz. entropy considerations for the bimolecular route suggest that at higher temperatures the energy barrier will increase; the lower concentration

sed for the line shape measurements will also increase the apparent barrier for he bimolecular mechanism; and the large errors involved in the spin saturation ransfer experiments, particularly the T_1 measurements, place a large uncertainty n the values obtained by that method. A possible fourth contribution to the ifference in values is the different solvent, which may have an appreciable effect on the rate of exchange, particularly the bimolecular contribution.

Insertion reactions

Insertion of 1,3-dienes such as butadiene and isoprene into π-allylic palladium complexes has become well known [5, 22]. Attempts to react 2-methylallyl-PdSal=N—C_6H_5 with isoprene resulted only in recovery of the starting material, even with reaction periods of up to 21 days. Only in the case of 2-chloroallylPd-Sal=N—CH_3 could a product be obtained. Reaction with isoprene in benzene for 24 h gave a viscous yellow oil as well as some Pd(Sal=N—CH_3)$_2$. The oil could be purified by extracting the product with hexane and evaporating the solution. Although no parent ion can be observed in the mass spectrum, and the ^{1}H NMR spectrum is ambiguous, indicating a mixture of isomers, the infrared spectrum indicates the presence of a Schiff base and elementary analyses correspond to insertion of one molecule of isoprene. The greater reactivity of the 2-chloroallyl group parallels the observations for hexafluoroacetylacetonato complexes [5], and also the lability expressed by the NMR measurements described above.

It appears from these results that the Schiff base ligands considerably lower the reactivity of the allyl group towards insertion reactions. As the insertion reaction appears to occur via a σ-bonded intermediate [5] this suggests that such intermediates are less readily formed in the Schiff base complexes. The ^{1}H NMR spectrum of 2-chloroallylPdSal=N—Me in the presence of isoprene shows no collapse of the *syn* and *anti* resonances due to exchange in a σ-intermediate, as is observed where reaction is reasonably rapid [5].

Experimental

Starting metarials

The chloro-bridged π-allylic palladium dimers [17, 23, 24, 25] and the thallium(I) Schiff base compounds [26] were prepared by the literature methods.

Syntheses

(a) from thallium salts

(All)PdSal=N—R (All and R as shown in Table 1). [(All)PdCl]$_2$ dissolved in benzene was treated with the stoichiometric quantity of solid TlSal=N—R and after stirring for 1-2 h the solution was filtered from TlCl and evaporated. (The filtration often proved difficult necessitating the use of glass fibre papers or cellulose sterilizing filter pads.) Crystallization of the residue (usually an oil) from the solvent mixture specified in Table 1 gave the pure product. Yields ranged from 55 to 90%. 2,3-Dimethyl-2-butenylPdSal=N—C_6H_5 could not be crystallized and remained as an oil.

[(All)Pd]$_2$Salen (All = allyl, 2-methylallyl, 2,4-cycloocta-dienyl, 4-methoxy-2-methyl-2-butenyl). [(All)PdCl]$_2$ dissolved in dichloromethane was stirred with the stoichiometric quantity of Tl$_2$Salen for 2-3 h and after filtering, the solution

evaporated. Recrystallization from the solvents stated in Table 1 gave the prod Yields were from 80 to 90%. When recrystallized from dichloromethane/benzer (2-methylallylPd)$_2$Salen incorporated two molecules of benzene of crystallizati

(All)PdSal (All = allyl, 2-methylallyl). These were prepared as above from [(All)PdCl]$_2$ and TlSal in benzene. Recrystallization was from dichloromethan hexane and the products were stored at 263 K to slow decomposition. Yields were 86 and 73% respectively.

(b) from free HSal=N—R

AllylPdSal=N—R (R = CH_3, p-$C_6H_4CH_3$). (*i*) [AllylPdCl]$_2$ suspended in methanol was treated with a slight excess of HSal=N—R and the stoichiometric amount of KOH (as 10% aqueous solution). After stirring for approx. 1 h all solid had dissolved, water was then added and the solution partly evaporated un reduced pressure. The yellow oil was extracted with chloroform, the chloroform evaporated and the residue crystallized from dichloromethane/hexane. Yields were 72 and 78% respectively for the methyl and *p*-tolyl Schiff base complexes. Made in this manner the compounds darkened after a few days, presumably due to trace impurities.

(*ii*) [AllylPdCl]$_2$ and HSal=N—CH_3 in methanol were treated with excess methylamine and stirred for 1 h. Similar work up to the above reaction gave the same product, allylPdSal=N—CH_3, in 63% yield. The analogous reaction with HSal=N—*p*-$C_6H_4CH_3$ and *p*-toluidine gave only allylPdCl(*p*-toluidine).

(c) from the salicylaldehyde complex

2-MethylallylPdSal=N—R (R = CH_3, C_6H_5), allylPdSal=N—CH_3. (All)PdSal freshly prepared from [(All)PdCl]$_2$ and TlSal, was dissolved in methanol and treated with a small excess of methylamine (25—30% aqueous solution) or anilin as appropriate. After standing for approx. 1 h water was added and the mixture partly evaporated under reduced pressure. Extraction of the oil which separated with dichloromethane, evaporation of this solution and crystallization from dich methane/hexane or ether/hexane (as in Table 1) gave the product. Yields for the three compounds were 68, 64 and 43% respectively.

Insertion reactions

Reactions of benzene solutions of 2-methylallylPdSal=N—CH_3 with isopren at room temperature for 21 days, 2-methylallylPdSal=N—C_6H_5 with butadiene at room temperature for 22 h, and allylPdSal=N—C_6H_5 with isoprene at 343 K for 0.5 h (longer heating caused decomposition to metallic palladium) all resulte in recovery of the starting complex.

2-ChloroallylPdSal=N—CH_3 (200 mg, 0.63 mmole) dissolved in benzene (8 ml) was treated with isoprene (1 ml, 10 mmole) and allowed to stand for 24 h Evaporation gave a mixture of solid and oil. Extraction with a little carbon tetra-chloride left the solid as fine yellow needles which were identified as Pd(Sal=N—CH_3)$_2$. After evaporation of the carbon tetrachloride the yellow oil was further purified by dissolving in hexane, filtering and evaporating. The infrared spectrum indicated the presence of Schiff base by bands near 1500 and 1600 cm^{-1} and the ^1H NMR spectrum indicated a mixture of isomers. (Found: C, 50.05; H, 5.45; Cl, 9.4; N, 3.29; Pd, 27.7. $C_{16}H_{20}ClNOPd$ calcd.: C, 50.02; H, 5.25; Cl, 9.2; N, 3.65; Pd, 27.7%. This corresponds to one mole of isoprene inserted.)

Mass spectra

These were measured on a Hitachi—Perkin—Elmer RMU-6E instrument using an ion chamber temperature of 473 K and an electron energy of 70 eV.

NMR spectra and rates of exchange

NMR spectra were obtained at 100 MHz with a Varian HA-100 spectrometer. Quantitative spin saturation transfer experiments were performed by integrating the resonance under study alternately with and without saturation of the position with which exchange is occurring. Due to large variation in the measurements of the integrated intensity the average of a number of runs was used, values for the ratio of the two integrated intensities showing a spread of ± 15% from the average. T_1 measurements were made by saturating the site under study and observing the recovery after removal of the saturating RF field. Analysis of the recovery curve was made using the equations of Forsén and Hoffman [13] assuming that T_1 for the site with which exchange occurs is equal to that under study and that elapsed time is sufficiently large for the equation:

$\ln(M_o - M_z) = \text{constant} - t/T_1$ (M_o and M_z defined as in [13])

to provide a reasonable approximation. This latter assumption will produce considerable errors in the early part of the curve where $t < \tau$. The short relaxation time made measurement of the recovery by repeated scanning of the signal difficult and the gradients of the semi-log plots showed a spread of from half to twice the average values. Hence the values found should be considered only as a rough estimate of T_1, and therefore the rates calculated treated similarly.

The elevated temperature spectra for lineshape analysis were measured using 1,1,2,2-tetrachloroethane as solvent, reference and lock. The spectra were digitized by measuring signal height at 1 Hz intervals and theoretical spectra with the rate of exchange being iterated, finally in intervals of 0.1 s^{-1}, were fitted using least squares methods. In the case of allylPdSal=N—CH_3 it was necessary to estimate the curve between H(2) and H(3) by interpolation, due to the presence of the non-exchanging resonance of the *N*-methyl group in this region. For 2-methylallylPdSal=N—CH_3 the region downfield of the midway point between H(2) and H(3) was excluded from the comparison with the theoretical spectrum as the former was obscured by the *N*-methyl resonance, and for 2-chloroallylPdSal=N—CH_3 only the shape of the upfield H(5) resonance was used as H(3) was more complex and H(3) and H(4) were obscured by the *N*-methyl resonances of both the compound and Pd(Sal=N—CH_3)$_2$ formed by decomposition. The rate for this latter compound must therefore be considered as of lower reliability than the others. Theoretical spectra were calculated on a Burroughs 6700 computer using a program for a number of uncoupled exchanging protons based on the many-site program of Saunders [27], and a program for an exchanging (coupled) AB system of our own design using the equations given by Heidberg, Weil, Janusonis and Anderson [28]. Appropriate combinations of these two were used to synthesize the spectra. In the allyl complex the separate lines due to the essentially first order coupling with H(1) for each resonance were considered as independent sites. The H(5) resonance in 2-chloroallylPdSal=N—CH_3 which is a doublet due to geminal coupling was treated similarly.

Line frequencies and line widths for the zero exchange limit were taken at

306 K, as below this temperature line broadening due to increasing viscosity be apparent. Although it is known (from spin saturation transfer experiments) tha some exchange is taking place at this temperature, this does not appear to great affect the line width. Certainly the width at this temperature is the best estimat available.

A difficulty with the fitting procedure was that the resonance positions sh a slight temperature dependence and therefore the calculated spectra based on lower temperature line positions tended to be somewhat offset from the experimental spectra. While this produced relatively large standard deviations in signal intensity at the given frequencies for the best fit spectrum, plotting of the two spectra showed excellent agreement in shape and degree of coalescence, with th apparently poor "best fit" being due only to a small shift of the peaks.

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