Organometallic Conformational Equilibria. X. Steric Factors and Their Mechanistic Implications in π-Allyl(amine)chloropalladium(II) Complexes[1-3]

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Abstract: Steric factors and their accompanying kinetic and thermodynamic parameters have been determined for certain 1,2,3-h^3-allyl(amine)chloropalladium complexes in which the allyl moiety is disubstituted, using a combination of nmr techniques. General rules for the establishment of the stereochemistry of allyl complexes have been determined. Placement of a bulky substituent at the central carbon causes the predominance of an anti configuration at the terminal carbon for the other substituent, whereas for a nonbulky group only ~5% is found in an anti configuration. Interconversion of isomers and epimerization occurs through formation of a σ-bonded intermediate. All other previously postulated mechanisms have been eliminated. A 1–3-kcal/mol *increase* in free energy of activation per substituent at the σ-bonded carbon atom was noted. Implications of these results in rearrangements and reactions of π-allyl complexes are discussed.

Considerable attention has focused on π-allyl palladium complexes and their rearrangement mechanisms because they are the postulated intermediates for certain homogeneously catalyzed reactions. Coordination of a reactive organic moiety to the transition metal often allows a configuration to be assumed which leads to stereoselectivity in the reaction products. Presumably, studies of these allyl complexes will lead to a greater understanding of the factors which influence these stereoselective reactions. Recent investigations have shown that pmr spectroscopy is a facile diagnostic tool for the elucidation of the mechanisms by which different configurations of these complexes may interconvert.[4-6]

When the halogen bridge of bis[1,2,3-h^3-(1-acetyl-2-methallyl)chloropalladium(II)][7,8] is cleaved with an optically active amine and the complex crystallized only one of the possible diastereoisomers is isolated.[9] This complex, $[\alpha]^{-50}D \sim -500°$, rapidly loses most of its optical activity at room temperature. Our studies establish that the epimerization does indeed proceed through formation of a σ-bonded intermediate, *i.e.*, a π–σ equilibrium leads to the loss of optical activity as previously postulated, but they also reveal that a more complicated situation exists and that isomerization occurs concurrently with epimerization.

Studies which demonstrate the generality of a σ-bonded intermediate have been concluded in two separate systems. Kinetic data for the complex 1,2,3,-h^3-allyl[(*S*)-α-phenethylamine]chloropalladium showed that additional epimerization occurred through formation of a σ-bonded intermediate rather than by the flip mechanism as had been previously proposed.[10] Investigations of 1,2,3-h^3-(1,1-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium and 1,2,3-h^3-(1,3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium have shown what limitations are placed on the behavior of a σ-bonded intermediate by the placement of substituent groups.

Results and Discussion

The 1,2,3-h^3-(1-Acetyl-2-methallyl)chloropalladium Complexes. A 1,2-disubstituted-h^3-allyl moiety can exist in two isomeric configurations, both of which are chiral (see Figure 1). These are, in the case of the 1-acetyl-2-methallyl moiety, a syn configuration where the acetyl group is "cis" to the methyl group or an anti configuration where the acetyl group is "trans" to the methyl group.

Previous studies have shown that the syn configuration predominates in mono-1-substituted-π-allyl (*e.g.*, π-crotyl) systems;[11] however, both the syn and the anti isomer have been reported to exist in solutions of certain 1,2-disubstituted-π-allyl complexes.[12]

In order to discuss the rearrangement mechanisms of the acetyl complexes, it will first be necessary to establish the stereochemistry of the species observed in solution.

The Stereochemistry of the Complexes. At room temperature the pmr spectrum of the 1,2,3-h^3-(1-acetyl-2-methallyl)(pyridine)chloropalladium complex shows ten resonances (Figure 2B), indicating the presence of two isomers in solution. While cis–trans isomerism within the square plane of the palladium complex (*i.e.*, isomerism of the amine ligand with respect to the acetyl-

(1) Part IX: J. W. Faller and M. J. Mattina, *Inorg. Chem.*, in press.

(2) This research was supported in part by the Connecticut Research Commission and the Petroleum Research Fund, administered by the American Chemical Society. Grant No. GP-6938 of the National Science Foundation provided funds for the Varian HA-100 spectrometer which was used in portions of this work. We thank Matthey Bishop, Inc. for the loan of palladium.

(3) The nomenclature for these complexes has been revised in keeping with general rules set by the IUPAC; *i.e.*, the previously reported complex 1,2,3-h^3-(3-acetyl-2-methallyl)[(*S*)-α-phenethylamine]chloropalladium(II) is now termed 1,2,3-h^3-(1-acetyl-2-methallyl)[(*S*)-α-phenethylamine]chloropalladium(II). This revision was deemed necessary when a large number of substituent groups are on the allylic moiety.

(4) J. W. Faller, M. J. Incorvia, and M. E. Thomsen, *J. Amer. Chem. Soc.*, **91**, 518 (1969), and references therein.

(5) J. W. Faller and M. J. Incorvia, *J. Organometal. Chem.*, **19**, P13 (1969).

(6) J. W. Faller and M. E. Thomsen, *J. Amer. Chem. Soc.*, **91**, 6871 (1969).

(7) I. I. Moiseev, E. A. Feodorovskaya, and Ya. K. Syrkin, *Zh. Neorg. Khim.*, **4**, 2641 (1959); *Russ. J. Inorg. Chem.*, **4**, 1218 (1959).

(8) G. W. Parshall and G. Wilkinson, *Inorg. Chem.*, **1**, 896 (1962).

(9) P. Corradini, G. Maglio, A. Musco, and G. Paiaro, *Chem. Commun.*, 618 (1966).

(10) P. Ganis, G. Maglio, A. Musco, and A. L. Segre, *Inorg. Chim. Acta*, **3**, 266 (1969).

(11) F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, **6**, 179 (1967).

(12) R. Huttel and H. Schmid, *Chem. Ber.*, **101**, 252 (1968).

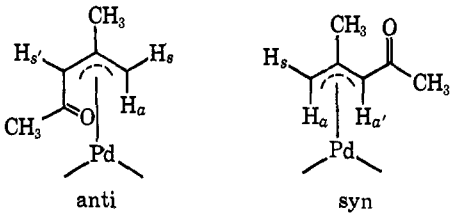


Figure 1. The two geometric isomers of a 1,2,3-h^3-(1-acetyl-2-methallyl) moiety.

substituted end of the π-allyl group) is possible and indeed has been observed in π-crotyl complexes,[1] we are not observing this phenomenon here. Amine ligand exchange in these complexes occurs rapidly even at temperatures well below room temperatures; hence, averaged spectra are observed and any effects due to cis–trans isomerism are thus "averaged out."[13] This suggests that the two isomers observed correspond to the *syn*- and *anti*-acetyl geometrical isomers shown in Figure 1. Integration of the resonances allowed the assignment of resonances 1, 2, 3, 7, and 10 to the major isomer in solution while resonances 4, 5, 6, 8, and 9 are assigned to the minor isomer (see Figure 2b). A tentative assignment of the resonances can be made on the basis of coupling among the protons in the allylic moiety. It has been found for most 1,2,3-h^3-allyl(amine)palladium halide complexes that the coupling between two syn protons is substantially greater than that between two anti protons or a syn and an anti proton.[1] This general property is also supported by the analysis of the AA'BB'X spectrum in 1,2,3-h^3-allyl[(*S*)-α-phenethylamine]chloropalladium(II) for which syn–syn coupling was found to be 2.05 Hz whereas all other syn–anti or anti–anti couplings were approximately 0.01 Hz.[10] Double-irradiation experiments showed that resonances 1 and 3 were coupled to each other ($J_{13} \cong 1.5$ Hz). Since this coupling is not observed for any of the resonances which are associated with the minor isomer, the presence of two syn protons is implied in the major isomer and the absence of two syn protons in the minor isomer. Consequently, the assignment of the anti geometrical configuration is made to the major isomer in solution.

This assignment is substantiated by comparison with model compounds. Bis[1,2,3-h^3-(1-ethoxycarbonyl-2-methallyl)chloropalladium(II)] has been reported to exist in solution as a mixture of syn and anti isomers with the ratio syn:anti of 65:35.[12] Cleavage of the chloride bridge with pyridine gave a derivative in which the ratio of isomers was 50:50 (see Figure 2C). The resonances of the ethoxycarbonylmethallyl complex correspond reasonably well to those of the acetylmethallyl complex. Resonances 1 and 3 are also coupled in this complex. Hence our assignment of the configurations of this particular complex is in agreement with that of Huttel and Schmid. Principally, however, this complex provides additional evidence of the generality of the relatively large magnitude of syn–syn coupling and a gauge of the reproducibility of chemical shifts between similar compounds.

Additional evidence for the assignment is put forward upon consideration of the 1,2,3-h^3-(1-acetylallyl)(pyridine)chloropalladium(II) complex. The room-temperature pmr spectrum indicated the presence of only one isomer in solution. It consisted of a low-field multiplet at δ 5.8, indicative of the central proton on the allylic moiety, a 7.5-Hz doublet at δ 3.79, an 11.0-Hz doublet at δ 3.57, a 12.5-Hz doublet at δ 2.32, and the acetylmethyl singlet at δ 2.29. It has been observed for a large number of allyl complexes that the coupling between the central proton and an anti proton is larger than that between a syn proton and the central proton; *i.e.*, J(anti–central) = 11–13 Hz whereas J(syn–central) = 6–8 Hz.[14] On the basis of the observed couplings one can assign the complex of syn configuration. The positions of the resonances of the 1-acetylallyl complex compare favorably with those of the minor species in the 1-acetyl-2-methallyl complex and, furthermore, the temperature dependence of the resonances (*vide infra*) exactly parallels those of the minor species of the 1-acetyl-2-methallyl complex. Additional shielding is expected for a proton adjacent to a carbonyl group; hence, the lower field anti proton (δ 3.57) is assigned to the proton adjacent to the *syn*-carbonyl group.

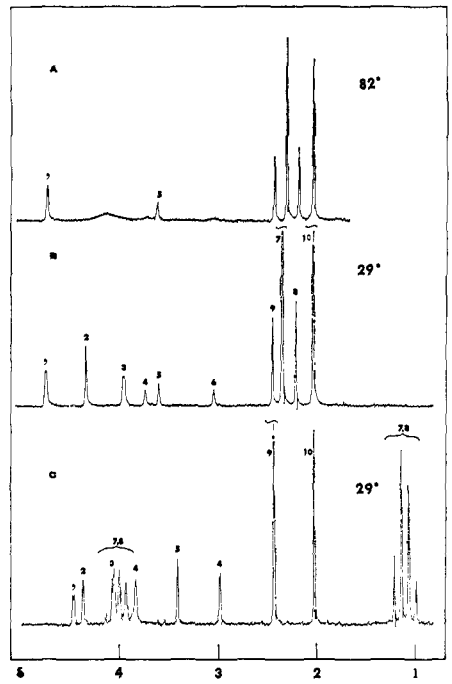


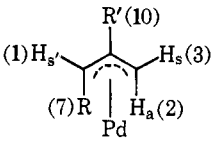
Figure 2. A. Pmr spectrum (100 MHz) of 1,2,3-h^3-(1-acetyl-2-methallyl)chloro(pyridine)palladium(II) in a 3:1 deuteriochloroform–benzene solution at 82°. B. Pmr spectrum (100 MHz) of 1,2,3-h^3-(1-acetyl-2-methallyl)chloro(pyridine)palladium(II) in a 3:1 deuteriochloroform–benzene solution at 29°. C. Pmr spectrum (100 MHz) of 1,2,3-h^3-(1-ethoxycarbonyl-2-methallyl)chloro(pyridine)palladium(II) in a 3:1 deuteriochloroform–benzene solution at 29°.

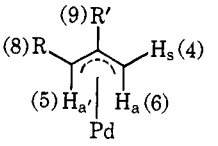
Comparison with the resonances of the model compounds just discussed allows the assignment of the proton resonances for the various amine derivatives of the 1-acetyl-2-methallyl moiety; see Table I. However, some ambiguity still arises concerning the assignments of the methyl groups, even though the acetylmethyl group might be expected to be at lower field owing to the deshielding of the carbonyl group. A

(13) This phenomenon will be considered later in this section in order to establish the configuration of the diastereoisomer obtained as the solid for the (*S*)-α-phenethylamine case.

(14) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, 3, 71 (1965).

Table I. Chemical Shifts of Allylpalladium Complexes





1-R-2-R′-Allyl(amine)chloropalladium(II)			Solvent ratio $CDCl_3$/ C_6H_6	Temp, °C	Anti isomer (1) $H_{s'}$	(2) H_a	(3) H_s	(7) H_R	(10) $H_{R'}$	Syn isomer (4) H_s	(5) $H_{s'}$	(6) H_a	(8) H_R	(9) $H_{R'}$
Amine	R	R′												
	(a) (b)							(a) ~3.96					(a) ~3.95	
Pyridine	$CO_2CH_2CH_3$	CH_3	3:1	29	4.46	4.37	4.07	(b) 1.12	2.02	3.83	3.41	2.98	(b) 1.12	2.44
Pyridine	$COCH_3$	H	3:1	29						3.79	3.57	2.82	2.29	5.81
Pyridine	$COCH_3$	CH_3	3:1	29	4.72	4.32	3.93	2.34	2.03	3.71	3.58	3.02	2.20	2.43
2-Picoline	$COCH_3$	CH_3	2:1	59	4.67	4.13	3.78	2.28	1.91	3.63	3.51	2.80	1.98	2.37
4-Picoline	$COCH_3$	CH_3	2:1	59	4.66	4.29	3.85	2.30	1.94	3.63	3.50	2.91	2.16	2.38
(*S*)-α-Phenethylamine	$COCH_3$	CH_3	3:1	29	4.48	3.76	3.46	2.25	1.57	3.32	3.28	2.47	2.21	2.12
						3.81	3.52		1.60			2.52	2.22	2.13

nuclear Overhauser effect was used to confirm the assignments. Under optimum conditions of relaxation times and when a site, A, is in close proximity to another site, B, irradiation of the resonance associated with A with a strong radiofrequency field will produce a change in the magnetization of the nuclei at site B. This change in magnetization is reflected in the intensity of the resonance associated with site B and directly related to the reciprocal of the cube of the distance between site A and site B. Hence, whichever nuclei are in closest proximity will show the greater nuclear Overhauser effect.

Intensity changes attributable to a nuclear Overhauser effect were observed in the pyridine derivative. When resonance 10, the higher field methyl resonance of the *anti*-acetyl isomer, was irradiated, the heights of both syn resonances, *i.e.*, 1 and 3, were affected (an intensity increase of ~25%), whereas the height of the anti proton resonance, 2, was only slightly affected (an intensity increase of ~3%). Since both syn protons were affected to approximately the same extent, the higher field methyl resonance (10) does indeed correspond to the methyl group attached directly to the 2 position of the π-allyl moiety.

When the lower field methyl resonance of the *anti*-acetyl isomer, resonance 7, was irradiated, resonance 1 was affected (an intensity increase of ~18%), while resonances 2 and 3 were barely affected (an intensity increase of <2%). Hence resonance 7 can be assigned to the methyl group on the acetyl portion. The magnitude of the observed effect might further imply that the acetyl group exists predominantly in a conformation such that the methyl group is essentially cis to the syn proton (note the conformation illustrated in Figure 1). Resonances 8 and 9 corresponding to the methyl groups of the *syn*-acetyl isomer could be assigned in a similar manner.

The overall assignment for the specific allylic resonances as shown in Figures 2 and 3 is given in Table I.

Rearrangement Mechanisms. Case 1. Epimerization and Isomerization through Formation of a σ-Bonded Intermediate. The nmr spectra of 1,2,3-h^3-(1-acetyl-2-methallyl)(pyridine)chloropalladium are temperature dependent. When the temperature was raised to +59°, resonances 2 and 3 and 4 and 6 began to broaden. At approximately 75° resonances 2 and 3 appeared to coalesce to a single broad peak. Clearly, by some mechanism the syn proton (H_s) and the anti proton (H_a) on both the *anti*-acetyl isomer and the *syn*-acetyl isomer were interconverting at a sufficient rate that an averaged resonance could be observed (see Figure 2a for the *anti*-acetyl isomer case). At much higher temperatures the samples decomposed to such a degree that reliable data were not obtainable. This fairly typical stumbling block can be circumvented by the use of spin-saturation experiments which effectively allow the labeling of a given proton position.[15] These experiments showed that resonance 1 ($H_{s'}$) and resonance 5 ($H_{a'}$), resonance 9 (CH_3-allyl) and resonance 10 (CH_3-allyl), and resonance 7 (CH_3-acetyl) and resonance 8 (CH_3-acetyl) were also interconverting, but at a somewhat slower rate than resonances 2 and 3 and 4 and 6. At a sufficiently high temperature (>85°) irradiation of the averaged resonance of resonances 2 and 3 showed that it was interconverting with the averaged resonance of resonances 4 and 6. Thus there are three separate and distinct processes which are occurring. The syn (H_s) and anti (H_a) protons on the *anti*-acetyl isomer are becoming equivalent, the syn (H_s) and anti (H_a) protons on the *syn*-acetyl isomer are becoming equivalent, and the *syn*-acetyl isomer is interconverting with the *anti*-acetyl isomer. Several mechanisms have been advanced to explain the observation of averaging of the syn and anti protons in various π-allyl complexes.

If an optically active amine such as (*S*)-α-phenethylamine is used, then a distinction can be made among all of the mechanisms which have been proposed through the utilization of the spin-saturation labeling technique. The formation of epimers by use of an optically active amine is reflected in small chemical shift differences for the resonances.

Thus the nmr spectrum at room temperature of 1,2,3-h^3-(1-acetyl-2-methallyl)[(*S*)-α-phenethylamine]chloropalladium consists of the same ten allylic resonances as the pyridine derivative except that each resonance has two components; see Figure 3. When a sample of 1,2,-3-h^3-(1-acetyl-2-methallyl)[(*S*)-α-phenethylamine]chloropalladium, the complex which exhibits the large optical activity at low temperature, was dissolved at −50°, the nmr spectrum showed five singlets whose positions

(15) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **89**, 760 (1967).

allowed their assignment as one of the epimers of the *anti*-acetyl isomer (see Figure 3).[16]

As the temperature was raised, five more resonances whose chemical shifts were very similar to those of the original epimer appeared. These are due to the appearance of the epimer of the complex found in the solid. When the temperature was raised still further, the resonances attributable to the *syn*-acetyl isomer appeared. Both epimers grew in simultaneously. As was the case with the pyridine derivative, the *anti*-acetyl isomer was always present to a greater degree than the *syn*-acetyl isomer.[17]

The temperature dependence of the (*S*)-α-phenethylamine derivative exactly parallels the temperature dependence of the pyridine derivative at high temperatures. Resonance 2 (H_a) and resonance 3 (H_s) and resonance 4 (H_s) and resonance 6 (H_a) begin to broaden above 50°. Each epimeric portion of resonances 1, 5, 7, 8, 9, and 10 also broadened. At 73° resonances 2 and 3 appeared to coalesce to a broad singlet, while the pairs of components of resonances 1, 7, and 10 had each coalesced to single resonances. Similar observations were made for resonances 4 and 6 as well for resonances 5, 8, and 9; *i.e.*, the epimers of the *syn*-acetyl isomer were interconverting as were the epimers of the *anti*-acetyl isomer. Spin-saturation labeling experiments showed that the averaged epimeric resonances 1 ($H_{s'}$) and 5 ($H_{a'}$) and resonances 9 (CH_3-allyl) and 10 (CH_3-allyl) were also exchanging, but at a somewhat slower rate. As was the case with the pyridine derivative, this third phase is due to the interconversion of the *syn*- and *anti*-acetyl isomers.

Each epimeric component of the various proton resonances can be labeled as possessing a (+) or a (−) absolute configuration.[4] If one assumes that the isomer in the solid is the (*S*)-*anti*-acetyl complex[18] then the syn (H_s) and anti (H_a) proton resonances which are present when the solid is dissolved at low temperature must be labeled with a (−) configuration. The adjacent epimeric components must therefore be labeled as being in a (+) configuration. At 44° saturation of the lower component of resonance 2, *i.e.*, the anti proton in the (−) configuration, caused a decrease in the intensity of the lower component of resonance 3, *i.e.*, the syn proton in the (+) configuration. Similarly, saturation of the higher component of resonance 2, *i.e.*, the anti proton in the (+) configuration, caused a decrease in the intensity of the higher component of resonance 3, *i.e.*, the syn proton in the (−) configuration (see Figure 3). Therefore, inversion of configuration occurs with the interconversion of the syn and anti protons. Because of this inversion of configuration the epimer of the complex isolated as the solid is initially formed.

(16) While the (*S*)-α-phenethylamine derivative crystallized as the *anti*-acetyl isomer the various substituted pyridine derivatives crystallized as either the *anti*-acetyl isomer, *i.e.*, the 4-picoline derivative, or the *syn*-acetyl isomer, *i.e.*, the 2-picoline derivative and the 2,6-lutidine derivative. These differences may be attributed to differences in packing forces in the crystal.

(17) The ratio of *anti*-acetyl isomer to *syn*-acetyl isomer is given for the series of amine derivatives as follows (derivative, anti/syn ratio): pyridine, 76/24; (*S*)-α-phenethylamine, 70/30; 2-picoline, 70/30; and 4-picoline, 75/25. It can thus be seen that a change of amine ligand does not substantially affect the ratio of *anti*-acetyl isomer to *syn*-acetyl isomer.

(18) The absolute configuration is irrelevant in this discussion of the pmr spectrum. If the opposite configuration were found in the solid, one could readily adapt the same discussion by considering the (*R*)-α-phenethylamine derivative rather than the (*S*)-α-phenethylamine derivative.

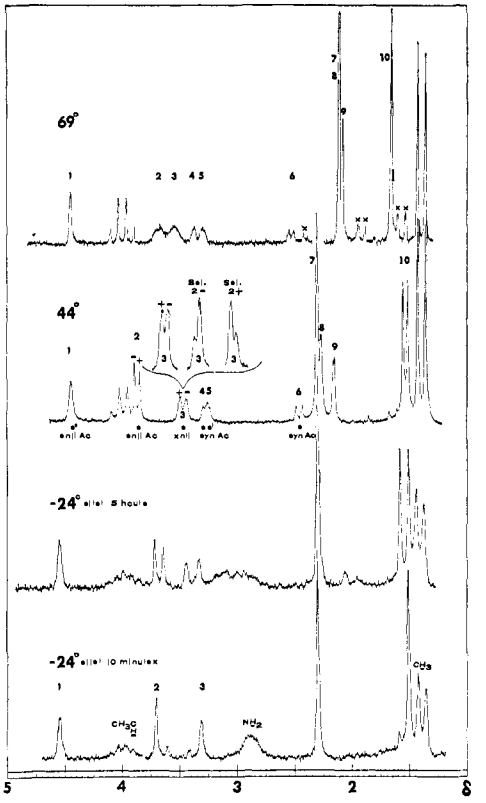


Figure 3. The 100-MHz pmr spectra of 1,2,3-h^3-(1-acetyl-2-methallyl)chloro[(*S*)-α-phenethylamine]palladium(II) in deuteriochloroform–benzene solution. The lower −24° spectrum was taken 10 min after the solid was added to a deuteriochloroform–benzene (5:1) solution at −50°. The 3:1 deuteriochloroform–benzene solution (44°) and the 5:1 solution (69°) were treated with D_2O to reduce the intensity of the amine proton resonances. The resonances marked with an × in the 69° spectrum are decomposition products. The insert in the 44° spectrum shows the effects on the components of **3** upon saturation of the component resonances of **2**.

Generally three types of mechanisms have been proposed to explain the observation of the interconversion of syn and anti protons: 1,3-h^2 flip, wherein the allylic moiety becomes coplanar with the metal atom;[19] an h^2-olefinic intermediate which allows free rotation of the uncoordinated end;[4] and a *monohapto* or σ-bonded intermediate.[4,9,20] Each of these mechanisms involves exchange of different proton sites (see Table II and Figure 4).

Table II. Site Interchanges Required by Different Mechanisms

(*S*)-*anti*-Ac $\overset{k_1}{\rightleftharpoons}$ (*R*)-*anti*-Ac

(*S*)-*syn*-Ac $\overset{k_2}{\rightleftharpoons}$ (*R*)-*syn*-Ac $\quad k_1 \gtrsim k_2 \gg k_3$

(*S*)-*anti*-Ac $\overset{k_3}{\rightleftharpoons}$ (*S*)-*syn*-Ac

(*R*)-*anti*-Ac $\overset{k_3}{\rightleftharpoons}$ (*R*)-*syn*-Ac

(*S*)-*anti*-Ac		1,3-h^2 flip	3-h σ allyl	1-h σ allyl	1,2-h^2 π olefin	2,3-h^2 π olefin
H_1	s′(*S*)	a′(R)	s′(R)	a′(*S*)	s′(*S*)	a′(*S*)
H_2	a(−)	s(+)	s(+)	a(+)	s(−)	a(−)
H_3	s(−)	a(+)	a(+)	s(+)	a(−)	s(−)
Me	Anti(*S*)	Syn(*S*)	Anti(*R*)	Syn(*S*)	Anti(*S*)	Syn(*R*)
Ac	Anti(*S*)	Syn(*S*)	Anti(*R*)	Syn(*S*)	Anti(*S*)	Anti(*R*)

(19) The planar-flip mechanism could occur either with or without interchange of syn and anti proton sites.[4,20]

(20) F. De Candia, G. Maglio, A. Musco, and G. Paiaro, *Inorg. Chim. Acta*, 2, 233 (1968).

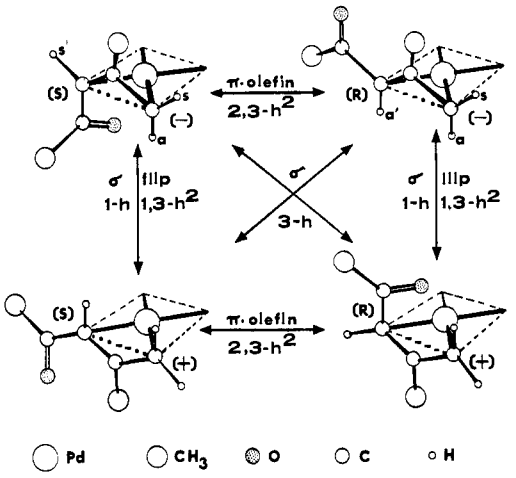


Figure 4. Modes of interconversion of the various diastereoisomers.

The 1,3-h^2-flip mechanism can be eliminated immediately, since simultaneous broadening of the syn (H_s) and anti (H_a) proton resonances and of the syn ($H_{s'}$) and anti ($H_{a'}$) resonances of the protons adjacent to the acetyl group was not observed.

The factor which differentiates between an end rotation, *i.e.*, formation of a 1,2-h^2 intermediate, and the postulated 3-h σ-bonded intermediate is the retention of configuration in the former and the inversion of configuration in the latter. The spin-saturation labeling data obtained showed that for 1,2,3-h^3-*anti*-(1-acetyl-2-methallyl)[(*S*)-α-phenethylamine]chloropalladium the interconversion of the syn (H_s) and anti (H_a) protons proceeded with inversion of configuration, *i.e.*, $H_s(+)$ to $H_a(-)$ or $H_s(-)$ to $H_a(+)$; thus the mechanism by which epimerization or racemization (in the case of the pyridine derivatives) occurs must be through formation of a 3-h σ-bonded intermediate. Similar observations on the *syn*-acetyl complex indicated that its epimerization or racemization also proceeded through the formation of a σ-bonded intermediate. Isomerization must therefore proceed through the formation of a 1-h σ-bonded intermediate.

Kinetic data for epimerization, racemization, and isomerization were obtained by two separate methods. Method I consisted of monitoring the rate at which either the epimer or isomer grew into the nmr spectrum. Method II employed the common technique of line broadening in the limit of slow exchange. Table III shows the data which were obtained for a few illustrative cases. It should be noted that the ΔF^* value obtained for the formation of the epimer of the *anti*-acetyl isomer found in the solid is in very good agreement with the data obtained using polarimetric methods.[21]

Table III. Kinetic Parameters for 1,2,3-h^3-(1-Acetyl-2-methallyl)(amine)chloropalladium Complexes

Isomer	Amine	*n*-h[a]	ΔF^*, kcal/mol	Temp, °C
Anti	(*S*)-α-Phenethylamine	3-h	18.5	53
		1-h	21.2[b]	12
Syn	(*S*)-α-Phenethylamine	3-h	18.8	55
Anti	2-Picoline	3-h	18.3	49
Syn	2-Picoline	3-h	18.6	52
Anti	4-Picoline	3-h	18.2	44
Syn	4-Picoline	3-h	18.3	55

[a] Denotes carbon atom at which the σ bond is formed. [b] For this case the rate constant was obtained by monitoring the rate at which the isomer appeared in the spectrum after dissolving the crystalline solid. In every other case the method of line broadening in the limit of slow exchange was used.

A comparison of the rates obtained for the various amine derivatives showed that the rate of syn (H_s) and anti (H_a) proton interconversion, *i.e.*, the formation of a 3-h σ-bonded intermediate, is virtually independent of the amine which is present as the ligand, nor is it dependent on the amount of free amine which is present in the sample. The reaction therefore is monomolecular.

Case 2. Cis–Trans Isomerism of the Amine Ligand. Cis–trans isomerism of the amine with respect to the 1 substituent on the allylic moiety would at no time have a bearing on the results for the interconversion of the epimers or of the *syn*- and *anti*-acetyl isomers; nevertheless, it was of interest to determine whether this phenomenon was present to a significant degree. The determination of the exact configuration of the diastereoisomer of the (*S*)-α-phenethylamine derivative found in the solid is important if one wishes to understand the driving force for the second-order asymmetric transformation which occurs in crystallization of the complex.

For the 1,2,3-h^3-(1-acetyl-2-methallyl)[(*S*)-α-phenethylamine]chloropalladium complex some broadening of the resonances was observed especially for the *syn*-acetyl isomer at lower temperatures, but at no time were resonances attributable to the presence of both *cis*- and *trans*-amine isomers observed. This implied that the (*S*)-α-phenethylamine derivative existed almost totally as one isomer. Further evidence for this observation concerned the behavior of the nmr spectra of 1,2,3-h^3-(1-acetyl-2-methallyl)[(*R*,*S*)-α-phenethylamine]chloropalladium as the temperature lowered. The single sharp resonances observed at room temperature had broadened and separated into their diastereoisomeric components, implying that amine exchange had been slowed down sufficiently that the chirality of the amine was no longer averaged. Since the amine exchange had been slowed down sufficiently, *cis–trans*-amine isomerism, if present, should have been observed, but the spectrum was identical with that observed for 1,2,3-h^3-(1-acetyl-2-methallyl)[(*S*)-α-phenethylamine]chloropalladium, implying that the complex exists in only one form.

No nuclear Overhauser effect could be observed upon irradiation of a sample of 1,2,3-h^3-(1-acetyl-2-methallyl)[(*S*)-α-phenethylamine]chloropalladium at both the amine protons and the methyl group associated with the amine. It thus cannot positively be concluded whether the 1,2,3-h^3-(1-acetyl-2-methallyl)[(*S*)-α-phenethylamine]chloropalladium exists in a *trans*-amine configuration or a *cis*-amine configuration.

Nevertheless, the behavior of certain substituted pyridine derivatives at low temperature implies that the (*S*)-α-phenethylamine derivative probably exists in a *trans*-amine configuration. *cis–trans*-amine isomerism has been observed for the 1,2,3-h^3-crotyl(2-picoline)-chloropalladium complex.[1] In that case the observa-

(21) The reported value obtained by polarimetric means for the free energy of activation was 18.6 ± 1.3 kcal/mol.[20]

tion at very low temperatures of three methyl-crotyl resonances led to the conclusion that there was hindered rotation about the metal–nitrogen bond for the *cis*-amine isomer. The isomers arising from the sterically hindered rotation were designated as endo and exo isomers.[22] Thus the identification of a *cis*-amine isomer from a *trans*-amine isomer is easily accomplished by observing which component of the original resonance is further split upon lowering the temperature.

At 59° the nmr spectrum of 1,2,3-h^3-(1-acetyl-2-methallyl)(2-picoline)chloropalladium is completely analogous to that of the 1,2,3-h^3-(1-acetyl-2-methallyl)-(pyridine)chloropalladium complex except for the additional methyl resonance at δ 2.62 due to the *o*-methyl substituent on the amine. This discussion will focus on the methyl region, since the behavior of the resonances in this region as the temperature was varied has most clearly shown which isomers were present and to what degree. At 29° resonance 7 (*anti*-CH_3-acetyl) had broadened and resonance 8 (*syn*-CH_3-acetyl) had become so broad that its position was not readily observed. Resonances 9 (*syn*-CH_3-allyl) and 10 (*anti*-CH_3-allyl) remained sharp. At −20° resonances 7 (*anti*-CH_3-acetyl) and 8 (*syn*-CH_3-acetyl) had each separated into two components. A shoulder had developed on resonance 10 (*anti*-CH_3-allyl) (see Figure 5). The identification of the components was made on the basis of spin-saturation labeling effects. Clearly amine exchange had been slowed down sufficiently that the individual resonances due to *cis*-amine isomer and the *trans*-amine isomer were observed. For the *syn*-acetyl isomer both forms were present in approximately equal amount, while for the *anti*-acetyl isomer the equilibrium was shifted overwhelmingly toward one form.

The upfield component of resonance 8 (*syn*-CH_3-acetyl), *i.e.*, resonance 8″ at δ 1.49, began to broaden at −55°. As the temperature was lowered still further it resolved into two components of approximately equal intensity (Figure 5). This implied that the temperature had been lowered sufficiently that the rate of rotation about the metal–nitrogen bond for the *cis*-amine isomer was slow enough that the resonances due to the presence of *exo*- and *endo*-picoline isomers were observable on the nmr time scale. No such observation was made for resonance 8′, the downfield component of resonance 8 (*syn*-CH_3-acetyl). Resonance 8′ must be due to the *trans*-amine isomer.

On the basis of chemical shifts it seems reasonable to assign resonance 7″ to the *cis*-amine isomer, although the separation of resonance 7″ into two components was not observed even though the temperature was lowered further (to −95°). This may imply that the *cis*-amine isomer of the *anti*-acetyl isomer exists predominantly as only one of the *exo*- and *endo*-picoline isomers or that there is a lower barrier for rotation in the *anti*-acetyl isomer. Nevertheless it is safe to conclude that the 1,2,3-h^3-(*anti*-1-acetyl-2-methallyl)(2-picoline)-chloropalladium complex exists mainly as the *trans*-amine isomer.

(22) The atoms Pd–C–C–Cl–N are depicted as forming a square plane. In the cis configuration the amine is located along the same edge of the square as carbon 1, the terminally substituted carbon of the allyl moiety; in the trans configuration the amine is located across the diagonal from the substituted carbon. In the endo isomeric form the *o*-methyl substituent of the pyridine is located on the same side of the square plane as the central carbon atom of the allyl; in the exo form the *o*-methyl is on the opposite side of the plane as the central carbon atom.

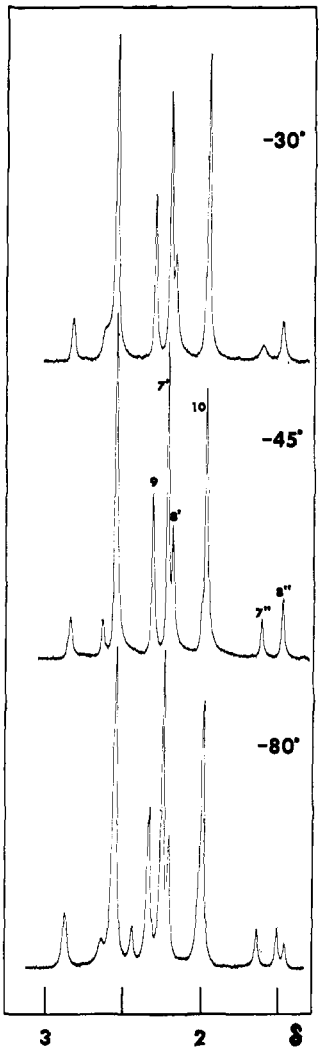


Figure 5. The effect of *cis–trans*-amine isomerism on the methyl region of the 100-MHz pmr spectra of 1,2,3-h^3-(1-acetyl-2-methallyl)-(2-picoline)chloropalladium(II) in dichlorofluoromethane as the temperature was lowered. The resonances between δ 2.5 and 3.0 are assigned to the methyl group on the 2-picoline.

1,2,3-h^3-(1-Acetyl-2-methallyl)(4-picoline)chloropalladium also exhibited *cis–trans*-amine isomerism. Since no *exo*- and *endo*-picoline isomers are possible in this case the assignment of the resonances was made on the basis of comparison of chemical shifts with the 2-picoline derivative. It was found for the 4-picoline derivative that both the *anti*-acetyl isomer and the *syn*-acetyl isomer exist mainly as the *trans*-amine isomer.

The observation that both the 2-picoline derivative and the 4-picoline derivative of the *anti*-acetyl isomer exist predominantly as the *trans*-amine isomer implies that the (*S*)-α-phenethylamine derivative would also exhibit similar behavior.

Considerations of Mechanisms Other Than σ-Bonded Intermediate Formation. The nmr spectrum of the 1,2,3-h^3-allyl[(*S*)-α-phenethylamine]chloropalladium complex at 35° corresponds to rapid epimerization by amine exchange which preserves the chirality of the terminal carbon atoms.[4] Recently a proposal has been advanced that the broadening observed above 35° due to the averaging of the chirality at the terminal carbon atoms may be attributed to a planar flip of the allylic ligand without *syn–anti* proton exchange.[10] Through

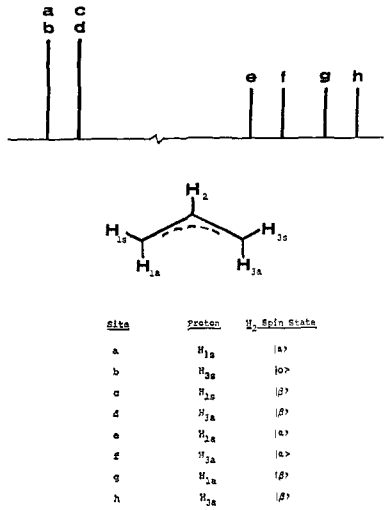


Figure 6. A schematic diagram of the resonances observed in the pmr spectrum of the syn and anti proton region of h^3-allylchloro-[(*S*)-α-phenethylamine)palladium (II) in chloroform at 30°.

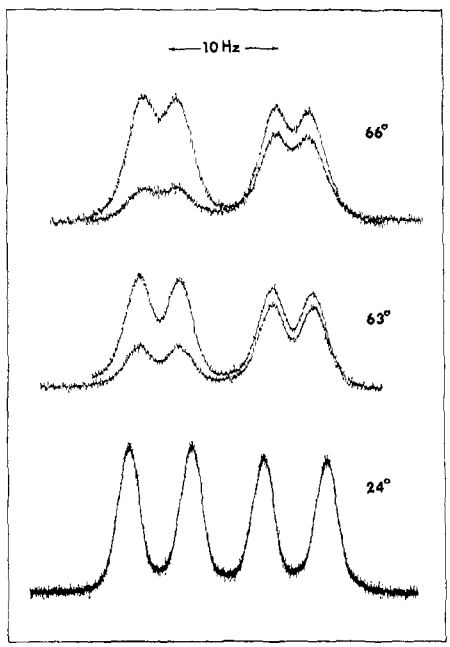


Figure 7. The temperature dependence of the anti proton resonances (e, f, g, and h) of h^3-allylchloro[(*S*)-α-phenethylamine]palladium(II) in benzene at 100 MHz. The lower traces in the 63 and 66° spectra illustrate the effect of spin saturation transfer upon irradiation of the syn resonances, a and b. The partial saturation of g and h arises principally from the inability of completely saturating a and b without some inadvertent saturation of c and d.

spin-saturation transfer experiments and line-shape analysis it has been possible to show that all spectral changes above 35° can be attributed to a π–σ equilibrium and that the planar flip mechanism is inadequate for explaining the experimental results.

The syn and anti proton region of the spectrum at 35° is indicated in Figure 6. Each component of a syn or anti doublet corresponds to a different spin state of the central allylic proton. If each of these components is separately labeled, the system may be treated formally as eight singlets with equal intensity. Since the chemically nonequivalent syn doublets are superimposed, only six resonances are observed with the intensity ratio 2:2:1:1:1:1.

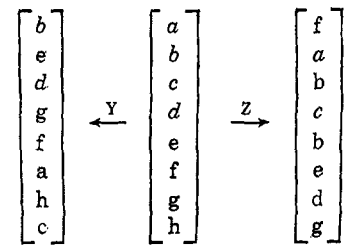


Figure 8. Site exchanges required by a σ-bonded intermediate.

Ganis, *et al.*,[10] report the observation that at 60 MHz as the temperature was raised e and f coalesced as did q and h, but the syn doublet remained unchanged. They proposed a flip mechanism which effectively averages the chirality at the terminal allyl carbon atoms but does not exchange syn and anti protons. Since the syn doublets corresponding to the (+) and (−) chirality of the terminal allylic carbon atoms are superimposed ($\delta\pm \cong 0$), the proposed mechanism should produce no changes in this region. On the other hand, there is a difference in chemical shift for the anti doublets ($\delta\pm$ = 0.049) ppm in benzene at 37°); thus, an allylic flip would lead to coalescence of these four resonances into a single doublet. As shown in Figure 7 one does observe broadening of these resonances above 40° at 100 MHz in benzene (coalescence occurs at ~76° at 100 MHz). Although the flip mechanism represented a logical postulate on the basis of the data that were in the hands of Ganis, *et al.*, at that time, we have shown to be erroneous the conclusion that these data require the intermediacy of a flip mechanism. Our studies have shown that the proposal of a flip mechanism is unnecessary and the rate of interconversion *via* the path involving a flip mechanism (if it exists) must be insignificant compared with the π–σ interconversion rate.

The site exchanges for a racemization pathway proceeding through a π–σ–π-allyl sequence is given in Figure 8. In this scheme, Z designates the pathway in which C_1 remains attached to the palladium atom *via* a σ bond and Y designates the pathway in which C_3 is σ bonded to palladium. It should be noted that since $\delta\pm \cong 0$ for the syn doublets, site a is equivalent to site b, and c is equivalent to d. Furthermore, J_{syn} and J_{anti} have the same sign, and only those site exchanges for which the spin state of the central carbon atom is preserved are permitted.[23] It is apparent from this scheme that for every site exchange of the syn protons accompanied by a chemical shift change, there are two such chemical shift changes of the anti protons. In other words, the lifetime of the syn protons is effectively twice as long as the lifetime of a proton in the anti site. Since in the slow-exchange limit the resonance peak width is inversely proportional to the lifetime of a proton in a given site, it follows that involvement of a σ-bonded allylic intermediate requires the anti resonances to broaden at twice the rate of the syn resonances. Hence, variations in the peak width resulting from a π–σ–π sequence should be considerably more noticeable in the

(23) Completely averaged spectra of allyl complexes invariably show an averaged coupling between the central proton and the terminal protons of approximately 10 Hz, which requires that J_{syn} and J_{anti} have the same sign. We assume that the signs are positive, as suggested by the coupling in substituted ethylenes.[24]

(24) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Elmsford, N. Y., 1966, p 681.

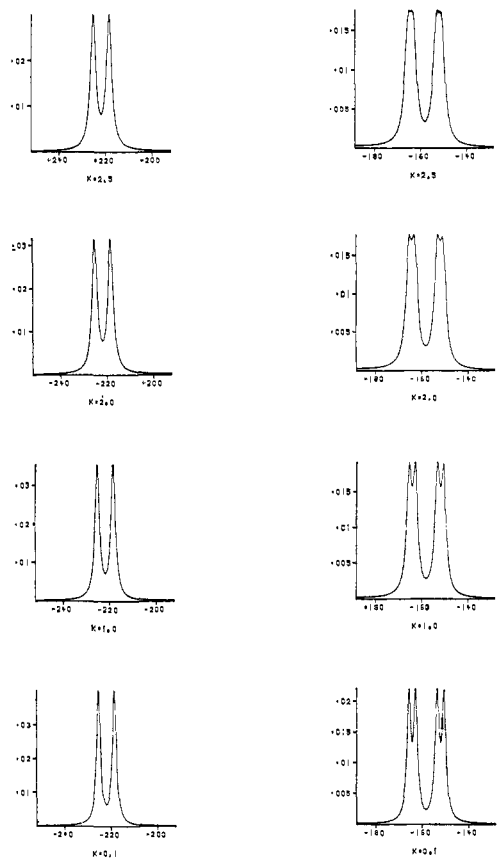


Figure 9. Calculated pmr spectra of the syn (left) and anti (right) region as a function of rate for h^3-allylchloro[(*S*)-α-phenethylamine]palladium(II) assuming the chemical shifts observed at 30° in chloroform at 60 MHz. The rate constant given is that for syn–anti exchange, k_{sa}.

anti resonances than in the syn resonances of the spectrum for the optically active complex. Figure 9 shows the computed nmr line shapes as a function of rate for interchange *via* a π–σ–π mechanism. The computation of the line shapes as a function of temperature is complicated by variations in chemical shifts,[25] but the general features of the spectra are illustrative of those expected on raising the temperature.[26] Of particular significance is the observation that the coalescence of the anti doublets to a single doublet occurs before appreciable broadening of the syn resonances. Assuming a π–σ process and using the chemical shifts appropriate to 69° (the coalescence temperature reported in chloroform[10]), a broadening of only about 1.0 Hz in the syn resonances would be expected at the coalescence of the anti doublets. As a result of these calculations, considerable doubt is cast upon the interpretation of the coalescence of the anti doublets in the "absence" of broadening of the syn doublets, as reported by Ganis, *et al.*[10]

(25) The chemical shift separation of the anti doublets was essentially a linear function of temperature in both chloroform-*d* and benzene. Some representative values for the chemical shift separation (100 MHz) in benzene as a function of temperature are (Hz) 5.5 (26°), 5.2 (31)°, 4.9 (37°), 4.5 (45°), and extrapolated to ~3.5 (63°), ~3.4 (66°), and ~3.2 (68°). The separations are about 0.5–1.0 Hz smaller in $CHCl_3$. The complication of chemical shift variations can be treated by computing the line shapes using the chemical shifts appropriate for each temperature.

(26) Since the rate constant necessary for coalescence is proportional to $\delta\pm$, the coalescence of the diastereotopic anti proton resonances occurs at a lower temperature and a slower rate than indicated in Figure 9 because $\delta\pm$ decreases with increasing temperature.

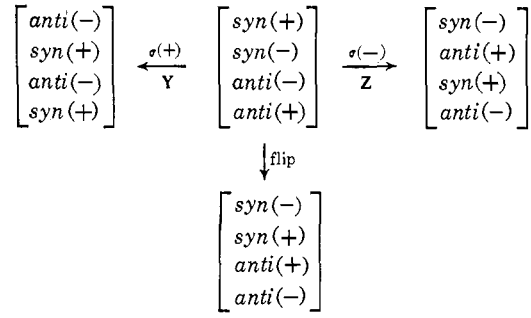


Figure 10. Site exchanges required by different mechanisms. σ-Bond formation at a terminal carbon with a (+) or (−) configuration is indicated by σ(+) or σ(−), respectively. The flip mechanism indicated is that in which no syn–anti exchange occurs.

Any significant involvement of a flip mechanism would imply that no syn–anti exchange should occur at a rate comparable to the (+)-anti to (−)-anti exchange by the flip. Spin-saturation transfer experiments, however, demonstrate unequivocally that syn–anti proton exchange is occurring. As shown in Figure 7 saturation of the syn resonances produced a partial saturation of the anti resonances. From the degree of saturation and the spin–lattice relaxation time of the anti resonances, it is possible to compute the rate constant for syn–anti exchange. This constant k_{sa} was found to be 2.3 ± 0.5 sec^{-1} at 66° and 1.4 ± 0.2 sec^{-1} at 63°.[27] One must now consider if these rates are compatible with the involvement of a flip mechanism. The mechanism involving a σ-bonded intermediate requires the site exchanges illustrated in Figure 10, which indicates that the first-order rate constant for interchange *via* this process is twice that for leaving a syn or anti site. This difference arises because the σ intermediate allows interchange of only one pair of syn and anti protons at a time; *i.e.*, only one end can turn over at a time. Hence, the first-order rate constant for rearrangement *via* the σ-bonded intermediate is related to that for syn–anti exchange by

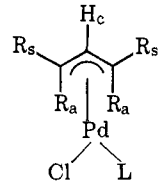
$$k_\sigma = 2k_{sa} \cong 5 \text{ sec}^{-1} \text{ (at } 66°)$$

If one computes the anti resonance line shape for this rate constant using the chemical shifts appropriate for 66°, one obtains a fairly close fit to the observed spectrum.[28,29] We feel that these experiments adequately

(27) The amount of saturation in the anti resonances is the same within experimental error in complexes prepared from either the (*S*)-amine or the (*R*,*S*)-amine. The behavior of the racemic amine complex provides corroborative evidence to the proposal above. Broadening of the syn and anti proton doublets is observed in the racemic amine complex, and since the chirality of the amine is totally averaged by intermolecular amine exchange at temperatures above 35°, syn–anti proton exchange is implicated. At 68° an additional line broadening of 1.0 Hz in the anti resonances was measured, which gives k_{sa} = 3.1 sec^{-1} using slow-exchange-limit line-shape expressions, whereas a saturation of 0.21 is measured, which corresponds to a rate constant of 3.5 sec^{-1}.

(28) The computed spectra show changes in the anti region qualitatively very similar to those in Figure 7 when k_{sa} is less than 10 sec^{-1}. A convenient method of matching calculated and observed spectra is comparison of valley minimum to peak maximum ratios. Although this approach is commonly used, it is very sensitive to the assumed natural line width and to deviations from Lorentzian line shapes. Deviations are particularly apparent at slow exchange rates when only slight broadening has occurred. At 63° the observed ratio for the valley between e and f to the height of e is ~0.61; at 66° it is ~0.85; and at 68° when k_{sa} ~3.2 sec^{-1}, it is ~0.99. Taking the natural line width as 2.0 Hz for a 3.5-Hz chemical shift difference between the anti doublets (appropriate for 63°), one obtains the following values (k_{sa}, sec^{-1}, ratio): 1.3, 0.77; 1.4, 0.79; and 1.5, 0.81. For a 3.3-Hz separation (appropriate for 66 and 68°) one obtains: 2.1, 0.92; 2.3, 0.94; 2.5, 0.96; 2.9, 0.99; 3.1, 0.996; and 3.3, 0.9998. Errors arising from

Table IV. Nmr Parameters for Model Compounds



L[a] Solvent	(*S*)-PEA C_6H_6	py $C_2H_2Cl_4$	(*S*)-PEA C_6H_6	py $C_2H_2Cl_4$	(*S*)-PEA C_6H_6	py $C_2H_2Cl_4$
δ H_c	4.75, 4.73[b,c]	5.01	4.71	5.07	~4.71	~5.07
δ H_s	3.49, 3.45	3.56			4.21	4.37
δ H_a	2.60, 2.48	2.76	3.31, 3.25	3.53	3.75, 3.69	3.99
δ Me_s	1.64, 1.63	1.30	1.36, 1.34	1.19	1.44	1.39
δ Me_a	1.19, 1.16	1.11			1.00, 0.97	1.01
$J(H_c\text{-}H_s)$	7.3	7.3			7	6.8
$J(H_c\text{-}H_a)$	12.8	12.8	12.4	12.2	12	12
$J(H_s\text{-}H_a)$	1.2	1.2				
$J(H_a\text{-}Me_s)$			6.1	6.3	6.4	6.2
$J(H_s\text{-}Me_s)$					6.8	6.7

[a] (*S*)-PEA = (*S*)-α-phenethylamine; py = pyridine. [b] δ is parts per million with respect to TMS; *J* is in hertz. The doublet at δ 1.59 and the quartet at δ 4.37 in Figure 11 are attributed to the (*S*)-α-phenethylamine.

demonstrate that the invocation of a flip mechanism which does not involve interchange of syn and anti protons is an unnecessary complication in considering the predominant pathways of rearrangement. Furthermore, the π–σ equilibrium successfully explains the rearrangements observed in the substituted allyl complexes reported in this paper and in the complex described by Tibbetts and Brown, 1,2-bis(diphenylphosphino)ethane(methallyl)palladium.[31] Therefore it appears to us that the weight of evidence suggests that the primary rearrangement pathways leading to inversion of configuration at the 1 and 3 carbon atoms of both substituted and unsubstituted π-allylpalladium complexes involve π–σ equilibria.

The 1,2,3-h^3-(Dimethylallyl)chloropalladium Complexes and Restrictions on Interconversions Imposed by π–σ Equilibria. Investigation of model systems has provided guidelines for predicting and determining stereochemistry and will allow some assessment of the restrictions upon isomer interconversion imposed by π–σ equilibria. The pmr spectra of the 1,1- and 1,3-dimethyl-h^3-allyl systems with (*S*)-α-phenethylamine are shown in Figure 11, and the assignments are summarized in Table IV. Syn and anti protons are readily assigned by the coupling to the central proton (7 Hz for syn and 12–13 Hz for anti). In the 1,1-dimethyl derivative the *syn*- and *anti*-methyl groups are readily assigned by the observed nuclear Overhauser enhancement of 29% in the central proton resonance upon irradiation of the *syn*-methyl resonances at δ 1.64, whereas an effect of less than 5% is noted upon irradiation of the *anti*-methyl resonance at δ 1.16 and 1.19. One also observes here, as in the case of the 1-acetyl-2-methallyl moiety, that the relative shielding due to the asymmetric amine on the syn protons is opposite to that on the anti protons. This is demonstrated by a decoupling experiment in which various components of the anti proton resonances are irradiated, the significant result of which is that irradiation of an upfield component in the anti resonance produces a decoupling in the downfield component of the syn resonance.[32] This compound thus provides the basis for the following

uncertainty in the natural line width are largest at the slower rates; *e.g.*, for a 1.9-Hz half-width and a 3.5-Hz chemical shift, a rate of 1.4 sec^{-1} gives a ratio of 0.77

(29) Line-shape analysis should in principle allow one to investigate the involvement of a flip mechanism which allows interchange of syn and anti protons.[30] The motion involved in this mechanism may be considered to resemble the inversion in cyclohexane (or cyclobutane) which exchanges axial and equatorial protons. This mechanism requires simultaneous interchange of both syn and anti protons; *i.e.*, both ends rotate simultaneously and in conjunction with the central carbon atom moving away from the metal atom. Since there is no exchange between (+)-anti and (−)-anti sites in this mechanism, the anti resonances do not coalesce as rapidly as in the π–σ equilibrium. That is, in the slow-exchange limit one notes the superposition of two doublets each broadened by $\pi^{-1}k_{ss}$.

The line shapes are quite sensitive to chemical shift separations and the assumed natural line widths. The narrowest line width observed for the anti resonances (2.0 Hz) is unusually large and although this is presumably attributable to small couplings and residual effects of intermolecular amine exchange, the subtle difference in line shape which need to be distinguished to determine the mechanism are of marginal reliability. More precise data taken at higher field strengths would probably be required if one wished to delineate this mechanism from the σ mechanism with confidence by this method. Our principal goal here was to demonstrate that the observed qualitative changes in the syn and anti region were compatible with a π–σ equilibrium alone and did not require the preliminary involvement of the flip mechanism discussed previously.

(30) F. A. Cotton, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, *1964*, **9**, 184 (1965).

(31) D. L. Tibbetts and T. L. Brown, *J. Amer. Chem. Soc.*, **92**, 3031 (1970).

(32) One can divide the molecules in solution into four groups on the basis of the spin state of the central proton and the absolute configuration at carbon-3. The nmr spectrum can then be treated as the superposition of four spectra, one for each of the four groups. Assuming *J* is positive[23] and that the anti proton resonance appears upfield when carbon-3 is in the (+) configuration,[18] the following assignments of the anti resonances may be made (Hz from TMS): $H_c(\beta)$ $C_3(+)$, 242; $H_c(\beta)$ $C_3(-)$, 254; $H_c(\alpha)$ $C_3(+)$, 254; and $H_c(\alpha)$ $C_3(-)$, 266. Each of these resonances is slightly split (1.2 Hz) by coupling to the syn proton. If the anti resonance of any particular group is decoupled, it will show up only as a removal of coupling from the syn proton of that same group. Consequently, it is straightforward to assign the syn resonances at 352, 348, 345, and 341 Hz downfield from TMS to the appropriate groups. Irradiation at 242 and 266 removes the coupling from 345 and 348, respectively; hence, 345 must arise from the group with H_c in the β spin state and C_3 in the (+) configuration, but 348 arises from $H_c(\alpha)$ and $C_3(-)$. Irradiation at 254 gives an ambiguous result, but the coupling constant of 7.3 Hz (checked at 60 MHz) requires that only one choice of assignment be made and one obtains: (β)(+), 242, 345; (β)(−), 254, 341; (α)(+), 254, 352; (α)(−), 266, 348.

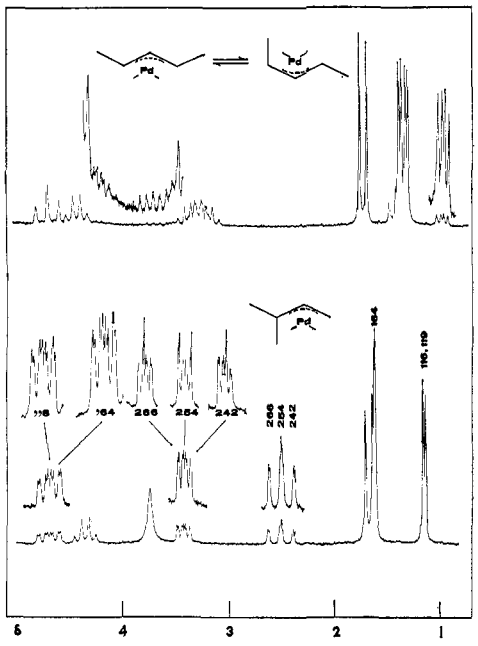


Figure 11. A comparison of the (*S*)-α-phenethylamine derivatives of the 1,1-dimethylallyl and the 1,3-dimethylallyl complexes in benzene at 26°. Inserts illustrate the effects of double-resonance experiments described in the text.[33] The Overhauser effects in the resonances at δ 3.49 and 3.45 were observed in perdeuteriotoluene.

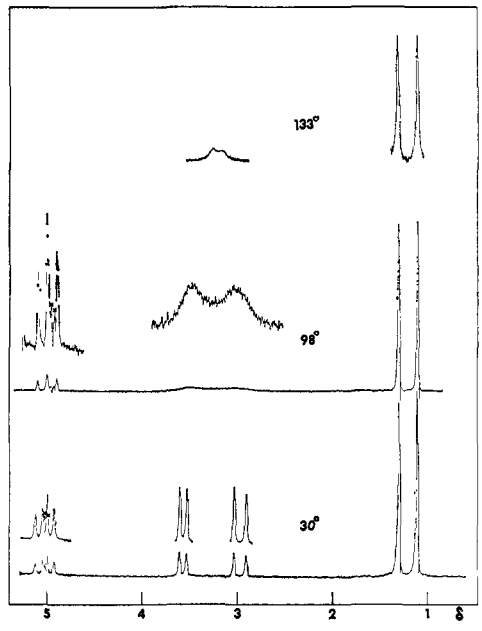


Figure 12. The temperature dependence of the pmr spectrum of 1,2,3-h^3-(1,1-dimethylallyl)chloro(pyridine)palladium(II) in *s*-tetrachloroethane. The resonances marked with an × near δ 5 are carbon-13 side bands of the solvent. Only the region of the terminal protons and the methyl groups are shown in the 133° spectrum owing to rapid and extensive decomposition at this temperature. The spectra are reproducible at elevated temperatures with freshly prepared samples.

criteria, which have been amply corroborated in the assignments of other substituted compounds: (1) for a given type of substituent (specifically protons or methyl groups), those in the syn position will usually give rise to resonances at lower field than those in the anti position, assuming the other allyl substituents are the same; (2) for a given substituent, the chemical shift difference arising from the asymmetry of the amine will be greater for the anti than for the syn substituent; (3) a substantial nuclear Overhauser effect can generally be observed in a proton in a "cis" relationship to a methyl group (*e.g.*, H_c when Me_s is irradiated); and, as previously mentioned, (4) the following magnitudes of coupling constants (Hz) are usually obtained: $J(H_c-H_s) \sim 7$, $J(H_c-H_a) \sim 13$, and $J(H_s-H_{s'}) \sim 1$. When there has been a conflict in the guidelines, coupling constants have proven to be more reliable criteria.

In the spectrum of the 1,3-dimethylallyl moiety one observes the presence of two isomers, and the above guidelines allow one to readily assign the configurations, which indicate the equilibrium to be *syn,syn*-1,3-dimethyl = *syn,anti*-1,3-dimethyl, with $K = 0.12$.

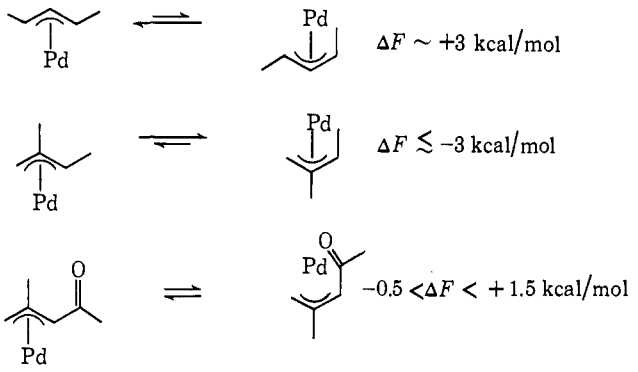
The temperature dependence of the pmr spectra, as shown in Figure 12, for the pyridine derivatives of the complexes may be interpreted as increased interchange of substituent orientation because of a faster rate of formation of the σ-bonded intermediate at higher temperatures. The significant feature of the 1,1-dimethyl-1,2,3-h^3-allyl complex is the broadening and coalescence of the syn and anti protons before any evidence of appreciable exchange of *syn*- and *anti*-methyl groups. This observation is consistent with a lower energy barrier associated with metal–carbon σ-bond formation at the unsubstituted end of the allyl, *i.e.*, a 3-*h* intermediate, and a much higher barrier associated with σ-bond formation at the disubstituted end. Averaging of the resonances of the two isomers of the 1,3-dimethylallyl complex occurs at intermediate temperatures. Hence, one obtains free energies of activation of 18.9, 20.9, and 23.7 kcal/mol, respectively, for formation of the σ-bonded intermediate at an unsubstituted carbon atom, a monomethyl-substituted carbon atom, and a dimethyl-substituted carbon atom.[33]

Thus one should expect a 1–3 kcal/mol increase in free energy of activation per substituent at the σ-bonded carbon atom. This expectation appears to hold true in practice; however, attempts to predict the actual barrier are difficult since the rate of interchange also depends markedly on the nature of the amine and the substituents on both the central and terminal carbon atoms.

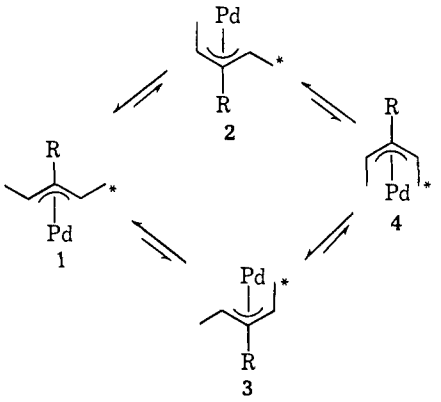
Some generalizations can be made concerning thermodynamic stability of certain isomers. For instance, with only a proton attached to the central carbon atom, the steric interactions are such that only a small percentage (usually 5–6%) of the *anti*-methyl isomer is observed in 1-substituted or 1,3-disubstituted complexes. Placement of a bulky substituent on the central carbon, however, may reverse this tendency in general so that the anti configuration is preferred.[34]

(33) The free energies of activation were determined from the additional broadening observed due to exchange from the slow-exchange-limit equation $k = \pi W$. For the pyridine derivatives, the following values were obtained: 3-*h*-(1,1-dimethylallyl), $\Delta F^*_{75} = 18.9$ kcal/mol; 1-*h*-(1,1-dimethylallyl), $\Delta F^* = 23.7$ kcal/mol; and for the syn,syn → syn,anti process, 1-*h*-(1,3-dimethylallyl), $\Delta F^* = 20.9$ kcal/mol. The rate of interchange does not depend on the concentration of excess amine in the solution, but does depend on the donor properties of the amine itself. For instance, the free energy of activation for the conversion of the (*S*)-α-phenethylamine derivative of the *syn,syn*-1,3-dimethyl-1,2,3-h^3-allyl complex to the syn,anti isomer at 80° is 22.3 kcal/mol.

(34) A small percentage of the anti isomers has frequently been observed in π-crotyl complexes.[1,5] The magnitude of the equilibium constant can be shifted significantly by the nature of the amine and the other substituents; nevertheless, within a series of complexes one can usually predict orders of the syn–anti ratio on the basis of steric interactions.

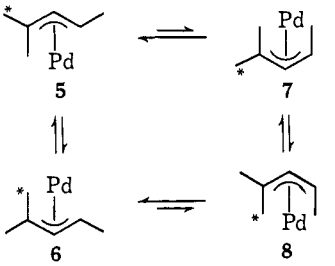


These thermodynamic and kinetic observations lead to some interesting predictions concerning possible isomer interconversions and racemizations. (1) *A 1,3-disubstituted allyl moiety with different substituents in the syn positions will not racemize if isolated optically pure.*[35,36] Each isomer accessible by rearrangements of **1** (R = H) that involve a σ intermediate is thermodynamically unfavorable; therefore, even though the barrier to rearrangement is ~21 kcal/mol, a pathway for rapid racemization is not available. (2) *If a 1,2,3- or*



1,1,3-trisubstituted allyl moiety has two different groups occupying the positions at the terminal carbon atoms, a chiral species will isomerize but not racemize. For the 1,2,3 case, *i.e.*, a methyl group in the 2 position, there would be a greater tendency for the terminal substituents to occupy anti positions; hence, contrary to prediction 1, isomer **3** or **4** should tend to remain in highest abundance, even though there is a fairly rapid equilibrium between isomers. An interesting application of this rule is the behavior of the 1-acetyl-2,3-dimethyl-1,2,3-h^3-allyl complex (the substituent which is marked with an asterisk in **1**–**4** would be the acetyl group and R = Me in **1**, **2**, **3**, and **4**). In this case either **4** and **2** or **3** and **1** would be expected to exist in appreciable concentrations, depending on the configuration about carbon-3. One diastereoisomer of the (*S*)-α-phenethylamine derivative is readily crystallized, and when dissolved at room temperature it equilibrates within minutes to a mixture having a specific rotation of ~+500°. This should be compared with the 1-acetyl-2-methallyl complex which equilibrates within seconds to a mixture having a specific rotation of −31°, which is attributable to the residual rotation resulting from the coordinated amine. The more rapid approach to an equilibrium rotation results from the ~3-kcal/mol lower barrier associated with σ-bond formation at an unsubstituted carbon atom compared to a monosubstituted carbon atom, and the difference in equilibrium specific rotation results from the thermodynamic restrictions on placement of a methyl group into an anti position.[37]

For the 1,1,3 case, one again notes that a pathway for racemization does not exist, but assuming the 3 substituent to be a methyl group, **5** would be expected to isomerize slowly to an equilibrium mixture with **6** (ΔF^* ~24 kcal/mol). Although isomerization about carbon-3 would be occurring over 100 times faster, appreciable concentrations of **7** and **8** would not be expected because of the unfavorable position of the *anti*-methyl group.



Principally, these studies have provided guidelines for synthetic studies and information basic to the understanding and interpretation of isomeric ratios and stereoselectivity of reactions involving π-allyl intermediates.

Experimental Section

Nmr spectra were measured on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. The temperature was measured with a copper–constantan thermocouple in an nmr tube with the junction at the level of the receiver coil or by calibration with a methanol or ethylene glycol sample.

Spin-saturation transfer experiments were performed as developed elsewhere.[15,38,39] Particular attention was paid to the following items to ensure accurate results: (1) high center-band power levels were used to minimize rf power loss at the observing frequency when the irradiating rf power was increased; (2) M_0 values were determined with irradiation at some irrelevant frequency ~100 Hz removed from the resonance to be totally saturated in the experiment; (3) the power of the irradiating frequency was increased several times after the apparent limit of saturation in the observed resonance was reached, to be certain of complete saturation of the irradiated resonance; and (4) low power levels were used for the observing frequency to avoid additional saturation of the observed resonance. Ordinarily, these experiments were performed as labeling studies such that T_1 measurements were not performed. Measurement of T_1 for the quantitative data followed the technique of Anet and Bourn[15] using magnetization recovery curves. The relatively short relaxation times were followed using a Honeywell 906c Viscorder oscillograph. This galvanometer recorder, which is frequently used on mass spectrometers, allows the signal to be recorded at several gain levels simultaneously, so that sufficient time can elapse for the short-lived exponential to become insignificant yet sufficient amplitude be observed for precise measurement.

(35) The palladium atom is considered to be below the plane of the paper in the diagrams.

(36) In principle the two methyl groups of the (*S*)-α-phenethylamine derivative of the 1,3-dimethylallyl complex should remain nonequivalent in the averaged spectra at high temperatures. Unfortunately, the decrease in chemical shift difference with increasing temperature and the onset of decomposition prevents reliable observation of the nonequivalence.

(37) A more detailed analysis of the isomerizations, as well as studies of the stereospecificity of insertion reactions of this and similar compounds will be published separately. It is interesting to compare these observations with the trends observed by J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Amer. Chem. Soc.*, 92, 4025 (1970), for the allyl cations.

(38) R. A. Hoffman and S. Forsen, *Progr. Nucl. Magn. Resonance Spectrosc.*, 1, 173 (1966).

(39) J. W. Faller in "Determination of Organic Structures by Physical Methods," Vol. III, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., in press.

Table V. Properties of 1,2,3-h^3-(1-Acetyl-2-methallyl)(amine)chloropalladium Complexes

Amine	Mp,[a] °C		C, %	H, %	Cl, %	N, %	Color
2-Picoline[b]	105–107	Calcd	43.40	4.86	10.67	4.22	Yellow
		Found	43.36	4.83	10.91	4.15	
4-Picoline[b]	94–96	Calcd	43.40	4.86	10.67	4.22	Light
		Found	43.26	4.95	10.81	4.34	Yellow
2,6-Lutidine[b]	130–132	Calcd	45.11	5.24	10.24	4.05	Yellow
		Found	44.99	5.23	10.46	4.07	

[a] All complexes were recrystallized from carbon tetrachloride and vacuum dried; they melted with decomposition. [b] Microanalysis done by Galbraith Laboratories, Knoxville, Tenn.

The relaxation times measured over the 5° temperature range did not differ significantly. The greatest source of error in measurements appears to be in the relaxation time measurement, which gave values of 1.1 ± 0.1 sec^{-1}. The amount of saturation, *i.e.*, $M_z(\infty)/M_0$ for (*S*)-α-phenethylamine was found to be 0.38 at 63°, 0.28 at 66°, and 0.22 at 68° (the value for the (*R*,*S*)-amine was found to be 0.21 at this temperature). Essentially the same results are obtained with freshly prepared samples of either the (*S*)- or the (*R*,*S*)-amine; however, on prolonged heating a lesser degree of saturation is noted, owing to decomposition. This presumably results from formation of bis[(*S*)-α-phenethylamine]dichloropalladium(II), which effectively "sequesters" the amine and causes the equilibrium between the bridged chloride dimer and the amine derivative to shift toward the dimer. Since the dimer does not undergo a rapid σ–π equilibrium, the effective exchange rate observed in the spectrum is less. This problem can be eliminated by adding a slight excess of amine, which does not affect the σ–π interconversion rate[1] but shifts the equilibrium overwhelmingly from the dimer toward the amine derivative.

Nuclear Overhauser effects were generally observed in samples prepared in deuterated solvents that were saturated with nitrogen and which contained a small percentage of benzene for the purpose of locking. Essentially the same precautions regarding power levels were used as in the spin-saturation transfer experiments. Relative peak areas were measured by tracing the resonances onto heavy paper, cutting them out, and comparing the weights.

The theoretical line shapes were calculated by the Kubo–Sack[40] method using a computer program developed by Professor Martin Saunders. The off-diagonal matrix elements for the probabilities in the symmetric kinetic-exchange matrix ($\mathbf{K}/k_\sigma$) were zero in the upper triangle except for p_{ab}, p_{af}, p_{be}, p_{cd}, p_{ch}, p_{dg}, p_{ef}, and p_{gh}, which were equal to 0.5. The frequencies for resonances a through h for the [(*S*)-α-phenethylamine]allyl complex at 60 MHz in benzene were taken as 225.4, 225.4, 218.6, 218.6, 165.8, 162.9, 153.6, and 150.7 Hz downfield from TMS. Half-widths were taken as 2.0 Hz, the narrowest line width observed for these resonances. These calculated spectra (Figure 9) represent an idealized case because there is a significant coupling (1.3 Hz) and a chemical shift difference (~0.01 ppm) between the syn protons. Since the chemical shift and the coupling between the syn protons are of the same magnitude, second-order effects make the calculation of the exact line shape of the syn resonances as a function of rate impossible by the method used here. Nevertheless, syn–anti and anti–anti coupling is negligible, so that the anti resonance line shape should be accurately reproduced at slow exchange rates. All attempts to compute rates from line-shape measurements were therefore confined to the behavior of the anti resonances.[28] *Note:* these comments refer to the precise measurement of the rates, but the observation of the coupling and chemical shift differences in the syn resonances in no way affects the qualitative conclusion that the anti resonances coalesce before the occurrence of appreciable broadening of the syn resonances.

Bis(π-allylchloropalladium) Complexes. Bis[1,2,3-h^3-(1-acetyl-2-methallyl)chloropalladium],[7] bis[1,2,3-h^3-(1-ethoxycarbonyl-2-methallyl)chloropalladium],[12] bis(1,2,3-h^3-allylchloropalladium),[41] bis-[1,2,3-h^3-(1,3-dimethylallyl)chloropalladium],[42] and bis[1,2,3-h^3-(1,1-dimethylallyl)chloropalladium][41] were prepared according to published methods. Bis[1,2,3-h^3-(1-acetylallyl)chloropalladium] was prepared from 3-penten-2-one using the same procedure as the 1-acetyl-2-methallyl preparation.[7]

π-Allyl(amine)chloropalladium Complexes. A suspension of the dimer (0.4 g) in 50 ml of ethyl acetate was treated with a 5% excess of the desired amine. After 30 min the solvent was removed and the residue crystallized from carbon tetrachloride to give the desired product (see Table V for certain representative amine derivatives).

The pyridine and (*S*)-α-phenethylamine derivatives not listed in Table V were not obtained in crystalline form, but deuteriochloroform and benzene solutions were prepared *in situ* in nmr sample tubes.

Isolation of the (*S*)-α-phenethylamine derivative of bis[1,2,3-h^3-(1-ethoxycarbonyl-2-methallyl)chloropalladium] in crystalline form has been unsuccessful.

(40) C. S. Johnson, Jr., *Advan. Magn. Resonance*, **1**, 33 (1965), and references therein.

(41) W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964).

(42) G. R. Davies, R. H. B. Mais, S. O'Brien, and P. G. Owsten, *Chem. Commun.*, 1151 (1967).