order conditions and to force the reactions to completion. The final spectra were generally in good agreement with those of the products prepared and characterized independently. The values of pseudo-first-order rate constants, k_{obsd} (sec^{-1}), were obtained from the slopes of plots of log $(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ are the optical densities of the reaction mixture at time t and after 7–8 half-lives, respectively. The values of k_{obsd} were reproducible to better than 10%.

Conductivity measurements on final reaction mixtures showed the presence of cationic carbene derivatives in negligible equilibrium amounts (some per cent units), which were not sufficiently high to affect the reliability of the kinetic results.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
YALE UNIVERSITY, NEW HAVEN, CONNECTICUT 06520

Organometallic Conformational Equilibria. IX. Isomerism and Hindered Rotation about Palladium–Nitrogen Bonds in π-Allyl Complexes[1]

BY J. W. FALLER* AND M. J. MATTINA

Received December 10, 1970

A study of variable-temperature behavior of the pmr spectra for some π-crotyl(amine)palladium(II) halide complexes from −100 to +100° is reported. The results are consistent with three pathways of isomerization and epimerization; the activation parameters of each route differ sufficiently to permit the observation of three distinct phases in the variable-temperature spectra of the complexes. In the lowest temperature phase the results are accounted for in terms of intramolecular hindered rotation about the palladium–amine bond. In the intermediate temperature phase intermolecular amine exchange is unequivocally established. The highest temperature phase is interpreted in terms of an equilibrium between π- and σ-bonded allylic forms. The variable-temperature studies were supplemented by double-resonance experiments.

Introduction

Several pathways of isomerization have been proposed for palladium complexes containing π-bonded allylic moieties. For L = amine and X = halide, (π-allyl)PdXL complexes have been shown to be structurally dynamic in solution by investigations of the temperature dependence of pmr spectra. Comparison of the unsymmetrical π-crotyl derivatives with their symmetrical π-allyl and π-2-methylallyl analogs has shown that throughout the observable temperature range the spectra may be entirely accounted for by the following mechanisms: (1) hindered rotation about the palladium–amine bond, (2) intermolecular amine exchange, and (3) an intramolecular π-allyl–σ-allyl equilibrium. Other previously proposed mechanisms are inconsistent with the evidence presented.

The relative magnitudes of the activation parameters for interconversion of certain isomers are readily interpreted in terms of intramolecular steric interactions. This is also true for establishing the relative populations of isomers. These results suggest that intramolecular steric interactions play a very important role in the determination of relative thermodynamic stabilities and in the selection of rearrangement pathways.

Results

Pertinent data from the pmr spectra of a series of (π-crotyl)PdXL species have been summarized in Table I. Broadening and coalescence of certain resonances occurred with variations in temperature, such that three separate and distinct phases of averaging could be distinguished. Rather than attempting to relate these phases to specific rearrangements in the entire series of complexes, the spectra of π-crotyl(2-picoline) halides will be discussed in detail in order to extablish the general pattern of stereochemical nonrigidity in these molecules.

Phase 1.—At −80° the spectrum of π-crotyl(2-picoline)palladium(II) bromide appears as recorded in Figure 1. On the basis of coupling constants and by analogy to the pmr spectra of 2-picoline and the $[(\pi\text{-crotyl})PdCl]_2$ dimer,[2] the following assignments are made. In region 1 is the sextet of the central allylic hydrogen; since $J_{H1-H2} \cong J_{H1-H6} \cong 12$ Hz (see the proton-labeling scheme accompanying Table I), the intensity ratio within the sextet is 1:1:2:2:1:1. In region 2 it is possible to detect a portion of the sextet assigned to the anti allylic proton geminal to the methyl substituent. An intensity ratio of 1:2:3:3:2:1 should derive from the coupling constants $J_{H1-H2} = 12$ Hz and $J_{H2-H8} = 6$ Hz. In region 3 the syn proton doublet is discernible. There are three singlets 4a, 4b, and 4c assigned to the methyl substituent in the picoline; these singlets partially obscure the methylene anti proton resonances, 6. Upfield are three doublets 8a, 8b, and 8c assigned to the methyl substituent in the allyl ligand.

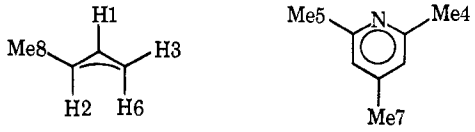
As the temperature drops below −80° some broadening is noted in resonance 8a; however, a more noticeable change occurs in resonance 4b which begins to broaden and collapse and at −100° appears as shown in Figure 1. If the temperature is raised above −80°, we observe the coalescence of resonances 8b and 8c to a single doublet at τ 8.90. Again the change in the pyridine methyl region is more dramatic than changes in the rest of the spectrum; resonances 4a and 4c broaden and coalesce to a single peak at their average value τ 7.17. Figure 1 shows the partially averaged peak at −60°. Between −60 and −30°, no significant

(1) Part VIII: J. W. Faller and M. E. Thomsen, *J. Amer. Chem. Soc.*, **91**, 6871 (1969). The work reported in this paper (IX) was presented in part at the Middle Atlantic Regional Meeting of the American Chemical Society, April 1970.

(2) H. C. Dehm and J. C. W. Chien, *J. Amer. Chem. Soc.*, **82**, 4429 (1960).

TABLE I

CHEMICAL SHIFT DATA (PPM) FOR SOME (π-crotyl)PdXL SPECIES[a]



L	X	Temp, °C	τ_1	τ_2	τ_3	τ_4[b]	τ_5[b]	τ_6	τ_7	τ_8
Pyridine	Cl									
Av		+4	4.62	6.11	6.19	...	...	7.13	...	8.62
Trans		−56						7.10[d]	...	8.50
			4.61[c]	6.16[c]	6.10[c]	...	...			
Cis		−56						7.08[d]	...	8.72
2-Picoline	Cl									
Av		+4	4.67	6.17	6.23	7.18	...	7.25	...	8.70
Trans		−56				7.20	...		...	8.48
Cis-endo		−56	4.64[c]	6.12[c]	6.22[c]	7.03[d]	...	7.22[c]	...	8.89
Cis-exo		−56				7.27[d]				
2-Picoline	Br									
Av		+11	4.69	6.11	6.18	7.20	...	7.35	...	8.67
Trans		−80			6.18	7.22	...			8.37
Cis-endo		−80	4.62[c]	6.08[c]	6.12	7.05[d]	...	7.22[c]	...	8.88[d]
Cis-exo						7.29[d]				8.91[d]
2,6-Lutidine[e]	Cl									
Trans		+4			6.42	7.01	7.28			8.50
			4.66[c]	6.16[c]				7.12[c]	...	
Cis		+4			6.19	6.97	7.23			8.97
Trans		−56			6.39	7.01	7.29			8.47
			4.67	6.17				*f*	...	
Cis		−56			6.17	6.98	7.26		...	8.96
2,6-Lutidine[e]	Br									
Trans		+11				7.04	7.28			8.36
			4.70	6.16[c]	6.16[c]			7.35[c]	...	
Cis		+11				7.00	7.25			8.94
Trans		−80			6.24	7.04	7.30			8.35
			4.65[c]	6.11[c]				7.23[c]	...	
Cis		−80			6.14	7.02	7.27			8.92
2,4,6-Collidine	Cl									
Trans		+4			6.38	7.07	7.34			8.47
			4.64[c]	6.18[c]				*f*	7.69[c]	
Cis		+4			6.18	7.04	7.31			8.95
Trans		−56			6.41	7.07	7.34			8.48
			4.47[c]	6.19[c]				*f*	7.70[c]	
Cis		−56			6.19	7.04	7.31			8.95
2,4,6-Collidine[e]	Br									
Trans		+11				7.10	7.34			8.36
			4.72[c]	6.18[c]	6.18[c]			7.30[c]	7.67[c]	
Cis		+11				7.05	7.31			8.93
Trans		−70			6.27	7.10	7.35			8.35
			4.66[c]	6.11[c]				7.25[c]	7.68[c]	
Cis		−70			6.14	7.07	7.33			8.92

[a] All spectra were recorded using samples prepared in dichlorofluoromethane with TMS as an internal standard. Coupling constants for individual cases are not reported but all fell in the following ranges: J_{12} = 12.0–13.0 Hz, J_{13} = 6.3–7.3 Hz, J_{16} = 12.0–13.0 Hz, and J_{28} = 6.3–7.3 Hz. [b] Assignments of the resonances to either the exo or endo methyl group have not been established; hence the designation τ_4 and τ_5 is arbitrary. [c] If for a given proton the resonances for the isomers are superimposed or if one of the two resonances is obscured by adjacent peaks, the chemical shift tabulated is approximate. [d] The assignment of resonances to a particular isomer has not been experimentally established and that given in the table is completely arbitrary. [e] Cis and trans isomers for the lutidine and collidine complexes were assigned on the basis of chemical shift comparisons with the picoline analogs. [f] The resonance is obscured by adjacent peaks.

changes, other than sharpening of some resonances, are observed.

Phase 2.—As the temperature is raised above −30° substantial changes occur throughout the spectrum. The resonances in regions 1–3 narrow considerably; in region 4 the singlets broaden until at +11° there is one pyridine methyl singlet permitting the observation of doublet 6. The doublets of region 8 broaden and average to one doublet. In the spectrum of Figure 2 these doublets, which are assigned to the allylic methyl substituent, are not fully averaged.

Phase 3.—The final phase of variable-temperature behavior occurs at temperatures above +30°. The syn and anti methylene protons undergo reversible broadening; *i.e.*, at +90° they are too broad to be observed; however, if the temperature is lowered, the spectrum at +30° may be reproduced. Changes are also noted in the region of resonance 1, but resonances 4 and 8 remain as sharp at +90° as they are at +30°.

Discussion

Phase 1.—Three superimposed $ABCDX_3$ allylic patterns and three methylpyridine singlets are observed in the spectrum of π-crotyl(2-picoline)palladium bromide at −80°. The three methyl resonances of the

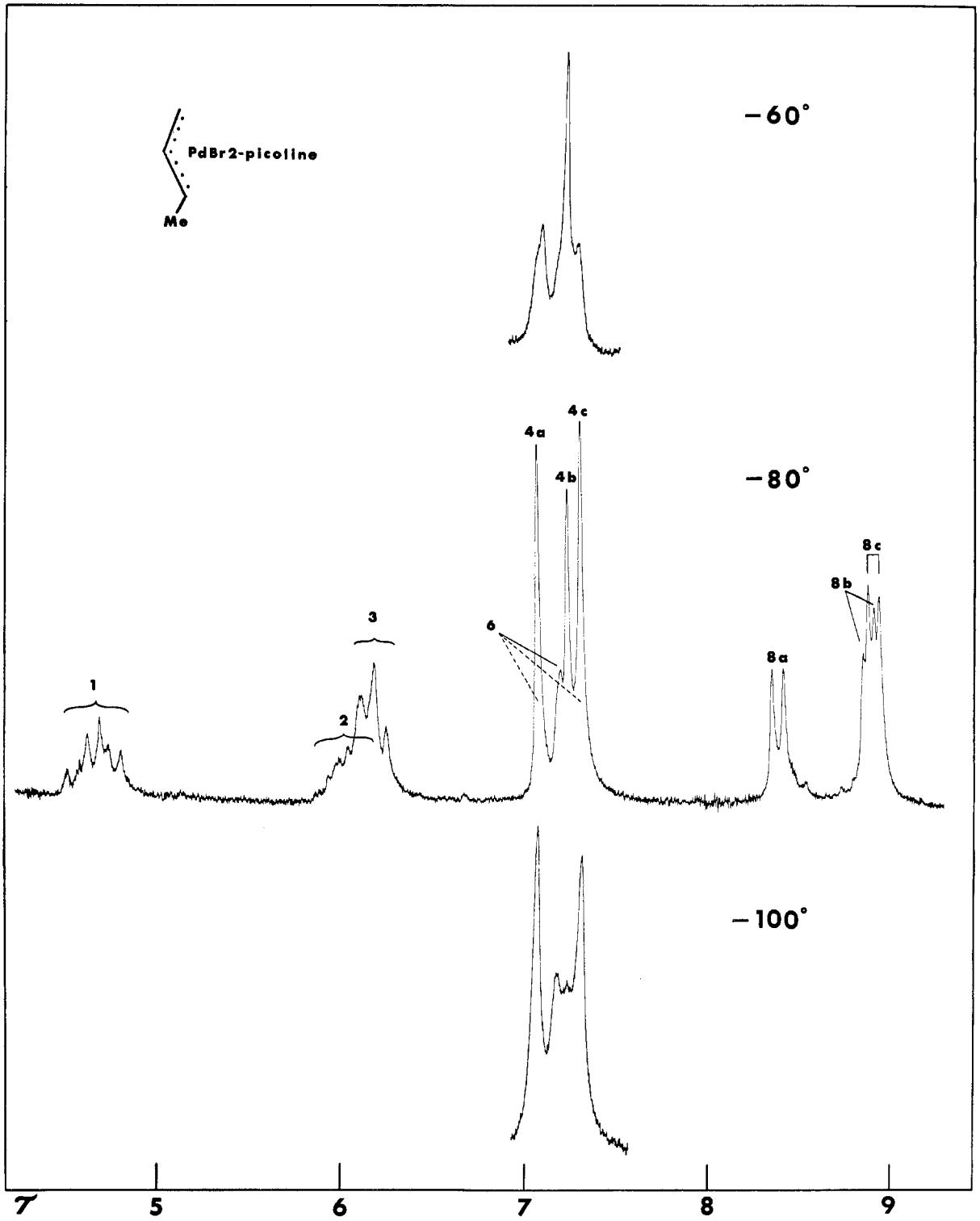


Figure 1.—The 100-MHz pmr spectra of π-crotyl(2-picoline)palladium bromide in CCl_2FH between $-100°$ and $-60°$.

picoline are designated 4a, 4b, and 4c in Figure 1. The three allylic patterns overlap extensively; nevertheless, their presence can be readily distinguished in the region of the doublets assigned to the methyl group of the crotyl moiety (8a, 8b, and 8c).[3] When the temperature is raised above $-80°$, two distinct picoline methyl singlets and two $ABCDX_3$ allylic patterns arise from averaging of the 4a and 4c singlets and the 8b and 8c doublets. These changes are more apparent in Figure 3 in which the spectra of the 2-picoline chloride complex are illustrated. The low-temperature singlets of the methyl substituent of the pyridine have coalesced to two singlets and resonances 8b and 8c have coalesced to one sharp doublet at $-35°$.

The changes noted when the temperature is lowered below $-80°$ are not so readily interpreted primarily because the limiting low-temperature spectrum could not be attained. These changes are the collapse of the 4b singlet and the broadening of the 8a doublet. They can reasonably be attributed to precursors of a limiting

(3) Splitting due to spin–spin coupling was distinguished from chemical shift differences by comparison of experiments at 100 and 60 MHz.

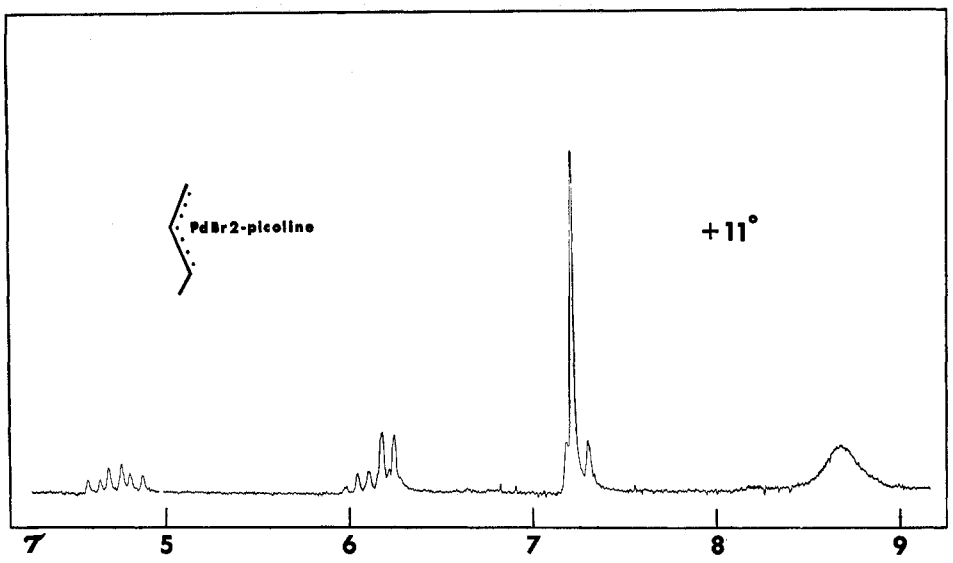


Figure 2.—The 100-MHz pmr spectra of π-crotyl(2-picoline)palladium bromide in CCl_2FH at +11°.

low-temperature spectrum with four pyridine methyl singlets and four $ABCDX_3$ allylic patterns.

The spectral variations comprising phase 1 may be interpreted in terms of interconversion between pairs of the four isomers shown in Figure 4. Molecular models indicate that the smallest intramolecular steric interactions should occur when the plane of the pyridine ring is approximately perpendicular to the Pd–C–C–X–N plane. Thus, one anticipates four isomers depending upon the relative orientation of the 2 substituent on the pyridine ring. The configurations in which the amine is located on the same edge of the square plane as the terminally substituted carbon atom are denoted as cis isomers (I), whereas configurations in which the amine is across the diagonal from the terminally substituted allyl carbon atom are denoted as trans isomers (II). These isomers can be further classified as endo or exo on the basis of the 2-methyl group being on the same (a) or the opposite side (b) of the square plane as the central allyl carbon atom. There is adequate precedent for suggesting this proposed orientation: (1) there is extensive evidence that steric interactions prevent free rotation about the nickel–carbon bond in square-planar complexes such as *trans*-$(R_3P)_2Ni(o\text{-tolyl})_2$ and it has been assumed that the planes of the aromatic rings are perpendicular to the plane containing the four nickel σ bonds,[4,5] (2) the collidine ring in (olefin)(2,4,6-collidine)$PtCl_2$ complexes is considered to be fixed perpendicular to the square plane of the platinum σ bonds,[6] and (3) the crystal structures of *trans*-$Pt(py)_2[Co(CO)_4]_2$ and *trans*-$Pt(py)_2[Mn(CO)_5]_2$ have shown the pyridine rings to be perpendicular to the plane of the platinum atom and the atoms attached directly to it.[7,8]

(4) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

(5) G. E. Coates and F. Glockling in "Organometallic Chemistry," H. Zeiss, Ed., American Chemicl Society Monograph Series, No. 147, American Chemical Society, Washington, D. C., 1960, Chapter 9.

(6) A. R. Brause, F. Kaplan, and M. Orchin, *J. Amer. Chem. Soc.*, **89**, 2661 (1967).

(7) D. Moras, J. DeLand, and R. Weiss, *C. R. Acad. Sci., Ser. C.*, **267**, 1471 (1968).

(8) In the trans platinum complexes the aromatic rings are expected to be perpendicular considering the symmetry of the molecules. In structures I and II, however, distortions are expected and the representations shown in the figure are idealized. Endo and exo would therefore apply to the methyl substituent being above or below the square plane, with no implications about exact angles.

For the 2-picoline complexes studied in this work and illustrated in Figure 4 molecular models confirm that rotation about the N–Pd bond in the cis isomer (I) is more sterically hindered than in the trans form (II). Accordingly in Figure 1 resonances 4a and 4c are assigned to the pyridine methyl substituent in the cis conformer and resonance 4b to the average of isomers IIa and IIb. Similarly, assuming the barrier to rotation to be larger in the cis form, then 8b and 8c can be assigned to it and 8a may be assigned to the average of the a and b rotamers of the trans isomer. Then as the temperature is lowered and the rate of interconversion between IIa and IIb decreases, resonances 4b and 8a begin to broaden and collapse as the first steps leading eventually to the four $ABCDX_3$ patterns and the four pyridine methyl singlets expected in the limiting low-temperature spectrum. On the other hand, raising the temperature above −80° increases the rate of interconversion between the two rotamers Ia and Ib until at −60° the averaged resonances of Ia and Ib as well as the average of IIa and IIb are observed.

These assignments of the resonances to the cis and trans conformations are confirmed by the data for the π-1,3-dimethylallyl(2-picoline)palladium chloride. In this complex the allyl moiety is symmetrical; hence there is no cis–trans isomerism. The two singlets assigned to the methyl substituent of the pyridine at −70° must correspond to the exo and endo orientations of the pyridine. Using the peak width at half-height of these two resonances the free energy of activation calculated for interconversion of the exo and endo forms is 11.1 kcal/mol (see Table II). This may be compared with the similar ΔF^* of 11.0 kcal/mol calculated from resonances 4a and 4c of the π-crotyl compound which corresponds to rotation about the N–Pd bond in the cis configuration of the π-crotyl complex. The agreement of the value of ΔF^* calculated from resonances 4a and 4c in the latter complex tends to corroborate the assignment of 4a and 4c to the cis configuration.

As the comparison of the activation energies given above implies, intramolecular steric interactions provide the basis for the interpretation of the phase 1 temperature behavior of the nmr spectra of these molecules.

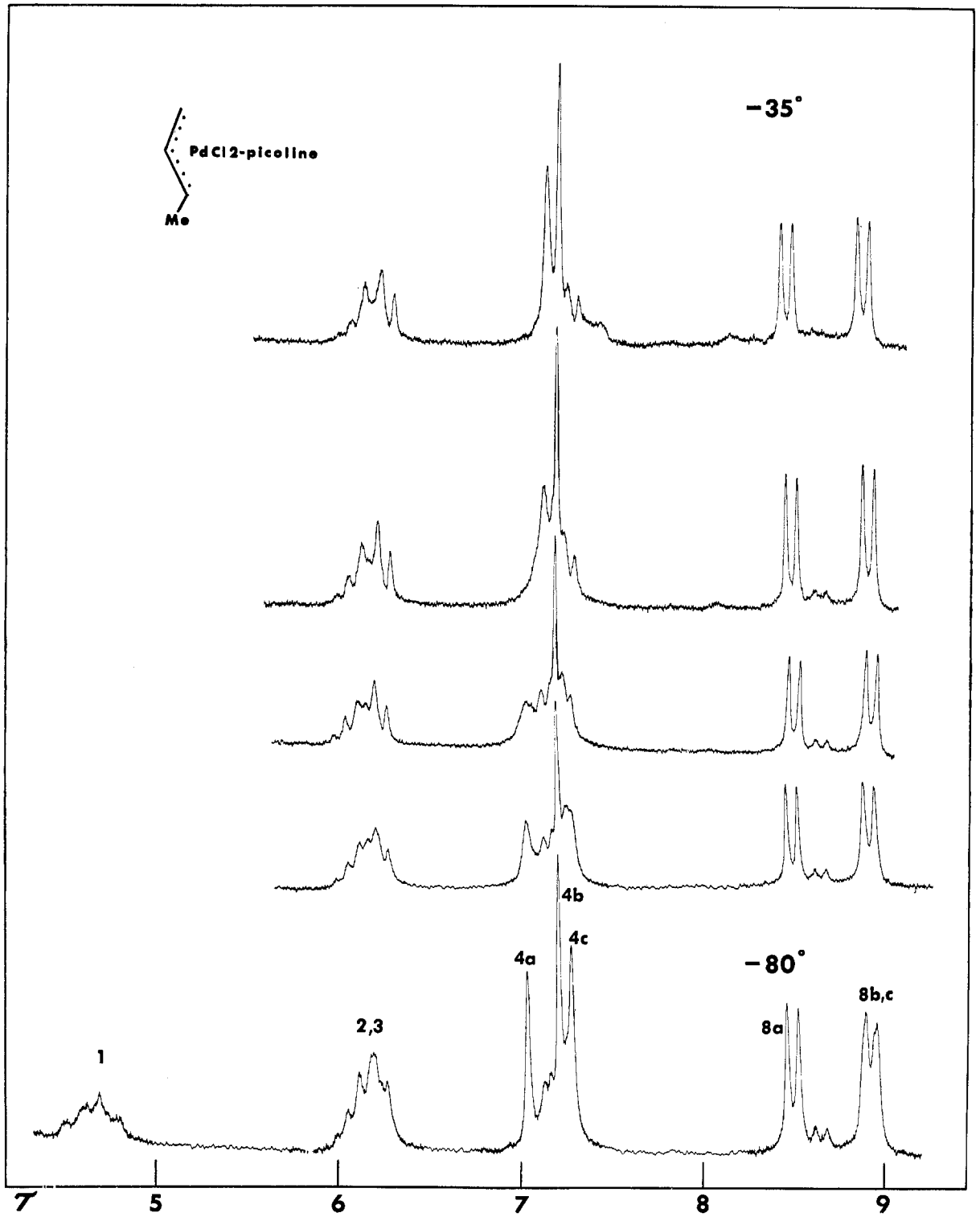


Figure 3.—The 100-MHz pmr spectra of π-crotyl(2-picoline)palladium chloride in CCl_2FH between −80° and −35°. The "impurity" at 8.7 is assigned to the crotyl methyl resonance of the dimer.

In the first place, interaction of the pyridine with the allyl substituents during rotation results in a difference of ~3 kcal mol^{-1} between the energy barriers for the cis and trans isomers. In addition, during the interconversion of the exo–endo forms the halogen will interact with the group in the 2 position of the pyridine, *i.e.*, either the hydrogen atom or the methyl substituent. Accordingly, a comparison of the activation energies for exo–endo interconversion in the analogous bromo and chloro complexes should tend to corroborate this interpretation. For the chloro complexes the activation energy for Ia ⇄ Ib is 11.0 kcal mol^{-1} and for IIa ⇄ IIb it is 8.0 kcal mol^{-1}. On replacing the chlorine ligand with the bromine the activation energies in both cases increase by 0.3–0.4 kcal mol^{-1}. The increased rate for IIa ⇄ IIb in the chloro complex is readily noted upon comparison of the relative height of 4b and 4a for the two complexes (Figures 1 and 3). Since resonance 4b should have twice the area of 4a, *i.e.*, it corresponds to the average of two methyl groups, a de-

TABLE II

FREE ENERGIES OF ACTIVATION FOR HINDERED ROTATION IN (π-allyl)(amine)PdX COMPLEXES[a]

Allyl	Amine	X	Method[b]	Interconversion	ΔF^*,[c] kcal/mol	Temp, °C
π-Allyl	Pyridine	Br	*d*		<8.0	
π-Crotyl	2-Picoline	Cl	A	IIa ↔ IIb	8.0	−85
π-Crotyl	2-Picoline	Br	A	IIa ↔ IIb	8.3	−85
π-Crotyl	2-Picoline	Cl	B	Ia ↔ Ib	11.0	−70
π-Crotyl	2-Picoline	Br	B	Ia ↔ Ib	11.3	−70
π-Crotyl	2,6-Lutidine	Cl	*d*	"Ia ↔ Ib" "IIa ↔ IIb"	>16.2	+20
π-Crotyl	2,4,6-Collidine	Cl	*d*	"Ia ↔ Ib" "IIa ↔ IIb"	>16.2	+20
π-1,3-Dimethylallyl	2-Picoline	Cl	*d*		11.1	−70

[a] Measurements were made on dichlorofluoromethane solutions of the complex. [b] Method A: fast exchange limit equation $k = \pi(\delta\nu)^2/2(\Delta\nu_{1/2}' - \Delta\nu_{1/2})$ assuming a separation $\delta\nu = 27$ Hz, as found in lutidine and collidine complexes. Method B: slow exchange limit equation $k = \pi(\Delta\nu_{1/2}' - \Delta\nu_{1/2})$. Method A was needed when measuring the narrowing of the picoline methyl resonance of the trans isomer, whereas method B was used when measuring the broadening of the picoline methyl resonance of the cis isomer. [c] Values of ΔF^* were calculated from $k = k_B T/h \exp(\Delta F^*/RT)$. See Experimental Section for discussion of errors. The temperature at which the line width was measured is given in the last column. [d] See Experimental Section.

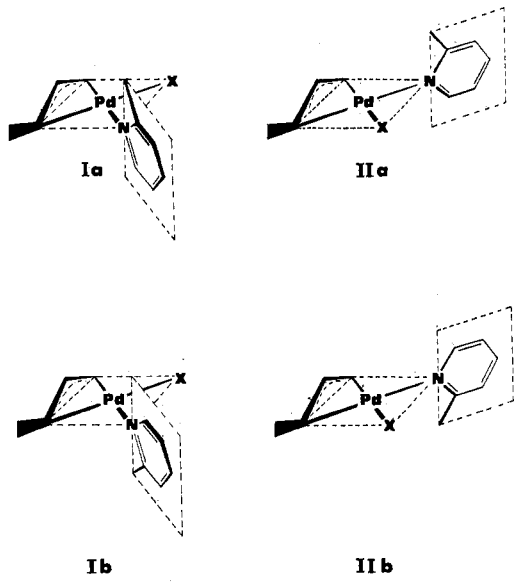


Figure 4.—Possible configurations of π-crotyl(2-picoline)palladium halide complexes.

crease in width of 4b due to faster exchange is indicated by an increase in relative height. The faster rate of Ia ⇄ Ib in the chloro complex is apparent upon consideration of the advanced stage of coalescence of 8b and 8c in the chloro complex compared to the relatively good resolution in the bromo complex. Apparently the larger radius of the bromide ligand results in greater interaction with the 2 substituent than that between the chloride and the 2 substituent. That the difference in ΔF^* for the bromo and chloro complexes is not greater than 0.4 kcal mol^{-1} is most likely due to the increased palladium–halogen bond length offsetting the increased van der Waals radius.

From consideration of either of the idealized configurations, it follows that there are two paths by which an endo isomer could be converted to an exo isomer—clockwise or counterclockwise rotation of 180°. Clarification of the "direction of rotation" about the N–Pd bond and the lowest barrier pathway is in order at this point. If we assume that the starting conformation is endo, the complex may be converted to the exo form by rotating about the N–Pd bond so that the 2-methyl substituent of pyridine moves either toward the halogen or toward the allyl ligand. It is reasonable to assume that one direction will be favored and that direction will be the one in which intramolecular interactions are minimized. Thus, a rotation of +180° followed by a rotation of −180° would be expected to be of lower energy than one of +360° to complete the sequence endo → exo → endo.[9]

Though it is not possible to establish conclusively the preferred direction of rotation about the N–Pd bond, examination of molecular models suggests that interaction between the α-methyl substituent of the picoline and the allyl is much more severe than interaction between the α-methyl group and the halogen. Therefore, it appears that for both cis and trans isomers of the π-crotyl complex the 2-picoline ligand prefers to rotate about the N–Pd bond in that direction for which the α-methyl substituent of the pyridine interacts with the halogen ligand and the α-hydrogen of the pyridine interacts with the allyl. In 2,6-lutidine square-planar complexes the interaction between the α-methyl substituent of the ring and the allyl is so sterically unfavored that ΔF^*(phase 2) < ΔF^*(phase 1). For the pyridine complexes with square-planar geometry steric interaction between the α-hydrogen and the allyl is substantially reduced so that ΔF^* for rotation is less than 8.0 kcal mol^{-1}.

There does not appear to be any significant thermo-

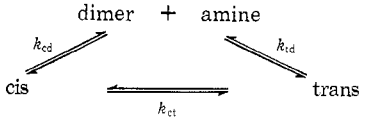
(9) In principle, one should be able to determine the preferred direction of rotation by considering differences and suitable combinations of barriers in a series of substituted derivatives. Assuming an observed barrier to be the sum of that due to the amine–halogen interaction and the amine–allyl interaction, one can obtain a set of values of barrier differences which allow the prediction of barriers and presumably should allow the determination of preferred direction. For instance, if a clockwise rotation of the picoline converts Ia to Ib, then the difference between the energy barriers for the chloride and bromide should be primarily due to the differences in interaction between the methyl of the picoline and the halogen: $\Delta\Delta F^* = \Delta F^*(\mathrm{Me_{py}}\text{–Br}) - \Delta F^*(\mathrm{Me_{py}}\text{–Cl})$. Likewise, for the same halogen in a comparison of Ia → Ib and IIa → IIb *via* rotations in which the picoline methyl group interacts with the halogen, one expects the major difference to be between the 2 hydrogen of the picoline and the substituents of the allyl: $\Delta\Delta F^* = \Delta F^*(\mathrm{H_{py}}\text{–CH}_2) - \Delta F^*(\mathrm{H_{py}}\text{–CHMe})$. Although based on very crude approximations, it does appear that these additivity relationships hold up reasonably well throughout the series (see Table II). It was hoped that comparisons with compounds such as the pyridine and 2,6-lutidine, for which the same barrier must be surmounted regardless of the direction of rotation, would allow the preferred direction of rotation in the picoline derivative to be determined. For example, if the direction is preferred in which the picoline methyl group passes by the halogen, then the difference in the activation energies for rotation in the π-crotyl(2-picoline)bromo and -chloro complexes should equal the difference in the activation energies for the (bromo)- and (chloro)-π-allyl(2,6-lutidine) compounds. On the other hand, if the opposite is favored, the difference for the π-crotyl(2-picoline) complexes would equal the difference for the π-1,3-dimethylallyl(4-picoline) complexes. Efforts to obtain the required activation energies were thwarted in the case of the 4-picoline derivative by low activation energies which would have required inaccessible temperatures and in the case of the lutidine derivatives by the activation energy for rotation increasing above that for exchange (phase 2).

dynamic preference for the endo or exo isomer in these complexes; *i.e.*, both rotamers are found in equal concentrations in solution. Nevertheless, in other cases where rotational barriers have been useful as criteria for determining cis and trans configurations,[1] slight differences have been observed.

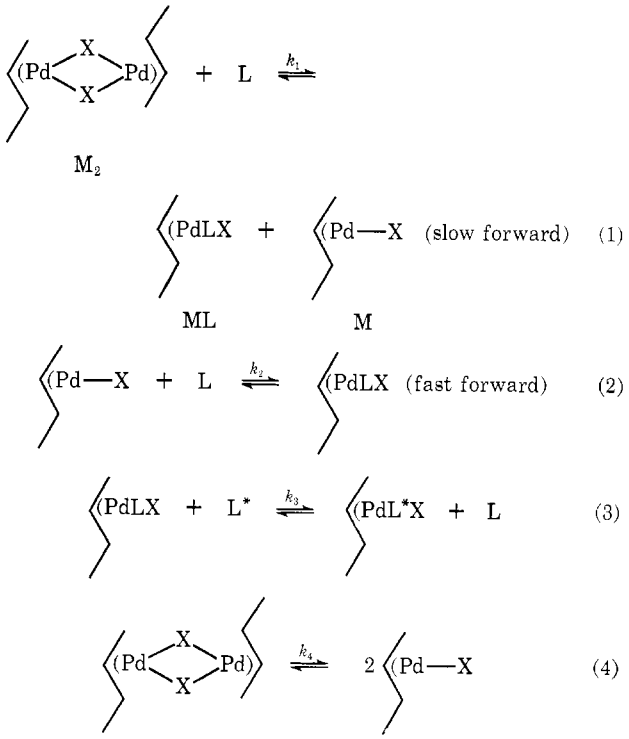
Phase 2.—When the temperature is raised above −35°, variations in the spectrum begin which lead eventually to the spectrum of the π-crotyl(2-picoline)-palladium bromide complex at +11° given in Figure 2. The most apparent changes again occur in regions 4 and 8. The two singlets assigned to the methyl substituent on the pyridine in the spectrum at −35° have coalesced to one sharp singlet. The two doublets assigned to the methyl group of the allyl have coalesced but are not completely averaged at +11°; at slightly higher temperatures one sharp doublet is observed. The clearly distinguishable sextet of the central proton of the allyl is in region 1; there are well-resolved doublets for the syn and anti protons of the allyl and half of the sextet of the anti proton on the methyl-substituted end of the allyl ligand is observed. Ample evidence has been presented that phase 2 spectral changes are associated with cis–trans isomerism *via* an intermolecular amine-exchange mechanism.[10,11] The pertinent conclusions from the previous work are developed below and provide a straightforward interpretation of the phase 2 changes.

The pmr spectrum of π-crotyl(2-picoline)palladium chloride in dichlorofluoromethane at −35° is consistent with the presence of both cis and trans isomers. The rate of rotation about the N–Pd bond is rapid enough at this temperature to average fully the resonances of the exo and endo isomers. When π-crotyl(chloro)-palladium dimer is added, resonances attributable to the dimer are observed at −60°. All these resonances, including those of the dimer, coalesce to give the averaged spectrum typical of a symmetrically substituted π-crotyl complex at +35°—a single $ABCDX_3$ allylic pattern. These observations indicate not only a rapid cis–trans interconversion but also a parallel equilibrium with the dimer or the direct involvement of the dimer as an intermediate.

Further elucidation of the pathway of amine exchange was provided by nuclear magnetic double-resonance techniques,[11,12] which showed that a given cis molecular configuration is most likely to be converted first to the dimer and then to the trans complex rather than proceeding directly from cis to trans. That is, considering the equilibria



one may conclude that $k_{cd} \gg k_{ct}$ and that $k_{td} \gg k_{tc}$. These studies demonstrated that the exchange occurs simultaneously by several different mechanisms and that at high concentrations of dimer, amine, or complex, bimolecular processes dominate the rate expression. At the concentrations consistent with good signal-to-noise ratios, these bimolecular contributions are appreciable and largely determine the broadening of the lines. Hence, one actually measures a pseudo-first-order rate constant from the line broadening; nevertheless it is this rate constant which is of practical utility when synthesis or isolation of a given complex is attempted. The following kinetic scheme was proposed tentatively to account for the observed concentration dependences; however, although it accounts for the major effects, other more subtle variations indicate that other equilbria must be taken into consideration, if one wishes to understand the kinetics in full.[13]



One may reasonably expect that nitrogen–palladium bond cleavage would be an integral part of the rate-determining step of any of the mechanisms and that rates would depend upon the Pd–N bond strength or, by inference, upon the basicity of the amine. A plot of the approximate activation energy based on the pseudo-first-order rate constants for cis–trans isomerism *vs.* pK_a of the protonated amine indicates an increasing order for structurally similar amines: pyridine < 2-picoline < 2,6-lutidine. The pertinent data are summarized in Table III. Although this correlation provides useful guidelines for the pyridine series, it cannot be generalized as indicated by the α-phenethylamine derivative.[14]

The activation energies cited above may be used to estimate the approximate rate constants for cis–trans isomerism at −50°: pyridine, 6 sec^{-1}; 2-picoline,

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

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

(12) J. W. Faller in "Determination of Organic Structures by Physical Methods," Vol. 5, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., in press.

(13) Other studies are in progress to untangle the concentration dependences of the concurrent reactions. It appears that at least four terms are needed in the summation describing the lifetime at a particular site. Above −40° in solutions ≥0.3 *M* in complex, sufficient amine is released by the reverse of steps 1 and 2 that $k_3[L^*] = k_{-3}[L] > k_{-2}$. (Note that k_{-2}, k_3, and k_{-3} would be slightly different for the cis and trans isomers.)

(14) The effects of hindered rotation about the Pd–N bond in the α-phenethylamine complex are not observed (at least not in the region studied, > −80°); nevertheless, the spectra are quite complicated due to effects of the chirality of the amine.[10]

TABLE III
APPROXIMATE KINETIC PARAMETERS FOR CIS–TRANS EXCHANGE IN π-ALLYL(AMINE)PALLADIUM CHLORIDE COMPLEXES

Allyl[a]	Amine	pK_a	ΔF^*,[b] kcal/mol	Temp, °C
π-Crotyl	Pyridine	5.23	12.2	−49
π-Crotyl	2-Picoline	5.96	13.4	−23
π-Crotyl	2,6-Lutidine	6.75	16.2	+22
π-Crotyl	2,4,6-Collidine	7.45	>16.2	
π-Allyl	α-Phenethylamine	9.08	~13	−30
π-Allyl	2,6-Lutidine		15.2	+10
π-1,3-Dimethylallyl	2,6-Lutidine		15.8	+20

[a] Samples were prepared in dichlorofluoromethane solution (0.3 *M*). [b] The slow exchange limit equation $k = \pi(\Delta\nu_{1/2}' - \Delta\nu_{1/2})$ was used to determine ΔF^*. The temperature at which the line width was measured is given in parentheses. The broadening of the methyl resonance attributed to the crotyl moiety in the trans isomer was measured for the π-crotyl complexes. The methyl resonance of the lutidine was measured in the allyl and dimethylallyl complexes. See Experimental Section for discussion of errors.

0.3 sec^{-1}; 2,6-lutidine, 10^{-3} sec^{-1}; 2,4,6-collidine, 10^{-5} sec^{-1}. With the order of magnitude of the rate constants established, it follows that the conformation of certain of the molecules in the solid could be determined by a simple pmr experiment. After adding CCl_2FH to the solid complex contained in an nmr tube and maintained at liquid nitrogen temperature, the spectrum of the solution was recorded at −50°. Provided that the rate of isomer interconversion was slow enough, only the resonances of one isomer were initially observed and they presumably corresponded to the isomer found in the solid. When this experiment was performed using the pyridine and 2-picoline complexes, the spectrum of the sample prepared at −196° and recorded at −50° was identical with the spectrum of the sample prepared at room temperature and recorded at −50°. In the light of the rate constants expected for these complexes these results are not surprising. When the experiment was performed on the (bromo)- and (chloro)-2,6-lutidine complexes two lutidine methyl singlets were observed at τ 6.17 and 6.98 and one allylic methyl doublet was observed at τ 8.96 (see Figures 5 and 6). The chemical shifts of these resonances correspond to the cis configuration. If the spectrum at −50° is recorded as a function of time, the second set of resonances assigned to the trans configuration gradually begins to grow in at τ 6.39 and 7.01 for the methyl resonances of the pyridine and at τ 8.47 for the methyl resonance of the allyl. The same experiment was carried out on the (bromo)- and (chloro)-2,4,6-collidine complexes; in this case the two collidine methyl singlets had chemical shifts of τ 6.41 and 7.07 and the allylic methyl doublet appeared at τ 8.48. As time passed a second set of pyridine methyl singlets grew in at τ 6.19 and 7.04 and the second allyl doublet grew in at τ 8.95. Thus for the 2,4,6-collidine complex the configuration in the solid is the trans isomer.

One can only speculate about the forces in the solid responsible for the preference for the cis configuration in the 2,6-lutidine complex and the trans configuration in the 2,4,6-collidine complex. In solution, however, the cis–trans equilibrium constants, which are summarized in Table IV, can be largely attributed to intramolecular steric interactions. For all of the complexes the ratio of cis to trans isomers at −70° is greater than 1. Molecular models suggest that the bulky halogen atom can interact to a greater extent with the methyl substituent of the allyl than the α-substituted pyridine ring, oriented "perpendicular" to the square plane, interacts with the allylic methyl substituent. Hence, in order to minimize halogen–allylic methyl interaction the cis configuration is favored over the trans. In addition K_{eq}(cis/trans) increases when the chlorine atom is replaced by bromine. The larger radius of the bromine relative to the chlorine would be expected to destabilize the trans configuration in the bromo complex even more than in the chloro complex due to the interactions discussed above.

TABLE IV
EQUILIBRIUM CONSTANTS FOR CIS–TRANS ISOMERISM FOR (π-crotyl)(amine)PdX COMPLEXES[a]

Amine	X	K(cis/trans)	Amine	X	K(cis/trans)
2-Picoline[b]	Cl	1.37	2,6-Lutidine	Br	1.54
2-Picoline[b]	Br	1.96	2,4,6-Collidine	Cl	1.08
2,6-Lutidine	Cl	1.10	2,4,6-Collidine	Br	1.48

[a] Measurements were made on dichlorofluoromethane solutions of the complex at −78°. Variations in *K* appear to be minimal (<1% over a 30° range). The pyridine chloride complex varies substantially, however: 1.13 (−86°), 1.18 (−75°), 1.22 (−64°), and 1.28 (−53°). [b] There appears to be no thermodynamic preference for the endo or exo isomers; *i.e.*, the endo:exo ratio is 1.00 (see exceptions in ref 1).

Phase 3.—The final observable spectral variations for π-crotyl(amine)palladium halide complexes occur above +30°. The spectral changes for π-crotyl(2-picoline)palladium chloride from 30 to 90° are shown in Figure 7. As the temperature is increased above +30°, both the syn and the anti doublets broaden considerably until at +90° they are no longer detectable. At the same time changes in the sextet of the central allylic hydrogen occur. When the temperature is lowered, the spectrum at +30° is reproduced. Reversible broadening of the syn and anti resonances is consistent with proton exchange between these two sites. The fully averaged syn–anti resonance would be a doublet giving an averaged coupling to the central proton of ≃10 Hz. Consequently, the central proton of the allyl ligand will be coupled by ≃12 Hz to the H2 proton and by ~10 Hz to the averaged syn and anti protons; the multiplet pattern should thus appear as a superimposed doublet of triplets as is beginning to occur at +91° in Figure 7.

Excessive decomposition of the complex at +90° and above makes this the upper limit of peak width measurements. In practice gradual thermal decomposition at temperatures below +90° decreases the range of valid peak width measurements. This problem can be circumvented by means of double-resonance techniques.[12] When exchange occurs between two sites, saturation of the resonance corresponding to one site will result in partial saturation of the resonance corresponding to the other site if the relaxation time of the second site is comparable to the reciprocal of the exchange rate. This spin saturation transfer technique is particularly advantageous because slower rates of exchange, hence lower temperatures, are required than in line width measurements. Saturation of the syn resonance led to partial saturation in the anti resonance, thus confirming syn–anti exchange. This interchange of syn and anti protons is consistent with a rearrangement involving σ-bond formation at the unsubstituted end of the crotyl moiety (3-*h*-1-methylallyl intermediate). It can be shown quite clearly in cases involving

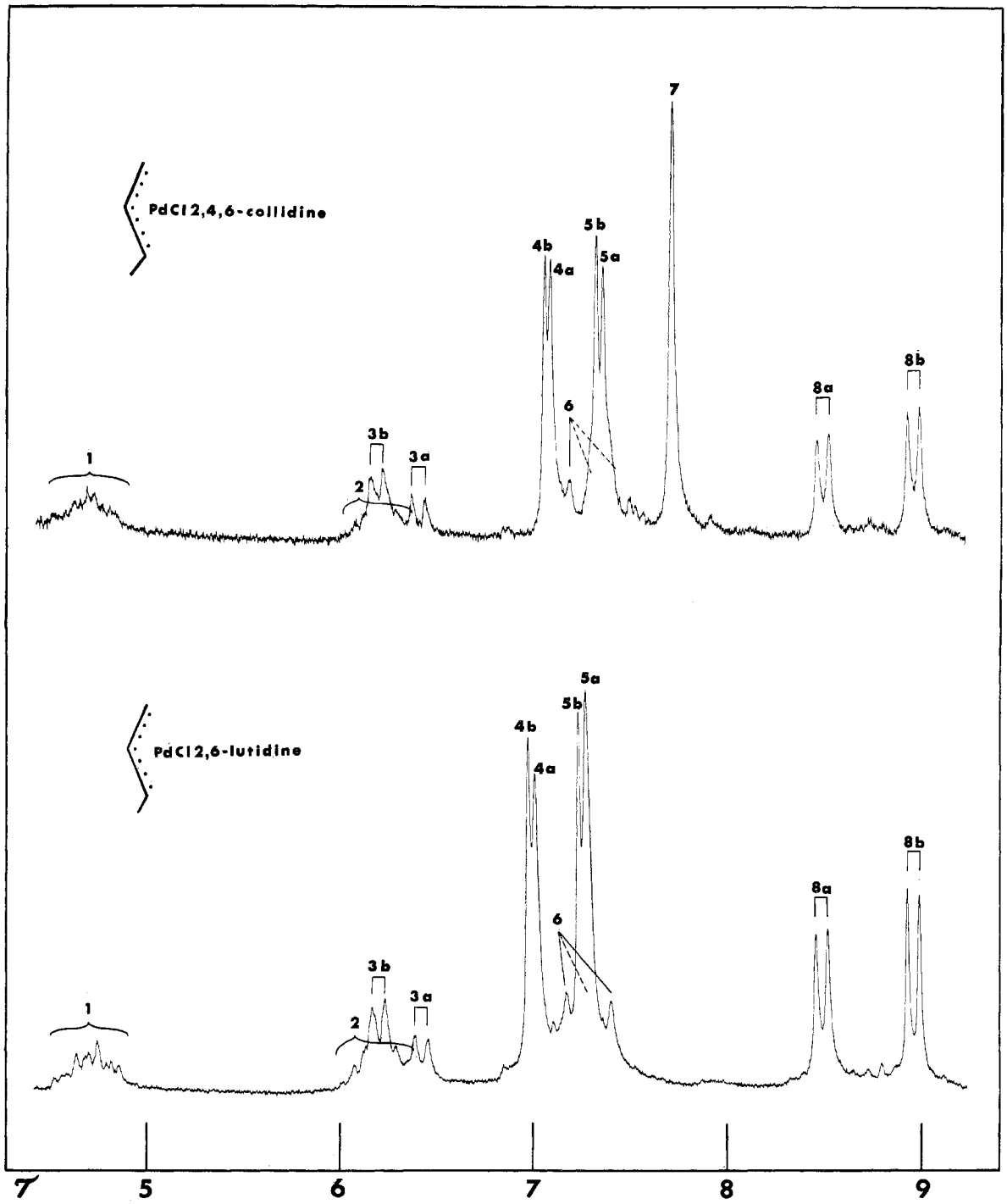


Figure 5.—The 100-MHz pmr spectra of π-crotyl(2,6-lutidine)palladium chloride and π-crotyl(2,4,6-collidine)palladium chloride in CCl_2FH at 0°. The spectra are effectively the same at −80°.

other substituents on the allyl moiety that the σ-bonded intermediate adequately explains isomerization and racemization pathways, whereas other suggested intermediates and mechanisms cannot adequately explain them.[1,10,11,15] Although the involvement of a σ-bonded intermediate has been strongly implicated in previous studies, the mechanism of its formation in these amine complexes is unusual in view of the results reported for the analogous phosphine and arsine complexes.[16] No significant dependence of the rate constant on complex concentration or excess amine was observed, which implies that the major pathway involves a simple intramolecular dissociation of one end of the allyl moiety to form the σ-bonded intermediate.[17] In the phosphine

(15) J. W. Faller, M. E. Thomsen, and M. J. Mattina, *J. Amer. Chem. Soc.*, **93**, 2642 (1971).

(16) K. Vrieze, H. C. Volger, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta Rev.*, **3**, 109 (1969).

(17) In general one would anticipate that there would be a different barrier associated with the formation of the σ bond at substituted and unsubstituted ends of the allyl moiety. In fact, it appears that about a 3 kcal/mol higher activation is involved for the 1-*h*-1-methylallyl intermediate.[15] The formation of the monohapto intermediate requires that a syn methyl complex isomerize to an anti methyl complex, which is unfavorable thermodynamically in this case. Details of these arrangements have been treated elsewhere[15] in consideration of complexes where these reactions are more important to the understanding of interconversions of major isomers in solution. Nevertheless, some anti crotyl isomers exist in the solution (~5%). The complications arising from considering the four additional isomers or, further, the effects of the chirality at the substituted end of the allyl did not appear to justify the confusion which would result in the discussion here.

TABLE V
ANALYSES OF SOME (π-allyl)PdLX COMPLEXES[a]

π-Allyl	X	L	Mp, °C	% C		% H		% N	
				Calcd	Found	Calcd	Found	Calcd	Found
Crotyl	Cl	Pyridine	66–69	39.16	39.05	4.38	4.43	5.07	4.95
Crotyl	Cl	2-Picoline	105–106	41.41	41.66	4.86	4.84	4.83	4.84
Crotyl (cis)	Cl	2,6-Lutidine	129–131	43.44	43.60	5.30	5.40	4.61	4.61
Crotyl (trans)	Cl	2,4,6-Collidine	>130 dec	45.30	45.58	5.70	5.80	4.40	4.31
Crotyl	Br	2-Picoline	112–114	35.90	35.90	4.20	4.20	4.19	4.15
Crotyl (cis)	Br	2,6-Lutidine[b]	136–140 dec	37.90	36.94	4.63	4.30	4.02	4.04
Crotyl (trans)	Br	2,4,6-Collidine	>145 dec	39.75	39.95	5.00	5.01	3.86	3.81
Allyl	Br	2,4,6-Collidine	163–165	37.90	37.78	4.63	4.57	4.02	3.90

[a] Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. [b] The nmr of the recrystallized material always indicated the presence of a small amount of the analogous dimer.

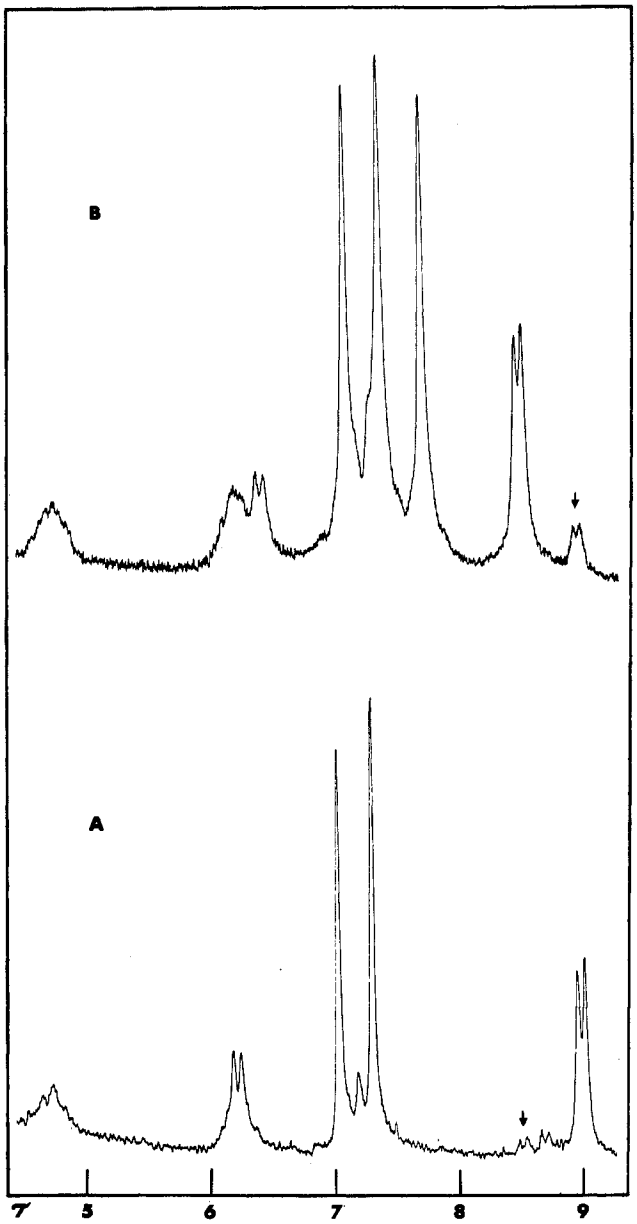


Figure 6.—Pmr spectra corresponding to the configuration found in the solid state of π-crotyl(2,6-lutidine)palladium chloride (A) and of π-crotyl (2,4,6-collidine)palladium chloride (B). The samples were prepared in CCl_2FH at −196° and the spectra recorded at −50°.

and arsine complexes, on the other hand, bimolecular mechanisms appear to predominate. Furthermore, no significant variations in rate constant with amine appear. This is unusual since it appears that the end of the allyl which becomes detached most easily in phosphine or arsine complexes is that end trans to the L group. In this case, the same type of effect may be partially masked by the tendency to form σ bonds at the unsubstituted end of the allyl.

Experimental Section

Preparation of Complexes. π-Crotyl(amine)palladium Halide Complexes.—These complexes were prepared by stirring an ethyl acetate solution of the di-μ-halo dimer with a fourfold excess of the amine under nitrogen for 0.5 hr at room temperature.[18] The white complexes which precipitated from solution were air stable and were recrystallized from methylene chloride–cyclohexane mixtures. (See Table V.)

Dimers.—The bis-π-crotyldi-μ-chloro-dipalladium complex (mp 142°) was prepared by the method of Dent, Long, and Wilkinson[19] and was mixed with a two- to threefold excess of lithium bromide in acetone at room temperature.[20] The solvent was removed and the residue was mixed with water. The bromo dimer was extracted from the aqueous layer with methylene chloride and the product (mp 163–165°) was crystallized from methylene chloride–cyclohexane mixtures.

Magnetic Resonance Measurements. Instrumentation.—Pmr spectra were obtained using a Varian Associates HA-100 spectrometer operating in frequency sweep mode. The probe temperature for kinetics experiments were measured by means of a copper–constantan thermocouple. Temperatures requiring less precision sometimes used an alternative calibration procedure based on the variation in chemical shift between the methyl and hydroxyl protons in methanol with temperature variations.

Rate Measurements.—The pseudo-first-order rate constants for leaving a given site were determined from the broadening of the resonance assigned to that site from the equation

$$k = \pi(\Delta\nu_{1/2}' - \Delta\nu_{1/2})$$

where $\Delta\nu_{1/2}'$ and $\Delta\nu_{1/2}$ refer the full widths of the resonances at half-height in the presence and absence of exchange, respectively. The line shape methods,[21] as well as the spin saturation methods,[12,22] have been discussed elsewhere. The following precautions were taken to ensure that the magnetization ratios, $M_z(\infty)/M_z(0)$, were accurate: (1) radiofrequency power loss at the observing frequency was minimized by using a high center band power level; (2) power levels of the observing channel were selected to avoid saturation of the resonance; (3) power levels at the saturating frequency were increased several times to ensure complete saturation of other sites; (4) values of magnetization were measured with the same value of power in the H_2 oscillator but set at an irrelevant frequency, in order to determine $M_z(0)$.

Kinetics.—Free energies of activation were calculated from $\log k = 10.321 + \log T - \Delta F^*/2.303RT$, using the line-broadening equations indicated above and in Table II. This equation requires only one rate constant at one temperature to evaluate ΔF^*. Temperatures were selected which allowed the greatest precision in the measurement of the broadening. That is, the temperature was adjusted such that the exchange broadening

(18) P. Corradini, G. Maglio, A. Musco, and P. Paiaro, *Chem. Commun.*, 618 (1966).
(19) W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964).
(20) J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1839 (1967).
(21) C. S. Johnson, *Advan. Magn. Resonance*, **1**, 33 (1965).
(22) R. A. Hoffman and S. Forsen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **1**, 15 (1966).

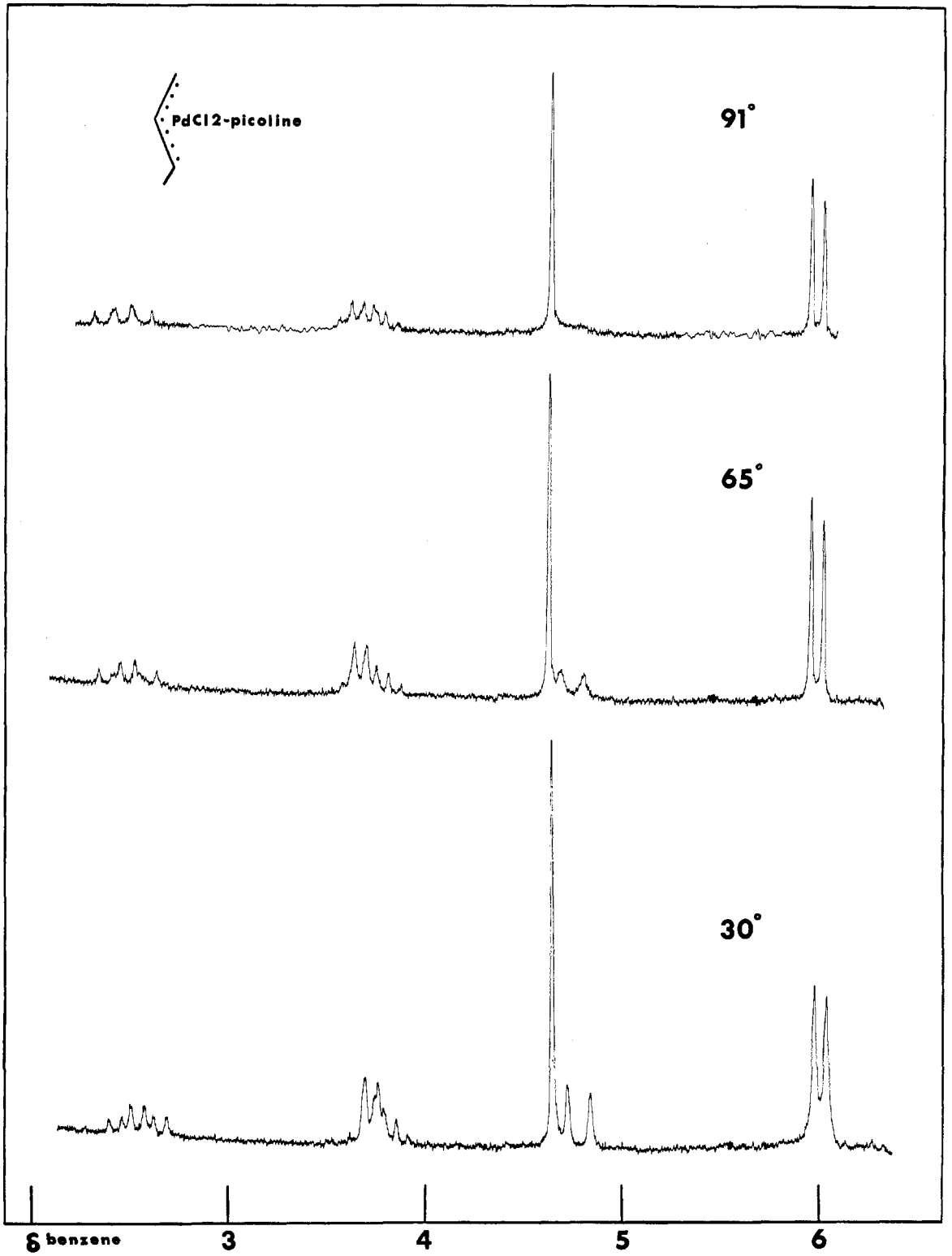


Figure 7.—The 100-MHz pmr spectra of π-crotyl(2-picoline)palladium chloride in benzene from +30° to +90°.

($\Delta\nu_{1/2}' - \Delta\nu_{1/2}$) was between 2.0 and 5.0 Hz. After temperature equilibration was attained, the rates determined at that temperature varied over a range of less than ±10% and standard deviations of the broadening were less than ±0.1 Hz. A ±10% range in rate constant corresponds to approximately a 0.03 kcal/mol range in ΔF^*. Furthermore, over a ±5° range of temperature the reported values of ΔF^* never varied by more than ±0.1 kcal/mol. The comparisons of data in Table II for the chloro and bromo compounds were taken under identical conditions; hence the difference of 0.3–0.4 kcal/mol between the halo complexes is significant.

Although the precision of the method allows significance to be attached to differences of 0.3 kcal/mol for samples under identical conditions; errors arising from variations in natural line widths, the complexity of competing reactions, errors arising from variations in natural line widths, overlap of resonances, approximations of chemical shift differences and errors in temperature measurement suggest that the accuracy of the method is less. That is, the differences in ΔF^* determined at a given temperature are significant; however, the uncertainty in the magnitude of ΔF^* might be as large as ±0.5 kcal/mol. In cases where it has been possible to measure rates over a range of temperature of 150°,[23]

(23) J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970).

log A values of ~12.8 have generally been observed for intramolecular first-order reactions. We have found that attempts to determine activation parameters from Arrhenius plots of rates determined from nmr data obtained over a very narrow temperature range generally give very misleading results. The predominant pathways in the reactions discussed in this paper have been shown to involve principally first-order kinetics and the large number of processes occurring limit the range over which the rate of any given process can be studied readily. Therefore, ΔF^* rather than E_a has been reported; nevertheless the expected values of log $A \approx 12.8$ and $\Delta S^* \approx 0$ suggest: (1) that ΔF^* will show only minor variations with temperature (such that no isokinetic temperature or reversal of trends would be expected) and (2) that relative rates at a given temperature should be adequately predicted using ΔF^* from a different temperature or by using E_a determined from a single rate at a single temperature and assuming log $A \approx 12.8$.

Cis–Trans Exchange Rates.—Some of the intricacies of the kinetics of cis–trans isomerization in these amine derivatives could be anticipated by consideration of the extensive studies of the phosphine and arsine complexes by Vrieze, *et al.*[16] The tentative kinetic scheme shown in the text is consistent with the major trends observed for concentration dependences in dilute solutions.[13] Since solubility limits one to fairly small concentration ranges of the complex, there is often difficulty in distinguishing orders of reaction with respect to certain components, particularly with respect to $^1/_2$- and $^1/_3$-order dependencies. Nevertheless, several paths are indicated by even the qualitative observation that the rate constant for leaving a trans site, $1/\tau(ML)$, increases with sufficient concentration of either the complex, amine, or the dimer. Increasing the concentration of the amine decreases the concentration of the dimer and *vice versa;* hence, the fact that increases in $1/\tau(ML)$ are observed with increasing concentrations of both suggests that at least two bimolecular pathways should be involved. The dependence of complex at high complex concentration appears to reflect the importance of a third bimolecular process; however, dependence is also observed due to its effect on increasing the concentrations of amine and dimer. It is apparent that a much more detailed study would be necessary to describe the kinetics in these systems in full; however, we have verified the qualitative observations indicated above for each of the complexes.

From the scheme suggested and taking $K_0 = [ML]^2/[M_2][L]^2$, one obtains the following relationships for the reciprocal lifetime of the complex: for high [L]

$$1/\tau(ML) = k_1K_0^{-1/2}[M_2]^{1/2} + k_3[L] + k_{-2}$$

and for high $[M_2]$

$$1/\tau(ML) = k_1K_0^{-1/2}[M_2]^{1/2} + k_3K_0^{-1/2}[ML]/[M_2]^{1/2} + k_{-2}$$

Actually other terms must be added to this expression to account for all of the concentration behavior.[13] The k_{-2} term makes a negligible contribution to the expression if there are appreciable concentrations of dimer or amine. Due to dissociation of the complex into dimer and free amine, the first two terms can become important even in the solutions prepared from the pure complex. It is difficult to assess the contribution of k_{-2} at high temperatures due to the effects of overlapping and competing processes; nevertheless it is obvious that k_{-2} is negligible compared to the other terms in solutions with complex concentrations ~0.3 M. Since the observed lifetime is a composite of several rate processes, ascribing a ΔF^* for the overall rate is inappropriate. Nevertheless, these free energies of activation provide a method of estimating rates at different temperatures in order to suggest conditions for the determination of solid-state configurations. Considering the difficulties which arise from standard kinetic approaches, spin saturation experiments[11] have often proven to be preferable in determining rearrangement pathways.

In order to estimate the order of magnitude of the rate constants some representative data from the π-crotyl(2-picoline)-palladium chloride complex were presented; however, it should be noted that there may be some hidden dependence on complex concentration in the constants derived from variation in dimer concentration.[13] Peak width measurements were taken for the resonance assigned to the methyl substituent of the allyl in the complex. From −55 to −38° in the absence of excess dimer or amine the line width in dilute CCl_2FH solution was 1.7 Hz. Measurements of the line widths for the trans isomer at −29° gave the following values as a function of complex concentration: 2.4 Hz (0.25 M), 2.6 Hz (0.33 M), 3.6 Hz (0.50 M), and 5.2 Hz (1.0 M). For variations in the dimer concentration at −60° the following line widths were observed for a complex concentration of 0.51 M: 2.8 Hz (0.11 M), 3.5 Hz (0.28 M), 4.3 Hz (0.50 M). As a function of amine concentration for a complex concentration of 0.20 M, the following were obtained at −60°: 2.4 Hz (0.02 M), 3.6 Hz (0.06 M), 4.7 Hz (0.10 M), 5.8 Hz (0.15 M), and 6.4 Hz (0.20 M). The following orders of magnitude at −60° are obtained: $K_0 \approx 10^4\ M^{-1}$; $k_1 \approx 10^3\ M^{-1}$ sec^{-1}; $k_3 \approx 10^2\ M^{-1}$ sec^{-1}.

π–σ Interchange Rates in π-Crotylpalladium Chloride Complexes.—The broadening is independent of complex concentration in dilute solutions. For instance, in the pyridine derivative the following widths were observed for the anti (H6) resonances in benzene at 55°: 3.6 Hz (0.13 M), 3.6 Hz (0.17 M), 3.5 Hz (0.25 M), and 4.0 Hz (0.51 M). Spin saturation transfer studies showed that the syn–anti interchange was independent of amine concentration. For a 0.20 M solution of the complex in benzene at 50° the following values of $M_z(\infty)/M_z(0)$ were observed upon total saturation of the syn resonance with variations in pyridine concentration: 0.41 (0.0 M), 0.41 (0.51 M), 0.40 (0.63 M), 0.40 (0.81 M), and 0.42 (1.41 M). To test the effect of base strength, broadening was measured on several amine derivatives in benzene solution at 56° and yielded 3.6 (pyridine), 3.6 (2-picoline), and 3.8 Hz (2,6-lutidine) ($\Delta F^* = 18.1$ kcal/mol).

Equilibrium Constants.—Peak areas were measured by cutting out traces of the doublets of the methyl substituent of the crotyl moiety and weighing them. The values cited are the average of several measurements. Standard deviations of the equilibrium constants indicated a precision of ±0.02.

Attempted Determination of Rotational Barriers.[9]—Efforts to obtain the required activation energy differences for the allyl and 1,3-dimethylallyl complexes were thwarted for several reasons. For the allyl(2,6-lutidine) complex the spectrum is unchanged from −80 to −15°. At −15° variations in the peak width of the pyridine 2-methyl substituent are first observed; these changes are accompanied by variations in the syn and anti resonances of the allyl. The concomitant changes in both the pyridine and allyl resonances must be interpreted in terms of the amine-exchange mechanism (see phase 2). These changes just described are comparable to those observed in the π-crotyl(2,6-lutidine) or -(2,4,6-collidine) complexes; the pmr spectrum is invariant from −80 to approximately 0°, at which temperature spectral variations associated with phase 2 begin. Figure 5 illustrates the spectral appearance up to 0° for these two compounds. For the π-1,3-dimethyl-4-picoline complex no alteration of the hydrogen resonance of the picoline was noted down to −100°. A similar result was observed for the π-crotyl(pyridine) compound.

Intramolecular interactions provide a consistent interpretation of these observations. In the ortho-disubstitued pyridine ligand steric interactions during rotation about the N–Pd bond raise the activation energy for phase 1 above that for phase 2. Since for the exchange of the 2,6-lutidine ligand in π-crotyl complexes $\Delta F^* = 16.2$ kcal mol^{-1}, for the 2,6-lutidine complexes of π-allyl and π-1,3-dimethylallyl the activation energy for rotation about the N–Pd bond must be >16.2 kcal mol^{-1}. For pyridine ligands unsubstituted in the ortho positions steric interactions between the pyridine 2 hydrogens and other atoms in the molecule during rotation are considerably reduced. Since the effects of a barrier of 8.0 kcal mol^{-1} can be observed at −96° (see Table II, the π-crotyl(2-picoline) complex), it must be concluded that $\Delta F^* <$ 8.0 kcal mol^{-1} for the pyridine and 4-picoline ligands.

Attempted Assignment of Endo and Exo Configurations.—Attempts to assign the endo and exo configurations to particular resonances *via* the nuclear Overhauser effect were unsuccessful. Irradiation of the methyl resonances of the amine ligands produced no intensity enhancement of the crotyl resonances, or *vice versa*.