# Isomerism Energetics and Mechanisms for Palladium(II) Phosphine Complexes Containing 5-Methyl- and 5-Trifluoromethyltetrazoles

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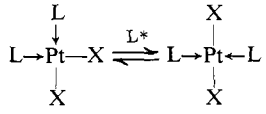
**Abstract:** These data pertain to the mechanisms of uncatalyzed and catalyzed cis–trans and linkage isomerization for 11 complexes of the type $(R_3P)_2Pd(tet)_2$, where $R_3P$ = $CH_3P(C_6H_5)_2$, $(CH_3)_2PC_6H_5$, $(C_6H_5)_3P$, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (abbreviated diphos), or $(C_6H_5)_{3-n}P(CH_2C_6H_5)_n$ ($n$ = 1–3) and tet = 5-methyl or 5-trifluoromethyl tetrazolate. Evidence is found for the ambidentate behavior of the tetrazoles, wherein coordination of either the $N_1$ or $N_2$ nitrogen is observed. The complexes have been studied in solution by proton and fluorine nuclear magnetic resonance, electronic and infrared spectroscopy, and conductometric methods. The ambidentate behavior of tetrazoles and the effects of solvent, phosphine, and the nature of the anion on the solution behavior and on the isomerization mechanisms were ascertained. When the isomerizations are catalyzed by phosphines, tetrazole exchange is more rapid than phosphine exchange, whereas in the absence of excess phosphine, phosphine exchange is more rapid than tetrazole exchange. Equilibrium and activation thermodynamics were determined and profile diagrams were constructed for these processes. A unified mechanism for isomerization of square-planar complexes is developed and discussed in terms of orbital symmetry selection rules.

The recent interest in the isomerization mechanisms of square planar platinum(II) and palladium(II) phosphine complexes[3–8] can be attributed in part to the importance of these metals and their complexes as catalysts. Although several other transition metals are now very important as laboratory and industrial catalysts, platinum and palladium continue to be widely investigated, perhaps because of their widespread catalytic activity, their relatively inert character, and the usual facile synthesis of their complexes. A major problem involved in the study of cis–trans isomerization of most platinum complexes investigated, however, is their nonlability, necessitating the use of phosphines to catalyze isomerization (eq 1).

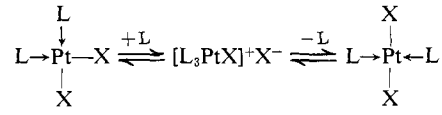


(1)

(L, L* are the same or different phosphines; X is a halide)

Recent investigations have demonstrated that isomerization catalyzed by L* results in no L and L* interchange.[3] This was taken to imply that any five-coordinate intermediate or transition state cannot have a regular geometry and must be distorted in such a way that L* and L can never become equivalent. This is not inconsistent with X-ray data which suggests nonregular geometry for a five-coordinate $d^8$ complex.[9]

Consecutive displacement was also proposed some time ago.[6] In this mechanism the excess phosphine displaces an anion to form an ionic intermediate of the type $[ML_3X]^+X^-$, from which L is then lost (or displaced by X) resulting in isomerization (eq 2). In the most recent



(2)

work,[7] in this area, the consecutive displacement mechanism has been upheld, since the ionic intermediate has been isolated as the $PF_6^-$ salt, when L = L* (eq 1). The difference in interpretation of the data which has given rise to the two mechanisms is whether the rate of isomerization is the same when catalyzed by L or L* (*i.e.*, is the isomerization rate sensitive to the nature of the catalyzing phosphine?). If the rate of isomerization is the same for L and L*, then a distorted pentacoordinated intermediate where L* occupies a unique position is required, as "no ligand mixing was observed."[3] If, on the other hand, the rates of isomerization are not the same, then consecutive displacement is the most probable mechanism.[7,8]

Only a few investigations of the isomerization behavior of similar palladium(II) complexes[6,8] have been reported; they are less detailed perhaps because the palladium(II) and platinum(II) complexes were expected to exhibit the same behavior. Nonetheless, isomerizations were catalyzed by excess ligand, consistent with a consecutive displacement mechanism, both for amine[6] and phosphine[8] complexes. Evidence supporting this mechanism for the phosphine complex was the isolation of the intermediate $[((CH_3)_2P\text{-}o\text{-}tolyl)_3PdCl]^+PF_6^-$.[8]

We recently reported solvent effects on the cis–trans equilibrium thermodynamics of $[(CH_3)_2PC_6H_5]_2PdCl_2$

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(3) P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 92, 4996 (1970).

(4) P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 92, 5243 (1970).

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and $[(C_6H_5)_2PCH_3]_2PdCl_2$ where we noted that isomerization was so rapid that on changing the temperature, equilibrium was reestablished within a few seconds.[10] While we were able to affect the position of the cis–trans equilibrium thermally, we were only able to monitor the chemical integrity of the phosphine and knew nothing of the fate of the anion. This made it nearly impossible to discern anything concerning the nature of the mechanism of isomerization. With the problem of nonlability surmounted, we prepared tetrazole complexes with these and similar phosphines which we hoped would be labile and where, *via* the tetrazole, we could monitor the behavior of the anion. We were able to follow the fate of the tetrazole, as well as the phosphine, *via* $^1H$ or $^{19}F$ nmr if the 5-position of the tetrazole was $CH_3$ or $CF_3$ substituted.

Tetrazole (Figure 1) was first explored as an anion for transition metals following the discovery of cyclopentadienyl sandwich complexes. Since tetrazole is an isoelectronic, aromatic, heterocyclic analog of cyclopentadiene, it was thought that tetrazole might also bond to transition metals through its $\pi$-electron cloud.[11] Contrary to initial reports of such behavior,[12,13] it was soon discovered that tetrazoles coordinate instead through the $C_5$ carbon or any of the nitrogen atoms.[14] When 5-R-substituted tetrazoles were used, only nitrogen metal bonds were formed, but still the exact structures of most complexes were not known because of the possibility of linkage isomerization (Figure 1)[15,16] and ambidentate behavior. More recently, quantum mechanical calculations have shown that the two possible bonding modes ($N_1$ *vs.* $N_2$) are essentially energetically equivalent,[16] and for the complexes *trans*-HPt[P-$(C_6H_5)_3]_2$(5-R-tet), R = $CH_3$, Cl, or $C_6H_5$, both $N_1$ and $N_2$ bound tetrazoles were shown to be present in solution in approximately equal amounts *via* $^1H$ nmr.[16]

The objectives of the work reported here were twofold: (1) to determine the mode of bonding of the tetrazole and the influence of substituents and other ligands on the bonding and (2) to use the substituents on the tetrazole as a probe, to follow the fate of the anion as the isomerization progresses, and thus determine the mechanisms of cis–trans isomerization. The results of this study are reported herein.

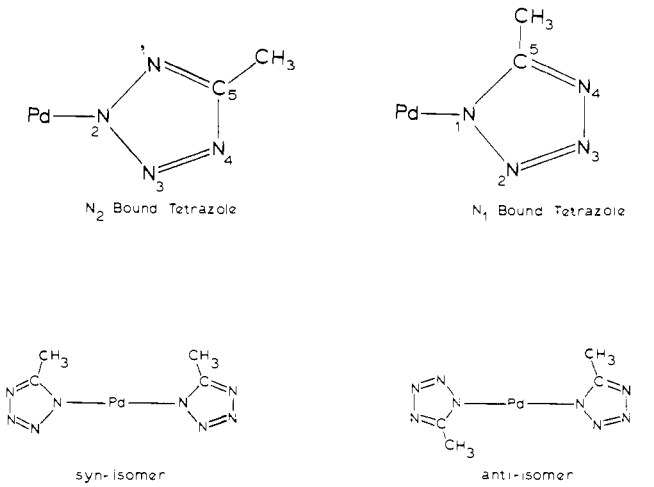


**Figure 1.** An illustration of the ambidentate possibilities for nitrogen coordination of the tetrazole ring system, also showing the geometrical relationship of the methyl group to the metal when coordinated by either the $N_1$ or $N_2$ nitrogen. The configurational interrelationship of two coordinated tetrazoles is also shown for the trans isomers illustrating the syn and anti conformations.

## Experimental Methods

**Nuclear Magnetic Resonance.** The $^{19}F$ nmr spectra were recorded at 94.1 MHz on a Jeolco 4-H 100 nuclear magnetic resonance spectrometer equipped with a JES-VT-3 variable temperature probe. Proton nmr spectra were recorded on the same instrument at 100 MHz, or at 60 MHz, on a Varian A-60 nuclear magnetic resonance spectrometer equipped with a V-6040 variable temperature controller. The $^{19}F$ chemical shifts are relative to internal perfluorobenzene while $^1H$ chemical shifts are relative to internal tetramethylsilane. In all cases, resonating nuclei were at higher shielding than the reference. Solvents used were commercial spectroscopy grade or were purified by standard procedures. Samples were prepared by dissolving in the appropriate solvent, heating if necessary, and filtering through Kleenex into the nmr tube to remove all insoluble material. Spectra were recorded immediately after solution preparation and subsequent to the temperature studies to check for decomposition and time-dependent phenomena. Thermodynamic data were obtained for at least six temperatures, some by heating and some by cooling as previously reported.[10] The coalescence was not accompanied by decomposition except for the tetrazole coalescence at 153° for $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$. However, cooling this sample yielded a spectrum which had the same cis–trans equilibrium mixture, but whose intensity was slightly less than the fresh sample. Equilibrium thermodynamics were calculated as before[10] and $\Delta G^{\ddagger}$'s were calculated by standard procedures from coalescence temperatures, by plots of $\Delta\nu$ *vs.* $1/T$, or line broadening.[17,18]

**Conductivity.** Conductivity studies were performed at 25 ± 0.1° and temperature regulation was achieved using a Brinkman Lauda K-2/R temperature controller. Conductance measurements were made using a Yellow Springs Instruments Co. conductivity cell, Model No. 3403, and measured on an Industrial Instruments conductivity bridge, Model RCl6B2, adapted in house for use with a Heathkit, Model E.U.W.-25 oscilloscope. Conductance ranges for electrolytes were taken from published literature values.[19–21]

**Infrared Spectra.** Low frequency infrared spectra were obtained using Beckman IR-12 or Perkin-Elmer 621 spectrometers, with samples prepared as Nujol mulls between CsBr plates. High frequency spectra used in determining the presence of tetrazoles and phosphines, were recorded on Perkin-Elmer 221 and 137 spectrometers as Nujol mulls between NaCl plates.

**Electronic Spectra.** Electronic spectra were recorded at room temperature on dichloromethane solutions using a Cary Model 14 spectrophotometer.

**Compound Preparation.** Phosphines were commercially available or prepared from commercial $PCl_3$, $(C_6H_5)PCl_2$, or $(C_6H_5)_2PCl$ by standard Grignard techniques and were stored under nitrogen or in sealed glass tubes under vacuum. All reactions involving phosphines were conducted under an atmosphere of dry nitrogen.

The 5-methyl-[22] and 5-trifluoromethyltetrazoles[23] were prepared by literature methods. The sodium tetrazolates were prepared by

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**Table I.** Analytical Data for the Complexes $(R_3P)_2Pd(5\text{-}R\text{-}tet)_2$

| Complex | Mp, °C | % C Calcd | % C Found | % H Calcd | % H Found | % N Calcd | % N Found | % P Calcd | % P Found |
|---|---|---|---|---|---|---|---|---|---|
| $[CH_3P(C_6H_5)_2]_2Pd(5\text{-}CH_3tet)_2$ | 189–190 | 53.54 | 53.60 | 4.79 | 4.72 | 16.65 | 17.28 | | |
| $[CH_3P(C_6H_5)_2]_2Pd(5\text{-}CF_3tet)_2$ | 176–178 | 46.14 | 45.98 | 3.36 | 3.38 | 14.34 | 14.30 | 7.93 | 7.70 |
| $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CH_3tet)_2$ | 206–208 | 43.92 | 43.23 | 4.78 | 5.18 | 20.50 | 20.15 | | |
| $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ | 197–198 | 36.58 | 36.35 | 3.38 | 3.42 | 17.05 | 16.87 | 9.43 | 9.27 |
| $[(C_6H_5)_3P]_2Pd(5\text{-}CH_3tet)_2$[a,b] | 225–228 | 60.27 | 59.60 | 4.55 | 4.58 | 14.06 | 14.48 | 7.77 | 8.48 |
| $[(C_6H_5)_3P]_2Pd(5\text{-}CF_3tet)_2$[a] | 255 | 53.09 | 52.80 | 3.34 | 3.36 | 12.38 | 12.01 | 6.84 | 7.02 |
| (diphos)$Pd(5\text{-}CH_3tet)_2$ | 181–183 | 53.75 | 53.71 | 4.51 | 4.56 | 16.70 | 16.54 | | |
| (diphos)$Pd(5\text{-}CF_3tet)_2$ | 283–284 | 46.26 | 46.25 | 3.11 | 3.07 | 14.38 | 14.15 | 7.95 | 7.82 |
| $[C_6H_5CH_2P(C_6H_5)_2]_2Pd(5\text{-}CF_3tet)Cl$ | 197–199 | 57.75 | 57.66 | 4.57 | 4.11 | 6.75 | 6.84 | | |
| $[(C_6H_5CH_2)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ | 239–241 | 54.99 | 54.87 | 3.99 | 3.92 | 11.65 | 11.47 | 6.44 | 6.31 |
| $[(C_6H_5CH_2)_3P]_2Pd(5\text{-}CH_3tet)_2$ | 193–196 | 62.69 | 62.16 | 5.49 | 5.62 | 12.71 | 11.84 | | |
| $[(C_6H_5CH_2)_3P]_2Pd(5\text{-}CF_3tet)_2$ | 187–192 | 55.85 | 56.28 | 4.27 | 4.22 | 11.13 | 11.03 | | |
| $\{[(CH_3)_2PC_6H_5]_3PdCl\}PF_6$ | 163–165 | No reasonable analyses were obtained | | | | | | | |
| $\{[(CH_3)_2PC_6H_5]_3Pd(5\text{-}CF_3tet)\}PF_6$ | 187–189 | No reasonable analyses were obtained | | | | | | | |

[a] W. Beck, K. Burger, and W. P. Fehlhammer, *Chem. Ber.*, **102**, 3637 (1969). [b] Reference 16.

addition of equimolar amounts of 0.1 *M* NaOH to an aqueous solution of the tetrazole, and either used *in situ* or as the water-recrystallized salt. The chloride complexes, $(R_3P)_2PdCl_2$, were prepared by literature procedures.[24,25]

All tetrazole complexes were prepared by simple metathesis of the corresponding chloride complexes in the following manner. To 0.4 g (0.0068 mol) of $[CH_3P(C_6H_5)_2]_2PdCl_2$ in sufficient chloroform to dissolve the complex was added 0.3 g (0.0191 mol) of sodium 5-trifluoromethyl tetrazolate dissolved in hot methanol. The resulting solution was heated at 50° and stirred for 1 hr, then evaporated to dryness on a flash evaporator. The resulting solid was washed with distilled water, then recrystallized from dichloromethane and triturated with diethyl ether or hexane to give white or light yellow crystals (Table I). We were unable to prepare $[(C_6H_5CH_2)P(C_6H_5)_2]_2$-Pd(5-trifluoromethyltetrazole)$_2$. All attempts resulted in the formation of light yellow crystals which proved to be $[(C_6H_5CH_2)P(C_6H_5)_2]_2Pd(Cl)$(5-trifluoromethyltetrazole). This is most likely due to the insolubility of this complex such that once formed it precipitates from solution and reacts no further.

**Attempted Preparations of $\{[(CH_3)_2PC_6H_5]_3Pd(Cl)\}PF_6$.** To 0.227 g (0.0005 mol) of $[(CH_3)_2P(C_6H_5)]_2PdCl_2$ in 30 ml of dichloromethane was added 0.0695 g (0.0005 mol) of $(CH_3)_2P(C_6H_5)$ and 0.50 g (0.0031 mol) of $NH_4PF_6$. Upon addition of the phosphine, the solution turns orange, then slowly turns light yellow. The solution was shaken for 55 hr, then concentrated to an oil and crystallized and recrystallized from dichloromethane–hexane, followed by methanol–water. A similar procedure was employed in an attempt to prepare $\{[(CH_3)_2PC_6H_5]_3Pd(5\text{-}CF_3tet)\}PF_6$. Both compounds gave inconsistent and unsatisfactory elemental analyses.

*Anal.* Calcd for $\{[(CH_3)_2PC_6H_5]_3Pd(Cl)\}PF_6$: C, 41.10; H, 4.75; P, 17.66. Found: C, 44.92, 44.83; H, 4.36, 4.49; P, 17.30, 17.55. Calcd for $\{[(CH_3)_2PC_6H_5]_3Pd(5\text{-}CF_3tet)\}PF_6$: C, 38.89; H, 4.15; P, 15.42. Found: C, 37.12; H, 3.13; P, 10.05.

Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. All samples melted without decomposition to red or yellow liquids.

Elemental analyses were performed either by Galbraith Laboratories, Knoxville, Tenn., or Chemalytics, Inc., Tempe, Ariz. The analytical results are listed in Table I.

## Results

**Infrared Spectral Studies.** Assignments of Pd–P stretching frequencies are generally believed to occur between 180 and 460 $cm^{-1}$.[26] Pd–N stretching frequencies occur in about this same general region, 600–200 $cm^{-1}$, with nitrogen heterocycles occurring in the lower portion. Both Pd–P and Pd–N absorptions are generally of medium or weak intensity.[26] We have compared the ir spectra in the 250–500 $cm^{-1}$ range of the palladium(II) phosphine tetrazole complexes with the ir spectra of the corresponding chloride complexes and the corresponding phosphines and report new peaks in the tetrazole complexes (Table II). The complex

**Table II.** Infrared Spectral Data for the Complexes $(R_3P)_2Pd(5\text{-}R\text{-}tet)_2$

| Complex | $\nu_{Pd-N}$ $\nu_{Pd-P}$[a] ($cm^{-1}$) | Solid state geometry |
|---|---|---|
| $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CH_3tet)_2$ | 350, 370, 386, 437 | Cis[b] |
| $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ | 320, 350, 372, 432 | Cis |
| $[CH_3P(C_6H_5)_2]_2Pd(5\text{-}CH_3tet)_2$ | 300, 372, 396, 435 | Cis |
| $[CH_3P(C_6H_5)_2]_2Pd(5\text{-}CF_3tet)_2$ | 335, 350, 400, 445 | Cis |
| $[(C_6H_5)_3P]_2Pd(5\text{-}CH_3tet)_2$[c] | 317, 355, 440, 463 | Cis |
| $[(C_6H_5)_3P]_2Pd(5\text{-}CF_3tet)_2$ | 330, 345, 390, 420 | Cis |
| (diphos)$Pd(5\text{-}CH_3tet)_2$ | 330, 345, 380, 430 | Cis |
| (diphos)$Pd(5\text{-}CF_3tet)_2$ | 325, 360, 400, 435 | Cis |
| $[(C_6H_5CH_2)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ | 310, 356 | Trans |
| $[(C_6H_5CH_2)_3P]_2Pd(5\text{-}CH_3tet)_2$ | 348, 382 | Trans |
| $[(C_6H_5CH_2)_3P]_2Pd(5\text{-}CF_3tet)_2$ | 348, 382 | Trans |

[a] From the data given by J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis, Jr., and A. S. Wilson, *Spectrochim. Acta, Part A*, **23**, 1121 (1967); G. E. Coates and C. Parkin, *J. Chem. Soc. A*, 421 (1963); P. S. D. Park and P. J. Hendra, *Spectrochim. Acta, Part H*, **25**, 227 (1967), it seems reasonable to assign $\nu_{Pd-N}$ to the lower energy vibrations and $\nu_{Pd-P}$ to the higher energy vibrations, although there is considerable disagreement over $\nu_{M-P}$, see *c* below. [b] X-Ray crystal structure of this complex shows it to be cis in the solid state. See ref 27. [c] K. Shobatake and K. Nakamoto, *J. Amer. Chem. Soc.*, **92**, 3332 (1970), and references contained therein, assigned $\nu_{Pd-P}$ at 191 $cm^{-1}$ for $[(C_6H_5)_3P]_2PdCl_2$.

$[(CH_3)_2P(C_6H_5)]_2Pd(5\text{-}CH_3tet)_2$ is known to be cis[27] from an X-ray crystal structure determination, and analysis of our ir spectra shows the presence of four new absorptions for this tetrazole complex in addition to those of the free phosphine. By standard group theoretical analysis,[28,29] if two Pd–P or Pd–N bonds are cis and the complex possesses $C_{2v}$ symmetry, then two absorptions are expected for both $\nu_{Pd-P}$ and $\nu_{Pd-N}$. If the two bonds are trans and the complex possesses $D_{2h}$ symmetry, then only one absorption for both the Pd–P and the Pd–N stretching frequencies should occur. Since this complex shows four new absorptions it is assigned the cis configuration in the solid state in agreement with

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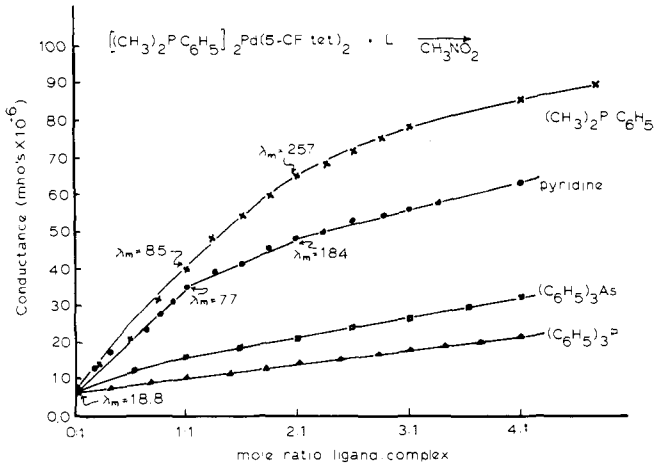


**Figure 2.** Results of conductometric titrations of a $4.56 \times 10^{-4}$ *M* solution of $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ with solutions containing $1.158 \times 10^{-3}$ *M* $(CH_3)_2PC_6H_5$ (×), $1.0 \times 10^{-3}$ *M* pyridine (○), $1.0 \times 10^{-3}$ *M* $(C_6H_5)_3As$ (□), and $1.0 \times 10^{-3}$ *M* $(C_6H_5)_3P$ (△), in nitromethane plotted as measured conductance *vs.* mole ratio of ligand:complex. See ref 19–21 for conductance values for various electrolytes in nitromethane.

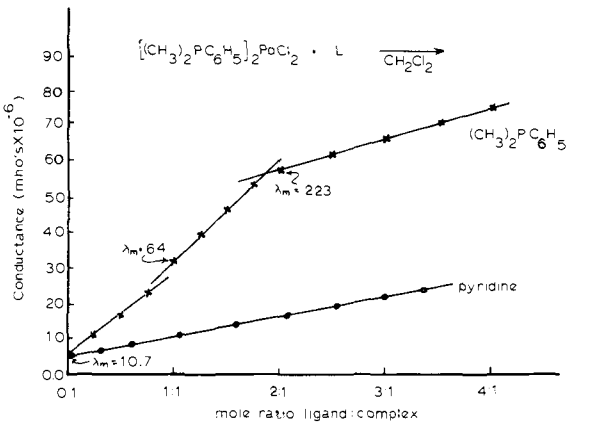


**Figure 3.** Results of conductometric titrations of a $5.00 \times 10^{-4}$ *M* solution of $[(CH_3)_2PC_6H_5]_2PdCl_2$ with solutions containing $1.58 \times 10^{-3}$ *M* $(CH_3)_2PC_6H_5$ (×) and $1.0 \times 10^{-2}$ *M* pyridine (○) in dichloromethane plotted as measured conductance *vs.* mole ratio of ligand:complex. Similar results were obtained for $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ in dichloromethane.

the crystal structure analysis.[27] Likewise the complexes of diphos, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, are required to be in the cis configuration and the ir spectra of the diphos tetrazole complexes show four peaks attributable to $\nu_{Pd-P}$ and $\nu_{Pd-N}$. The benzylphosphine complexes, on the other hand, show only two additional absorptions and are consequently assigned as trans in the solid state entirely consistent with $^1H$ nmr results which demonstrate that in all cases the benzylphosphine tetrazole complexes are trans in solution (*vide infra*). A summary of complexes in this paper and their configuration in the solid state is found in Table II.

**Conductometric Studies.** Since Powell[7,8] has isolated both palladium and platinum ionic species and has $^1H$ nmr evidence for their existence in solution, a conductometric study was undertaken to test the supposition that for the catalyzed consecutive displacement mechanism an ionic intermediate is formed. It was also found that the solvent has a marked effect on the cis–trans equilibrium and dramatic effects on the isomerization rates.

The plots of conductance *vs.* moles of base per mole of complex are shown in Figures 2 and 3 for $[(CH_3)_2P(C_6H_5)]_2Pd(5\text{-}CF_3tet)_2$ and $[(CH_3)_2P(C_6H_5)]_2PdCl_2$, respectively. Parallel studies were conducted in both dichloromethane and nitromethane for both complexes. Titration of either complex with additional solvent in all cases produced no change in conductivity, indicating that neither dichloromethane nor nitromethane caused dissociation. Bases against which the complexes were titrated were triphenylphosphine, triphenylarsine, pyridine, and dimethylphenylphosphine.

For the complex $[(CH_3)_2P(C_6H_5)]_2Pd(5\text{-}CF_3tet)_2$ in nitromethane, both triphenylphosphine and triphenylarsine give straight line plots of slowly increasing conductivity. Pyridine and dimethylphenylphosphine, on the other hand, plot as a long curve with two inflection points, one at 1:1 ($\lambda_m$ = 77 or 85 $cm^2\ \Omega^{-1}\ mol^{-1}$) and one at 2:1 ($\lambda_m$ = 184 or 257 $cm^2\ \Omega^{-1}\ mol^{-1}$) electrolytes with dimethylphenylphosphine showing the higher conductivity (see Figure 2). In dichloromethane, $[(CH_3)_2P(C_6H_5)]_2Pd(5\text{-}CF_3tet)_2$ had straight line plots which slowly increased in conductivity for pyridine and triphenylphosphine; a curve with two inflection points, however, was obtained for dimethylphenylphosphine at molar ratios of 1:1 ($\lambda_m$ = 99.7) and 2:1 ($\lambda_m$ = 167.5). (The molar conductances at these two points are in accord with 1:1 and 2:1 electrolytes, respectively.) It is important to notice the difference in behavior of pyridine in the two different solvents. Whereas ionic species are formed on addition of pyridine in nitromethane, a solvent capable of supporting such species, no evidence is found for ionic species in dichloromethane.

When various bases were added to $[(CH_3)_2P(C_6H_5)]_2PdCl_2$, ionic species were only found for $(CH_3)_2P(C_6H_5)$ in either solvent. Furthermore in nitromethane, pyridine produces no ionic species for the chloride complex, but they are formed with the tetrazole complex (*vide supra*). This suggests that the ionic species not only require a solvent which can stabilize them but their formation is also dependent on the particular anion.

Similar to the other complexes, $[(C_6H_5)_3P]_2PdCl_2$ in dichloromethane and nitromethane gave straight lines; however, with $(CH_3)_2P(C_6H_5)$ in nitromethane, the plot gave a curve with only one inflection point at 2:1 molar ratios of phosphine to complex. The molar conductance at this point is that of a 2:1 electrolyte ($\lambda_m$ = 223 in $CH_3NO_2$).

A similar study involving $C_3H_7(C_6H_5)_2P$ and *cis*-$[C_3H_7(C_6H_5)_2P]_2PtCl_2$[24] in dichloromethane indicated a 1:1 electrolyte which was isolated as the $(C_6H_5)_4B^-$ salt. A number of cationic palladium and platinum complexes having the general formulas $[ML_4]^{2+}$ and $[ML_3X]^+$ where L is phosphites,[30] phosphonites,[30] phosphinites,[30] trimethylphosphine,[31] trimethylarsine,[31] or methyldiphenylarsine[32] have also been isolated.

We were unable to isolate either the 1:1 or 2:1 electrolytes studied herein as the $PF_6^-$ salts in a pure form with satisfactory elemental analyses. However, in-infrared, nmr, and conductometric data indicated that they had been formed in solution (Table III).

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(31) D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc. A*, 545 (1970).
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Table III. Nmr Data for Solutions of $PF_6^-$ Complexes

| Complex | Phosphine resonances[a] ($\tau$) | Tetrazole resonances ($\delta$) |
|---|---|---|
| $\{[(CH_3)_2PC_6H_5]_3PdCl\}PF_6$ | 8.10 (t), 8.22 (t)<br>8.75 (d), 8.85 (d) | |
| $\{[(CH_3)_2PC_6H_5]_3Pd(5\text{-}CF_3tet)\}PF_6$ | 8.60 (t) | 13.68 (s) |

[a] Phenyl resonances not reported: infrared, $\nu_{Pd-P}$ and $\nu_{Pd-N}$, 300, 350, 412, 416, 505 and 295, 350, 365, 435, 450, and 485 $cm^{-1}$, respectively (see ref 30–32); $\nu_{3(flu)}$, 850 $cm^{-1}$; $\nu_{4(flu)}$, 565 $cm^{-1}$; for $PF_6^-$, see A. De Lettre, *J. Chem. Phys.*, **19**, 1610 (1951); nmr $^{19}F$, $PF_6^-$ $\delta$ 85.24 $'J_{PF}$ = 712 Hz for $\{[(CH_3)_2PC_6H_5]_3PdCl\}PF_6$, see M. Grayson and E. J. Griffith, Ed., *Top. Phosphorus Chem.*, **5**, 446 (1967); conductance, $\lambda_m$ = 57.2 mhos for a $1 \times 10^{-3}$ *M* $CH_2Cl_2$ solution of $\{[(CH_3)_2PC_6H_5]_3PdCl\}PF_6$. Thus, the ionic chloro complex is formed in solution but the ionic tetrazolato complex is only present as a rapidly equilibrating mixture of $[(R_3P)_3Pd(tet)]^+$ and $(R_3P)_2Pd(tet)_2$.

**Electronic Spectral Studies.** In an effort to further substantiate our conductometric results, we attempted to follow the cis–trans isomerization *via* electronic spectroscopy.[8] It was impossible to distinguish cis and trans isomers in this manner for either the chloride or tetrazole complexes, even in solvents where nmr data indicate that both isomers are present. This can be due to one or all of the following: (1) the superposition of the absorbances of the cis complexes with phosphine absorptions; (2) very little difference in the spectra of the cis and trans isomers as was previously noted for $[PdCl_2\{(CH_3)_2\text{-}\alpha\text{-naphthylP}\}_2]$,[8] or (3) to the lability of the complexes.

In agreement with (1) above, upon addition of $(CH_3)_2P(C_6H_5)$ to solutions of $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$, a color change from colorless to light yellow was noted accompanied by a shift of the absorption at 310 nm to one at 325 nm. The absorption at 325 nm did not change in either position or intensity with further addition of phosphine through a 3:1 molar excess although absorptions below 300 nm increased in intensity. Similarly, solutions of the complex $[(CH_3)_2PC_6H_5]_2PdCl_2$ show a color change from light yellow to gold upon addition of excess phosphine but no changes occur in the electronic spectrum other than increases in intensity for phosphine absorptions below 300 nm.

**Nuclear Magnetic Resonance Studies. Structure Identification and Behavior.** A survey of recent investigations on transition metal complexes with tetrazole anions demonstrates the ability of unsubstituted tetrazole to bond through the carbon $C_5$,[33] or nitrogens $N_1$ or $N_2$. In complexes of 5-substituted tetrazolates the interesting M–C bond possibilities are eliminated, but the two possible metal nitrogen bonding modes can be exhibited. For several platinum(II) tetrazolates it has been shown that both $N_1$ and $N_2$ linkage isomers occur in solution; the existence and identification of the two modes have, however, not been as firmly established for solutions of palladium(II) complexes.

Several X-ray crystal structure determinations have been conducted on transition metal tetrazolato complexes, examining the mode of tetrazolato bonding. These include $Cu_2(5\text{-}CF_3CN_4)_2(diphos)_3$,[34] which has both tetrazoles $N_2$ bound; $[(Ph_3P)_2Ag(\mu\text{-}5\text{-}CF_3CN_4)_2$,[35] where the tetrazoles bridge two silver ions and bond through the $N_2$ and $N_3$ nitrogens, $ZnCl_2(1\text{-}CH_3tetrazole)_2$,[36] which is the $N_4N_4$ isomer and tetrahedral, $[(C_6H_5)_3P]_2Pd(5\text{-}C_6H_5tet)_2$,[15] in which the tetrazoles are trans and both $N_2$ bound, and $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CH_3tet)_2$,[27] where both tetrazoles are cis and $N_1$ bound and the tetrazole methyl groups are anti to one another (Figure 1).

We have investigated several palladium(II) phosphine complexes of 5-methyl- and 5-trifluoromethyltetrazole (hereafter denoted as 5-$CH_3$tet and 5-$CF_3$tet, respectively) *via* $^1H$ and $^{19}F$ nmr spectroscopy. In many instances the specific isomers present in solution have been identified and their interconversion with changing temperature have been followed; a summary of the nmr data is given in Table IV.

Before proceeding with discussion of actual spectra, it is informative to first discuss the possible geometrical and linkage isomers and to predict their $^1H$ spectra. Since 5-R tetrazolate may be bound *via* either the $N_1$ or $N_2$ nitrogens (Figure 1) (*vide supra*), it is possible to have $N_1N_1$, $N_2N_2$, and $N_1N_2$ combinations of tetrazoles bound to the metal. Considering both the cis and trans geometries, six isomers are possible,[16] *viz.*, cis-$N_1N_1$, cis-$N_2N_2$, cis-$N_1N_2$, trans-$N_1N_1$, trans-$N_2N_2$, and trans-$N_1N_2$. In addition, if Pd–N bond rotation is restricted, then each of the above isomers would be paired as syn and anti conformers such that 12 isomers are possible. These 12 isomers could result in 16 distinct resonances with one resonance arising from each $N_1N_1$ and $N_2N_2$ isomer and two resonances arising from each $N_1N_2$ isomer (*i.e.*, whereas for the $N_1N_1$ or $N_2N_2$ isomers both tetrazole methyl resonances will occur at the same chemical shift, but for the $N_1N_2$ isomers, there should be a resonance for each of the $N_1$ and $N_2$ bound tetrazole methyls). If Pd–N rotation is not restricted, *i.e.*, there will be no syn–anti pairs of isomers, then eight distinct resonances could arise, again one resonance for each $N_1N_1$ or $N_2N_2$ isomer and two resonances for the $N_1N_2$ isomers. If, on the other hand, Pd–N rotation is occurring in the trans isomer, but is hindered in the sterically more hindered cis isomer, then 12 resonances could arise.

Assume that only one geometrical isomer is present. If both tetrazoles are $N_1$ bound, a singlet should be observed for the tetrazole methyl resonance, unless Pd–N rotation is restricted and then two singlets should be observed, *i.e.*, one for each of the syn and anti isomers. This analysis can be carried further, that is if only one geometrical isomer is present and the isomers $N_1N_1$ and $N_2N_2$ are present, then either two or four resonances would be found.

If it is again assumed that only one geometrical isomer is present but the $N_1N_1$, $N_2N_2$, and $N_1N_2$ tetrazole bonding isomers are present, then four resonances could arise. If we further examine the two resonances arising from the $N_1N_2$ isomer, however, it would seem reasonable that the $N_2$ tetrazole methyl might occur at the same chemical shift as for the $N_2N_2$ isomer. Furthermore, the $N_1$ tetrazole methyl would not occur at the same chemical shift as the $N_1N_1$ isomer. If a model of the complex is examined, it is seen that the methyl of

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**Table IV.** Summary of 100-MHz Nmr Data for LPd(5-R-tet)$_2$ Complexes

| Ligand | R | Solvent | Phosphine resonances[a] ($\tau$) | Tetrazole resonances |
|---|---|---|---|---|
| $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ | $CH_3$ | $CDCl_3$ | 7.40 (d) | $\tau$ 7.80 (sb), 8.10 (s) |
| $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ | $CH_3$ | $C_6H_5NO_2$ | 6.98 (d) | $\tau$ 7.34 (s), 7.65 (s) |
| $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ | $CF_3$ | $CDCl_3$ | Insoluble | |
| $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ | $CF_3$ | $C_6H_5NO_2$ | 6.95 (d) | $\delta$ 14.80 (s) |
| $(C_6H_5)_3P$[b] | $CH_3$ | $CDCl_3$ | | $\tau$ 8.05 (s), 8.15 (s), 8.25 (s), 8.50 (s) |
| $(C_6H_5)_3P$[b] | $CH_3$ | $C_6H_5NO_2$ | | $\tau$ 7.80 (s), 7.90 (s), 8.02 (s), 8.22 (s) |
| $(C_6H_5)_3P$ | $CF_3$ | $CDCl_3$ | Insoluble | |
| $(C_6H_5)_3P$ | $CF_3$ | $C_6H_5NO_2$ | Insoluble | |
| $(CH_3)_2PC_6H_5$ | $CH_3$ | $CDCl_3$ | 8.40–9.1 (m) | $\tau$ 7.47 (s), 7.65 (s), 8.05 (s), 8.45 (s) |
| $(CH_3)_2PC_6H_5$ | $CH_3$ | $C_6H_5NO_2$ | 8.50 (d) | $\tau$ 7.65 (s), 8.00 (s) |
| $(CH_3)_2PC_6H_5$ | $CF_3$ | $CDCl_3$ | 8.61 (t) | $\delta$ 13.82 (s), 13.91 (s), 13.98 (s) |
| $(CH_3)_2PC_6H_5$ | $CF_3$ | $C_6H_5NO_2$ | 8.72 (t), 8.38 (d) | $\delta$ 15.58 (sb), 15.00 (s) |
| $(CH_3)_2PC_6H_5$ | $CF_3$ | $CD_3NO_2$ | 8.51 (d), 8.64 (t) | $\delta$ 16.31 (sb), 15.93 (s) |
| $(CH_3)_2PC_6H_5$ | $CF_3$ | $C_6D_6$ | 9.31 (t) | $\delta$ 15.08 (s) |
| $(CH_3)_2PC_6H_5$ | $CF_3$ | $m$-$Cl_2C_6H_4$ | 8.87 (t) | $\delta$ 14.02 (s), 13.80 (s) |
| $(C_6H_5)_2PCH_3$ | $CH_3$ | $CDCl_3$ | 8.30–8.70 (m) | $\tau$ 7.80 (s), 7.90 (s) |
| $(C_6H_5)_2PCH_3$ | $CH_3$ | $C_6H_5NO_2$ | Insoluble | |
| $(C_6H_5)_2PCH_3$ | $CF_3$ | $CDCl_3$ | 8.31 (t), 8.59 (d) | $\delta$ 13.72 (s), 13.67 (s), 13.61 (s) |
| $(C_6H_5)_2PCH_3$ | $CF_3$ | $C_6H_5NO_2$ | 7.98 (d), 8.18 (t) | $\delta$ 15.24 (sb), 14.97 (s) |
| $(C_6H_5)_2PCH_3$ | $CF_3$ | $CD_3NO_2$ | 8.82 (d), 8.97 (t) | $\delta$ 16.21 (sb), 15.75 (s), 15.70 (s), 15.62 (s) |
| $(C_6H_5)_2PCH_3$ | $CF_3$ | $C_6D_6$ | 8.84 (t) | $\delta$ 16.18 (s) |
| $(C_6H_5)_2PCH_3$ | $CF_3$ | $m$-$Cl_2C_6H_4$ | 8.53 (t) | $\delta$ 14.22 (asym S) |
| $(C_6H_5CH_2)_3P$ | $CH_3$ | $CDCl_3$ | 7.20 (t) | $\tau$ 7.55 (s), 7.62 (s), 7.68 (s) |
| $(C_6H_5CH_2)_3P$ | $CF_3$ | $CDCl_3$ | 6.89 (t), 7.11 (t) | $\delta$ 14.36 (s) |
| $(C_6H_5CH_2)_3P$ | $CF_3$ | $C_6H_5NO_2$ | 6.77 (t), 6.98 (t) | $\delta$ 15.32 (s) |
| $(C_6H_5CH_2)_2PC_6H_5$ | $CF_3$ | $CDCl_3$ | 6.78 (q of t) | $\delta$ 13.82 (s) |
| $(C_6H_5CH_2)P(C_6H_5)_2$ | (5-$CF_3$tet)(Cl) | $CDCl_3$ | 6.12 (t) | $\delta$ 13.77 (s), 13.84 (s) |

[a] Phenyl resonances not reported. Key: s ≡ singlet, sb ≡ broad singlet, asym s ≡ asymmetric singlet, m ≡ multiplet, d ≡ doublet, t ≡ triplet, q ≡ quartet, $|^3J_{PH} + {}^4J_{PH}|$ = 7–9 Hz and 8–11 Hz for the triplets and doublets, respectively. [b] At 60 MHz; data at 100 MHz is $\tau$ 8.02, 8.15, 8.16, 8.27, 8.47 and 7.80, 7.82, 7.90, 8.05, 8.20, respectively (all singlets). These singlets change chemical shifts and cross as a function of temperature.

the $N_1$ bound tetrazole is directed toward the bulk of the complex and should feel significantly different through space, and also through bond, interactions depending on whether the second tetrazole is $N_1$ or $N_2$ bound. The methyl group of the $N_2$ bound tetrazole, on the other hand, is one bond further away, so that through bond interactions should be minimized, and is directed away from the bulk of the complex so that through space interactions should also be minimized (Figure 1). Thus, there should be little if any chemical shift difference if the second tetrazole was $N_1$ or $N_2$ bound. Under this set of circumstances, only three resonances would arise, one for the $N_1N_1$ isomer, one for the $N_1$ tetrazole of the $N_1N_2$ isomer, and one for the $N_2N_2$ isomer and the $N_2$ methyl of the $N_1N_2$ isomer.

This same treatment can be applied to either geometrical isomer, but the cis isomer is sterically more hindered, and if the syn and anti isomers occur, they would most likely occur for the cis isomer.

**Nuclear Magnetic Resonance Behavior of Solutions Containing Only the Complexes.** **$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Pd(CH_3tet)_2$.** The $^1H$ nmr spectrum of this complex in deuteriochloroform exhibits a 1:1 doublet, as expected for the diphos methylenes. In addition to this, the spectrum also contains two singlets in the methyl region. The singlet at higher shielding is broad and of low intensity while the resonance at lower shielding is intense and sharp; the relative integrated intensities are 1:19, respectively. The spectrum is temperature independent over a 50° temperature range. The two resonances in the methyl region arise from the tetrazole methyl group. Since the diphos ligand locks the complex in the cis configuration, and since the two resonances are in a ratio of 1:19, they must arise from at least two isomers in solution. (If only cis-$N_1N_2$ were present, two 1:1 singlets would arise.) From the previous discussion, it is seen that two resonances, for only one geometrical isomer can arise from the presence of the $N_1N_1$ and $N_2N_2$ isomers. The $N_1N_2$ isomer might also be present (*vide supra*) if there is no chemical shift difference between its $N_1$ and $N_1N_1$ and its $N_2$ and $N_2N_2$; however, it would be extremely difficult to rationalize, particularly that the methyl of the $N_1$ tetrazole would not occur at a different chemical shift than the resonance of the $N_1N_1$ isomer (*vide infra*).

The small broad resonance at higher shielding is assigned to the $N_1N_1$ isomer because of its broadness. This might arise from quadrupolar broadening, which would be much greater for the methyl in the $N_1$ bonded tetrazole, or from hindered rotation of $N_1$ tetrazole (the $N_2$ tetrazole is free to rotate[16]) or both. The larger sharp resonance then corresponds to the $N_2N_2$ isomer and, in solution, 95% of the complex is the $N_2N_2$ isomer.

This complex shows almost exactly the same spectrum in nitrobenzene as in deuteriochloroform. Again the small broad resonance at higher shielding must arise

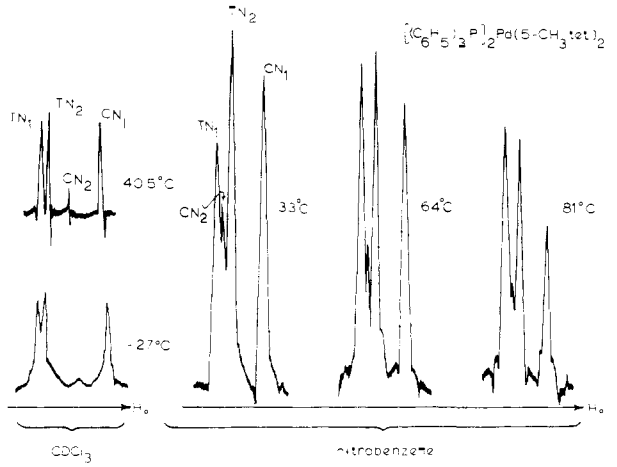


Figure 4. Temperature effects upon the 60-MHz $^1$H nmr spectra of $[(C_6H_5)_3P]_2Pd(5\text{-}CH_3tet)_2$ for $CDCl_3$ and nitrobenzene solutions. The resonances are assigned to their corresponding isomers: $TN_2$ = trans-$N_2$ bonded tetrazoles, $TN_1$ = trans-$N_1$ bonded tetrazoles, $CN_2$ = cis-$N_2$ bonded tetrazoles, and $CN_1$ = cis-$N_1$ bonded tetrazoles. The assignments were made using arguments developed in the text.

from less than 10% of the complex being the $N_1N_1$ isomer; the $N_2N_2$ isomer is assigned the large sharp resonance at lower shielding. These data indicate that slightly more of the $N_1N_1$ isomer is present in nitrobenzene than in deuteriochloroform (*viz.*, 10% *vs.* 5%). It is significant that in neither case are the syn and anti isomers observed as this is a very sterically hindered complex.

**$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Pd(5\text{-}CF_3tet)_2$.** This complex is not sufficiently soluble in nitrobenzene to obtain either $^{19}$F or $^1$H nmr spectra. The $^{19}$F spectrum in deuteriochloroform is a sharp singlet which is invariant over a 50° temperature range and is assigned as the $N_2N_2$ isomer by comparison to the data obtained for the analogous 5-$CH_3$tet complex. Thus the amount of $N_2$ bonded tetrazole increases upon changing from 5-$CH_3$- to 5-$CF_3$tetrazole (*viz.*, 90–95% *vs.* 100%).

**$[(C_6H_5)_3P]_2Pd(5\text{-}CH_3tet)_2$.** The $^1$H methyl resonances for this complex in deuteriochloroform at 100 MHz appear as five singlets. For this complex, as well as all others following, additional isomers are possible since both cis and trans geometries about the metal are now likely. Consequently, disregarding conformers, six possible isomers result[16] (*vide supra*). Since five resonances are observed, it is definitely possible that each of these isomers is present in solution.

At 60 MHz where chemical shift differences are less magnified, this complex shows only four resonances in both deuteriochloroform and nitrobenzene. It has been observed that when an equilibrium mixture of cis and trans palladium(II) phosphine complexes is heated the amount of the higher energy trans isomer increases.[10] For mixtures of $N_1$ and $N_2$ bonded tetrazoles the $N_1$ bonded tetrazole is more sterically hindered to rotation and therefore the higher energy one, and the one which will increase in amount when the mixture is heated. If it is assumed that the four resonances represent the trans-$N_1N_1$, cis-$N_1N_1$, trans-$N_2N_2$, and cis-$N_2N_2$ isomers, the $N_1N_2$ isomer is absent, or that at 60 MHz the chemical shifts of the $N_1$ and $N_2$ resonances are indistinguishable from those of the corresponding $N_1N_1$ and $N_2N_2$ isomers (*vide supra*), then it should be possible to describe the behavior of the isomer population from the change in the appearance of the $^1$H nmr with changing temperature. As the temperature increases, the trans isomers should increase in abundance as should the $N_1$ bonded isomer while the cis isomers and the $N_2$ bonded isomer should decrease in abundance. Therefore, the resonance whose intensity increases most is trans-$N_1N_1$, which should increase more than trans-$N_2$-$N_2$; at the same time cis-$N_1N_1$ should decrease only slightly whereas cis-$N_2N_2$ should decrease much more. The resonances were assigned, using these arguments (Figure 4). At 100 MHz, the additional resonance indicates that one of the $N_1N_2$ isomers are present, but their behavior cannot be predicted as a function of temperature, and further assignment is not possible. The 5-$CF_3$tet analog, unfortunately, is too insoluble to record reproducible $^{19}$F spectra in either deuteriochloroform or nitrobenzene.

**$[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ and $[(C_6H_5)_2PCH_3]_2$-$Pd(5\text{-}CF_3tet)_2$.** In these and the remaining complexes the methyl or methylene resonances from the phosphines complicate the $^1$H nmr spectra. Even though the overlap of phosphine methyl resonances (abbreviated phosphine resonances) with tetrazole methyl resonances occurs in these two complexes, which makes specific isomer assignments impossible, these phosphines exhibit the phenomenon of virtual coupling.[37] In virtual coupling when the phosphines are mutually cis and $J_{pp}$ is very small (approximately = 0 Hz), the phosphine methyl resonances appear as a 1:1 doublet. However, if the phosphines are mutually trans and $J_{pp}$ is large, on the order of 100 Hz, then the phosphine methyl resonances appear as a 1:2:1 triplet. Thus the gross geometry in solution can be determined *via* the phosphine resonances and an attempt can be made to correlate directly the cis–trans behavior of the phosphines with the behavior of the tetrazoles. In several cases both a doublet and a triplet arising from the phosphine methyls are present in the $^1$H nmr spectrum, indicative of both cis and trans isomers in solution,[10] as previously argued for the triphenylphosphine complexes[16] (*vide supra*).

For these complexes in deuteriochloroform the $^1$H nmr of the tetrazole shows at least four singlets. However, some of the tetrazole methyls overlap with the phosphine methyls and they themselves give rise to several overlapping doublets and triplets, indicative of the presence of several isomers (both cis and trans). Because of the complexity of the spectra any specific isomer assignments are impossible. The complex $[(C_6H_5)_2PCH_3]_2Pd(5\text{-}CF_3tet)_2$ is too insoluble in nitrobenzene to obtain nmr spectra, and although $[(CH_3)_2$-$PC_6H_5]_2Pd(5\text{-}CH_3tet)_2$ is also quite insoluble, poor quality spectra are obtainable in which the tetrazole methyl resonances are exhibited as two singlets while the phosphine resonance appears as only a doublet indicating that the phosphines and consequently the tetrazoles are cis. The X-ray crystal structure of this complex[27] (crystals grown from nitrobenzene solution) shows the tetrazoles to be only $N_1$ bonded in the solid state, but the solution nmr spectra require the existence in solution of the $N_1N_1$ isomer and either the $N_2N_2$ or $N_1N_2$ isomers to account for the number of resonances. The presence of these isomers can be

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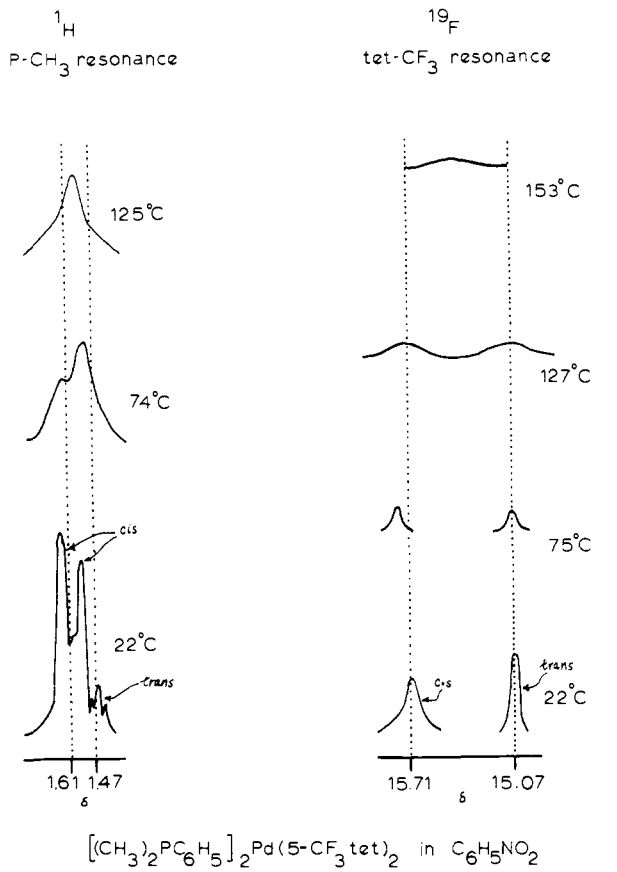


**Figure 5.** Temperature effects upon the $^1$H (100 MHz) and $^{19}$F (94.1 MHz) nmr spectra for a nitrobenzene solution of $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ illustrating rapid isomerization at 125° and rapid tetrazole exchange at 153°. Rapid trans phosphine exchange occurs at 70°.

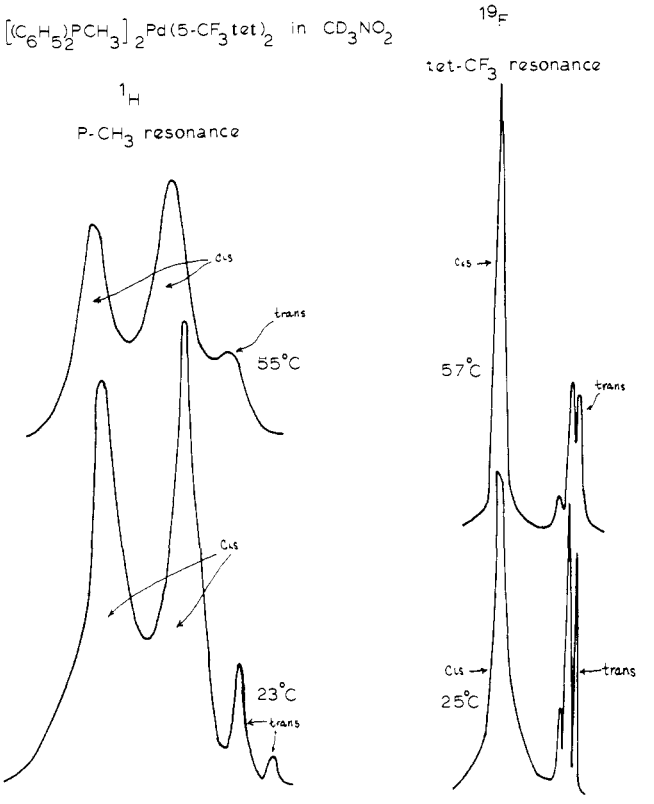


**Figure 6.** Temperature effects upon the $^1$H (100 MHz) and $^{19}$F (94.1 MHz) nmr spectra for a nitromethane-$d_3$ solution of $[(C_6H_5)_2PCH_3]_2Pd(5\text{-}CF_3tet)_2$ illustrating that while the trans phosphine is rapidly exchanging the trans tetrazoles are not.

accounted for only if $N_1$ to $N_2$ interchange occurs upon dissolution.

**$[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ and $[(C_6H_5)_2PCH_3]_2Pd(5\text{-}CF_3tet)_2$.** These two complexes are quite soluble enabling us to obtain both $^1$H and $^{19}$F spectra in a variety of solvents. The complex $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ shows for the proton phosphine resonances in nitrobenzene both a doublet and a triplet and, for the tetrazole $^{19}$F resonances, two singlets (Figure 5). Cis and trans phosphines are indicated by the doublet and triplet. With increasing temperature the triplet intensity increases at the expense of the doublet intensity; simultaneously, the $^{19}$F spectra show a singlet at lower shielding which increases in intensity at the expense of the singlet at higher shielding. It was also found that the ratio of the integrated intensities of the doublet *vs.* triplet was the same as that of the more shielded singlet *vs.* the less shielded singlet. The singlets were therefore assigned as arising from cis and trans tetrazoles, respectively. The complex $[(C_6H_5)_2PCH_3]_2Pd(5\text{-}CF_3tet)_2$ exhibits the same spectral behavior in nitrobenzene, and assignments were made in the same way. The ratio of doublet to triplet for the two complexes at the same temperature, however, is different leading to a difference in $K_{eq}$ = cis/trans for the two complexes.

The complex $[(C_6H_5)_2PCH_3]_2Pd(5\text{-}CF_3tet)_2$ in nitromethane-$d_3$ exhibited a strikingly different spectrum (Figure 6). Whereas the $^1$H phosphine resonances again appeared as a doublet and a triplet, the $^{19}$F spectrum showed a broad singlet at higher shielding and three closely grouped singlets at less shielding. The singlet at higher shielding loses intensity with increasing temperature to the three singlets, as does the $^1$H doublet to the triplet; it is therefore assigned as arising from the cis tetrazoles. In assigning the three singlets of the trans tetrazoles, they seem to represent the isomers trans-$N_1N_1$, trans-$N_2N_2$, and trans-$N_1N_2$ where the $N_2$ resonance occurs at the same chemical shift as the trans-$N_2N_2$ isomer (*vida supra*). However, these three could also represent trans-$N_2N_2$, and syn and anti trans-$N_1N_1$[16] (Figure 1). It was found that when the temperature of the solution was increased to 55° the trans triplet in the $^1$H spectra had coalesced to a singlet, indicative of trans phosphine exchange. In the $^{19}$F spectra, however, the three trans singlets retain their integrity at 55°. If two of the resonances were the result of syn and anti isomers, they should have coalesced at 55° as the phosphine which was the physical barrier to their rotation now rapidly exchanges from the complex. The three peaks must therefore represent the presence of trans-$N_1N_1$, trans-$N_2N_2$, and trans-$N_1N_2$ (*vide supra*). However, it is not possible to assign specific resonances to their corresponding isomers.

The complex $[(CH_3)_2PC_6H_5]_2Pd(5CF_3tet)_2$ in nitromethane-$d_3$ has a similar $^1$H spectrum, but shows only two singlets in the $^{19}$F spectrum. On heating the lower shielded singlet increases in intensity at the expense of the singlet at higher shielding. As in the previous assignment, the singlet at higher shielding represents the cis tetrazoles and that at lower shielding the trans.

In deuteriochloroform, the proton nmr spectra of $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ show a single triplet indic-

ative of only the trans isomer while the $^{19}F$ spectrum shows three closely grouped singlets indicative of the presence of the three isomers, trans-$N_1N_1$, trans-$N_2N_2$, and trans-$N_1N_2$. In the same solvent, $[(C_6H_5)_2PCH_3]_2$-$Pd(5\text{-}CF_3tet)_2$ exhibits both a doublet and triplet in the $^1H$ spectra, while the $^{19}F$ spectra show a broad singlet at higher shielding and again the three singlet group. On the basis of the above arguments and the temperature variations, the $^{19}F$ spectrum resonances are assigned as cis tetrazoles at higher shielding and the three trans isomers, $N_1N_1$, $N_2N_2$, and $N_1N_2$, at lower shielding.

Both complexes in *m*-dichlorobenzene exhibit only a triplet in their proton nmr spectra, but the $^{19}F$ nmr spectrum of $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ shows two singlets (approximately 1:2) representing the trans-$N_1N_1$ and trans-$N_2N_2$ isomers while the $^{19}F$ nmr spectrum of $[(C_6H_5)_2P(CH_3)]_2Pd(5\text{-}CF_3tet)_2$ shows only one sharp asymmetric resonance, indicative of the presence of at least one of the trans isomers.

In perdeuteriobenzene both complexes exhibit a single triplet for the proton spectra and a single sharp singlet for the fluorine spectra. In both cases then, only one isomer is present in solution which is probably the trans-$N_2N_2$ isomer. It should also be noted that all $^{19}F$ singlets assigned as cis were quite broad which might indicate some type of hindered rotational behavior in the cis complexes.

**$[(C_6H_5CH_2)_3P]_2Pd(5\text{-}CF_3tet)_2$ and $[(C_6H_5CH_2)_3P]_2Pd(5\text{-}CH_3tet)_2$.** The complex $[(C_6H_5CH_2)_3P]_2Pd(5\text{-}CH_3tet)_2$ has an $^1H$ nmr spectrum in deuteriochloroform which consists of a single triplet for the phosphine resonances, indicative of trans isomers and three singlets for the tetrazole resonances of the $N_1N_1$, $N_2N_2$, and $N_1N_2$ isomers. The complex $[(C_6H_5CH_2)_3P]_2Pd(5\text{-}CF_3tet)_2$ has an $^1H$ nmr spectrum which possesses two triplets with relative integrated intensities of 2:1 for the phosphine resonances in both deuteriochloroform and nitrobenzene. The $^{19}F$ spectra in either solvent shows only one sharp singlet. The appearance of two triplets has been previously described[38,39] and attributed to the lack of a plane of symmetry through the P–Pd–P bonds. However, in these cases, the two triplets must have 1:1 relative intensities. It could be argued that the two triplets might represent two rotamers,[40] but this is also unlikely as the $^{19}F$ spectra in this case would be expected to show a separate fluorine resonance for each rotamer. In addition, the spectra would be expected to be temperature dependent[41] but both the $^1H$ and $^{19}F$ spectra are temperature independent from 23 to 170° in nitrobenzene. These data may indicate that this complex is locked in a particular configuration such that the resonances are the result of an $A_2B_4$-$XX'B_4'A_2'$ spin system with $J_{AB} = 0$. This could only occur with Pd–P but not P–C or tetrazole hindered rotation. Since the $N_1$ bonded tetrazoles would be hindered to rotation, the tetrazoles seem to be $N_2$ bonded. This complex is believed to be trans-$N_2N_2$ and locked in either the gauche or eclipsed conformation.[42] The fact that the tetrazole methyl resonance is a singlet for the complex $[(C_6H_5CH_2)_3P]_2Pd(5\text{-}CF_3tet)_2$ indicates for this trans complex that even when Pd–P rotation is restricted, Pd–N rotation is not, as the syn and anti isomers would give rise to two singlets.

**Nuclear Magnetic Resonance Behavior on Addition of Excess Phosphines.** To compare these complexes to others whose catalyzed cis–trans isomerization mechanism has been studied,[3-5,7,8] a slight amount of excess phosphine was added to their nmr solutions, and their $^1H$ and $^{19}F$ spectra were observed. In all cases the phosphine methyl and the tetrazole resonances collapsed to a singlet indicative of rapid exchange of both phosphines[43] and tetrazoles, even at room temperature. When a solution of $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ containing excess $(CH_3)_2PC_6H_5$ was cooled to 0.0°, the $^1H$ phosphine[8] resonance appears as a broad doublet, while the $^{19}F$ of the tetrazole still appeared as a sharp singlet. On further cooling to −10.0°, the $^1H$ spectrum remained nearly the same while the tetrazole resonance was split into two singlets, indicating that upon catalysis tetrazole exchange is more rapid than phosphine exchange.

**Variable Temperature Studies on Solutions of $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ and $[(C_6H_5)_2PCH_3]_2Pd(5\text{-}CF_3tet)_2$.** Cis–trans isomerization occurred for these complexes in deuteriochloroform, nitromethane-$d_3$, and nitrobenzene but not in benzene-$d_6$ or *m*-dichlorobenzene. In nitrobenzene, however, other important observations were also made. For $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$, on increasing the temperature from 22 to 70°, the $^1H$ triplet:doublet ratio, *i.e.*, trans:cis ratio, increased; at 70°, the trans triplet coalesced to a singlet while the doublet, *i.e.*, the cis resonance, retained its integrity and decreased in intensity relative to the collapsed triplet (Figure 5). The coalescence indicates that the trans complex is more labile than the cis and proceeds to some intermediate with a lower $\Delta G^{\ddagger}$ than the cis complex; this would be expected from the known trans effect if phosphine, but not tetrazole, exchange occurs. At 70° no rapid exchange of tetrazole occurred as indicated by the two singlet tetrazole resonances. At 125° the doublet and the coalesced triplet coalesced (Figure 5) indicating that isomerization is now rapid on the nmr time scale. The $^{19}F$ nmr spectrum at 127° still showed two singlets (Figure 5) indicating that tetrazole exchange did not occur simultaneously with isomerization; at 153°, however, tetrazole exchange becomes rapid on the nmr time scale.

For $[(C_6H_5)_2PCH_3]_2Pd(5\text{-}CF_3tet)_2$, trans exchange occurs at 111°, rapid isomerization at 143°, and tetrazole exchange was not rapid even at 153°. The nature of the solvent has a dramatic effect on the various rates as in nitromethane-$d_3$, trans exchange for this complex occurs at 55° (Figure 6). Uncatalyzed phosphine exchange was observed only in coordinating solvents indicating that the solvent must participate in some manner in the isomerization mechanism.

Whenever both cis and trans isomers are present in solutions of these complexes, the equilibrium can be shifted to produce more of the trans isomer by heating the solution. The equilibrium thermodynamics, *i.e.*, $\Delta H_{eq}$ and $\Delta S_{eq}$, can then be obtained by plotting the

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(40) A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc. A*, 1826 (1971).
(41) A. J. Cheney and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 860 (1972).
(42) J. H. Nelson and D. A. Redfield, *Inorg. Nucl. Chem. Lett.*, **9**, 807 (1973).
(43) J. D. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, **91**, 1941 (1969).

**Table V.** *cis*-$L_2PdX_2 \rightleftharpoons$ *trans*-$L_2PdX_2$

| | $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ | $[(C_6H_5)_2PCH_3]_2Pd(5\text{-}CF_3tet)_2$ | $[(CH_3)_2PC_6H_5]_2PdCl_2$ | $[(C_6H_5)_2PCH_3]_2PdCl_2$ |
|---|---|---|---|---|
| | | In $CDCl_3$ | | |
| $\Delta G_{305}$[a] | | −1.13 | 0.36 | −0.54 |
| $\Delta H_{eq}$[a] | All trans | 1.7 | 3.1 | 5.3 |
| $\Delta S_{eq}$[b] | | 9.4 | 9.0 | 19.1 |
| | | In $C_6H_5NO_2$ | | |
| $\Delta G_{305}$[a] | 0.88 | 0.91 | 1.57 | 0.26 |
| $\Delta H_{eq}$[a] | 4.6 | 3.6 | 7.7 | 8.1 |
| $\Delta S_{eq}$[b] | 12.1 | 12.2 | 20.2 | 25.7 |
| $\Delta G^{\pm}$(phos exch)[a] | 18.6 at 343°K | 20.8 at 384°K | | |
| $\Delta S^{\pm}$(phos exch)[b] | | 20.0 | | |
| $\Delta G^{\pm}$(isom)[a] | 20.7 at 398°K | 21.6 at 416°K | | |
| $\Delta G^{\pm}$(tet exch)[a] | 27.2 at 426°K | >27.2 | | |
| $\Delta G^{\pm}$(catyl isom)[a] | 14.4 at 278°K | | | |
| $\Delta G^{\pm}$(catyl tet exch)[a] | 13.0 at 263°K | | | |
| $\Delta G^{\pm}$(catyl phos exch)[a] | >13.0 | | | |
| $\Delta G$(eq at isom)[a] | −0.19 at 396°K | −1.28 at 400°K | | |
| | | In $CD_3NO_2$ | | |
| $\Delta G_{305}$[a] | −1.14 | 1.21 | 1.38 | 1.36 |
| $\Delta H_{eq}$[a] | 6.5 | 4.8 | 4.4 | 5.7 |
| $\Delta S_{eq}$[b] | 16.3 | 11.8 | 16.2 | 14.9 |
| $\Delta G^{\pm}$(phos exch)[a] | | 17.3 at 328°K | | |

[a] $\Delta G$, $\Delta G^{\pm}$, and $\Delta H$ data given in kcal/mol. [b] $\Delta S$ data given in eu. The accuracies of the data are $\Delta G \pm 1$ kcal/mol, $\Delta S \pm 1$ eu, $\Delta H \pm 0.5$ kcal/mol, and $\Delta G^{\pm} \pm 0.5$ kcal/mol.

ratio of the isomers in terms of the ratio of the integrated intensities of the doublet and triplet *vs.* reciprocal temperature.[10] Once $\Delta S_{eq}$ and $\Delta H_{eq}$ are found, $\Delta G_{eq}$ can be calculated at any temperature desired. A $\Delta G^{\pm}$ can be obtained for any process if a coalescence phenomena occurs for that process, *e.g.*, if the triplet coalesces, then $\Delta G^{\pm}$ for trans phosphine exchange can be obtained; if the doublet and triplet coalesce then a $\Delta G^{\pm}$ isomerization can be obtained, and if tetrazole resonances coalesce, then $\Delta G^{\pm}$ for tetrazole exchange can be obtained. In addition, for trans phosphine exchange, $\Delta S^{\pm}$ can be obtained from line broadening by plotting $k/T$ *vs.* reciprocal temperature ($k$ is calculated from the corrected line width at half height). A $\Delta G^{\pm}$ for trans phosphine exchange may be calculated by using either a standard lifetime of $\tau = 0.225$ at coalescence or by using the corrected line width at half height to calculate the lifetime. These two methods yielded values which are within experimental error of each other when applied to these complexes. The results of such calculations from variable temperature data are given in Table V.

## Discussion

**Thermodynamic Data.** The equilibrium thermodynamic data collected for the tetrazoles, although not as extensive as that collected for $[(CH_3)_2PC_6H_5]_2PdCl_2$ and $[(C_6H_5)_2PCH_3]_2PdCl_2$,[10] are very informative (Table V) and exhibit some of the same trends. As shown by the data in deuteriochloroform and nitrobenzene, the amount of cis isomer generally increases with increasing solvent dipole moment and the trans isomer becomes more abundant as the temperature increases. However, while the dipole moment of the solvent seems to have a large effect on $K_{eq}$, it may not necessarily be the controlling factor since limits in solubility did not permit a study of the $K_{eq}$ in a much wider range of solvents where other solvent characteristics could be compared, as Burmeister suggests.[44]

(44) J. L. Burmeister, R. L. Hassell, and R. J. Phelan, *Inorg. Chem.*, **10**, 2032 (1971).

As was found for the chloride complexes, $\Delta S_{eq}$ also seems to control $\Delta G_{eq}$ for the tetrazole complexes. For the tetrazoles, however, $\Delta S_{eq}$ is smaller than for the corresponding chlorides as expected if $\Delta S_{eq}$ is controlled by steric and statistical factors; the larger size of the tetrazole would result in fewer changes in the number of rotational degrees of freedom on change in geometry from cis to trans since even the trans complexes have a great amount of steric hindrance. This is substantiated by the $^{19}F$ nmr of the complexes $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ and $[(C_6H_5)_2PCH_3]_2Pd(5\text{-}CF_3tet)_2$ where the cis tetrazole resonances are very broad singlets indicative of intermediate, on the nmr time scale, rotational activity. Also solvation differences should be less for the tetrazole complexes than for the smaller and more polar chloride complexes.

An important difference between the chloride and tetrazole complexes is the reversal in order of $\Delta H_{eq}$ (Table V). In the chlorides, $\Delta H_{eq}$ was larger for the $(C_6H_5)_2PCH_3$ complex and the weaker base $(C_6H_5)_2PCH_3$ would be expected to have a lower $\Delta H$ than the more basic $(CH_3)_2PC_6H_5$, if $\sigma$ bonding was controlling $\Delta H_{eq}$. If, on the other hand, $\pi$ bonding is more important, then $(C_6H_5)_2PCH_3$ would be expected to have the larger $\Delta H_{eq}$ which was found for the chlorides. The reversal of the order of $\Delta H_{eq}$ in these tetrazole complexes indicates that perhaps $\sigma$ bonding is now more important than $\pi$ bonding since the stronger base, $(CH_3)_2PC_6H_5$, forms the stronger bond.

It could be argued that $\Delta H$ is more a function of solvation than of Pd–P and/or Pd–N bond strengths; however, the order of $\Delta S$'s (Table V) for these complexes seems to be inconsistent with this proposal. If solvation interactions were more important for $\Delta H$, then these same interactions must also be important for $\Delta S$. Thus, a large difference should be seen when comparing $\Delta S$'s for $[(C_6H_5)_2PCH_3]_2PdCl_2$ in nitrobenzene and deuteriochloroform and a difference of 6.6 eu is found. However, when comparing $\Delta S$'s for $[(CH_3)_2PC_6H_5]_2PdCl_2$ with those for $[(C_6H_5)_2PCH_3]_2PdCl_2$ in deuterio-

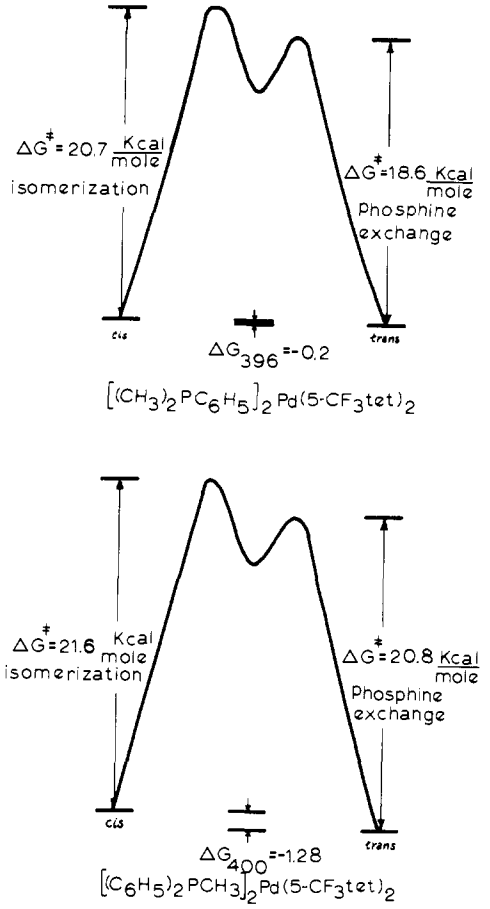


**Figure 7.** Energy profile diagrams drawn to scale for the cis–trans isomerizations of $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$, $\Delta G$ calculated from equilibrium data at 376°K, and $[(C_6H_5)_2PCH_3]_2Pd(5\text{-}CF_3tet)_2$, $\Delta G$ calculated from equilibrium data at 400°K in nitrobenzene solution.

chloroform and nitrobenzene, differences of 10.1 and 5.5 eu, respectively, are found. In each case the larger phosphine shows the larger $\Delta S$. The change in $\Delta S$ with change in phosphine which is of the same order or larger than the change in $\Delta S$ with changing solvents, seems to suggest that $\Delta S$ obtains greater contributions from steric factors than from solvation interactions, especially since the change in phosphine is less dramatic than the change in the nature of the solvents. If $\Delta S$ is dominated by steric factors and not solvation interactions, $\Delta H$ must be dominated by factors other than solvation interactions. This leads to the conclusion that $\Delta H$ predominantly measures changes in Pd–P and/or Pd–X bond energies.

For the tetrazole complexes, whereas, $\Delta S$ for both complexes in nitrobenzene is nearly the same, 12.1 *vs.* 12.2 eu (within experimental error); the $\Delta H$'s are considerably different, 4.6 *vs.* 3.6 kcal/mol (outside experimental error). If solvation interactions are not very important for $\Delta S$, they are also not very important for $\Delta H$, and it seems likely that, in these complexes also, $\Delta H$ is dominated by Pd–P and/or Pd–X bond energies.

It was also found that the rate of uncatalyzed isomerization, *i.e.*, $\Delta G^{\ddagger}$ isomerization, was phosphine dependent. This, however, cannot be a function of the strength of the bond broken since the $\Delta H$'s are in just the reverse order of what was found for the $\Delta G^{\ddagger}$'s such that the complex with the stronger bonds isomerizes at a faster rate. It seems that upon changing the phosphine from $(CH_3)_2PC_6H_5$ to $(C_6H_5)_2PCH_3$ the effect must be due to the additional bulk which the additional phenyl group adds. This phosphine then acts as a more effective block toward associative attack by the solvent. This necessitates a larger $\Delta G^{\ddagger}$ for that process consistent with $\Delta G^{\ddagger}$ isomerization for $(CH_3)_2PC_6H_5$ *vs.* $(C_6H_5)_2PCH_3$ being 20.7 *vs.* 21.6 kcal/mol. It is also in line with known mechanisms of substitution reactions of palladium(II) and platinum(II) complexes.[45] It was also found that $\Delta S^{\ddagger}$ for phosphine exchange = 20.0 eu for $[(C_6H_5)_2PCH_3]_2Pd(5\text{-}CF_3tet)_2$ indicating that, in nitrobenzene, phosphine exchange is a dissociate process. Since the isomerization rates are sensitive to both the leaving group (phosphine) and the entering group (solvent), it seems that the isomerization mechanism involves SN2 processes.

These data make it possible to develop an energy level diagram (Figure 7) for the isomerization process as $\Delta G_{eq}$, the energy difference between the two isomers; $\Delta G^{\ddagger}$ for trans phosphine exchange, $\Delta G^{\ddagger}$ for isomerization, and $\Delta G^{\ddagger}$ for tetrazole exchange are known.

For tetrazole exchange for $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tet)_2$ in nitrobenzene, $\Delta G^{\ddagger}$ is 27.1 kcal/mol which compares favorably with rough calculations for some of Beck's data[15] for $[(C_6H_5)_3P]_2Pd(5\text{-}CH_3tet)_2$ in *o*-$Cl_2C_6H_4$ where $\Delta G^{\ddagger}$ tetrazole exchange is 27.8 kcal/mol. This indicates that in each case tetrazole exchange is not rate controlling for isomerization. In addition, a $\Delta S^{\ddagger}$ for catalyzed isomerization of $-36.9$ eu[5] has been calculated by Haake, indicating that the rate determining step for catalyzed isomerization is associative, as suggested earlier.[10]

**Catalyzed Isomerization Mechanism.** These data for the phosphine catalyzed isomerization are consistent with the proposed consecutive displacement mechanism in that more-highly ionic species were found to be present as the base strength of the catalyst increases. The nature of the isomerization intermediate then seems to be dependent on the base. With phosphine, a strong base, as a catalyst, a fully dissociated ionic species is formed, whereas with pyridine, a weaker base, an intimate ion pair is formed. Finally, when only the solvent is present in the isomerization process no ionic intermediate is formed. The observation that when $[(CH_3)_2PC_6H_5]_2Pd(5\text{-}CF_3tetrazole)_2$ is catalyzed by excess phosphine, tetrazole exchange ($\Delta G^{\ddagger}$ = 13.0 kcal) is more rapid than isomerization ($\Delta G^{\ddagger}$ = 14.4 kcal) is, also in line with a consecutive displacement mechanism.

## Conclusion

The behavior of platinum and palladium complexes in solution is of considerable importance as these metals and their complexes are important catalysts in various processes. The postulated mechanisms for much of their catalytic behavior requires coordinatively unsaturated intermediates, where the nature of the solvent is very important, and small amounts of various bases poison the catalyst. The ability to establish the identity of species in solution and their behavior, such as cis–trans isomerization, and the mechanism for that behavior is most helpful in our understanding of the mechanism of catalysis.

It has been possible to identify the $N_1N_2$, $N_2N_2$, and

(45) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, pp 18–51.

$N_1N_2$ isomers for both 5-$CF_3$tet and 5-$CH_3$tet complexes in solution for most of these palladium(II) phosphine tetrazole complexes. In the organic alkylation of tetrazole salts, electronegative substituents in the 5-position give predominantly 2-isomers while those with electropositive groups in the 5-position give predominantly 1-isomers.[46] If the metal acts essentially like an organic substituent and "alkylates," a difference in the amount of isomers for the $CH_3$ *vs.* the $CF_3$ tetrazoles should be detected as in fact it is. While the $CF_3$tet $N_1N_1$ and $N_2N_2$ isomers are generally about equal in population, the $CH_3$tet appears to favor the $N_1N_1$ isomer.

We have also shown that the solvent and the anion have a large effect on both the thermodynamics of equilibrium and the $\Delta G^{\ddagger}$ for some processes. The mechanism for uncatalyzed isomerization is not precisely that of consecutive displacement since the nature of the intermediate is considerably different depending on the solvent and/or catalytic agent. The conductometric studies showed that the nature of the ionic species, *i.e.*, the conductivity, was directly dependent on the basicity of the catalytic agent. When no catalytic agent is present, *i.e.*, the strongest base is a weakly coordinating solvent molecule, no ionic species is present.

All of this seems to indicate that transition states are five-coordinate trigonal bipyramidal species with coordinated solvent and fluxional behavior; the intermediate is a four-coordinate species where solvent has displaced phosphine. When phosphine, a strong base, is added, the intermediate becomes ionic as the base displaces an anion rather than a phosphine to form the proposed consecutive displacement intermediate. The fact that a complex whose X-ray crystal structure shows only $N_1$ bonded tetrazole[27] but whose $^1H$ nmr in two solvents shows both $N_1$ and $N_2$ bonded tetrazole anions, indicates that some albeit slow, tetrazole exchange occurs even when no strong base is present. Since the rates of isomerization vary with changes in both coordinated and catalytic phosphine, the previously suggested[3] unique Pd–L* bonds in the intermediate are not necessary when the catalytic phosphine and the ligating phosphine are not the same.[47]

(46) R. A. Henry and W. G. Finnegan, *J. Amer. Chem. Soc.*, **76**, 923 (1954).

(47) However, no one has been able to isolate mixed phosphine complexes from these solutions. This must be a thermodynamic effect rather than a kinetic effect such that in general $LL'MX_2$ complexes, M = Pd, Pt, are thermodynamically less stable (as well as probably kinetically less stable) than $L_2MX_2''$, M = Pd, Pt, complexes. The $LL'MX_2$ complexes still may however, have a transient existence in solution.

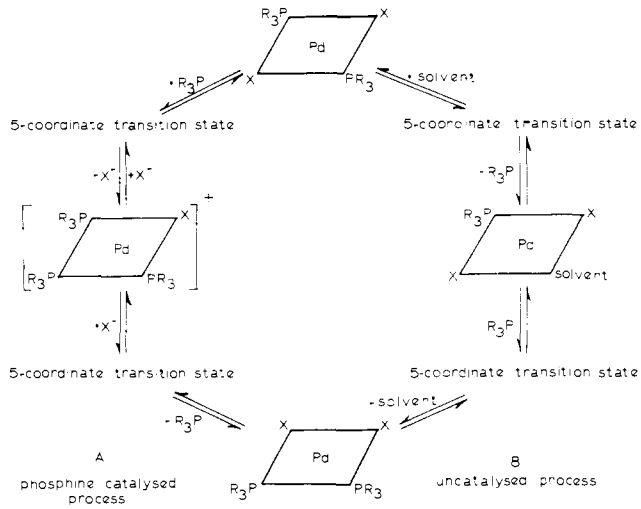


**Figure 8.** Postulated isomerization mechanisms for the phosphine catalyzed (process A) and the uncatalyzed (process B) cis–trans isomerizations of the complexes $(R_3P)_2Pd(5\text{-R-tet})_2$. The geometry of the 5-coordinate transition states is unknown but it is believed to be irregular (J. Burgess, *Inorg. React. Mech., Part 2*, 135 (1972)).

The selection rules for cis–trans isomerizations proposed by Eaton[48] are pertinent to these data and discussion which state that phosphine catalyzed thermal cis–trans isomerization of square planar complexes should lie between allowed tetrahedral substitution and disallowed cis–trans isomerization. Uncatalyzed isomerization should therefore be slower than catalyzed isomerization where substitution occurs more readily and this is indeed consistent with our data. It is also proposed that the selection rules are in agreement with the allowed fluxional behavior of trigonal bipyramidal species in line with the assignment of five-coordinate transition states here.

The isomerization mechanism shown in Figure 8 is consistent with all the available data for both platinum and palladium; it is a very general mechanism which accounts for solvent, anion, ligand steric considerations, basicity, and catalytic effects. Further work in this area is under way.

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(48) D. R. Eaton, *J. Amer. Chem. Soc.*, **90**, 4272 (1968).