be derived (in thought) by substituting $(NH_3)_5Co^{III}$ for an alkyl group. A similarly large gap separates the reported pK_A for the protonated acetato complex (-0.60 at $\mu = 1.0$[4b]) from the acidities of protonated acetate esters. The aquo complex $H_2O\text{-}Co(NH_3)_5{}^{3+}$ ($pK_A = 6.21$[20]) and the protonated alcohols $H_2O^+\text{-}R$ (for which pK_A's lie between -2 and -4[19]) are functionally interrelated in an analogous fashion, and here an even greater acidity difference exists. If, as we suspect, the acetato complex is protonated at the carbonyl oxygen whereas the unsaturated complexes are protonated at the double or triple bond, the acid dependencies observed in this series suggest that the strong base-strengthening action of $(NH_3)_5Co^{III}$ (when substituted for hydrogen or alkyl) is transmitted remarkably effectively through conjugated systems. Why such action is not observed also with the formato, benzoato, or trimethylacetato[4b] complexes remains a puzzling point.[21]

Registry No. Table II I, 21035-07-4; II, 36191-54-5; III, 15558-13-1; IV, 36191-56-7; V, 36191-57-8; VI, 36191-58-9; acetylenecarboxalato, 15603-19-7; *o*-hydroxycinnamato, 36191-60-3; *m*-methoxycinnamato, 36191-61-4; *p*-hydroxycinnamato, 36191-62-5; *m*-hydroxycinnamato, 36245-47-3; 2-thiopheneacrylato, 36191-63-6. Cr, 7440-47-3.

(19) Since pK_A's for such unsaturated esters have not yet been reported, it is assumed that interposition of a $-CH{=}CH-$ linkage between an aromatic ring and a carboxylate group increases the pK_A of an ester by about 1 unit, as has been observed for the protonated (monopositive) forms of the corresponding carboxylic acids. Appropriate data have been compiled by E. M. Arnett, *Progr. Phys. Org. Chem.*, 1, 223-402 (1963). This author also emphasizes the conceptual and experimental obstacles associated with fixing a meaningful pK_A value for water. Arguments here are presented in terms of esters and alcohols, rather than carboxylic acids, to avoid this difficulty.

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(21) An additional unexpected item in the report of Barrett and coworkers[4b] is the marked decrease in K_A of the acetato complex from 4.0 M at $\mu = 1.0$ to 0.45 M at $\mu = 4.0$, implying that reduction rates should vary more drastically, in the range 0.1-1.0 M $HClO_4$, at the higher ionic strength than at the lower. Since a tenfold change in K_A with only a fourfold change in μ appeared unusually large and because one of Barrett's values was obtained spectrophotometrically whereas the other was obtained kinetically, a confirmation of K_A at high μ was undertaken. Rate measurements at $\mu = 4.0$ by J. R. Barber, Jr., Kent State University, 1971, yield a K_A value of 0.44 for the acetato complex, in excellent agreement with the spectrophotometric value. Moreover, in accord with Barrett's findings, no evidence for protonation of the formato complex is obtained, even on extending measurements to $\mu = 4.0$.

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Equilibrium Energetics of Cis-Trans Isomerization for two Square-Planar Palladium(II)-Phosphine Complexes

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Received March 9, 1972

Equilibrium thermodynamics for the cis-trans isomerization of the compounds $[PhP(CH_3)_2]_2PdCl_2$ and $(Ph_2PCH_3)_2PdCl_2$ in a series of 11 solvents as determined by variable-temperature proton nuclear magnetic resonance are reported. It is found that for both complexes in most solvents the cis isomer is thermodynamically more stable than the trans isomer, that polar solvents favor the cis isomer, and that the isomerization process is entropy controlled and probably occurs *via* a solvent association mechanism.

Introduction

It has long been known that the cis isomers of square-planar platinum(II)-phosphine complexes are thermodynamically more stable than the trans isomers.[1,2] The trans isomers have, however, been isolated in several cases and the ability to isolate both isomers has been attributed to a kinetic phenomenon (*viz.*, the robust nature of these complexes).[3]

Electronic spectral studies, X-ray crystallography, and dipole moment measurements have shown that in general for the platinum complexes, the trans isomers are yellow and the cis isomers are colorless.[4] By analogy with these results, the palladium complexes $(R_3P)_2PdX_2$, which are nearly always various shades of yellow and possess low dipole moments in benzene solution, have been assigned the trans configuration.[4] In only three cases have both isomers been isolated for palladium.[3] The tendency for isomerization of the relatively labile palladium complexes makes these assignments tenuous since the less polar trans complexes are favored in solvents such as benzene.[5] In fact, more recent studies using infrared and nmr methods have shown that the cis complexes of palladium are indeed more common than originally believed.[6-12]

In addition, it has recently been shown by X-ray crystallography that the yellow complex $[PhP(CH_3)_2]_2PdCl_2$, originally believed to be trans, is cis in the solid state.[13] Jenkins and Shaw[12] found that this complex existed as a mixture of 67% cis and 33% trans in deuteriochloroform

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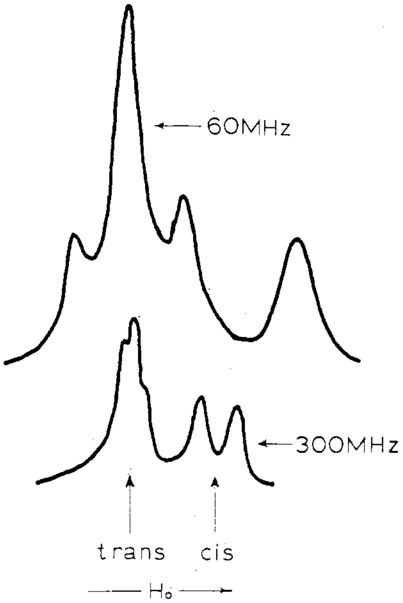

Figure 1. The 60- and 300-MHz ^1H nmr spectra in the methyl region of a cis–trans mixture of $(Ph_2PCH_3)_2PdCl_2$ in deuteriochloroform at 33°. The upfield doublet represents the cis isomer and the downfield triplet the trans isomer.

and that it was 100% cis in methanol–carbon disulfide and the chloroform results have been affirmed by the ^{31}P nmr studies of Grim and Keiter.[9] Jenkins and Shaw[12] further reported that this complex was too insoluble to obtain nmr spectra in nonpolar solvents such as benzene.

We have obtained the ^1H nmr spectrum of $[PhP(CH_3)_2]_2PdCl_2$ in deuteriobenzene and found that this complex is, within instrumental limitations, wholly trans in this solvent. We also discovered that the ratio of cis to trans isomers in other solvents was a function of both the solvent and the temperature, and that equilibrium was rapidly established. We therefore performed systematic variable-temperature ^1H nmr investigations in a series of 11 solvents on the two complexes $[PhP(CH_3)_2]_2PdCl_2$ and $(Ph_2PCH_3)_2PdCl_2$. The results of these studies including the thermodynamic parameters ΔS, ΔH, and ΔG are reported herein.

Experimental Section

Proton nmr spectra were obtained on a Varian A-60 nuclear magnetic resonance spectrometer, equipped with a V-6040 variable-temperature controller. Temperatures were measured to within ±1° with ethylene glycol and methanol as calibrants. The two complexes were prepared as described by Keiter and Grim.[9] The phosphines were prepared from commercial (Aldrich) dichlorophenylphosphine and chlorodiphenylphosphine by standard Grignard reactions. All reactions involving tertiary phosphines were conducted under an atmosphere of nitrogen. Saturated solutions for nmr were prepared by dissolving the complexes in hot solvents, allowing the solutions to cool to room temperature, and filtering. Solvents were commercial grade and purified by standard methods when necessary.

Results

We have prepared the two yellow complexes $[PhP(CH_3)_2]_2PdCl_2$ and $(Ph_2PCH_3)_2PdCl_2$ and found that they are sufficiently soluble in a variety of solvents to obtain ^1H nmr spectra, contrary to previous statements.[12] It has been shown[14] that, apart from a few exceptions, the geometric configurations of planar and octahedral transition metal complexes of methylphosphines can be discerned from the appearance of the ^1H nmr resonance of the methyl group. In general, when two equivalent phosphines occupy mutually trans positions, this resonance appears as a 1:2:1 triplet, whereas when the phosphines are cis to one another, it appears as a 1:1 doublet, the difference arising[15] through differences in the magnitude of $^2J_{(P-P)}$. This phenomenon, known as "virtual coupling", has been used to assign the geometry of a large number of transition metal phosphine complexes in solution.[9,10,12,14,16-29] In addition the conditions necessary for observation of the phenomenon, the theory, and the appearance of the resulting spectra have been discussed.[15,28,30-33]

It had previously been reported[9,12] that the methyl resonance of $[PhP(CH_3)_2]_2PdCl_2$ in deuteriochloroform solution consists of an overlapping doublet and triplet indicating the presence of both the cis and trans isomers in solution. Even though these two sets of resonances overlap, each is clearly discernible. However, the methyl resonance of $[Ph_2PCH_3]_2PdCl_2$ in deuteriochloroform appears as four lines at 60 MHz. To show that this complex also existed as a cis–trans mixture (*i.e.*, that the resonance was an overlapping doublet and triplet) we obtained the 300-MHz spectrum shown in Figure 1. It should be apparent from this spectrum that the 60-MHz spectrum (also shown in Figure 1) is an overlapping doublet and triplet as well. We then obtained 60-MHz spectra at several temperatures for both compounds and noticed changes typical of those illustrated in Figure 2. The spectra in this figure show that there is a pronounced temperature effect upon equilibrium 1. It can be seen that if no other species are present in solution, at the lower temperature illustrated the

$$\textit{cis}\text{-}(Ph_2PCH_3)_2PdCl_2 \rightleftharpoons \textit{trans}\text{-}(PH_2PCH_3)_2PdCl_2 \qquad (1)$$

solution contains a great deal more of the cis isomer than it does at the higher temperature.

It was established that the cis and trans isomers were the only species present in solution based on the following observations. The starting complex could be recovered quantitatively from each solution by evaporation of solvent; thus no decomposition or conversion to, for example, a halide-

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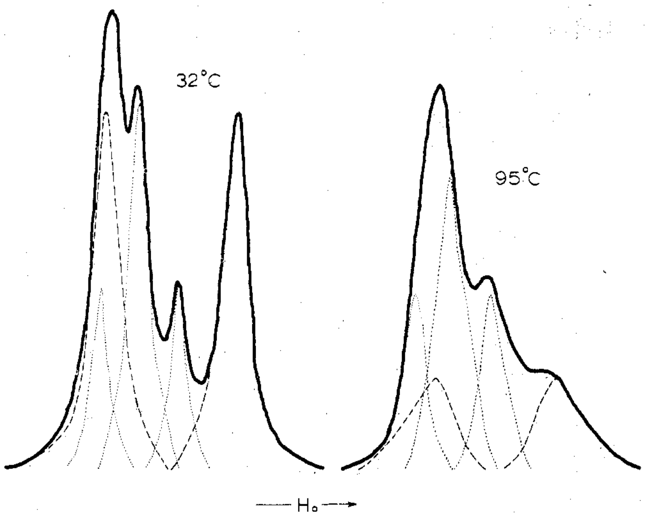

Figure 2. A typical gaussian analysis of the 60-MHz ^1H nmr spectra of a cis-trans mixture of $(Ph_2PCH_3)_2PdCl_2$ in nitrobenzene at 32 and 95° illustrating the effect of temperature on the equilibrium: · · · ·, trans isomer; - - -, cis isomer.

bridged dimer had occurred. When the solutions were heated, rapid equilibrium was established (in *ca.* 5 min after temperature equilibration) and the spectra were reproducible over an extended period of time (months) at the same temperature through both heating and cooling cycles; spectra taken on different samples of the same or different preparations were identical at the same temperature and no additional resonances appeared in any of the spectra. In addition, the coupling constants were very nearly constant over the temperature ranges investigated.

The ratios of the isomers in solution were then determined by integration of the nmr methyl resonances using three different techniques: (1) triangulation, (2) machine integration, and (3) cutting and weighing. All data reported herein were obtained by the cutting and weighing technique, which is commonly considered to be the most accurate spectral integration technique. If peaks overlapped, as they usually did, gaussian analyses were performed, and the ratios were determined using those peaks having least overlap. (A typical gaussion analysis is shown in Figure 2.) Temperature and solvent studies were repeated on several samples of complexes prepared from at least two different syntheses; the ratios were compared and found to be the same for all samples at the same temperature. Data from variable-temperature studies were determined during both heating and cooling cycles with consistent results, with the spectra being identical at the same temperatures during, before, and after temperature cycles. All samples during the variable-temperature measurements were given sufficient time to equilibrate before final spectra were recorded, with the spectrum followed until no further change occurred (usually complete in less than 5 min after instrument temperature equilibration). Each temperature study contained at least six temperatures over a minimum temperature range of 60°.

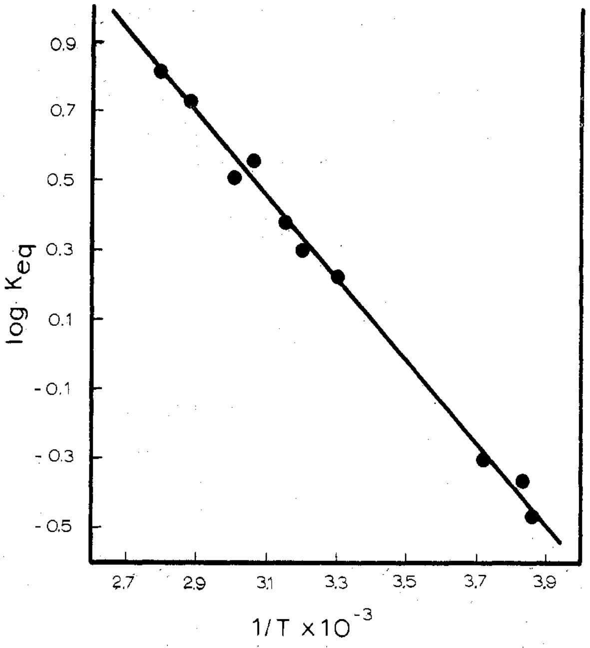

Figure 3. A representative least-squares plot of log K_{eq} *vs.* $1/T$ for the isomerization of $(Ph_2PCH_3)_2PdCl_2$ in deuteriochloroform.

The thermodynamic properties were obtained by least-squares analysis of log K *vs.* $1/T$ plots. Nearly all values were within experimental error of the least-squares line (Figure 3 shows a representative plot). Those not within experimental error showed signs of crystallization of the less soluble cis isomer from the solution resulting in spuriously high but constant trans:cis ratios (low temperatures) or contained insufficient amounts of one of the isomers for accurate gaussian analysis. These data were not used in the determination of ΔH and ΔS. The estimated uncertainties in ΔH, ΔS, and ΔG are 0.5 kcal, 1 eu, and 1 kcal, respectively. In some of the solvents investigated it was impossible to obtain the thermodynamic quantities due to the presence of overlapping solvent resonances, making exact data analysis impossible, since the resonances of the solvent and complex move relative to one another as a function of temperature. However, peaks attributable to the individual isomers were identifiable in most cases at ambient temperature.

The chemical shifts of the methyl resonances are slightly solvent and temperature dependent. These varied from τ 7.80 to 8.03 for *trans*-$(Ph_2PCH_3)_2PdCl_2$, from τ 7.85 to 8.13 for *cis*-$(Ph_2PCH_3)_2PdCl_2$, from τ 8.09 to 8.55 for *trans*-$[PhP(CH_3)_2]_2PdCl_2$, and from τ 8.03 to 8.38 for *cis*-$[PhP(CH_3)_2]_2PdCl_2$ at room temperature with the chemical shifts increasing from solvents with lowest dipole moment (benzene) to those with highest dipole moment (nitrobenzene). A nearly regular trend between chemical shift and solvent dipole moment was observed for each of the isomers. The methyl resonance of the trans isomer always occurred at lower field than that of the corresponding cis isomer, and either the resonance for the cis isomer moves upfield or that for the trans isomer moves downfield with respect to TMS or both occur as the temperature is raised. The methyl resonances of the methyldiphenylphosphine complexes always occurred at lower field than the methyl resonances of the corresponding isomers of the dimethylphenylphosphine complexes.

The apparent coupling constants $|^2J(P\text{-}H) + {}^4J(P\text{-}H)|$ were found to be only very slightly solvent or temperature dependent. These varied from 3.4 to 3.8 Hz and from 11 to 11.6 Hz for the trans and cis isomers of both complexes, respectively. The higher coupling constants were observed in the solvents with higher dipole moments. The coupling constants had decreased by only 0.2 Hz at the maximum temperature of the measurements.

Table I. Equilibrium Thermodynamic Data for the Reaction *cis*-$[PhP(CH_3)_2]_2PdCl_2 \leftrightarrows$ *trans*-$[PhP(CH_3)_2]_2PdCl_2$

Solvent	μ,[a] D	ΔH, kcal/mol	ΔS, eu	$\Delta G_{305°}$, kcal/mol	Line shape[b] at room temp
Nitrobenzene	4.22	7.7 ± 0.5	20.2 ± 1	1.57	d, t
o-Dichlorobenzene	2.52	4.6	14.0	0.33	d, t
m-Dichlorobenzene	1.72	4.4	16.1	−0.51	d, t
Toluene-d_8	0.36				t[c]
Benzene-d_6	0				t[c]
Nitromethane-d_3	3.44	4.4	16.2	1.38	d, t
Acetone-d_6	2.88	2.8	7.9	0.39	d, t
sym-Tetrachloroethane	1.36	5.8	15.3	1.13	d, t
1,2-Dichloroethane	1.19			0.62[d]	d, t
1,1,2-Trichloroethane	1.22				t[c]
Deuteriochloroform	1.01	3.1	9.0	0.36	d, t

[a] Dipole moment (Debye units): R. C. Weast, Ed., "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969, pp E-61–E-71. [b] d = doublet (representing cis isomer) and t = triplet (representing trans isomer) observed at room temperature. [c] Limited solubility precluded low-temperature measurements where the cis isomer may be present. The cis isomer precipitates from these solutions. [d] Obtained from the equation $\Delta G = -RT \ln K_{eq}$ using the measured value of $K_{eq} = 0.36$ at 305°K.

Table II. Equilibrium Thermodynamic Data for the Reaction *cis*-$(Ph_2PCH_3)_2PdCl_2 \rightleftarrows$ *trans*-$(Ph_2PCH_3)_2PdCl_2$

Solvent	μ,[a] D	ΔH, kcal/mol	ΔS, eu	$\Delta G_{305°}$, kcal/mol	Line shape[b] at room temp
Nitrobenzene	4.22	8.1 ± 0.5	25.7 ± 1	0.26	d, t
o-Dichlorobenzene	2.52				d, t
m-Dichlorobenzene	1.72			−1.05[d]	d, t
Toluene-d_8	0.36				t[c]
Benzene-d_6	0				t[c]
Nitromethane-d_3	3.44	5.7	14.9	1.16	d, t
sym-Tetrachloroethane	1.36	6.4	18.9	0.64	d, t
1,2-Dichloroethane	1.19			0.30[d]	d, t
1,1,2-Trichloroethane	1.22				t
Deuteriochloroform	1.01	4.6	20.2	−1.56	d, t
Deuteriochloroform[e]	1.01	5.3	19.1	−0.54	d, t

[a] Dipole moment (Debye units): R. C. Weast, Ed., "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969, pp E-61–E-71. [b] d = doublet (representing cis isomer) and t = triplet (representing trans isomer) observed at room temperature. [c] Limited solubility precluded low-temperature measurements where the cis isomer may be present. The cis isomer precipitates from these solutions. [d] Obtained from the equation $\Delta G = -RT \ln K_{eq}$ using the measured values of K_{eq} at 305°K: *m*-dichlorobenzene, $K_{eq} = 5.7$; 1,2-dichloroethane, $K_{eq} = 0.61$. [e] Run on a Jeolco 4H-100 to verify these seemingly anomalous results.

Discussion

The results of temperature studies in 11 different solvents are listed in Tables I and II. It can be seen from the data in these tables that in all the solvents investigated except *m*-dichlorobenzene and deuteriochloroform (for $(Ph_2PCH_3)_2PdCl_2$ only) the cis isomer is thermodynamically more stable than the corresponding trans isomer. In all solvents, heat is consumed in the transformation of the cis into the trans isomers. Also, the amount of trans isomer increases as the dipole moment decreases (*vide infra*). In addition, ΔH for the isomerization process is small (2.8–8.1 kcal/mol) but larger than for similar platinum complexes (1.2–2.5 kcal/mole)[1,2,34] $\Delta G_{305°}$ is small in all cases and ΔS is rather large (7.9–25.7 eu, which is larger than ΔS for similar platinum complexes, 9.4–14.2 eu).[34] These data indicate, as had previously been concluded for the platinum complexes,[1,2,34] that the isomerization process is entropy controlled.

There should be two major contributions to both ΔH and ΔS. For ΔH these are ΔH for internal bond strength changes and ΔH of solvation. Both of these favor the cis isomer, since the palladium–phosphorus bonds would be stronger in the cis than in the trans isomer (using either σ- or π-bonding arguments[34]) and since the dipole–dipole interactions between the complex and the solvent would also be greater in the cis than in the trans isomer.[1,2,34] For ΔS the major contributions are ΔS of solvation and ΔS of internal steric crowding. Since ΔS of internal steric crowding should be small, as it involves only the loss of some rotational and vibrational degrees of freedom, ΔS of solvation should be the larger and more significant term. Since ΔS favors the trans geometry and ΔH the cis and since both are dominated by the dipole–dipole interaction between the solvent and complex, the trans complex should be most abundant in the solvents with the lowest dipole moments. Thus, since this is the case, it appears that the solvent dipole moment is the most important factor in determining the geometry of the complex in solution. Chatt and Wilkins[1] have previously argued that solvent association is greater for the cis platinum complexes of this type than for the trans isomers and that ΔS involves a release of two molecules of solvent during the course of the isomerization process. The orders of the ΔH values are in agreement with this and suggest that the solvent is bound more strongly to the cis isomer than to the trans isomer. In concert with these arguments, if the solvents are ordered according to dipole moment into three separate groups ((1) chlorinated hydrocarbons, (2) aromatics, and (3) acetone and nitromethane) a trend in ΔH, ΔS, and ΔG with solvent dipole moment is evident where ΔH, ΔS, and ΔG generally increase as the solvent dipole moment increases.[35] The separation of the three groups of solvents seems reasonable since the exact nature of the complex–solvent interaction is probably different in the three groups. The chlorinated hydrocarbons are most likely participating in hydrogen bonding to the

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(34) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 424.

(35) There seems to be no correlation of ΔH or ΔS with either solvent dielectric constant or internal pressure.

coordinated chlorides, acetone and nitromethane are probably effectively engaged in coordination to the two vacant axial coordination sites on palladium, and the aromatics may be participating in a π–π interaction with the phenyl groups attached to the phosphine.

By comparing the data in Tables I and II it can be seen that in all solvents both ΔH and ΔS are larger for $(Ph_2PCH_3)_2PdCl_2$ than for $[PhP(CH_3)_2]_2PdCl_2$. It was anticipated that ΔS should be larger for $(Ph_2PCH_3)_2PdCl_2$ than for $[PhP(CH_3)_2]_2PdCl_2$ since the steric requirement of Ph_2PCH_3 should be greater and the basicity less[34,36] than those of $PhP(CH_3)_2$. The fact that ΔH is also greater seems to imply that the Pd–P bond is stronger for the cis isomer of $(Ph_2PCH_3)_2PdCl_2$ than for the cis isomer of $[PhP(CH_3)_2]_2PdCl_2$. Since Ph_2PCH_3 is a weaker base[36] than $PhP(CH_3)_2$, we take this to be a manifestation of greater π back-bonding in the Ph_2PCH_3 complex. This is reasonable since this ligand contains two electron-withdrawing phenyl groups whereas $PhP(CH_3)_2$ contains only one. It has previously been suggested for the platinum-phosphine complexes that the cis isomers were favored due to dπ–dπ back-bonding.[1,2,34]

If one compares data for similar platinum complexes to those reported here, it appears that the cis palladium complexes are more stable relative to the trans than are the cis platinum complexes. This is completely contrary to our expectations based upon previous arguments regarding palladium(II)- and platinum(II)-phosphine complexes.[4] It can be rationalized, however, by considering that either palladium-phosphorus dπ–dπ bonding is greater than platinum-phosphorus dπ–dπ bonding or that palladium-phosphorus σ bonding is greater than platinum-phosphorus σ bonding.[37] Until we have more data on similar systems, we are unable to distinguish between these two possibilities.

Another interesting comparison obtained by this investigation is the relative rates of isomerization of the palladium and platinum complexes. The greater lability of the palladium complexes is shown by the fact that isomerization occurs spontaneously and rapidly in all solvents studied without the addition of excess phosphine, whereas the platinum complexes require the catalysis of excess phosphine.[3] When excess phosphine is added to solutions of the palladium complexes, very rapid phosphine exchange occurs as also observed by other workers.[38]

Also of interest is the fact that only the trans isomers could be detected in the three solvents—benzene, toluene, and 1,1,2-trichloroethane. The trichloroethane result is especially surprising since both isomers are present in either dichloroethane or tetrachloroethane. All three solvents should show the same effect on the isomerization process[39] if one can apply Burmeister's arguments regarding solvent control of linkage isomerism to solvent control of geometrical isomerism.

Since Burmeister[39] found very similar solvent control on the nature of bonding of the ambidentate ligands thiocyanate and selenocyanate and since it has been shown that these modes of bonding are sensitive to the nature of the trans ligand,[40,41] it is tempting to suggest that he is also seeing the results of cis–trans isomerism at least for the palladium and platinum complexes.

Burmeister[39] has established that the linkage isomerism process involves dissociation of either the neutral group V ligand or the anionic ligand. We find, as have others,[12] that for the complexes $(R_3P)_2PdX_2$, where $R_3P = Ph_2PCH_3$ or $PhP(CH_3)_2$ and X = SCN or OCN, exchange of the anionic ligand is much more rapid than exchange of the phosphine. This suggests that, for the palladium complexes of these ambidentate ligands, linkage isomerism predominantly occurs through anion exchange.

For the chloride complexes, both phosphine and chloride exchange in the absence of excess phosphine are slow on the nmr time scale. However, phosphine exchange is rapid in the presence of excess phosphine. We are thus inclined to believe that the geometric isomerization process probably occurs through rapid solvent association followed by slow exchange of either phosphine or chloride or both.

Registry No. $[PhP(CH_3)_2]_2PdCl_2$, 29484-66-0; $[Ph_2PCH_3]_2PdCl_2$, 29484-75-1; $[PhP(CH_3)_2]_2PdCl_2$, 29484-74-0; $[Ph_2PCH_3]_2PdCl_2$, 26973-01-3.

Acknowledgments. We are pleased to acknowledge the financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Nevada, Reno Research Advisory Board. We also wish to thank Mr. Lew Carey of Varian Associates for obtaining the 300-MHz spectrum.

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