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Equilibrium Energetics of Cis–Trans Isomerization for a Series of Palladium(II)–Phosphine Complexes. Study of Phosphine Electronic Effects[1]

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Equilibrium thermodynamics for the cis–trans isomerization of the series of para-substituted phosphine complexes $[(p\text{-}ZC_6H_4)_nP(CH_3)_{3-n}]_2PdX_2$ ($n = 1$, $Z = OCH_3$, CH_3, H, Cl; $n = 2$, $Z = CH_3$, H, Cl; $X^- = Cl^-$, N_3^-) have been determined in a series of four solvents by variable-temperature proton NMR spectra. It is found that for both the chloride and azide complexes the cis isomer is thermodynamically more stable than the trans. The cis isomer is more predominant in solutions of the azide complexes and is favored by polar solvents. The isomerization process is entropy controlled and probably occurs via a solvent-association mechanism. Linear correlations of both ΔH and ΔS with Hammett σ constants of Z are found and discussed. The enthalpy and entropy of the reaction $cis\text{-}(R_3P)_2PdX_2 \rightleftharpoons trans\text{-}(R_3P)_2PdX_2$ both increase as the basicity of the phosphine increases.

Introduction

The existence of cis and trans isomers has long been known for square-planar platinum(II) complexes[2,3] but only recently established for square-planar palladium(II) complexes.[4-20] The ability to isolate both isomers of the platinum(II) complexes has been attributed to the robust nature of the complexes, a kinetic phenomenon.[12] For platinum the isomers generally possess distinct color differences. The trans isomers are usually yellow whereas the cis isomers are usually colorless.[13,14] They have been studied extensively by electronic spectroscopy, X-ray crystallography, and dipole moment measurements so that there is no doubt about the structural assignments.[13,14] The analogous palladium(II) complexes are various shades of yellow and have often been erroneously assigned the trans configuration.[11,13,14] The reliability of structural assignments based on color trends is of dubious value[19] when one notes that palladium(II)–phosphite complexes often exhibit the reverse trends.[14] For a series of palladium(II)–phosphite complexes we have found colorless and yellow compounds which are both cis or two colorless compounds, one which is cis and one which is trans.[15] In few cases have both the cis and trans isomers been isolated for palladium.[12,14,20] Previous failures to identify cis–trans isomerization of the relatively labile palladium complexes by dipole moment measurements are a result of stabilization of the trans isomer by low dipole solvents such

as benzene.[11] Recently, NMR and infrared studies have shown that the palladium(II) complexes often exist as cis–trans mixtures in solution.[4-11,16,18-20] X-Ray crystallography of the yellow complex $[C_6H_5P(CH_3)_2]PdCl_2$ originally believed to be trans and of the colorless complex $[C_6H_5P(CH_3)_2]_2Pd(5\text{-}CH_3tetrazolate)_2$ show that they are both cis in the solid state.[17,21] We have consistently found that cis palladium(II) complexes are thermodynamically more stable than the trans isomers.[16,18,22-24]

The NMR spectrum of $[C_6H_5P(CH_3)_2]_2PdCl_2$ has been studied by a number of workers.[8,10,16] Equilibrium thermodynamics have been obtained for this complex as well as several others through variable-temperature proton NMR spectra.[16,22-24] In an effort to study ligand electronic effects on the thermodynamics of cis–trans isomerization for palladium(II)–phosphine complexes, a systematic study by variable-temperature ^1H NMR was performed in a series of four solvents on five para-substituted chloro and five para-substituted azido complexes. The previously studied[16,22] Z = H compounds are included for comparison.

Experimental Section

Proton NMR spectra were obtained on a Varian A-60 spectrometer, equipped with a V-6040 variable-temperature controller, and on a Jeolco 4H-100 spectrometer, equipped with a JES-VT-3 variable-temperature probe. The temperatures were measured to within $\pm 1°$

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with ethylene glycol and methanol as calibrants. The preparation of the complexes has been previously described.[19] Saturated solutions for NMR were prepared as previously described.[16] The solvents were purged with nitrogen and checked spectroscopically prior to use. Thermodynamic data were obtained as previously described.[16,22,23]

Conductivity studies were performed at $25 \pm 0.1°$ as previously described.[22,23] Conductance ranges for electrolytes were taken from published values.[25-28]

Results

The ability of ^1H NMR to follow the cis–trans isomerization of methylphosphine complexes is limited only by compound solubility, lability, and interferences between solute and solvent resonances. It is reliable for most planar and octahedral transition metal complexes[29] except for a few Cr, Mo, W, and Mn complexes.[30-32] In general, where two equivalent phosphines are mutually trans, the methyl resonance appears as a 1:2:1 triplet; two equivalent phosphines cis to one another give rise to a 1:1 doublet. The difference in the line shapes is a function[33] of the magnitude of $^2J_{PP}$. This phenomenon, known as "virtual coupling", has been used to assign the geometric configurations of a multitude of transition metal–phosphine complexes in solution.[8,10,16,18,19,33-47] The reasons that $^2J_{PP}$ is greater than 500 Hz for two mutually trans phosphines and less than 50 Hz for two mutually cis phosphines, the theoretical line shapes, and the spectral results have been discussed by a number of authors.[32,45,47-51]

The appearance of the ^1H methyl resonances for these complexes has previously been described.[8,10,16,19] For the [ArP(CH₃)₂]₂PdCl₂ series in CDCl₃, the methyl resonance consists of an overlapping doublet and triplet indicating the presence of both the cis and trans isomers. For the [Ar₂P-CH₃]₂PdCl₂ series the methyl resonances are difficult to discern at 60 MHz; however, at 100 MHz the spectra clearly exhibit four lines.[16] The assignments were confirmed by $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra.[19] The ^1H NMR spectra of the azide complexes are more complex as the chemical shift differences between the two resonances are small, the coupling constants are similar, and the resonances overlap. The methyl resonances of the [ArP(CH₃)₂]₂Pd(N₃)₂ compounds often appear as a 1:1:1 triplet at room temperature. At higher temperatures the separate resonances are more clearly defined. All assignments were confirmed by $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR. Equilibrium constants were only determined when the isomers could be clearly distinguished at 100 MHz. The usual precautions[16] were taken to establish that the spectral changes could be completely accounted for by eq 1. Special precautions

$$cis\text{-}(R_3P)_2PdX_2 \rightleftharpoons trans\text{-}(R_3P)_2PdX_2 \qquad (1)$$
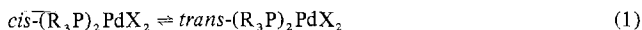
must be taken with the azide complexes in nitrobenzene; decomposition occurred at temperatures in excess of 140° and turned the yellow solutions to black. The recovered material was palladium black and charred organics which were not characterized. By avoiding excessive temperatures one can recover the azide complexes from the nitrobenzene solutions without decomposition or structural change. The studies were checked by obtaining spectra over a period of 6 months after the initial runs. Spectra were obtained on several preparations of the complexes to guarantee consistency of results and to check coupling constants. Temperature stability and sample equilibration were ensured by multiple runs at each temperature.

The ratios of the isomers in solution were determined primarily by cutting and weighing. Triangulation and integration (machine) were used to check the accuracy. Where peak overlap occurred, especially in the azides, gaussian analyses were performed, with the isomer ratios determined from the peaks with least overlap. Spectra were identical for the same temperatures attained by either heating or cooling of the sample. Each temperature study contained at least six

Table I. Equilibrium Thermodynamics for the Reactions
$cis\text{-}[(p\text{-}ZC_6H_4)P(CH_3)_2]_2PdCl_2 \rightleftharpoons$
$trans\text{-}[(p\text{-}Z(C_6H_4)P(CH_3)_2]_2PdCl_2$

Z	ΔS, eu	ΔH, kcal/mol	ΔG_{300}, kcal/mol	$\Delta G^{\ddagger}$, kcal/mol
		Solvent: $C_6H_5NO_2$; $\mu = 4.22$ D		
Cl	18.8 ± 1	6.3 ± 0.1	0.7 ± 0.1	23.5 ± 0.5
H	20.2	7.7	1.6	
CH₃	21.1	8.6	2.3	24.0
CH₃O	22.0	9.2	2.6	24.0
		Solvent: $o\text{-}C_6H_4Cl_2$; $\mu = 2.52$ D		
Cl	13.6	2.1	−2.0	21.5
H	14.0	4.6	0.4	
CH₃	19.8	5.9	0.04	23.5
CH₃O^a	20–21	7	0.4–1.0	21.0
		Solvent: $sym\text{-}C_2H_2Cl_4$; $\mu = 1.36$ D		
Cl	14.2	5.1	0.8	
H	15.3	5.8	1.2	
CH₃	27.0	10.2	2.1	
CH₃O	31.3	12.6	3.2	21.5
		Solvent: $CDCl_3$; $\mu = 1.01$ D		
Cl	4.8	1.2	−0.2	
H	9.0	3.1	0.4	
CH₃	13.3	4.8	0.8	
CH₃O	16.4	5.7	0.8	

^{a} Complex insoluble; values are predicted.

temperatures over a minimum temperature range of 80°.

Thermodynamic values were obtained by standard least-squares analyses of plots of log K_{eq} vs. $1/T$. Nearly all values were within the experimental error of the least-squares line. Where values fell outside experimental error, either crystallization of one isomer had begun to occur or insufficient amounts of one isomer caused erroneous gaussian analysis; these data were not used in the determination of ΔH and ΔS. The estimated uncertainties for ΔH, ΔS, and ΔG are 0.1 kcal, 1 eu, and 0.1 kcal, respectively. In some solvents, especially with the azide complexes, investigation of thermodynamic properties was impossible due to nearly overlapping resonances or lack (near) of one isomer.

Methyl resonance chemical shifts depend upon both solvent and temperature. The room-temperature shifts increase with increasing solvent dipole moment. They also depend on the para substituent of the phosphine.[19] In most cases, they are linearly related to Hammett σ constants as discussed in the preceding paper.[19]

The apparent coupling constants $|^2J(P-H) + {}^4J(P-H)|$ varied from 6.6 to 7.4 Hz for trans and from 11.1 to 11.6 Hz for cis isomers of all complexes. At the maximum temperatures used and in the absence of exchange the coupling constants usually decreased by less than 0.3 Hz over those observed at room temperature. Coalescence of the resonances and loss of P–H coupling was observed for some of the complexes in some solvents. Isomerization activation energies were calculated (Table I) in these cases and found to be 21.0–24.0 kcal/mol with no apparent dependence upon phosphine basicity. $\Delta G^{\ddagger}$ does increase slightly with increasing solvent dipole moment, suggesting stabilization of cis isomers as concluded previously.[16,22,23]

Discussion

Thermodynamics. It has been shown[19] that each of these complexes is cis in the solid state and that equilibrium mixtures of cis and trans isomers are rapidly formed upon dissolution. Results of studies in four solvents are listed in Tables I–IV. It can be seen that the cis isomers are generally thermodynamically more stable than the trans isomers, consistent with all previous observations.[16,22-24] In general, the amount of the trans isomer decreases as the basicity of the phosphine or dipole moment of the solvent increases. The isomerization

Table II. Equilibrium Thermodynamics for the Reactions
cis-$[(p$-$ZC_6H_4)_2PCH_3]_2PdCl_2 \rightleftharpoons trans$-$[(p$-$ZC_6H_4)_2PCH_3]_2PdCl_2{}^a$

Z	ΔS, eu	ΔH, kcal/mol	ΔG, kcal/mol
Solvent: $C_6H_5NO_2$; $\mu = 4.22$ D			
Cl	22.9 ± 1	5.5 ± 0.1	-1.4 ± 0.1
H	25.7	8.1	0.4
CH$_3$	27.5	9.7	1.5
Solvent: sym-$C_2H_2Cl_4$; $\mu = 1.36$ D			
Cl	10.6	3.5	0.3
H	18.9	6.4	0.7
CH$_3$	24.8	8.1	0.7
Solvent: CDCl$_3$; $\mu = 1.01$ D			
Cl	9.6	2.2	-0.7
H	20.2	4.6	-1.5
CH$_3$	29.2	8.0	-0.8

^{a} In o-$C_6H_4Cl_2$ these complexes are greater than 95% cis.

Table III. Equilibrium Thermodynamics for the Reactions
cis-$[p$-$ZC_6H_4P(CH_3)_2]_2Pd(N_3)_2 \rightleftharpoons$
$trans$-$[p$-$C_6H_4P(CH_3)_2]_2Pd(N_3)_2{}^a$

Z	ΔS, eu	ΔH, kcal/mol	ΔG, kcal/mol
Solvent: sym-$C_2H_2Cl_4$; $\mu = 1.36$ D			
Cl	19.2 ± 1	6.2 ± 0.1	0.4 ± 0.1
H	22.6	9.6	2.8
CH$_3$	25.4	8.2	0.6
CH$_3$O	26.8	8.7	0.7
Solvent: CDCl$_3$; $\mu = 1.01$ D			
Cl	Spectrum poor; appears to be all cis		
H	13.6	5.5	1.4
CH$_3$	16.1	7.1	2.3
CH$_3$O	18.8	9.1	3.5

^{a} These complexes are greater than 95% cis in o-$C_6H_4Cl_2$ and $C_6H_5NO_2$.

Table IV. Equilibrium Thermodynamics for the Reactions
cis-$[(p$-$ZC_6H_4)_2PCH_3]_2Pd(N_3)_2 \rightleftharpoons$
$trans$-$[(p$-$ZC_6H_4)_2PCH_3]_2Pd(N_3)_2$ (Solvent: sym-$C_2H_2Cl_4$; $\mu =$ 1.36 D)^a

Z	ΔS, eu	ΔH, kcal/mol	ΔG, kcal/mol
Cl	9.0	4.2	1.5
H	11.4	4.6	1.2
CH$_3$	13.2	6.1	2.1

^{a} These complexes are greater than 95% cis in CDCl$_3$, o-$C_6H_4Cl_2$, and $C_6H_5NO_2$.

enthalpy is in general much larger than that found for platinum complexes.[13,22,52]

The isomerization entropy and enthalpy exhibit large ranges (Table I–IV) and both are excellently correlated (with correlation coefficients generally greater than 0.915) (Table V) with phosphine basicity as reflected by Hammett σ constants.[53]

There should be two major contributions to both ΔH_{eq} and ΔS_{eq}. For ΔH_{eq} these are solvation effects (ΔH_{sol}) and changes in internal bond strengths (ΔH_{bond}). For ΔS_{eq} these are solvation effects (ΔS_{sol}) and changes in internal degrees of freedom (ΔS_{free}). Thus
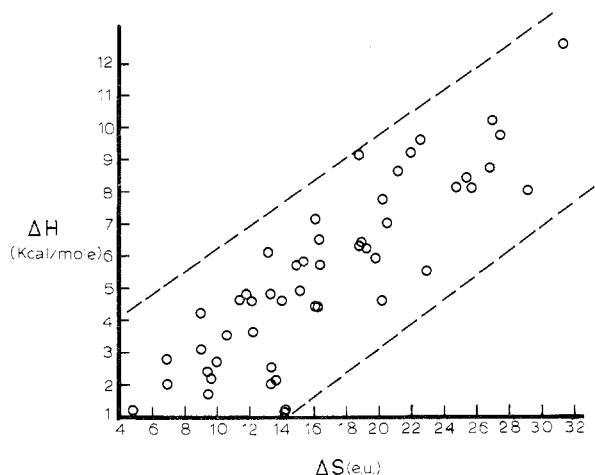
$$\Delta H_{eq} = \Delta H_{sol} + \Delta H_{bond} \qquad (2)$$

and

$$\Delta S_{eq} = \Delta S_{sol} + \Delta S_{free} \qquad (3)$$

Using these equations and the data in Table V the following conclusions may be drawn. (1) There is an electronic effect on the isomerization equilibrium as the basicity of the phosphine changes. (2) There is a steric effect on both ΔH and ΔS as ρ for all the correlations decreases upon going from the [ArP(CH$_3$)$_2$]$_2$PdX$_2$ complexes to the [(Ar)$_2$PCH$_3$]$_2$PdX$_2$ complexes. The steric effect on ΔH seems to be larger than that on ΔS. This seems reasonable as ΔH does not contain a direct steric contribution as does ΔS, but rather an indirect one. As steric interactions increase, the metal–ligand bonds become longer and consequently weaker and the fifth and sixth coordination positions become effectively blocked resulting in a decrease in the magnitude of ΔH_{sol}. (3) There is a dramatic solvent effect upon the isomerization as the ρ's are markedly solvent dependent. This is reasonable as both ΔH and ΔS (eq 2 and 3) contain a direct contribution from the solvent effect. The relative magnitude of the ρ's should reflect the relative magnitudes of the solvent effects with the smallest ρ's indicating the largest solvent effects. Since the solvent–solute interaction can occur in any of at least three ways (dipole–dipole, hydrogen bonding, or coordination) it is not too surprising that the ρ's are not directly related to solvent dipole moment. Were the solvent donor abilities[54–56] known for each of these solvents, it might be that the ρ's would correlate with these. Nevertheless, the ρ's usually increase as the solvent dipole moment decreases as would be anticipated from eq 2 and 3.

We have previously shown that these isomerizations are entropy controlled. This is also evidenced by the data presented here. Both ΔH_{sol} and ΔH_{bond} (using either σ- or π-bonding arguments) favor the cis isomer and both ΔS_{sol} and ΔS_{free} favor the trans isomer. Why then are the cis isomers favored in polar solvents if ΔS controls the isomerization, favors the trans isomer, and usually increases as the solvent dipole moment increases? The answer to this question and to the question of the relative magnitudes of the terms contributing to ΔH and ΔS can be found from the information contained in Figure 1. In this figure ΔH is plotted vs. ΔS for all the compounds in all the solvents thus far investigated.[16,22,23,57] Included in these data are changes in anions Cl$^-$ and N$_3^-$, in metals Pd(II) and Pt(II), in neutral ligands (Ar)$_2$PCH$_3$, ArP(CH$_3$)$_2$, C$_6$H$_5$CH$_2$P(C$_6$H$_5$)$_2$, (C$_6$H$_5$CH$_2$)$_2$PC$_6$H$_5$, (C$_2$H$_5$)$_3$P, (C$_3$-H$_7$)$_3$P, (C$_2$H$_5$)$_3$As, and (C$_2$H$_5$)$_3$Sb, and in solvents (eleven different with dipole moments ranging from 0 to 4.22 D). There is a regular trend between ΔH and ΔS such that they

Table V. Regression Analyses Parameters^a for the Relationships $\Delta H_{eq} = \rho \Sigma \sigma + B$ and $\Delta S_{eq} = \rho \Sigma \sigma + B$

		ρ		B		$\Sigma \Delta y \times 10^{-9}{}^b$		r^c	
Compd	Solvent	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS
[4-ZC$_6$H$_4$P(CH$_3$)$_2$]$_2$PdCl$_2$	CDCl$_3$	-9.12	-23.12	3.21	9.64	0.6	-0.29	0.999	0.994
	sym-C$_2$H$_2$Cl$_4$	-15.38	-36.22	7.61	20.02	0	-0.1	0.934	0.926
	o-C$_6$H$_4$Cl$_2$	-9.67	-15.48	4.39	16.15	0.6	-0.2	0.997	0.915
	C$_6$H$_5$NO$_2$	-5.79	-6.25	7.64	20.19	-0.7	-0.2	0.999	0.996
[4-ZC$_6$H$_4$P(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$	CDCl$_3$	-12.92	-18.77	5.34	13.41	3.0	-0.8	0.977	0.985
	sym-C$_2$H$_2$Cl$_4$	-4.19	-15.42	7.95	22.68	0.5	-0.8	0.633	0.999
[(4-ZC$_6$H$_4$)$_2$PCH$_3$]$_2$PdCl$_2$	CDCl$_3$	-7.20	-24.61	5.21	20.60	1.0	-9	0.983	0.999
	sym-C$_2$H$_2$Cl$_4$	-5.83	-17.91	6.22	18.78	0.1	0.7	0.998	1.000
	C$_6$H$_5$NO$_2$	-5.31	-5.81	7.97	25.59	1.9	-9.7	0.999	0.999
[(4-ZC$_6$H$_4$P)$_2$PCH$_3$]$_2$Pd(N$_3$)	sym-C$_2$H$_2$Cl$_4$	-2.31	-5.29	5.05	11.40	-1.3	0.5	0.919	1.000

^{a} ΔH in kcal/mol; ΔS in eu. ^{b} $\Sigma \Delta y$ is the standard deviation defined as $\Sigma \Delta y = \Sigma y_{obsd} - \Sigma y_{calcd}$. ^{c} r is the correlation coefficient defined as $(\Sigma xy - \Sigma x \Sigma y/N)/[\Sigma x^2 - \Sigma x^2/N(\Sigma y^2 - (\Sigma y)^2/N)]^{1/2}$.

Figure 1. Plot of ΔH vs. ΔS for all Pd(II) and Pt(II) compounds of the type L_2MX_2 where X = tetrazolate, chloride, or azide. Data were taken from this work and ref 2, 3, 16, 22–24, and 57.
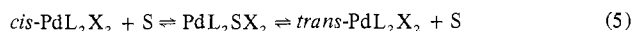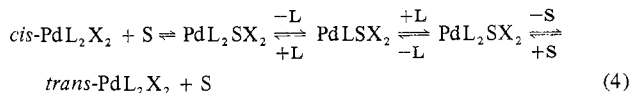
both increase in a parallel fashion. There is, however, considerable scatter of the points. Since the only terms common to ΔH_{eq} and ΔS_{eq} involve solute–solvent interactions, one can conclude that the major contributions to ΔH_{eq} and ΔS_{eq} are ΔH_{sol} and ΔS_{sol}. If these were the only important terms, ΔH_{eq} and ΔS_{eq} should be linearly related. Thus, it is the ΔH_{sol} term primarily which gives rise to the cis isomer stabilization in polar solvents.

The fact that there is scatter in this trend (ΔH vs. ΔS) indicates that the terms ΔH_{bond} and ΔS_{free} are also important. The cis isomers are in most cases thermodynamically more stable than the trans isomers and the cis isomer stability increases with increasing basicity of the phosphine and upon changing anions from Cl^- to N_3^- in addition to the solvent effects discussed above. Thus, as the phosphine basicity increases, ΔH_{bond}, ΔH_{sol}, and ΔS_{sol} increase. The increase in ΔH_{bond} with increasing basicity of the phosphine can be rationalized by σ-bonding arguments but not by π-bonding arguments since the stronger bases yield larger ΔH's.[58,59] Consequently, for these complexes, at least, it seems that σ bonding is more important than π bonding. Were Pd–P π bonding important, this should be apparent in the complex of $(4\text{-}ClC_6H_4)_2PCH_3$, the weakest base and the ligand with the greatest propensity for π bonding. Since ΔH is greater for the $4\text{-}ClC_6H_4P(CH_3)_2$ complexes than for those of $(4\text{-}Cl\text{-}C_6H_4)_2PCH_3$, we conclude that ΔH_{bond} mostly reflects σ-bonding effects. Of the four terms, ΔH_{sol}, ΔH_{bond}, ΔS_{sol}, and ΔS_{free}, the most important terms are the solvation terms ΔH_{sol} and ΔS_{sol}. The difficulty in separating ΔH_{bond} from ΔH_{sol} presents problems in bonding discussions. The two terms work in concert; that is, the more basic phosphine produces stronger metal–phosphorus bonds, causing greater polarization of the complex which, in turn, promotes increased solute–solvent interaction. Thus, as Drago has suggested,[60,61] it is nearly impossible to eliminate solvent contributions to ΔH. Of the solvents used in this study, $CDCl_3$ and *sym*-tetrachloroethane appear to provide the smallest solvent effects whereas nitrobenzene seems to show larger solvent effects; the ρ's decrease from $CDCl_3$ to nitrobenzene. The cis isomer stability, upon changing anions, Cl^- to N_3^-, may be either steric in origin or may be a result of differences in Pd–X bond strengths. By comparison, the complexes $[(CH_3)_{3-n}P(C_6H_5)_n]_2PdX_2$ (n = 1, 2; X^- = Br^-, I^-) are only trans[10] in solution, which is in line with both steric effects and accepted palladium–halogen bond strengths.

Conductivity Studies. Since ionic species have been previously isolated for similar complexes and since there is evidence for an ionic pathway for catalyzed isomerization, we

wished to determine if ionic species are formed for these complexes when phosphine catalysts are added.[64] Consequently, a known volume and concentration of the complexes that most rapidly and most slowly isomerize was titrated with the respective phosphine to a 4:1 mole ratio conductometrically in nitromethane. The four complexes were dichloro- and diazidobis(*p*-anisoledimethylphosphine)palladium(II) and dichloro- and diazidobis(methyldi-*p*-chlorophenyl-phosphine)palladium(II) (concentrations from 1 to 5 × 10⁻⁴ *M*). In all cases, the plot of volume-corrected conductance (range 14–17 × 10⁻⁶ mho) vs. moles of ligand was a straight line. Since the conductance of the ligands alone in this concentration range is 8–10 μmhos, very little ionic species is indicated.[22] We have found evidence for ionic species in this manner for other complexes.[22,23] The original complex could be recovered in nearly quantitative yield from these solutions. The P-CH_3 doublet collapses to a singlet in the ¹H NMR spectra of these complexes with excess ligand (1:1) in *sym*-tetrachloroethane, indicating that phosphine exchange occurs rapidly.

Where measurable, the isomerization activation energy was found to lie in the range 21.0–24.0 kcal/mol in keeping with previously reported values.[16,22,23,64] These data indicate that the predominant isomerization mechanism for these complexes is probably a solvent-assisted consecutive displacement of phosphine,[23,65] which proceeds through transition states or intermediates of the type PdL_2SX_2 where S represents the solvent or catalyzing phosphine. Thus, the mechanism is best described by eq 4 or 5.

$$cis\text{-}PdL_2X_2 + S \rightleftharpoons PdL_2SX_2 \underset{+L}{\overset{-L}{\rightleftharpoons}} PdLSX_2 \underset{-L}{\overset{+L}{\rightleftharpoons}} PdL_2SX_2 \underset{+S}{\overset{-S}{\rightleftharpoons}}$$

$$trans\text{-}PdL_2X_2 + S \tag{4}$$

$$cis\text{-}PdL_2X_2 + S \rightleftharpoons PdL_2SX_2 \rightleftharpoons trans\text{-}PdL_2X_2 + S \tag{5}$$

Registry No. *cis*-[C₆H₅P(CH₃)₂]₂PdCl₂, 29484-66-0; *cis*-[(*p*-ClC₆H₄)P(CH₃)₂]₂PdCl₂, 54832-73-4; *cis*-[(*p*-CH₃C₆H₄)P-(CH₃)₂]₂PdCl₂, 54832-74-5; *cis*-[(*p*-CH₃OC₆H₄)P(CH₃)₂]₂PdCl₂, 54832-75-6; *trans*-[C₆H₅P(CH₃)₂]₂PdCl₂, 29484-74-0; *trans*-[(*p*-ClC₆H₄)P(CH₃)₂]₂PdCl₂, 54910-28-0; *trans*-[(*p*-CH₃C₆H₄)P-(CH₃)₂]₂PdCl₂, 54869-03-3; *trans*-[(*p*-CH₃OC₆H₄)P(CH₃)₂]₂PdCl₂, 54910-41-7; *cis*-[(C₆H₅)₂PCH₃]₂PdCl₂, 29484-75-1; *cis*-[(*p*-ClC₆H₄)₂PCH₃]₂PdCl₂, 54869-04-4; *cis*-[(*p*-CH₃C₆H₄)₂PCH₃]₂PdCl₂, 54869-05-5; *trans*-[(C₆H₅)₂PCH₃]₂PdCl₂, 26973-01-3; *trans*-[(*p*-ClC₆H₄)₂PCH₃]₂PdCl₂, 54832-68-7; *trans*-[(*p*-CH₃C₆H₄)₂PCH₃]₂PdCl₂, 54832-69-8; *cis*-[C₆H₅P(CH₃)₂]₂Pd(N₃)₂, 52810-36-3; *cis*-[(*p*-ClC₆H₄)P(CH₃)₂]₂Pd(N₃)₂, 54832-70-1; *cis*-[(*p*-CH₃C₆H₄)P(CH₃)₂]₂Pd(N₃)₂, 54832-71-2; *cis*-[(*p*-CH₃OC₆H₄)P(CH₃)₂]₂Pd(N₃)₂, 54832-72-3; *trans*-[C₆H₅P-(CH₃)₂]₂Pd(N₃)₂, 52881-92-2; *trans*-[(*p*-ClC₆H₄)P(CH₃)₂]₂Pd(N₃)₂, 54869-00-0; *trans*-[(*p*-CH₃C₆H₄)P(CH₃)₂]₂Pd(N₃)₂, 54869-01-1; *trans*-[(*p*-CH₃OC₆H₄)P(CH₃)₂]₂Pd(N₃)₂, 54869-02-2; *cis*-[(C₆H₅)₂PCH₃]₂Pd(N₃)₂, 52881-91-1; *cis*-[(*p*-ClC₆H₄)₂PCH₃]₂Pd(N₃)₂, 54832-66-5; *cis*-[(*p*-CH₃C₆H₄)₂PCH₃]₂Pd(N₃)₂, 54832-67-6; *trans*-[(C₆H₅)₂PCH₃]₂Pd(N₃)₂, 27285-41-2; *trans*-[(*p*-ClC₆H₄)₂PCH₃]₂Pd(N₃)₂, 54868-98-3; *trans*-[(*p*-CH₃C₆H₄)₂PCH₃]₂Pd(N₃)₂, 54868-99-4.

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Lewis Base Properties of Platinum(0) Complexes. III. Adducts between Platinum and Titanium Tetrachloride[1a]

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Treatment of tris- and tetrakis(triphenylphosphine)platinum(0) complexes with titanium tetrachloride affords bis(titanium tetrachloride)tris(titanium tetrachloride–triphenylphosphine)platinum(0) (I). Thermolysis of I results in the formation of tris(titanium tetrachloride–triphenylphosphine)platinum(0) (II). Reaction of I with triphenylphosphine or methyl-diphenylphosphine also affords II. Treatment of I with boron trichloride affords titanium tetrachloride. Subsequent thermolysis of the reaction residue results in the evolution of additional titanium tetrachloride, boron trichloride–triphenylphosphine adduct, and bis(titanium tetrachloride–triphenylphosphine)platinum(0).

Introduction

The nucleophilic character of triphenylphosphineplatinum(0) complexes has been demonstrated with the isolation of adducts with boron trichloride, silicon tetrafluoride, and aluminum trimethyl.[2,3] Silicon tetrafluoride reacts with $[(C_6H_5)_3P]_3Pt$ to afford a 1:1 adduct, with elimination of one $(C_6H_5)_3P$ ligand, whereas boron trichloride forms an adduct but without ligand displacement. These facts may be rationalized on the basis of silicon exhibiting a trans effect via overlap of vacant 3d orbitals with platinum 5d orbitals thereby decreasing the phosphorus–platinum π-bond strength. When complexed, boron trichloride has no suitable low-lying vacant orbitals; hence trans-ligand labilization is not expected. In an effort to investigate further the nucleophilic character of platinum(0) complexes with strong Lewis acids capable of π bonding, the system $[(C_6H_5)_3P]_3Pt–TiCl_4$ was investigated.

Results and Discussion

Treatment of tris(triphenylphosphine)platinum(0), $[(C_6H_5)_3P]_3Pt$, with titanium tetrachloride, $TiCl_4$, results in formation of an emerald green crystalline complex of composition $(TiCl_4)_2Pt[TiCl_4·P(C_6H_5)_3]_3$. A variety of reaction conditions have been employed in studying this system and a summary of the pertinent data from six reactions is presented in Table I. The measured weight gain of the contents of the reaction apparatus can be directly related to the amount of $TiCl_4$ that has been coordinated to the starting platinum compound because (1) only $TiCl_4$ is added to $[(C_6H_5)_3P]_3Pt$, (2) unreacted $TiCl_4$ is the only volatile material detected at the conclusion of the reaction, (3) $P(C_6H_5)_3$ is not permanently displaced, (4) neither $TiCl_4·P(C_6H_5)_3$ nor $TiCl_4·2P(C_6H_5)_3$ is a reaction by-product, and (5) I represents a single material based on its microcrystalline homogeneous appearance. Based