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Isomerization Energetics for Palladium(II) Complexes of 1-Substituted 3,4-Dimethylphospholes

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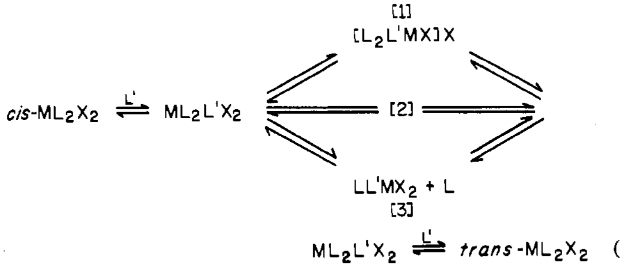
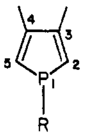
There has been a great deal of interest in square-planar bis(phosphine)(transition metal) complexes, especially since many of these complexes homogeneously catalyze a wide variety of organic reactions. The bis(phosphine) complexes of palladium(II) and platinum(II) have been widely used as models for studying this catalytic behavior and are themselves excellent catalysts.[2] Although bis(phosphine)platinum(II) complexes are rather robust, palladium(II) bis(phosphine) complexes are so labile that they often exist as mixtures of cis and trans isomers in solution[3-5] and are believed to isomerize spontaneously at ambient temperatures without catalysis.[6] An investigation into the cis–trans isomerization thermodynamics and mechanism is important because in several proposed mechanisms for the catalytic behavior of complexes of these metals, cis–trans isomerism is postulated.[7,8]

Recent investigations[5,9-19] of the geometrical isomerization of complexes of the type L_2PdX_2 have indicated that the isomerization process is associative, proceeding through pentacoordinate transition states as illustrated in eq 1. The various conditions under which each pathway occurs have been discussed previously.[15] At the moment there is not much information on the solution behavior of pentacoordinate palladium(II) species. In addition, there have been few pentacoordinate complexes of palladium(II) with monodentate ligands reported,[20-25] and all but one[25] involve sterically undemanding phosphole ligands; however, each of these complexes is extensively dissociated in solution. There is evidence[26] to suggest that the relative stabilities of ML_2X_2 and ML_3X_2 species depend upon a subtle interplay of steric and electronic effects, although there are no clear reasons why this may be so. We have recently shown[27] that the sterically undemanding 1-substituted 3,4-dimethylphospholes (I) form stable L_2MX_2 complexes with palladium(II). Spectroscopic and X-ray data[27] indicate that the Pd–P bonds in these complexes are as strong as, if not stronger than, Pd–P bonds in similar phosphine complexes. With this in mind we have investigated, via variable-temperature $^{31}P\{^1H\}$ NMR, the solution behavior of L_2PdX_2 complexes of 1-R-3,4-dimethylphospholes (R = CH_3, n-C_4H_9, t-C_4H_9, C_6H_5, and $CH_2C_6H_5$; X = Cl^-, Br^-, N_3^-) in three solvents in order to better understand the interplay of ligand size and electronic character and their effects on the geometrical isomerization process for palladium(II).



(1)



I

phosphole structure and ring numbering scheme

Experimental Section

Proton-decoupled phosphorus-31 NMR spectra were recorded at 40.26 MHz on a JEOL FX-100 NMR spectrometer in Fourier transform mode, equipped with a variable-temperature probe. The preparation of the complexes,[27] as well as the preparation of the saturated solutions for NMR,[5] has been previously described.

Conductivity studies were performed at 25 ± 0.1 °C as previously described.[16,18] Conductance ranges for electrolytes were taken from published values.[28]

Results

The $^{31}P\{^1H\}$ NMR spectra are straightforward in that only one singlet is observed for each isomer present in solution. When both cis and trans isomers are present in solution, the cis $^{31}P\{^1H\}$ resonance is broader than the trans resonance and appears downfield of the trans resonance in all cases.

The ratios of isomers in solution were determined primarily by cutting and weighing, with integration by the FX-100 computer employed as an accuracy check. Each temperature

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Table I. Equilibrium Thermodynamics for the Reactions *cis*-$L_2PdX_2 \rightleftharpoons$ *trans*-L_2PdX_2

		benzene (μ = 0 D)			chloroform (μ = 1.01 D)			nitrobenzene (μ = 4.22 D)		
R[a]	X	ΔG_{303}, kcal/mol	ΔH, kcal/mol	ΔS, eu	ΔG_{303}, kcal/mol	ΔH, kcal/mol	ΔS, eu	ΔG_{303}, kcal/mol	ΔH, kcal/mol	ΔS, eu
CH_3	Cl		insol			all cis			all cis	
	Br		mixture[b]		0.697	5.69	16.48	2.10	4.44	7.73
	N_3		insol			all cis			all cis	
n-Bu	Cl	0.023	6.11	20.09		all cis			all cis	
	Br		all trans		0.701	5.34	15.31		all cis	
t-Bu	Cl		all trans		−0.622	4.52	16.97	0.303	3.16	9.43
	Br		all trans			all trans			all trans	
	N_3		insol			all cis			all cis	
Ph	Cl	−0.422	2.76	10.50		all cis			all cis	
	Br		all trans		0.432	5.35	16.23	1.36	3.16	5.95
	N_3		insol			all cis			all cis	
Bzl	Cl		insol			all cis			all cis	
	Br	−0.353	7.14	24.73	1.84	9.01	23.66		all cis	
	N_3		insol			all cis			all cis	

[a] See structure I in text. [b] Trans predominant.

study contained at least four temperatures over a minimum range of 40 °C.

Thermodynamic values (Table I) were obtained by standard least-squares analyses of plots of log K_{eq} vs. $1/T$. The correlation coefficients for the least-squares lines ranged from 0.78 to 0.99 and were typically greater than 0.90. The estimated uncertainties for ΔH, ΔG, and ΔS are 0.1 kcal/mol, 0.1 kcal/mol, and 1 eu, respectively.

Care must be taken when the azide complexes are studied at temperatures over 100 °C in nitrobenzene, as decomposition occurs resulting in Pd metal and a tarry organic residue which was not characterized.

Discussion

We have previously shown[27] that each of these complexes exists as the cis isomer in the solid state. Previous work[5,15,16] has shown that for L_2PdX_2 the cis isomers are generally thermodynamically more stable than the trans isomers, and the data for the bis(phosphole)palladium(II) complexes (Table I) are consistent with this observation.

For phosphine as well as phosphole complexes there should be two major contributions to both ΔH and ΔS of isomerization. For ΔH these are solvation effects (ΔH_{sol}) and changes in internal bond strengths (ΔH_{bond}), both of which favor the cis isomer. For ΔS these are solvation effects (ΔS_{sol}) and changes in internal degrees of freedom (ΔS_{free}), both of which favor the trans isomer. Therefore

$$\Delta H_{eq} = \Delta H_{sol} + \Delta H_{bond} \quad (2)$$

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

For bis(phosphine)palladium(II) complexes, solvation effects were shown[5,18,19] to be dominant in the cis–trans isomerization process. An increase in the solvent dipole moment brought about an increase in the cis isomer population, along with a concurrent increase in ΔH_{eq} and ΔS_{eq}.

For bis(phosphole)palladium(II) complexes, increasing the solvent dipole moment favors the cis isomer; however, ΔS_{eq} and ΔH_{eq} both decrease concurrently with increasing μ_{sol}. It appears that solvation effects, while still important, are not dominant in the cis–trans isomerization process for these complexes. Equation 1 would indicate the ΔH_{sol} is now not necessarily larger than ΔH_{bond}. This tenet is supported by X-ray data[27] which suggest that Pd–P and Pd–X bonds in phosphole complexes are shorter than those in phosphine complexes. This would point to an increase in bond strengths (increase ΔH_{bond}) and a decrease in bond dipoles (decrease ΔH_{sol}).

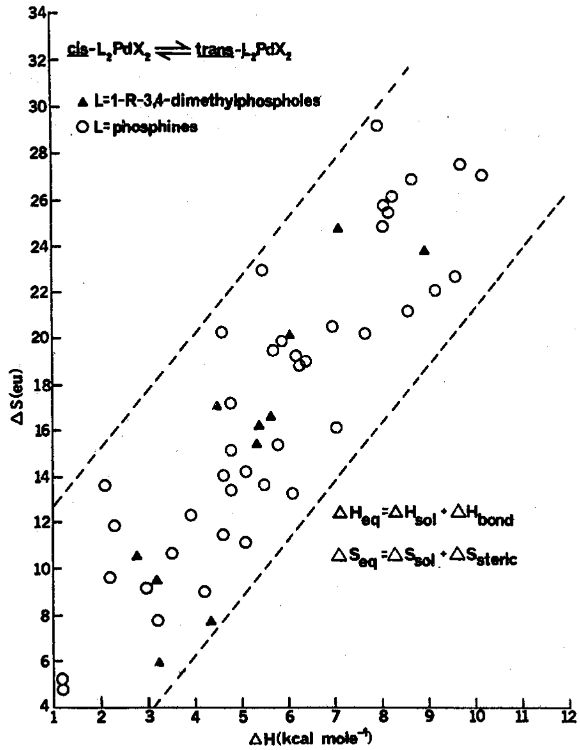

Figure 1. Plot of ΔS vs. ΔH for Pd(II) compounds of the type L_2PdX_2 where X = Cl^-, N_3^-, or Br^-. Data taken from this work and ref 19 and 29 (▲) represent the (1-R-3,4-dimethylphosphole)palladium(II) complexes.

Thus even though the phospholes appear to be a completely different ligand system in comparison to phosphines, solvation effects are still important in their isomerization thermodynamics. *Only because the Pd–P and Pd–X bonds are stronger*[27] *in phosphole complexes* than in phosphine complexes does ΔH_{eq} approach $T\Delta S_{eq}$. A similar situation is observed[29] for palladium(II) isocyanate phosphine complexes. This is not the case for many palladium(II) bis(phosphine) complexes, where $T\Delta S$ is usually much larger than ΔH.

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A plot of ΔS_{eq} vs. ΔH_{eq} (Figure 1) demonstrates that the equilibrium thermodynamic values for palladium(II) phosphole complexes lie well within the range observed for palladium(II) phosphine complexes. The scatter of the points indicates that ΔH_{bond} and ΔS_{free} are important in the thermodynamic process as discussed previously.[19] The information in Figure 1 suggests that the relative energies between the cis and trans isomers for the palladium(II) phosphole complexes are not radically different from those for palladium(II) phosphine complexes. It also supports our contention that these phospholes coordinate as strongly as do phosphines—a prime question at the beginning of our study into the coordination chemistry of these phospholes.

Conductivity studies of these complexes in $CHCl_3$ at 25 °C do not indicate the existence of ionic species in the presence or absence of excess ligand. This would indicate that in $CDCl_3$ the cis–trans isomerization is proceeding through either pathway 3 (eq 1), consecutive neutral ligand displacement, or pathway 2 (pseudorotation of pentacoordinate transition states). Upon addition of excess ligand to the complexes in nitromethane, 1:1 electrolytes are detected in solution, suggesting that in nitromethane or other polar solvents such as nitrobenzene, the isomerization mechanism involves consecutive anion displacement (pathway 1). Since these phospholes are small and seem to have a propensity[30] for π bonding, the likelihood of pentacoordination is greater for the 1-R-3,4-dimethylphospholes than for phosphines in $CHCl_3$, and most likely in benzene as well. The solution behavior in nitromethane further suggests that the Pd–phosphole bond strengths are greater than the Pd–X bond strengths.

Support for the existence of pentacoordinate transition states in $CHCl_3$ comes from the observation that addition of 1:1 excesses of phospholes to their complexes gives rise to single, broad ^{31}P NMR resonances at room temperature, suggesting rapid exchange between free and coordinated phosphole. When the solution is cooled to −50 °C, the broad line is replaced by a complex set of narrow lines, some exhibiting P–P coupling. This suggests the presence of species having increased coordination numbers in solution. The number of lines and temperature behavior of these solutions indicate that an equilibrium between several species is occurring in these solutions. Further studies to elucidate the nature of these species are in progress and will be discussed elsewhere.

Acknowledgment. The financial support of the University of Nevada, Reno, Research Advisory Board and of the National Science Foundation (Grant No. CHE77-08937), which provided funds to purchase the FT NMR spectrometer, is gratefully acknowledged.

Registry No. *cis*-L_2PdX_2 (R = CH_3, X = Cl), 72402-81-4; *cis*-L_2PdX_2 (R = CH_3, X = Br), 72402-85-8; *trans*-L_2PdX_2 (R = CH_3, X = Br), 72442-16-1; *cis*-L_2PdX_2 (R = CH_3, X = N_3), 72402-90-5; *cis*-L_2PdX_2 (R = *n*-Bu, X = Cl), 72402-82-5; *trans*-L_2PdX_2 (R = *n*-Bu, X = Cl), 72937-29-2; *cis*-L_2PdX_2 (R = *n*-Bu, X = Br), 72402-86-9; *trans*-L_2PdX_2 (R = *n*-Bu, X = Br), 72442-17-2; *cis*-L_2PdX_2 (R = *t*-Bu, X = Cl), 72402-83-6; *trans*-L_2PdX_2 (R = *t*-Bu, X = Cl), 72442-15-0; *trans*-L_2PdX_2 (R = *t*-Bu, X = Br), 72442-18-3; *cis*-L_2PdX_2 (R = *t*-Bu, X = N_3), 72402-91-6; *cis*-L_2PdX_2 (R = Ph, X = Cl), 66368-11-4; *trans*-L_2PdX_2 (R = Ph, X = Cl), 72937-30-5; *cis*-L_2PdX_2 (R = Ph, X = Br), 72402-88-1; *trans*-L_2PdX_2 (R = Ph, X = Br), 72442-19-4; *cis*-L_2PdX_2 (R = Ph, X = N_3), 72402-92-7; *cis*-L_2PdX_2 (R = Bzl, X = Cl), 72402-84-7; *cis*-L_2PdX_2 (R = Bzl, X = Br), 72402-89-2; *trans*-L_2PdX_2 (R = Bzl, X = Br), 72442-20-7; *cis*-L_2PdX_2 (R = Bzl, X = N_3), 72402-93-8.

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Reactions of Tetrakis(triphenylphosphine)platinum(0) and (Ethylene)bis(triphenylphosphine)platinum(0) with Strong Proton Acids[1]

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This paper outlines a brief study of the reactions of two soluble platinum(0) complexes—(ethylene)bis(triphenylphosphine)platinum(0) (**1**) and tetrakis(triphenylphosphine)platinum(0) (**2**)—with sulfuric acid and trifluoromethanesulfonic acid (triflic acid). These studies are pertinent to an appreciation of the reactivity of low-valent transition-metal complexes in strongly acidic media and suggest processes which may be important in catalytic oxidation–reduction reactions and hydrogenations in these media.[2]

Results

Reaction of **1** with triflic acid yields ethane as the only volatile product: the yield varies from ca. 70% for heterogeneous reactions between acid and either solid **1** or a heptane slurry of **1** to ca. 30% for homogeneous reaction with a benzene solution of **1** (Scheme I).[3] The reaction is complete in less than 2 min at 0 °C. GLC detects no ethylene in these experiments, but control experiments indicate that ethylene, if produced, would be consumed rapidly by reaction with the strong acid. Dihydrogen was also not detected. Removal of excess triflic acid at the conclusion of a reaction and treatment of the platinum-containing residue with lithium chloride generated dichlorobis(triphenylphosphine)platinum(II) (**3**); we assume that ditriflylbis(triphenylphosphine)platinum(II) is the precursor of this substance.

Qualitatively similar results were obtained on treatment of **1** with sulfuric acid. Treatment of **1** in ether with anhydrous hydrogen chloride generated ethylene and *trans*-hydridochlorobis(triphenylphosphine)platinum(II) (**4**).[3] Reaction of **2** with triflic or sulfuric acid immediately generated dihydrogen (85% yield); reaction of **2** with hydrochloric acid is reported to yield **4** by a path which involves $[(Ph_3P)_3PtH]^+Cl^-$ as an intermediate.[4]

In order to examine the influence of medium acidity on the partitioning of the ethylene moities of **1** between ethane and ethylene, we determined the yield of ethane following reaction in sulfuric acid–tetrahydrofuran mixtures. Typical results are summarized in Figure 1. Ethane generation requires a very strongly acidic medium: in mixtures containing less than 70% w:w H_2SO_4 (1.75 mol of H_2SO_4 to 1 mol of THF), no significant yield of ethane is produced. At these lower acidities, the reaction of ethylene with sulfuric acid is relatively slow, and ethylene is readily detected, although the observed yields are only qualitative. Isotopic-exchange experiments carried out at high and low acidities are pertinent to the mechanism of ethane production. Ethane produced by reaction of solid **1** with deuterated acids was polydeuterated: from CF_3SO_3D, 27% d_6, 32% d_5, 22% d_4, 15% d_3, 4% d_2; from 100% D_2SO_4, 38% d_6, 32% d_5, 14% d_4, 10% d_3, 6% d_2. Ethane itself does not exchange hydrogen for deuterium with D_2SO_4 (99% D)

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