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Palladium(II) Complexes of the Para-Substituted Phenylphosphines $(4\text{-}ZC_6H_4)_nP(CH_3)_{3-n}$ (n = 1, 2). Preparation, Characterization, and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ Nuclear Magnetic Resonance Spectra[1]

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A series of para-substituted aryl(tertiary phosphines) $(4\text{-}ZC_6H_4)_nP(CH_3)_{3-n}$ (n = 1, Z = Cl, H, CH_3, CH_3O; n = 2, Z = Cl, H, CH_3), their derivatives (oxides, sulfides, methiodides, benzyl chlorides, and phosphonium salts), and their palladium(II) complexes (PdL_2X_2, X^- = Cl^-, N_3^-) have been prepared and characterized by elemental analyses, physical properties, infrared and electronic spectroscopy, and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra. The complexes are all cis in the solid state but spontaneously isomerize to equilibrium mixtures of cis and trans isomers in solution with the cis isomers generally predominating. Linear correlations are found between Hammett σ constants and ^1H chemical shifts for the free phosphines, phosphine oxides, phosphine sulfides, and most of the palladium(II) complexes. The azide complexes have larger $^2J_{PP}$ values and smaller coordination chemical shifts than the chlorides.

Introduction

Palladium(II) reacts with various tertiary phosphines, R_3P, to form square-planar complexes of the type $(R_3P)_2PdX_2$ where X represents a monodentate uninegative anion.[3] Palladium(II) and platinum(II) complexes of this type are model systems for square-planar substitution and isomerization reactions since these reactions are easily followed by ordinary techniques.[4,5] Substitution of arylphosphines in the para (4) position changes their basicity in a way which parallels Hammett σ constants.[6-9] We anticipated that varying the para substituent would affect the ease of complex formation and the relative ratio of isomers.

Palladium-phosphine complexes and their reactions are easily studied by NMR if the phosphine contains either an α-methyl or -methylene group. These groups allow assignment of geometry through either ^1H or $^{13}C\{^1H\}$ NMR because of the "virtual coupling" phenomenon.[10-14] There is some disagreement over the interpretation of the $^{13}C\{^1H\}$ NMR spectra of complexes of this type[15] which merited further investigation.

Although complexes of palladium(II) are thermodynamically stable, they are kinetically more labile than analogous complexes of platinum(II),[11] as evidenced by their spontaneous isomerization in solution; photolysis[16] or catalysis[17,18] is necessary to isomerize the platinum(II) complexes. This ease of isomerization coupled with its likely relationship to the palladium(II)-catalyzed isomerization of olefins[19-21] has prompted us to investigate further the cis-trans isomerization mechanism. From our previous studies[11,22-24] we anticipated that the basicity of the phosphorus ligands would affect the relative stabilities of the isomers. We have now prepared and characterized a series of para-substituted arylphosphines $(4\text{-}ZC_6H_4)_nP(CH_3)_{3-n}$ (n = 1, Z = Cl, H, CH_3, CH_3O; n = 2, Z = Cl, H, CH_3), their derivatives (oxides, sulfides, methiodides, benzyl chlorides, and phosphonium salts), and their palladium(II) complexes $(R_3P)_2Pd(X)_2$ (X^- = Cl^-, N_3^-). These phosphines were chosen to vary electronic effects systematically with concomitant minimal variation in steric effects. The following paper[25] will discuss the isomerization thermodynamics and mechanism.

Experimental Section

A. Reagents and Physical Measurements. Chemicals were reagent grade and used as received or synthesized as described below. All solvents, when necessary, were dried by standard procedures and stored over Linde 4A molecular sieves for at least 2 days prior to use. All reactions involving the phosphines were conducted in a prepurified nitrogen atmosphere. The nitrogen-stored phosphines are stable indefinitely when kept refrigerated; oxidation was prevented in this manner. Melting points were determined on Fisher-Johns and Meltemp apparatus and are uncorrected. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz. 85282.

Infrared spectra were recorded on a Beckman IR-8 spectrometer (high frequency only) as $CDCl_3$ solutions in 0.1-mm NaCl cavity cells or on a Beckman IR-12 spectrometer as $CHCl_3$ solutions in 0.2-mm NaCl sealed solution cells for the high-frequency region and as Nujol mulls between CsBr plates for the low-frequency region.

Electronic spectra were recorded on a Cary 14 spectrophotometer as $CHCl_3$ solutions in 1-cm quartz cells or as Nujol mulls supported on Whatman No. 1 filter paper with Nujol-saturated filter paper as the reference.

The ^1H NMR spectra were recorded at 100 MHz on a Jeolco 4H-100 spectrometer equipped with a V-6040 variable-temperature controller. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian XL-100-15 spectrometer in Fourier transform mode as previously described.[23] Proton and ^{13}C chemical shifts are relative to internal TMS while the ^{31}P shifts are relative to external 85% H_3PO_4 (capillary). Solvents were spectroscopic grade and used as received from the manufacturer after a routine check for purity. Samples were prepared as previously described.[11] Spectra were recorded immediately and were recorded after a minimum of 20 hr to see if they changed with time.

B. Syntheses. 1. Phosphines and Their Derivatives. The phosphines are only moderately air sensitive. They were always prepared, handled, and allowed to react with other chemicals under a nitrogen atmosphere (except for the oxides). All of the phosphines were prepared by standard Grignard reactions on the respective phosphonous dihalides.[27-34] Bis(p-chlorophenyl)methylphosphine was prepared in like manner; yield 31.2%, bp 235° (4 mm). The derivatives were prepared by standard literature methods.[6,36]

2. Bis(phosphine)palladium(II) Complexes. The bis(phosphine)palladium(II) chloride complexes were prepared by reaction of the phosphine with sodium tetrachloropalladate(II). The azido complexes were, in turn, prepared by metathesis of the chlorides. Representative examples are described below.

a. Dichlorobis(p-anisoledimethylphosphine)palladium(II). To 0.500 g (1.7×10^{-3} mol) of sodium tetrachloropalladate(II) in 50 ml of 95% ethanol was added 0.574 g (3.4×10^{-3} mol) of phosphine. After 1 hr of stirring, the sodium chloride was filtered off and the filtrate reduced to 15 ml on a rotary evaporator. The resultant yellow crystals were triturated by slow addition of distilled water in an ice bath. The yellow crystals were recrystallized from chloroform-benzene (1:1 by volume) and washed with cold pentane to yield 0.41 g (48.0%) of complex.

b. Diazidobis(p-anisoledimethylphosphine)palladium(II). To 0.513 g (10^{-3} mol) of dichlorobis(p-anisoledimethylphosphine)palladium(II) in 50 ml of hot dimethylformamide was added 9.32 g (2.3×10^{-3} mol) of sodium azide in 50 ml of warm methanol. After stirring the solution for 1 hr and filtering to remove the sodium chloride, the filtrate stood in the dark overnight and bright yellow crystals deposited on the flask walls. After recrystallization from dimethylformamide-ethyl ether (1:1 by volume) and washing with ether, 0.285 g (54.0%) of complex was obtained.

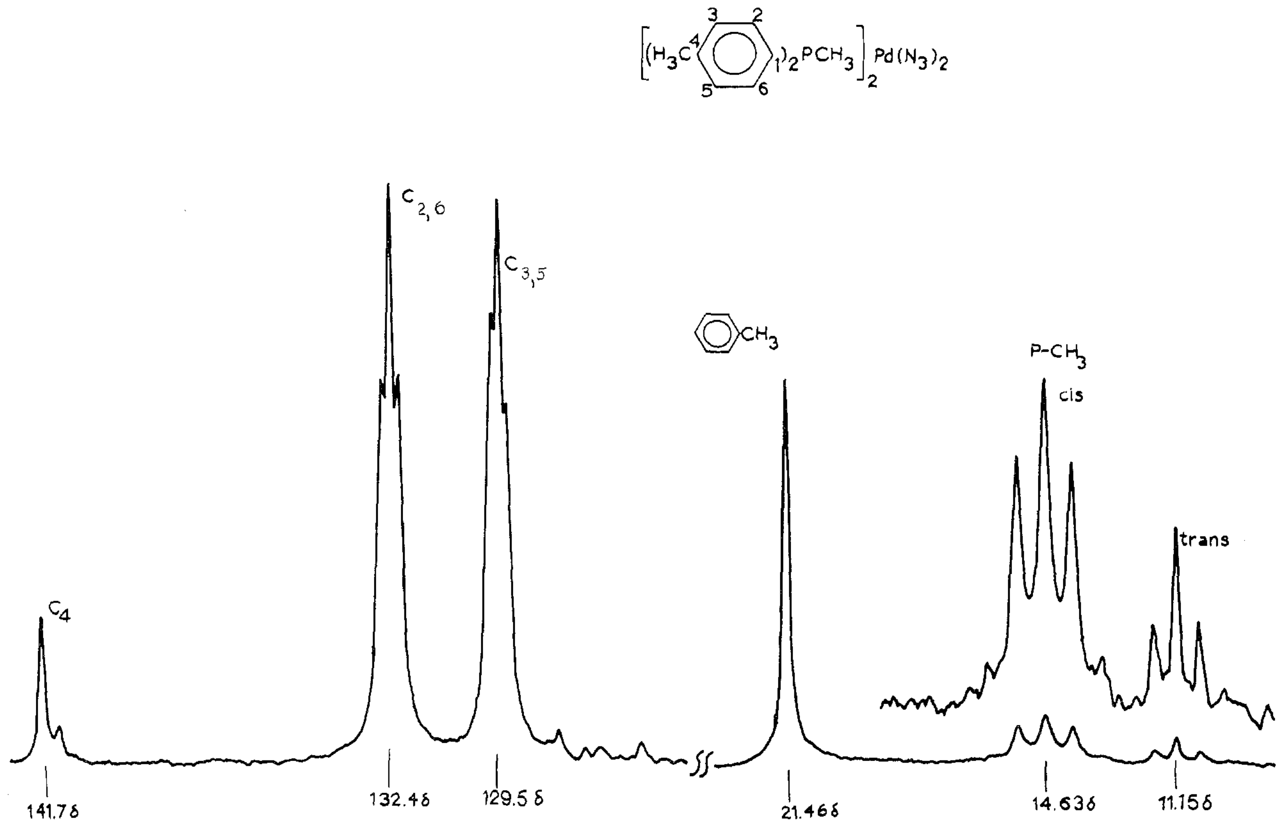

Figure 1. The 25.2-MHz $^{13}C\{^1H\}$ NMR spectrum of $[(p\text{-}CH_3C_6H_4)_2PCH_3]_2Pd(N_3)_2$ in $CDCl_3$ at room temperature. The methyl region appears as a five-line multiplet (deceptive non 1:2:1 triplet) for the cis isomer and as a triplet (1:2:1) for the trans isomer at higher field relative to the cis isomer. The para methyl resonance is insensitive to different isomeric forms.

Results and Discussion

^1H Nuclear Magnetic Resonance—the Complexes. It has been amply demonstrated for complexes of the type $(R_3P)_2PdX_2$ containing phosphines with α-methyl or -methylene groups that the shape of their NMR resonances is determined by the magnitude of $^2J_{PP}$. The spin systems of these complexes are $A_nXX'A'_n$ or $[A_nX]_2$. Where $^2J_{PP}$ is large (mutually trans phosphines)[26] this multiplet is generally a 1:2:1 triplet. Where $^2J_{PP}$ is small (mutually cis phosphines)[26] this multiplet is generally a 1:1 doublet. Thus the NMR offers a tool with which the geometry in solution may be assigned.

The phosphine ^1H methyl resonance (Table I) for the chloride complexes generally appears as an overlapping doublet and triplet at room temperature in low dipole moment solvents and as a doublet when $n = 2$ in high dipole moment solvents. For the azide complexes this resonance appears as a "filled in" doublet in most solvents at room temperature. This paper will discuss the spectra, and the following paper,[25] the equilibria involved. The chloride complexes in $CDCl_3$ are primarily cis when $n = 1$ and trans when $n = 2$. The azides show more cis isomer than the analogous chloride complexes. For the chloride complexes the trans isomers are always found slightly downfield of the cis. The ^1H NMR line shapes alone for the azide complexes at room temperature are not always conclusive in the absolute assignment of geometries; however, use of $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ along with the ^1H spectra permitted conclusive assignments in each case.

Carbon-13 Nuclear Magnetic Resonance Spectra. The $^{13}C\{^1H\}$ NMR spectra (Table II) offer complementary data to those obtained from ^1H NMR. Phosphorus methyl resonances for the cis isomers may appear as a quintet, a non 1:2:1 triplet, a doublet of doublets, or a doublet in the $^{13}C\{^1H\}$ spectra[15] (Figures 1–3). The methyl resonances of the trans isomer always appear as 1:2:1 triplets. There are linear relationships between $\delta(^{13}C)$ for the methyl resonances of the chloride complexes and Hammett σ constants. There is also an anion effect on the chemical shifts of the cis isomers. The chloride complexes are found between 16.0 and 17.9 ppm, and the azido complexes, between 13.45 and 14.6 ppm. This difference may be a manifestation of the size of the anion (chloride larger than azide) or it may reflect a difference in metal–phosphorus bond strengths.

Table I. ^1H NMR Data for $CDCl_3$ Solutions of the Complexes $[(4\text{-}ZC_6H_4)_nP(CH_3)_{3-n}]_2PdX_2$ [a]

Z	n	X	$\delta(^1H)_{p\text{-}CH_3}$, $\lvert ^2J_{PH} + {^4J_{PH}} \rvert$		δ_Z
			Cis	Trans	
CH_3O	1	Cl	1.70, 11.0	1.73, 7.6	3.91
CH_3	1	Cl	1.72, 11.25	1.75, 7.7	2.05 cis 1.8 trans
H	1	Cl	1.75, 11.4	1.78, 7.4	
Cl	1	Cl	1.80, 12.0	1.84, 7.4	
CH_3O	1	N_3	1.62, 11.0	1.62, 7.4[c]	3.94
CH_3	1	N_3	1.68, 10.9	1.67, 7.4[c]	2.39
H	1	N_3	1.60, 12.5	1.76, 7.0	
Cl	1	N_3	1.78, 11.5	1.78, 7.6[c]	
CH_3	2	Cl	1.90, 11.0	1.90, *d*	2.65 trans 2.45 cis
H	2	Cl	1.94, 11.3	2.15, 7.4	
Cl	2	Cl	2.0, 12.0		
CH_3	2	N_3	1.87, 10.9		2.45
H	2	N_3	1.68, 10.5	2.02, 7.0	
Cl	2	N_3	1.96, 11.2		
$((CH_3)_3P)_2PdCl_2$ [b]			1.68, 10.6	1.42, 7.4	

[a] δ in ppm; *J* in Hz. [b] Reference 38. [c] At −2°. [d] Ambiguous; appears all cis.

In the cases of $[4\text{-}CH_3C_6H_4P(CH_3)_2]_2Pd(N_3)_2$ and $[4\text{-}CH_3OC_6H_4P(CH_3)_2]_2PdCl_2$ the para CH_3 and OCH_3 carbons appear as two adjacent singlets (Figure 2); their relative intensities reflect the ratio of isomers determined from the ^1H and $^{31}P\{^1H\}$ spectra. The resonances of the ortho aromatic

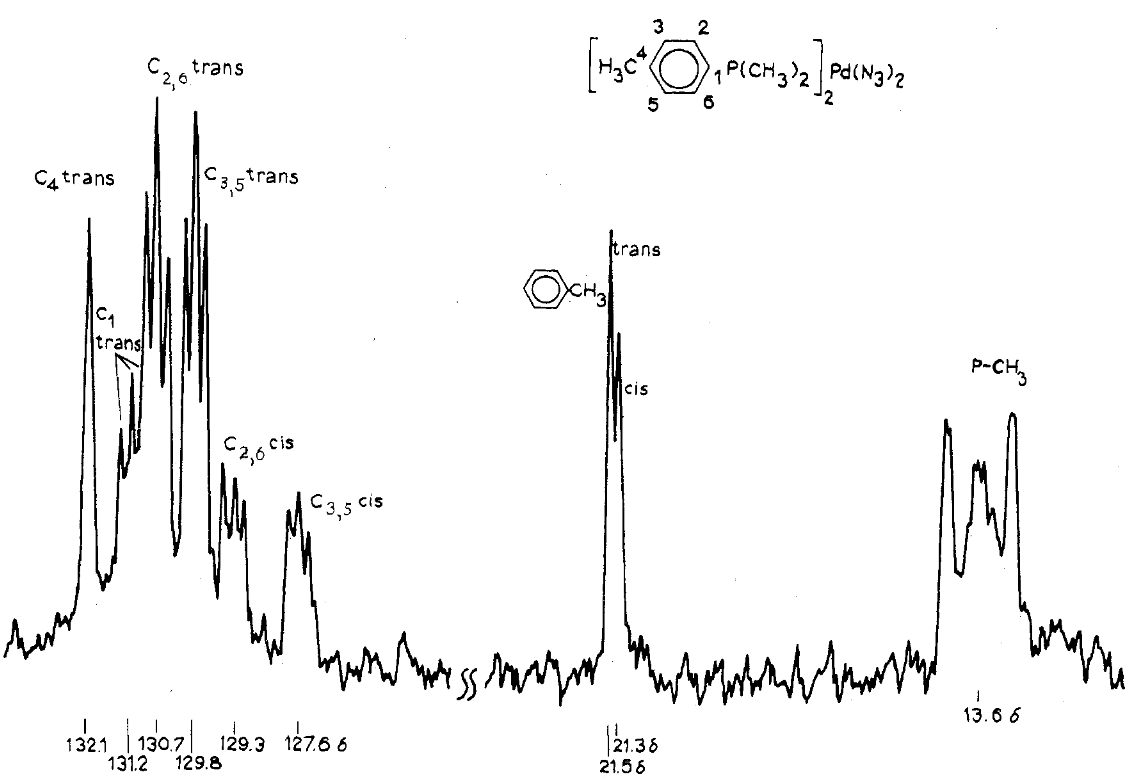

Figure 2. The 25.2-MHz $^{13}C\{^1H\}$ NMR spectrum of $[(p\text{-}CH_3C_6H_4P(CH_3)_2]_2Pd(N_3)_2$ in $CDCl_3$ at room temperature. The phosphorus methyl region appears to be a filled-in doublet. The methyl region provides no stereochemical information; however, the para methyl resonances indicate the presence of two isomers. The phenyl carbon resonances are indicative of two isomers: a doublet or filled-in doublet for cis and a triplet for trans.

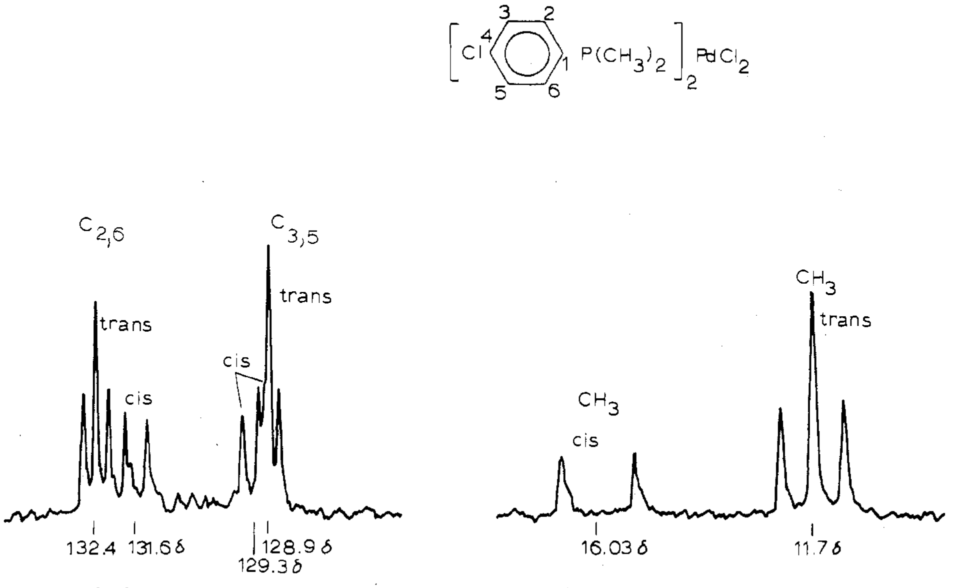

Figure 3. The 25.2-MHz $^{13}C\{^1H\}$ NMR spectrum of $[(p\text{-}ClC_6H_4P(CH_3)_2]_2PdCl_2$ in $CDCl_3$ at room temperature. The phosphorus methyl resonances are useful for stereochemical assignment in that the cis isomer gives a simple 1:1 doublet while the trans isomer gives a 1:2:1 triplet. This straightforward behavior is also seen in the phenyl carbon resonances.

carbons, C(2) and C(6), and the meta aromatic carbons, C(3) and C(5), indicate the presence of two isomers as shown in Figures 2 and 3. The much lower intensities of the C(1) and C(4) resonances are a reflection of the nuclear Overhauser effect.[37] The exact assignment of these resonances is tentative. All compounds exhibit normal coupling patterns in each of the phenyl carbon resonances except $[(C_6H_5)_2PCH_3]_2PdCl_2$ where each of the phenyl resonances is a singlet. We have no explanation for this anomalous result.

The coupling constants for the phosphorus methyl resonances usually cannot be obtained directly from the spectra as the splitting represents $|^1J_{PC} + {}^3J_{PC}|$ in most cases. For three cases—*cis*-diazidobis(anisoledimethylphosphine)palladium(II), *cis*-diazidobis(tolyldimethylphosphine)palladium(II), and *cis*-diazidobis(methylditolylphosphine)palladium(II)—a quintet was observed for the P-CH_3 carbon resonance which allowed calculation of all the coupling constants. The method used for these calculations is a standard geometric analysis.[38] It was found that $^1J_{PC}$ varies from 31.8 to 36.2 Hz, $^3J_{PC}$ from 0 to 3.16 Hz, and $^2J_{PP}$ from 33.9 to 41.3 Hz. These values have a confidence level of greater than 98% and each spectrum was matched very well by a computer-simulated spectrum.

Table II. $^{13}C\{^1H\}$ Nuclear Magnetic Resonance Data for the Complexes $[(4\text{-}ZC_6H_4)_nP(CH_3)_{3-n}]_2PdX_2$, Given as $\delta(^{13}C)$ (ppm), Line Shape, $|^nJ_{PC} + {}^{n+2}J_{P'C}|$ (Hz)

			P-CH$_3$		Para substituent			(C3), C(5)		C(2), C(6)		
Z	*n*	X	Cis	Trans	Cis	Trans	C(1)	Cis	Trans	Cis	Trans	C(4)
CH_3O	1	Cl	16.25, d, 37.85	12.17, t, 32	55.5, s	55.3, s	123.0, d, 22	114.54, d, 12.3	114.52, t, 12.3	132.66, d, 12.7	132.39, t, 13.2	161.91, s
CH_3	1	Cl	16.02, d, 37.2	11.89, t, 32	21.47, s	21.47, s	114.53, d, 16 114.30, t, 24	129.63, d, 11.5	129.53, t, 11.5	130.70, d, 11.5	130.62, t, 11.5	141.63, s
H	1	Cl	15.89, d, 38	11.78, t, 33			128.54, t, 10	128.9, d, 12	128.9, t, 12	130.56, d, 11	130.56, t, 11	133.27, d, 5 131.12, s
Cl	1	Cl	16.02, d, 37.1	11.70, t, 32.5			?	129.25, d, 11.6	128.94, t, 10.3	131.6, d, 13.6	132.4, t, 12.6	136.88, s
CH_3	2	Cl	17.9, d, 39	12.24, t, 33			128.35, t, 52	129.22, d, 11	129.08, t, 10	132.72, d, 11	133.14, t, 10	141.36, d, 3 140.61, s
H	2	Cl	17.67, d, 39	12.05, t, 33			130.57, s, *d*	128.4, s	128.4, s	133.1, s	133.1, s	130.57, s, *d*
Cl	2	Cl		12.06, t, 33			129.53, t, 50		129.14, t, 11		134.4, t, 13	137.5, s
CH_3O	1	N_3	13.95, 5 line[a]		55.5, s		131.7, *d*	114.71, t, 11		132.31, t, 12.2		162.04, s
CH_3	1	N_3	13.64, 5 line[b]	13.24, *d*	21.47, s	21.32, s	131.2, t, 12	127.6, t, 10	129.8, t, 11	129.3, t, 11	130.6, t, 12	141.88, s 132.1, s
H	1	N_3	13.45, t, 34.5	13.03, t, 32					129.15, t, 9.7		130.51, t, 10.6	131.28, s
Cl	1	N_3	Limited solubility						129.42, t, 11		131.62, t, 12	138.06
CH_3	2	N_3	14.63, 5 line[c]	11.15, t, 30	21.46, s	21.46, s	127.3	129.5, d, 13	129.5, t, 13	132.4, d, 11	132.4, t, 11	141.7, s 141.2, s
H	2	N_3	14.28, t, 32.5	11.15, t, 30			?	129.01, d, 9.8	129.01, t, 9.8	131.20, d, 7	131.20, t, 7	132.34, s 132.54, s
Cl	2	N_3	Limited solubility	10.86, t, 33					129.6, t, 10.2		133.76, t, 13.6	

[a] $^1J_{PC} = 34.57$, $^3J_{PC} = 0.52$, $^2J_{PP} = 34.22$ Hz. [b] $^1J_{PC} = 31.83$, $^3J_{PC} = 3.16$, $^2J_{PP} = 41.30$ Hz. [c] $^1J_{PC} = 36.21$, $^3J_{PC} = 0.1$, $^2J_{PP} = 33.86$ Hz. [d] Assignment questionable.

Other coupling constants for the aromatic carbons are listed in Table II. For the ortho and meta aromatic carbons $|^nJ_{PC} + {}^{n+2}J_{PC}|$ values are similar and in the range of 7–13 Hz for both the cis and the trans isomers.

From previous studies[24,26,39-44] and the data presented in Tables I and II one can make the following statements about the various coupling constants. For the cis chloride complexes $^2J_{PP}$ = 0 to −0.5 Hz, $^3J_{PC}$ = 0 to +0.5 Hz, $^1J_{PC}$ varies from 37.1 to 39 Hz and is probably positive, $^2J_{PH}$ is approximately −11 Hz, and $^4J_{PH}$ varies from 0 to +1 Hz. For the trans chloride complexes $^2J_{PP}$ is large ($\gtrsim$+61 Hz), and if $^1J_{PC}$ and $^2J_{PH}$ are similar to what they are in the cis complexes (+37 to +39 and −11 Hz, respectively), then $^3J_{PC}$ varies from −4 to −7 Hz and $^4J_{PH} \simeq +7$ Hz. For the cis azide complexes $^2J_{PP}$ varies from 33 to 41 Hz, $^3J_{PC}$ varies from +0.1 to +3.15 Hz, $^1J_{PC}$ varies from +31 to +36 Hz, $^2J_{PH}$ is approximately −11 Hz, and $^4J_{PH}$ is approximately 0. For the trans azide complexes $^2J_{PP}$ is large ($\gtrsim$+61 Hz), $^1J_{PC}$ varies from +31 to +36 Hz, $^3J_{PC}$ varies from −2 to −6 Hz, $^2J_{PH}$ is approximately −11 Hz, and $^4J_{PH}$ is approximately +7 Hz. Thus upon changing the anion in the cis complexes from chloride to azide, there is a marked increase in the magnitude of $^2J_{PP}$ from 0 to ~37 Hz and in $^3J_{PC}$ from 0 to ~1.5 Hz and a decrease in $^1J_{PC}$ from ~38 to ~33 Hz; the rest of the coupling constants remain relatively constant. When comparing cis and trans isomers $^2J_{PP}$, $^3J_{PC}$, and $^4J_{PH}$ are uniformly larger for the trans isomers. The anion effect is difficult to explain at this point. The trans to cis changes are more easily rationalized in terms of a trans influence.[45]

Phosphorus-31 Nuclear Magnetic Resonance. The $^{31}P\{^1H\}$ NMR provides the best indication of the presence of two isomers in solution as there are clean, well-separated signals for each isomer (Table III). Mann et al.[43] have shown that there is a linear relationship between the ^{31}P coordination chemical shift, Δ, and the ^{31}P chemical shift of the free phosphine, δ. The compounds studied here have extended the equations of Mann and will be discussed elsewhere. There is an anion effect on the coordination chemical shift as the ^{31}P shift difference of cis and trans isomers is −11.27 ± 0.54 ppm for the chloride and −8.25 ± 0.79 ppm for the azide complexes. The ^{31}P chemical shifts and methyl carbon ^{13}C chemical shifts are related in each series of compounds. In each case $\delta(^{13}C) = -A\delta(^{31}P) + C$; i.e., the methyl carbon shielding decreases as the phosphorus shielding increases, and the slopes (A) of these correlations are similar.[46]

The concentration ratios of isomers, K_{eq}, can be established from the NMR spectra of the three different nuclei (Table III). The agreement of K_{eq} as determined for the three different nuclei is generally good except when one of the isomers greatly predominates. The problem in determining this ratio in the carbon spectra is to obtain the intensities of outside lines in the five-line multiplets. The agreement of the carbon-derived ratios with those from phosphorus and hydrogen, expecially in the case of the azide complexes, lends credence to the coupling constant data as extracted from the five-line multiplets.

These ratios indicate a general trend within a series of para-substituted L_2PdX_2 complexes. On going from para chloro to para methoxy substituents K_{eq}, the cis:trans ratio, increases as the basicity increases. The effect of the basicity on K_{eq} and other thermodynamic parameters will be developed further in the following paper.[25]

Proton Nuclear Magnetic Resonance—the Phosphines and Their Organic Derivatives. Table IV shows that methyl hydrogens appear as doublets with small $^2J_{PH}$ values (3.0–3.2 Hz) for the phosphines or as doublets with large $^2J_{PH}$ values (11.7–15.5 Hz) for their derivatives. There is a rough correlation of $^2J_{PH}$ and $\delta(^1H)$ for the methyl groups with the

Table III. $^{31}P\{^1H\}$ NMR Data for $CDCl_3$ Solutions of the Complexes $[(4\text{-}ZC_6H_4)_nP(CH_3)_{3-n}]_2PdX_2$

			$\delta(^{31}P)$, ppm			$K_{eq} = C/T$		
Z	*n*	X	Cis	Trans	Cis − trans	From ^{31}P	From ^1H data	From ^{13}C data
CH_3O	1	Cl	−5.54	6.17	−11.71	4.04	4.28	4.41
CH_3	1	Cl	−5.75	5.67	−11.42	5.31	4.08	4.09
H	1	Cl[a]	−6.60	5.23	−11.83	2.03	3.47	5.42
Cl	1	Cl	−5.72	4.86	−10.58	0.4	0.67	0.28
CH_3O	1	N_3	−4.15	4.50	−8.65	60	263	
CH_3	1	N_3	−4.35	3.98	−8.33	28.3	42	
H	1	N_3	−5.20	2.02	−7.22	3.85	8.33	Overlapped
Cl	1	N_3	−4.57	2.83	−7.40	1.4	1.35	
CH_3	2	Cl	−17.85	−6.25	−11.60	1.14	1.20	0.87
H	2	Cl[a]	−19.10	−7.80	−11.30	0.41	0.46	0.55
Cl	2	Cl	−17.78	−7.40	−10.38	0.03	Very small	Very small
CH_3	2	N_3	−16.19	−6.82	−9.37	2.27	2.42	2.30
H	2	N_3	−17.01	−9.14	−7.87	1.67	1.69	1.72
Cl	2	N_3	−16.44	−7.53	−8.91	0.32	0.42	

[a] References 14, 48, and 49.

Table IV. ^1H Chemical Shifts and $^2J_{PH}$ for the CH_3 Doublets of the Phosphines and Their Derivatives: δ_{CH_3} $(^2J_{PH})$[a]

Phosphine	Free	Oxide	Sulfide	Methiodide	Benzyl chloride[b]	Phosphonium ion[c]
$4\text{-}CH_3OC_6H_4P(CH_3)_2$	1.26 (3.2)	1.7 (13.3)	2.03 (13.5)	2.6 (15.0)	2.48 (14.5)	1.79 (11.7)
$4\ CH_3C_6H_4P(CH_3)_2$	1.28 (3.2)	1.76 (13.3)	2.02 (13.5)	2.67 (15.0)	2.56 (13.5)	1.82 (13.0)
$C_6H_5P(CH_3)_2$	1.30 (3.1)	1.90 (13.0)	2.00 (13.2)	2.67 (14.0)	2.49 (14.0)	2.21 (15.2)
$4\text{-}ClC_6H_4P(CH_3)_2$	1.32 (3.0)	2.08 (14.0)	2.00 (13.5)	3.05 (15.0)	2.61 (14.7)	2.42 (14.7)
$(4\text{-}CH_3C_6H_4)_2PCH_3$	1.33 (3.0)	2.02 (13.5)	2.30 (14.0)	2.86 (14.5)	2.75 (14.4)	2.18 (15.0)
$(C_6H_5)_2PCH_3$	1.31 (3.2)	1.96 (13.6)	2.01 (13.0)	2.89 (13.5)	2.68 (13.0)	2.51 (15.0)
$(4\text{-}ClC_6H_4)_2PCH_3$	1.26 (3.0)	1.80 (13.8)	2.31 (14.0)	2.72 (15.0)	2.83 (14.0)	2.71 (15.5)
$P(CH_3)_3$[d]	0.89 (2.7) (neat)	1.93 (13.4)	1.74 (13.0)	2.47 (14.4)		2.3 (15.7)

[a] $CDCl_3$ solutions; δ in ppm from internal TMS; $^2J_{PH}$ in Hz. [b] δ_{CH_2} $(^2J_{PH})$ values for the compounds are 4.59 (16.0), 4.68 (16.5), 4.56 (16.0), 4.78 (16.5), 4.98 (16.2), 4.91 (15.0), and 5.34 (16.0), respectively. [c] In 1:1 CF_3CO_2H–$CDCl_3$. [d] Data taken from ref 39.

electronegativity of Y in the compounds $(4\text{-}ZC_6H_4)_nP(Y)(CH_3)_{3-n}$. Generally, the greater the electronegativity of Y the greater the chemical shift and the smaller $^2J_{PH}$ among the phosphorus(III) compounds whereas the converse seems true for the phosphorus(V) compounds. It is known that $^2J_{PH}$ may be either positive or negative with reference to α-methyl or -methylene protons[47,48] and that its magnitude depends upon the s character of the phosphorus and carbon bonding orbitals.[47,49] Our observation that $^2J_{PH}$ is insensitive to para substituent electronic effects is in keeping with earlier observations[9] and indicates that the s character in both the phosphorus and carbon bonding orbitals remains essentially constant.

A large series of compounds of the type $ZC_6H_4Y(CH_3)_n$ where Y is C, Si, and Ge (n = 3), N, P, and As (n = 2), and O and S (n = 1) has been investigated[9] and linear relationships have been observed where the equation $\delta(^1H)_{CH_3} = \rho\sigma + C$ (σ's are the ordinary Hammett constants[50]) is obeyed. Similar behavior is found (Tables I and IV) for the free phosphines, phosphine oxides, phosphonium ions, palladium complexes, and phosphine sufides, for n = 2. For the methiodides and benzyl chlorides (n = 2) the unsubstituted compounds deviate markedly from the lines defined by the other compounds in the series. The ρ values are generally believed to be indicative of the systems' ability to transmit the electronic effects of the substituent, although such interpretations with chemical shift data have been cautioned against.[51] From the data given in Tables I and IV it can be seen that the free phosphines, the benzyl chloride derivatives, and the complexes display similar transmitting abilities for substituent effects but the oxides, sulfides, methiodides, and phosphonium ions are markedly different. For the oxides and sulfides this probably reflects a difference in phosphorus polarizability as a function of formal oxidation state.[49] The large ρ values for the oxides, methiodides, and phosphonium ions suggest that the phosphorus atom in these compounds is very polarizable whereas the very small ρ value for the sulfides suggests that for these compounds it is not. Since good linear correlations, as judged by the high correlation coefficients and low standard deviations, are found for the dimethylarylphosphines and derivatives, it is somewhat surprising that they are not also found for the methyldiarylphosphines and derivatives. In each case the unsubstituted compound deviates from the value anticipated from those of the other compounds. If one compares ^1H chemical shifts for each of the series of compounds $(CH_3)_2P(Y)(aryl)$ and $CH_3P(Y)(aryl)_2$, it is apparent that there is no group contribution from either the methyl or phenyl groups and no additivity relationships of chemical shifts are found.

The chemical shifts of the methyl hydrogens decrease in the order methiodide > benzyl chloride > sulfide > phosphonium ion > oxide > complex > free phosphine and usually decrease from the chloro- to the methoxy-substituted compounds. This sequence probably reflects the decrease in positive charge on the phosphorus. There is one anomalous trend. When n = 2 the chemical shifts generally increase from chloro to methoxy (except for the phosphonium ions). This may be a result of increased steric effects in the n = 2 series of compounds.

Infrared and Electronic Spectroscopy. Infrared data on the phosphines and their complexes are given in Table V. Most of the phosphines show three distinct bands in the low-frequency region whereas each of the complexes show seven to eight. The additional bands are attributable to metal–phosphorus and metal–chlorine or metal–nitrogen stretches, especially in the 370–425-cm^{-1} region.[52,53] The strong assymetric azide[23,53] stretching band ν_{N_3} is found between 2010 and 2055 cm^{-1}. This band should be a single sharp band for the trans geometry with D_{2h} symmetry and two closely spaced bands for the cis geometry with C_{2v} symmetry. The trans isomer would exhibit single Pd–P, Pd–N, and/or Pd–Cl vibrations while the cis isomer would exhibit two vibrations for each group. The infrared data indicate that each of the complexes is cis in the solid state. The solid-state electronic spectral data and solution spectral data are very similar (Table V). This coupled with the fact that these complexes are cis

Table V. Infrared and Electronic Spectral Data

	Ir spectra, ν, cm^{-1}		Electronic spectra	
Compd	Low freq, solid (CsBr plates)	High freq, $\nu_{as}(N_3)$	λ, nm (log ϵ)^a (CHCl$_3$ soln)	λ, nm (solid state, Nujol mull)
p-CH$_3$OC$_6$H$_4$P(CH$_3$)$_2$	280, 370, 496			
[*p*-CH$_3$OC$_6$H$_4$P(CH$_3$)$_2$]$_2$PdCl$_2$	280, 299, 370, 420, 435, 496, 540		280 (4.120), 325 (4.049)	283, 328
[*p*-CH$_3$OC$_6$H$_4$P(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$	301, 364, 381, 395, 415, 540, 565	2012, 2048	255 (4.4969), 300 (4.4969)	260, 310
p-CH$_3$C$_6$H$_4$P(CH$_3$)$_2$	280, 380, 518			
[*p*-CH$_3$C$_6$H$_4$P(CH$_3$)$_2$]$_2$PdCl$_2$	280, 330, 380, 390, 425, 440, 518		259 (4.255), 331 (4.000)	268, 335
[*p*-CH$_3$C$_6$H$_4$P(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$	295, 368, 380, 415, 442, 505, 537	2020, 2055	260 (4.292), 315 (4.2922)	265, 320
p-ClC$_6$H$_4$P(CH$_3$)$_2$	270, 385, 510, 525			
[*p*-ClC$_6$H$_4$P(CH$_3$)$_2$]$_2$PdCl$_2$	275, 305, 360, 385, 416, 510, 525		295 sh,^{b} 392 (4.198)	290, 383
[*p*-ClC$_6$H$_4$P(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$	290, 349, 377, 406, 450, 503, 539	2000, 2040	268 sh, 315 (4.279)	273, 320
(*p*-CH$_3$C$_6$H$_4$)$_2$PCH$_3$	286, 390, 508			
[(*p*-CH$_3$C$_6$H$_4$)$_2$PCH$_3$]$_2$PdCl$_2$	286, 305, 395, 410, 460, 510, 565		276 (3.886), 341 (4.016)	283, 346
[(*p*-CH$_3$C$_6$H$_4$)$_2$PCH$_3$]$_2$Pd(N$_3$)$_2$	292, 372, 386, 423, 444, 506, 556	2005, 2030	320 (4.785)	267, 320
(*p*-ClC$_6$H$_4$)$_2$PCH$_3$	280, 390, 505, 567			
[(*p*-ClC$_6$H$_4$)$_2$PCH$_3$]$_2$PdCl$_2$	282, 305, 380, 400, 420, 505, 567		273 sh, 337 (4.292)	296, 348
[(*p*-ClC$_6$H$_4$)$_2$PCH$_3$]$_2$Pd(N$_3$)$_2$	286, 310, 381, 420, 430, 501, 540, 550	2012, 2045	258 sh, 305 (4.415)	265, 310

^{a} Extinction coefficients based upon total complex concentration. ^{b} Shoulder.

in the solid state and rapidly equilibrating mixtures of cis and trans isomers in solution suggests that assignment of geometry solely on the basis of electronic spectral data is extremely difficult. Evidently, both the cis and trans isomers exhibit two electronic transitions, both of which occur at very nearly the same wavelength and differ only in extinction coefficient.[18] This explains the difficulties arising from attempts at correlating geometry with colors of the complexes.

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Registry No. *cis*-[*p*-CH$_3$OC$_6$H$_4$P(CH$_3$)$_2$]$_2$PdCl$_2$, 54832-75-6; *trans*-[*p*-CH$_3$OC$_6$H$_4$P(CH$_3$)$_2$]$_2$PdCl$_2$, 54910-41-7; *cis*-[*p*-CH$_3$C$_6$H$_4$P(CH$_3$)$_2$]$_2$PdCl$_2$, 54832-74-5; *trans*-[*p*-CH$_3$C$_6$H$_4$P(CH$_3$)$_2$]$_2$PdCl$_2$, 54869-03-3; *cis*-[PhP(CH$_3$)$_2$]$_2$PdCl$_2$, 29484-66-0; *trans*-[PhP(CH$_3$)$_2$]$_2$PdCl$_2$, 29484-74-0; *cis*-[*p*-ClC$_6$H$_4$P(CH$_3$)$_2$]$_2$PdCl$_2$, 54832-73-4; *trans*-[*p*-ClC$_6$H$_4$P(CH$_3$)$_2$]$_2$PdCl$_2$, 54910-28-0; *cis*-[*p*-CH$_3$OC$_6$H$_4$P(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$, 54832-72-3; *trans*-[*p*-CH$_3$OC$_6$H$_4$P(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$, 54869-02-2; *cis*-[*p*-CH$_3$C$_6$H$_4$P(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$, 54832-71-2; *trans*-[*p*-CH$_3$C$_6$H$_4$P(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$, 54869-01-1; *cis*-[PhP(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$, 52810-36-3; *trans*-[PhP(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$, 52881-92-2; *cis*-[*p*-ClC$_6$H$_4$P(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$, 54832-70-1; *trans*-[*p*-ClC$_6$H$_4$P(CH$_3$)$_2$]$_2$Pd(N$_3$)$_2$, 54869-00-0; *cis*-[(*p*-CH$_3$C$_6$H$_4$)$_2$PCH$_3$]$_2$PdCl$_2$, 54869-05-5; *trans*-[(*p*-CH$_3$C$_6$H$_4$)$_2$PCH$_3$]$_2$PdCl$_2$, 54832-69-8; *cis*-[Ph$_2$PCH$_3$]$_2$PdCl$_2$, 29484-75-1; *trans*-[Ph$_2$PCH$_3$]$_2$PdCl$_2$, 26973-01-3; *cis*-[(*p*-ClC$_6$H$_4$)$_2$PCH$_3$]$_2$PdCl$_2$, 54869-04-4; *cis*-[(*p*-CH$_3$C$_6$H$_4$)$_2$PCH$_3$]$_2$Pd(N$_3$)$_2$, 54832-67-6; *cis*-[Ph$_2$PCH$_3$]$_2$Pd(N$_3$)$_2$, 52881-91-1; *trans*-[Ph$_2$PCH$_3$]$_2$Pd(N$_3$)$_2$, 27285-41-2; *cis*-[(*p*-ClC$_6$H$_4$)$_2$PCH$_3$]$_2$Pd(N$_3$)$_2$, 54832-66-5; *trans*-[(*p*-ClC$_6$H$_4$)$_2$PCH$_3$]$_2$PdCl$_2$, 54832-68-7; *trans*-[(*p*-CH$_3$C$_6$H$_4$)$_2$PCH$_3$]$_2$Pd(N$_3$)$_2$, 54868-99-4; *trans*-[(*p*-ClC$_6$H$_4$)$_2$PCH$_3$]$_2$Pd(N$_3$)$_2$, 54868-98-3; (*p*-MeOC$_6$H$_4$)P(Me)$_2$, 20717-52-6; 4-CH$_3$C$_6$H$_4$P(CH$_3$)$_2$, 20676-64-6; C$_6$H$_5$P(CH$_3$)$_2$, 672-66-2; 4-ClC$_6$H$_4$P(CH$_3$)$_2$, 33733-56-1; (4-CH$_3$C$_6$H$_4$)$_2$PCH$_3$, 1486-25-5; (C$_6$H$_5$)$_2$PCH$_3$, 1486-28-8; (4-ClC$_6$H$_4$)$_2$PCH$_3$, 54844-83-6; 4-CH$_3$OC$_6$H$_4$P(O)(CH$_3$)$_2$, 54844-84-7; 4-CH$_3$C$_6$H$_4$P(O)(CH$_3$)$_2$, 53888-89-4; PhP(O)(CH$_3$)$_2$, 10311-08-7; 4-ClC$_6$H$_4$P(O)(CH$_3$)$_2$, 22605-49-8; (4-CH$_3$C$_6$H$_4$)$_2$P(O)(CH$_3$), 723-45-5; Ph$_2$P(O)(CH$_3$), 2129-89-7; (4-ClC$_6$H$_4$)$_2$P(O)CH$_3$, 54844-85-8; 4-CH$_3$OC$_6$H$_4$P(S)(CH$_3$)$_2$, 54844-86-9; 4-CH$_3$C$_6$H$_4$P(S)(CH$_3$)$_2$, 54844-87-0; PhP(S)(CH$_3$)$_2$, 1707-00-2; 4-ClC$_6$H$_4$P(S)(CH$_3$)$_2$, 54844-88-1; (4-CH$_3$C$_6$H$_4$)$_2$P(S)(CH$_3$), 54844-89-2; Ph$_2$P(S)CH$_3$, 13639-74-2; (4-ClC$_6$H$_4$)$_2$P(S)CH$_3$, 54844-90-5; 4-CH$_3$OC$_6$H$_4$P(CH$_3$)$_2$·MeI, 54844-91-6; 4-CH$_3$C$_6$H$_4$P(CH$_3$)$_2$·MeI, 54844-92-7; C$_6$H$_5$P(CH$_3$)$_2$·MeI, 1005-21-6; 4-ClC$_6$H$_4$P(CH$_3$)$_2$·MeI, 54844-93-8; (4-CH$_3$C$_6$H$_4$)$_2$PCH$_3$·MeI, 1499-36-1; (C$_6$H$_5$)$_2$PCH$_3$·MeI, 1017-88-5; (4-ClC$_6$H$_4$)$_2$PCH$_3$·MeI, 54844-94-9; 4-CH$_3$OC$_6$H$_4$P(CH$_3$)$_2$·PhCH$_2$Cl, 54869-89-5; 4-CH$_3$C$_6$H$_4$P(CH$_3$)$_2$·PhCH$_2$Cl, 54844-95-0; C$_6$H$_5$P(CH$_3$)$_2$·PhCH$_2$Cl, 54844-96-1; 4-ClC$_6$H$_4$P(CH$_3$)$_2$·PhCH$_2$Cl, 54844-97-2; (4-CH$_3$C$_6$H$_4$)$_2$PCH$_3$·PhCH$_2$Cl, 54869-90-8; (C$_6$H$_5$)$_2$PCH$_3$·PhCH$_2$Cl, 54844-98-3; (4-ClC$_6$H$_4$)$_2$PCH$_3$·PhCH$_2$Cl, 54844-99-4; 4-CH$_3$OC$_6$H$_4$P(CH$_3$)$_2$·H$^+$, 54845-00-0; 4-CH$_3$C$_6$H$_4$P(CH$_3$)$_2$·H$^+$, 54845-01-1; C$_6$H$_5$P(CH$_3$)$_2$·H$^+$, 24151-41-5; 4-ClC$_6$H$_4$P(CH$_3$)$_2$·H$^+$, 54845-02-2; (4-CH$_3$C$_6$H$_4$)$_2$PCH$_3$·H$^+$, 54845-03-3; (C$_6$H$_5$)$_2$PCH$_3$·H$^+$, 54845-04-4; (4-ClC$_6$H$_4$)$_2$PCH$_3$·H$^+$, 54845-05-5; ^{13}C, 14762-74-4; ^{31}P, 7723-14-0.

Supplementary Material Available. The elemental analyses, melting points, and colors of the complexes and statistical analyses of the correlations will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC40574R.

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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*-$(R_3P)_2PdX_2 \rightleftharpoons$ *trans*-$(R_3P)_2PdX_2$ 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-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 ±1°