to the sum of the two inversion rate constants. Because of the much lower concentrations used in the kinetic experiments (dictated by the high activity of the resolved complexes), the $\Delta\epsilon_\infty$ value could not be obtained with high precision. It was calculated from the equilibrium data and we find that the observed rate constants for approach to equilibrium are identical for the two isomers (3.25×10^{-2} hr^{-1}). A least-squares treatment of the data between 6 and 26 hr gave a correlation coefficient of 0.999 for all 10 points. The two rates of inversion are, for (+), 1.67×10^{-2} hr^{-1} and, for (−), 1.57×10^{-2} hr^{-1}. This 6% difference is also obtained by extrapolating the data in Figure 2 to zero time where the kinetics are controlled only by the forward inversion rates of the two enantiomers.

(c) Instrumentation. The instruments used were a Roussel-Jouan Dichrographe, maximum sensitivity 1×10^{-5}, a Varian T-60 nmr spectrometer, a Unicam SP800A spectrophotometer, and a Perkin-Elmer Model 141 electric polarimeter.

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Registry No. $Ni(phen)_3^{2+}$, 17085-38-0; (+)-$Ni(phen)_3^{2+}$, 31933-96-7; (−)-$Ni(phen)_3^{2+}$, 23385-79-7; (−)-2,3-butanediol, 7225-57-2.

References and Notes

(1) By diastereotopic interaction we mean the difference in interaction between each enantiomer and another chiral molecule of the same or different chemical species; thus it only includes that part of the total interaction which is discriminatory. It is important to make this distinction between the total interaction and the discriminatory part for it is only the latter which causes enantiomerization.
(2) E. E. Turner and M. M. Harris, *Quart. Rev., Chem. Soc.*, **1**, 299 (1947).
(3) B. Bosnich, "Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism," F. Ciardelli and P. Salvadori, Ed., Heyden and Son Ltd., London, 1973, p 254.
(4) R. Kuhn, *Ber. Deut. Chem. Ges. B*, **65**, 49 (1932).
(5) P. Pfeiffer and K. Oruehl, *Ber. Deut. Chem. Ges. B*, **64**, 2667 (1931).
(6) F. P. Dwyer, E. C. Gyarfas, and M. F. O'Dwyer, *Nature (London)*, **167**, 1036 (1951).
(7) B. Bosnich, *J. Amer. Chem. Soc.*, **88**, 2606 (1966).
(8) B. Bosnich and D. W. Watts, *J. Amer. Chem. Soc.*, **90**, 5744 (1968).
(9) S. Kirschner and N. Amad, *J. Amer. Chem. Soc.*, **90**, 1910 (1968).
(10) D. P. Craig, *Proc. Roy. Aust. Chem. Inst.*, **41**, 1 (1974).
(11) The solubilities in ref 6 are incorrect. The correct ones, quoted here, were obtained by Dwyer and were communicated to us by Professor D. P. Mellor *via* Professor D. P. Craig.
(12) D. P. Craig, E. A. Power, and T. Thirunamachandran, *Proc. Roy. Soc., Ser. A*, **322**, 165 (1971).
(13) B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Aust. J. Chem.*, **27**, 477 (1974).
(14) G. B. Kauffman and L. T. Takahashi, *J. Chem. Educ.*, **39**, 481 (1962).
(15) Assusming the optically pure diol has a rotation of −13° ("Handbook of Chemistry and Physics," 48th ed, CRC Press, Cleveland, Ohio, 1967), then our solvent contains 93% (−)-2,3-butanediol and, presumably, the rest is the (+) isomer. The alcohol is obtained from a somewhat capricious biological culture and there may be some of the meso form present. The values of the enantiomerization constants could be about 10% low throughout.
(16) These values are calculated from our kinetic results and the racemization activation energies of $[Ni(phen)_3]^{2+}$ in ethylene glycol (N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 24, 1325 (1954)).

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Equilibrium Thermodynamics and Mechanism of Cis–Trans Isomerization for Diazidobis(methyldiphenylphosphine)palladium(II) and Diazidobis(dimethylphenylphosphine)palladium(II)

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The complexes $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ and $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$ were prepared and characterized by nuclear magnetic resonance (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}), infrared, and electronic spectroscopy and conductometric methods. It is shown that the magnitude of the phosphorus–phosphorus coupling constant, $^2J_{PP}$, is greater for the azido complexes than for the analogous chloro complexes. These complexes are cis in the solid state but spontaneously isomerize to produce equilibrium mixtures of the cis and trans isomers in a variety of solvents. Equilibrium energetics for the isomerizations were determined by variable-temperature ^{1}H nmr and compared with the results obtained for the analogous chloride and tetrazole complexes. The mechanism of base-catalyzed and uncatalyzed isomerization was ascertained. Evidence is presented for nonionic five-coordinate intermediates in solutions containing the complexes and amines or phosphines.

Introduction

The cis–trans isomerization of square-planar bis(phosphine)(transition metal) complexes has recently received considerable attention.[2-11] One reason for this interest is the importance of these and similar complexes as catalysts. It is well known that bis(phosphine)platinum(II) complexes are robust and isomer interconversion normally requires either extended periods of refluxing or catalysis by excess phosphine. It is not as widely known that the analogous palladium(II) complexes are so labile that often mixtures of the isomers exist in solution simultaneously and that isomerization occurs spontaneously requiring only a few minutes with no heating and no catalysis.[6-8]

It has been shown that the gross geometry of bis(phosphine)palladium(II) complexes of phosphines containing α-methyl or -methylene groups can be determined by ^{1}H nmr as the phosphines are virtually coupled.[5-8,11-14] More recently, it has also been shown that, at least for some complexes, the gross geometry can be determined by ^{13}C{^{1}H} nmr.[8,11,15-19] The spin systems for these complexes are $A_nXX'A'_n$ or $[A_nX]_2$[20] for ^{1}H nmr and AXX' or $A[X]_2$ for ^{13}C{^{1}H} nmr of the phosphine methyl or methylene groups. The shape of the multiplets in the ^{1}H and ^{13}C{^{1}H} nmr arising from these groups is dependent upon the magnitude of $^2J_{PP}$,[21,22] and $^2J_{PP}$ is different for the cis and trans isomers[22] so that it is possible to determine from the nmr spectra whether the phosphines are mutually cis or trans. Although, many complexes containing halide ions have been investigated in this manner, few containing pseudohalides, especially azide, have.

The chemistry of coordinated azides[23] has received increased attention in recent years primarily due to the multifarious reactions which these complexes undergo. For example, it has been shown that coordinated azides react with metal hydrides to produce amino complexes[24] and with oxygen to produce coordinated nitrites.[25] They are also precursors to molecular nitrogen complexes.[26] The relatively weak N–N bond of the azide moiety (the bond between the middle nitrogen and the nitrogen coordinated to the metal) leads to the conversion of N_3^- to NCO^- [27] by reaction with carbon monoxide and to a coordinated triphenylphosphoimido group[28] by reaction with

Table I. Nuclear Magnetic Resonance Data for the Complexes $(R_3P)_2Pd(N_3)_2$

R_3P	Nucleus	Chem shift (line shape, *J*), isomer assignment[a]
$(C_6H_5)_2PCH_3$	^1H	1.68 (d, 10.5 Hz), C; 2.02 (t, 7 Hz), T
	$^{13}C\{^1H\}$	11.15 (t, 30 Hz), T; 14.28 (t, 32.5 Hz), C
	$^{31}P\{^1H\}$	−9.14 (s), T; −17.01 (s), C
$(C_6H_5)P(CH_3)_2$	^1H	1.59 (d, 12.5 Hz), C; 1.76δ (t, 7 Hz), T
	$^{13}C\{^1H\}$	13.03 (t, ~32 Hz[b]), T; 13.45 (t, 34.5 Hz), C
	$^{31}P\{^1H\}$	+2.02 (s), T; −5.2 (s), C

[a] Data for $CDCl_3$ solutions at ambient temperature, chemical shifts, δ, in ppm relative to TMS internal standard for ^1H and $^{13}C\{^1H\}$ and H_3PO_4 external standard for $^{31}P\{^1H\}$. Chemical shifts are accurate to ±0.05 ppm. Abbreviations: d, doublet; t, triplet; s, singlet; C, cis isomer; T, trans isomer; $J = |^2J_{PH} + {}^4J_{P'H}|$ or $|^1J_{PC} + {}^3J_{P'C}|$. Only the methyl resonances are reported for the ^1H and $^{13}C\{^1H\}$ spectra. [b] This resonance is poorly defined as it overlaps with that of the cis isomer.

Table II. Equilibrium Thermodynamic Data for the Reaction *cis*-$(R_3P)_2PdX_2 \rightleftharpoons$ *trans*-$(R_3P)_2PdX_2$[a]

	$R_3P = C_6H_5P(CH_3)_2$			$R_3P = (C_6H_5)_2PCH_3$		
	$X = Cl^-$	$X = N_3^-$	X = 5-CF_3-trifluoromethyltetrazolate	$X = Cl^-$	$X = N_3^-$	X = 5-trifluoromethyltetrazolate
			Solvent $CDCl_3$			
ΔG_{305}[b]	0.36	1.39	All trans	−0.54	0.35	−1.13
ΔH_{eq}	3.1	5.47	All trans	5.3	4.93	1.70
ΔS_{eq}	9.0	13.59	All trans	19.1	15.24	9.40
			Solvent *sym*-Tetrachloroethane			
ΔG_{305}	1.13	2.82	*c*	0.64	1.22	*c*
ΔH_{eq}	5.8	9.62	*c*	6.4	4.64	*c*
ΔS_{eq}	15.3	22.62	*c*	18.9	11.39	*c*
			Solvent *o*-Dichlorobenzene			
ΔG_{305}	0.33	All cis	*c*	Cis + trans[d]	0.65	*c*
ΔH_{eq}	4.6	All cis	*c*	Cis + trans	10.69	*c*
ΔS_{eq}	14.0	All cis	*c*	Cis + trans	30.03	*c*

[a] Both azido complexes were wholly cis in nitrobenzene, perfluoronitrobenzene, CD_3NO_2, and *m*-dichlorobenzene. The complex $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ was wholly trans in toluene-d_8 and wholly cis in 1,1,1-trichloroethane. [b] ΔH in kcal/mol is believed to be accurate to ±0.1 kcal/mol; ΔS in eu is believed to be accurate to ±1 eu; ΔG in kcal/mol. These data were obtained as previously described: chlorides,[6] tetrazolates.[7] All the azido ^1H nmr temperature studies were run on a Jeolco 4H-100. [c] Limited solubility precluded measurements in these cases. [d] Both cis and trans isomers are present but overlapping solvent resonances precluded accurate data analysis.

triphenylphosphine. The well-known organic 1,3-dipolar cycloaddition reaction,[29] which has been reviewed for organic azides,[30] has been shown to produce a number of heterocycles from azido complexes.[31] It has been found that many of these products do not have the same geometry as the starting azido complexes; *e.g.*, the azido complexes are predominantly cis (*vide infra*) whereas the tetrazolato complexes[7] are predominantly trans.

We have recently reported the equilibrium thermodynamics of cis–trans isomerization for dichlorobis(methyldiphenylphosphine)palladium(II)[6] and dichlorobis(dimethylphenylphosphine)palladium(II)[6] and for several bis(phosphine)palladium(II) complexes of 5-methyl- and 5-trifluoromethyltetrazolate.[7] It is very desirable to investigate the effects which different anions and phosphines have on this isomerization process. It is also of interest to determine whether the isomerization mechanism is influenced by the presence of weak bases or phosphines as catalysts. These effects are particularly important since cis–trans isomerization has been postulated in many catalysis mechanisms and it is known that small amounts of various bases poison the catalysts. We report herein the effect on the cis–trans equilibrium thermodynamics of changing the anion to azide. In addition the mechanisms of catalyzed and uncatalyzed isomerization were studied by variable-temperature ^1H nmr, electronic spectroscopy, and conductometric methods.

Experimental Section

1. Instrumental Methods. (A) Nuclear Magnetic Resonance. The ^1H nmr spectra were recorded at 100 MHz on a Jeolco 4H-100 nuclear magnetic resonance spectrometer equipped with a JES-VT-3 variable-temperature probe, at 60 MHz on a Varian A-60 nmr spectrometer equipped with a V-6040 variable-temperature controller, and at 300 MHz on a Varian instrument at Varian Associates, Palo Alto, Calif. $^{13}C\{^1H\}$ nmr spectra were recorded at 25.2 MHz and $^{31}P\{^1H\}$ nmr spectra were recorded at 40.5 MHz on a Varian XL-100-15 nmr spectrometer in Fourier transform mode. Several tens of thousands transients for $^{13}C\{^1H\}$ and several hundred transients for $^{31}P\{^1H\}$ were accumulated with typical acquisition times of 0.8 sec. Line positions were determined automatically by computer software using the Varian S-124X1 Fourier transform accessory. $^{13}C–^1H$ and $^{31}P–^1H$ couplings were eliminated using broad-band ^1H noise-modulated decoupling. ^1H and $^{13}C\{^1H\}$ chemical shifts are relative to internal TMS while $^{31}P\{^1H\}$ chemical shifts are relative to external H_3PO_4 (capillary). Solvents used were commercial spectroscopy grade or were purified by standard procedures. Samples were prepared by dissolving in the appropriate solvent, heating if necessary, and filtering through Kleenex into the nmr tube to remove all insoluble material (primarily trace amounts of palladium metal). Spectra were recorded immediately after solution preparation and subsequent to temperature studies to check for decomposition and time-dependent phenomena; the results are given in Table I. Equilibrium thermodynamics were calculated as before.[6] The results are given in Table II.

(B) Conductivity Measurements. Conductivity studies were performed at 25 ± 0.1° and temperature regulation was achieved using a Brinkman Lauda K-2/R temperature controller. Conductance measurements were made using a Yellow Springs Instruments conductivity cell, Model No. 3403, and measured with an Industrial Instruments conductivity bridge, Model RC16B2, adapted in house for use with a DuMont 401 R oscilloscope. Conductance ranges for electrolytes were taken from published values.[32-35] Base conductance corrections were made by plotting the results of titrations of base into pure solvent. The base-corrected conductance was then determined by subtracting the conductance due to the base from the measured conductance.

(C) Infrared Spectra. Low-frequency infrared spectra were recorded on a Beckman IR-12 infrared spectrometer with samples prepared as Nujol mulls between CsBr plates. High-frequency spectra were recorded on Beckman IR-8 and IR-12 spectrometers with samples as solutions in 0.1-mm NaCl cavity cells or as Nujol mulls between NaCl plates. The results are given in Table III.

(D) Electronic Spectra. Electronic spectra were recorded at room

Table III. Infrared and Electronic Spectral Data for the Complexes $(R_3P)_2Pd(N_3)_2$

Phosphine	State	$\nu_{as}(N_3)$, cm^{-1}	Electronic transitions, kK (log ϵ)[b]	ν_{Pd-P} and ν_{Pd-N},[c] cm^{-1}
$(C_6H_5)_2PCH_3$	Solid, Nujol	2000, 2025[a]	40, 29.4	349, 360, 374, 478
	$CHCl_3$	2032, 2045	40 (4.35), 31.5 (4.30)	
	Toluene	2030, 2045	33.9 (3.77), 29.4 (3.55)	
	1,1,1-Trichloroethane	2018 w, 2035, 2045	38 (4.12), 30.3 (4.05)	
$C_6H_5P(CH_3)_2$	Solid, Nujol	2012, 2040[a]	38.4, 31.8	345, 370, 445, 450
	$CHCl_3$	2040	42.6 (4.30), 31.3 (4.35)	
	1,1,1-Trichloroethane	2030, 2048	40 (3.87), 31 (3.82)	

[a] This vibration exhibits a severe Christiansen effect in the solid state and it is very difficult to define the absorption maximum. It is probably for this reason that the values reported in ref 38 (2020, 2044 cm^{-1}) differ from those which we report. The $CHCl_3$ data agree. For a discussion of the Christiansen effect see W. J. Potts, "Chemical Infrared Spectroscopy," Vol. 1, Wiley, New York, N. Y., 1963, pp 137–140. [b] These transitions are a combination of overlapping intraligand and charge-transfer transitions. Extinction coefficients were calculated from the total concentrations. [c] From the data given by J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis, Jr., and A. S. Wilson, *Spectrochim. Acta, Part A*, **23**, 1121 (1967); G. E. Coates and C. Parkin, *J. Chem. Soc. A*, 421 (1963); P. S. D. Park and P. J. Hendra, *Spectrochim. Acta, Part A*, **25**, 227 (1967); it seems reasonable to assign ν_{Pd-N} to the lower energy vibrations and ν_{Pd-P} to the higher energy vibrations.

temperature on a Cary Model 14 spectrophotometer as chloroform solutions and as Nujol mulls supported on Whatman No. 1 filter paper with Nujol-saturated filter paper as reference. The results are given in Table III. Job's law studies were performed on dichloromethane solutions in the following manner.[36] The method of Job is to plot the deviation from Beer's law as the concentration of the complex and coordinating ligand are varied such that the total concentrations remain constant in a constant volume of solution. This amounts to a variation of the mole fractions of complex and ligand. The change in the absorbance of the solution at a particular wavelength is then followed. If A is the absorbance measured at a particular wavelength and for a particular mole fraction of ligand, X, and if A_0 is the absorbance when no ligand has been added, then a plot of Y, where $Y = A - (1 - X)A_0$, *vs.* X will yield a straight line at $Y = 0$ if no new species are formed. Thus, if no new species are formed in solution, there should be no deviation from Beer's law. If new species are formed, the average number of new coordinated ligands, $\bar{n}$, can be calculated from the formula $\bar{n} = X/(1 - X)$ where X is the mole fraction of ligand at maximum deviation (*i.e.*, Y_{max} or Y_{min}). If the extinction coefficient for the new species is greater than the extinction coefficient for the original complex, then the deviation should be positive. If the extinction coefficient for the new species is less than that for the original complex, then the deviation should be negative. If more than one new species is formed, the curve may have "humps" or may, if $\epsilon_{new} > \epsilon_{original}$ for one species and $\epsilon_{new} < \epsilon_{original}$ for another species, cross $Y = 0$ and have both positive and negative deviations.

(E) Compound Preparation. The amines and trimethyl phosphite were commercially available. Pyridine was dried over sodium hydroxide, distilled therefrom, and used immediately after distillation. Trimethyl phosphite was distilled and utilized immediately. The phosphines were prepared by standard Grignard reactions from commercially available (Aldrich) $(C_6H_5)PCl_2$ and $(C_6H_5)_2PCl$ and were stored and handled under nitrogen. All reactions involving phosphines were conducted under an atmosphere of dry nitrogen. The azido complexes were prepared by simple metathesis of the analogous chloride[6,12] complexes in the following manner.[37,38] To 0.453 g (1 × 10^{-4} mol) of $[(CH_3)_2PC_6H_5]_2PdCl_2$ dissolved in *ca.* 50 ml of 5:1 chloroform–ethanol was added 0.260 g (4 × 10^{-4} mol) of sodium azide (2 molar excess). The resulting solution was stirred several hours with mild heating and evaporated to dryness with a flash evaporator. The resulting solid was extracted with dichloromethane (100 ml) and the extract filtered to remove undissolved NaCl and excess NaN_3. The solvent was again removed on the flash evaporator. The resulting yellow crystals were dissolved in a minimum amount of hot dichloromethane; the solution was filtered and cooled. The cold solution was triturated with hexane to yield yellow-orange crystals of $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$, mp 170–172° dec. *Anal.* Calcd for $C_{16}H_{22}N_6P_2Pd$: C, 41.15; H, 4.74; N, 18.01. Found: C, 41.09; H, 4.72; N, 18.22. $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ was prepared similarly. Yellow-orange crystals, mp 172–174° dec. *Anal.* Calcd for $C_{26}H_{26}N_6P_2Pd$: C, 52.87; H, 4.40; N, 14.22. Found: C, 52.89; H, 4.49; N, 13.89.

(F) Melting Points and Elemental Analyses. Melting points were determined on a Fischer-Johns melting point apparatus and are uncorrected. When melted, both compounds formed red liquids which on further heating bubbled as if releasing a gas (presumably N_2). The compounds are photosensitive and should be stored in the dark. When stored in foil-wrapped vials in a desiccator, they seem stable indefinitely. Elemental analyses were performed by Chemalytics, Tempe, Ariz.

Results

Proton Nmr. It has been well established that the geometry of most[29] square-planar bis(phosphine)(transition metal) complexes can be determined *via* ^1H nmr if the phosphines contain α-methyl or -methylene groups.[5-8,11-14,21,22] This is possible because the α-methyls or -methylenes are virtually coupled and in trans complexes $^2J_{PP}$ is usually large[22,39] (approximately 400 Hz) such that the phosphine resonances (*i.e.*, the α-methyl or -methylenes) appear as a 1:2:1 triplet. When the phosphines are mutually cis, these resonances normally appear as a 1:1 doublet since $^2J_{PP}$ is usually small[22,39] (0–15 Hz). This doublet often appears to have fine structure between the two outer members.[40] In some cases the appearance is such that the doublet is almost filled in and may or may not have what appears to be another resonance rising between the outer resonances. This filled-in doublet arises because of larger values of $^2J_{PP}$ which give rise to "intermediate coupling."[41] The spin systems which describe these multiplets are $A_nXX'A'_n$ or $[A_nX]_2$[20] where A is ^1H and X is ^{31}P. These spin systems have been treated theoretically[41] and coupling constant requirements for the different multiplet shapes can be deduced from the equations describing the spin system.[41] A 1:2:1 triplet will be observed when[21,42] $|J_{AX} - J_{AX'}|^2 < 2J_{XX'}\Delta\nu_{1/2}$, where $\Delta\nu_{1/2}$ is the resolving power of the spectrometer, typically about 0.5 Hz. A 1:1 doublet will be observed[21,41] when $|J_{AX} - J_{AX'}|^2 > 4J_{XX'}\Delta\nu_{1/2}$. Intermediate coupling is defined as occurring when neither of the above conditions are fulfilled and filled-in doublets will normally be observed.

For the complex $[C_6H_5P(CH_3)_2]_2Pd(N_3)_2$ the ^1H nmr spectrum in $CDCl_3$ consists of a large filled-in doublet and a small triplet at δ 1.59 and 1.76, respectively (Table I and Figure 1). To corroborate the argument that the filled-in doublet is precisely that and not two overlapping multiplets, a 300-MHz spectrum was obtained which shows exactly the same line shapes at precisely the same chemical shifts. The triplet and the doublet are therefore assigned as arising from the trans and cis isomers, respectively. The fact that the cis isomer of the analogous chloride complex shows a 1:1 doublet for the ^1H resonance while that for the azido complex is a filled-in doublet indicates that $^2J_{PP}$ is larger for the azido complex than for the chloro complex. This is also evidenced in the $^{13}C\{^1H\}$ spectra (*vide infra*).

The ^1H nmr spectrum of $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ in $CDCl_3$ also contains a 1:2:1 triplet and a filled-in doublet which are likewise assigned as arising from the trans and cis isomers, respectively. The isomer populations of both complexes in $CDCl_3$ and other solvents are temperature dependent and the

Table IV. ^{31}P Chemical Shifts (δ) and Coordination Chemical Shifts (Δ) for the Complexes $(R_3P)_2PdX_2$

R_3P	X	δ(phosphine)[a]	δP(complex)[b]		Δ (found) δ(complex) − δ(phosphine)		Δ (calcd)[c]		Error Δ(found) − Δ(calcd)	
			Cis	Trans	Cis	Trans	Cis	Trans	Cis	Trans
$(CH_3)_2PC_6H_5$	Cl^-	47.55	−6.60	5.23	−54.15	−42.32	−46.11	−45.08	−8.04	+2.76
	N_3^-	47.55	−5.20	2.02	−52.75	−45.53	−46.11	−45.08	−6.64	−0.45
$CH_3P(C_6H_5)_2$	Cl^-	27.68	−19.10	−7.80	−46.78	−35.48	−46.82	−37.94	+0.04	+2.46
	N_3^-	27.68	−17.01	−9.14	−44.69	−36.82	−46.82	−37.94	+2.13	+1.12

[a] $\delta(^{31}P)$ data are taken from B. E. Mann, C. E. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *Inorg. Nucl. Chem. Lett.*, 7, 881 (1971). [b] $\delta(^{31}P)$ data for the chloride complexes were taken from the same reference and from S. O. Grim and R. L. Keiter, *Inorg. Chim. Acta*, 4, 56 (1970). [c] The equations for calculating the coordination chemical shifts, Δ, are given in the reference cited in *a* above.

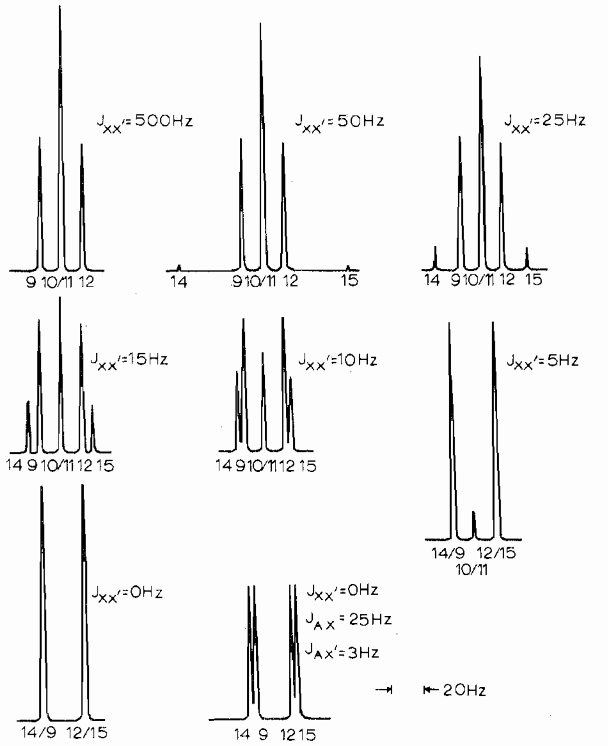

Figure 1. Computer simulation of the $A[X]_2$ spin system where $J_{AX} = 25$ Hz, $J_{AX'} = 0.5$ Hz, and $J_{XX'}$ is varied between 500 and 0.0 Hz. Similar spectra are obtained using differing values of J_{AX} and $J_{AX'}$ which exhibit the same general changes with changing $J_{XX'}$. The line width at half-height for these simulations is 0.8 Hz.

ratio of the relative intensities of the respective resonances is the ratio of the isomers. In none of the solvents investigated did these resonances overlap, therefore making integration straightforward. By plotting ln K_{eq} *vs.* T^{-1} it is possible to calculate the equilibrium thermodynamics for cis–trans isomerization. The results are given in Table II.

In all cases where comparisons can be made, there is an increased amount of the more sterically hindered cis isomer for the azido complexes over that found for the chloro complexes.

$^{31}P\{^1H\}$ Nmr. For both complexes two singlets were observed in $CDCl_3$, each representing one isomer, and were assigned by comparing their relative integrated intensities with K_{eq} in $CDCl_3$. It was noted that for both cases, the $^{31}P\{^1H\}$ resonance assignable to the cis isomer had a much greater line width ($\Delta\nu_{1/2}$) than that assignable to the trans isomer (see for example Figure 1). The observation of two phosphorus nuclei with different chemical shifts for each complex confirms the presence of two isomers in solution. The $^{31}P\{^1H\}$ data are given in Table II.

Phosphorus-31 coordination chemical shifts have been reported for the chloro complexes. In addition, an equation has been formulated with which the expected coordination chemical shifts may be calculated. Comparisons of the observed and calculated coordination chemical shifts are presented in Table IV for both the chloro and azido complexes. It seems that the trans complexes generally give better agreement than the cis complexes and that the azido complexes generally give better agreement than the chloro complexes. This seems to be a manifestation of the lower steric requirements of the trans complexes and the azido group (*vide infra*).

$^{13}C\{^1H\}$ Nmr. Initially, investigation of similar complexes by $^{13}C\{^1H\}$ nmr led to the expectation that $^{13}C\{^1H\}$ nmr would be more useful in determining the geometry of virtually coupled phosphine complexes than ^1H nmr, especially when the ^1H spectrum exhibited intermediate coupling.[15,16] It was not realized at that time, however, that because of the very low natural abundance of ^{13}C, the spin systems for the $^{13}C\{^1H\}$ nmr spectra of these complexes must be treated[17-20] as AXX' or $A[X]_2$ and not $[A_nX]_2$. For this spin system, the conditions for the occurrence of a 1:2:1 triplet in terms of coupling constants are that a triplet will be observed when $|J_{AX} - J_{AX'}|^2 < 8J_{XX'}\Delta\nu_{1/2}$. By comparing the conditions for the observation of a 1:2:1 triplet for the $[A_nX]_2$ spin system[20] ($|J_{AX} - J_{AX'}|^2 < 2J_{XX'}\Delta\nu_{1/2}$) with the above conditions, it is readily apparent that for similar values of J_{AX} and $J_{AX'}$, $J_{XX'}$ may be 4 times smaller for $^{13}C\{^1H\}$ than for ^1H nmr and a 1:2:1 triplet will be observed. This suggests that if the ^1H spectrum is a filled-in doublet, the $^{13}C\{^1H\}$ spectrum will most likely be a triplet.[43] This then can account for the appearance of a triplet in the $^{13}C\{^1H\}$ nmr spectra of several cis complexes.[18,19]

If the appearance of the phosphine carbon multiplet in the $^{13}C\{^1H\}$ nmr spectrum is considered as a function of decreasing $J_{XX'}$, it is seen that when $J_{XX'}$ is large, a 1:2:1 triplet is observed. As $J_{XX'}$ decreases, the center line of the triplet decreases in intensity with the simultaneous appearance of weak combination transitions on each side of the original triplet. If these lines are too weak to be observed, the triplet will still consist of three observable lines but it will *not* be a 1:2:1 triplet. As $J_{XX'}$ decreases further, a five-line multiplet should be observed. If $J_{XX'}$ is zero, a doublet of doublets should be observed[44] as long as $J_{AX'}$ is greater than the resolving power of the instrument (*i.e.*, >0.5 Hz). If both $J_{XX'}$ is zero and $J_{AX'} < 0.5$ Hz, then a single doublet will be observed. When a single doublet is observed, the splitting is, for all practical purposes, equal to J_{PC}. Therefore, if two phosphines are mutually cis in a bis(phosphine) complex and $^2J_{PP'}$ is small, then either a five-line multiplet, a non-1:2:1 triplet, or a doublet of doublets should be seen[18,19] (remembering that a doublet may be seen if $J_{PP} = 0$ and $J_{P'C} < 0.5$ Hz).[11,16] In all cases where the phosphines are mutually trans in a bis(phosphine) complex and $^2J_{PP'}$ is large, a 1:2:1 triplet should be observed. In Figure 1 the changes in line shape as a function of $^2J_{PP}$ are illustrated.

The $^{13}C\{^1H\}$ nmr spectrum of $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ in $CDCl_3$ was found to consist of two triplets (Figure 2). The ratio of the integrated intensities of the two triplets was found to be 0.60 (higher shielding:lower shielding), and by comparison with K_{eq} = [trans]/[cis] of 0.59 from the ^1H nmr spectrum

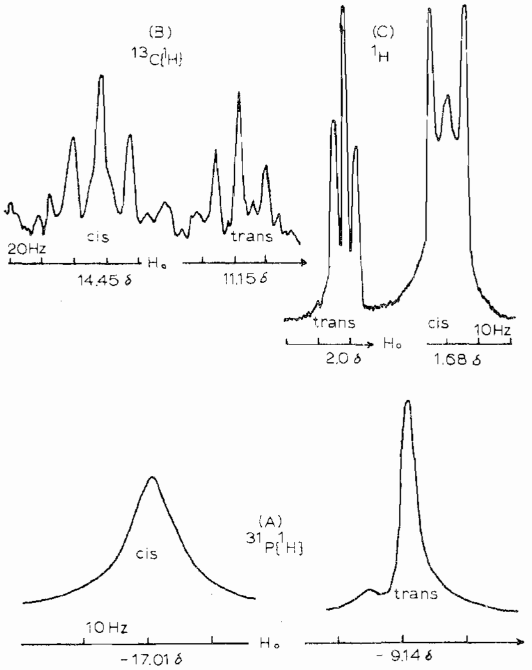

Figure 2. Nmr spectra at ambient temperature for $CDCl_3$ solutions of $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$: (A) 40.5-MHz $^{31}P\{^1H\}$, H_3PO_4 external reference; (B) 25.2-MHz $^{13}C\{^1H\}$ in the methyl region, TMS internal reference; (C) 100-MHz ^1H in the methyl region, TMS internal reference.

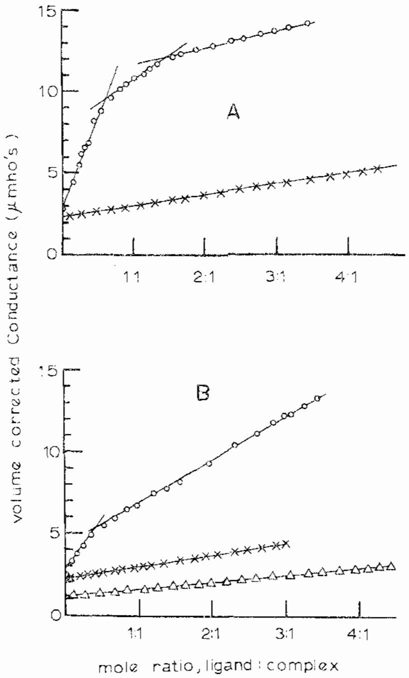

Figure 3. Results of conductometric titrations: (A) 4.8×10^{-4} *M* solution of $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$ with solutions containing 4.45×10^{-3} *M* $(CH_3)_2PC_6H_5$ (○) and 2.47×10^{-3} *M* pyridine (×); (B) 5×10^{-4} *M* $[(CH_3)P(C_6H_5)_2]_2Pd(N_3)_2$ with 4.45×10^{-3} *M* $(CH_3)_2P\text{-}C_6H_5$ (○) and 2.47×10^{-3} *M* pyridine (×) and 1×10^{-4} *M* $[CH_3P\text{-}(C_6H_5)_2]_2Pd(N_3)_2$ with 9.95×10^{-5} *M* $(CH_3O)_3P$ (Δ), all in nitromethane plotted as volume-corrected conductance *vs.* ligand:complex mole ratio.

they are assigned to the trans and cis isomers, respectively. The effect of the spin system differences in the ^1H and $^{13}C\{^1H\}$ nmr is seen here since the $^{13}C\{^1H\}$ resonance of the cis isomer is a triplet whereas the ^1H resonance is a filled-in doublet.

For the complex $[C_6H_5P(CH_3)_2]_2Pd(N_3)_2$, the $^{13}C\{^1H\}$ spectrum again possesses two triplets which in this case overlap. By comparison of the ratio of integrated intensities of these two triplets to K_{eq} found from the ^1H nmr they were assigned as trans at higher shielding and cis at lower shielding. It should be noted that for both complexes the trans isomers gave rise to 1:2:1 triplets while the cis isomers gave rise to triplets that are not 1:2:1.

Conductivity Studies. Since ionic species have been previously isolated for similar complexes and since there is evidence for an ionic pathway for catalyzed isomerization,[11] we wished to determine if ionic species are formed for these complexes when weak bases or phosphine catalysts are added. If ionic species were formed, we hoped to determine whether some behavior of these species showed parallel behavior to the order of K_a's (as determined in H_2O) of the bases. This is important in light of the ability of weak bases to poison catalysts. Consequently, a known volume and concentration of the complexes were titrated with various bases conductometrically. The bases investigated were dimethylphenylphosphine, dimethyl sulfoxide, methyldiphenylamine, *N,N*-dimethylaniline, *N,N*-diethylaniline, pyridine, isoquinoline, and trimethyl phosphite. The only base for which any evidence for ionic species was obtained was dimethylphenylphosphine (Figure 3). Even with this base the conductivity never reached that of a 1:1 electrolyte even when a 3 molar excess of base was added. When the volume-corrected conductance was plotted against the mole ratio of dimethylphenylphosphine to $[C_6H_5P(CH_3)_2]_2Pd(N_3)_2$ there was obtained a curve with two inflection points at approximately 1:1 and 2:1 ligand:complex mole ratios (Figure 3). This seems to indicate that although the conductivities are not those of 1:1 or 2:1 electrolytes, some new species with higher conductivities are formed with probable stoichiometries of $L_3Pd(N_3)_2$ and $L_4Pd(N_3)_2$, L = $C_6H_5P(CH_3)_2$. For the complex $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ a curve was also found when $C_6H_5P(CH_3)_2$ was added. This curve, however, had only one break at approximately a 1:1 phosphine:complex ratio. This might suggest the formation of a species $L'L_2Pd(N_3)_2$, where L = $(C_6H_5)_2PCH_3$ and L' = $C_6H_5P(CH_3)_2$, which is not a 1:1 electrolyte.

On the other hand, since addition of $(CH_3)_2PC_6H_5$ to either of these two complexes resulted in increased conductivity but the conductivity never approached that of a 1:1 or 2:1 electrolyte, especially when corrected for the conductivity of the base, a small amount of the ionic species might be formed. If it is assumed that the increase in conductivity is the result of an increased amount of the more conducting base in conjunction with the formation of a small amount of ionic species of the types $[ML_2L'X]^+$ and $[ML_2L'_2]^{2+}$ and if the conductance resulting from the base can be subtracted out (see the Experimental Section), then the remaining conductivity can be assumed to arise from the formation of a small amount of the ionic species. If λ_m's for 1:1 and 2:1 electrolytes are assumed to be 80 and 130, respectively (λ_m's near 80 were found for 1:1 electrolytes of similar complexes[7]), then the concentration of the ionic species, [C], can easily be calculated from $[C] = (\lambda_m(\text{exptl}))[C°]/\lambda_m(1{:}1)$ where $\lambda_m(\text{exptl})$ is the molar conductivity found experimentally after subtraction of the base conductivity and [C°] is the concentration of the complex at the new volume (*i.e.*, original volume plus volume of base added). The results of these calculations are that [C]:[C°] upon addition of $(CH_3)_2PC_6H_5$ to $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$ for a 1:1 addition is 1.62×10^{-5} *M*:4.36×10^{-4} *M* and for a 2:1 addition is 1.77×10^{-5} *M*:4.17×10^{-4} *M*; for addition of $(CH_3)_2PC_6H_5$ to $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ for a 1:1 addition [C]:[C°] = 1.21×10^{-5} *M*:2.11×10^{-4} *M*. These data suggest that up to 10% of the $ML_2L'X$ complex ionizes to $[ML_2L'X]^+ + X^-$. These data seem to be internally consistent in that for $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$ there is a lesser

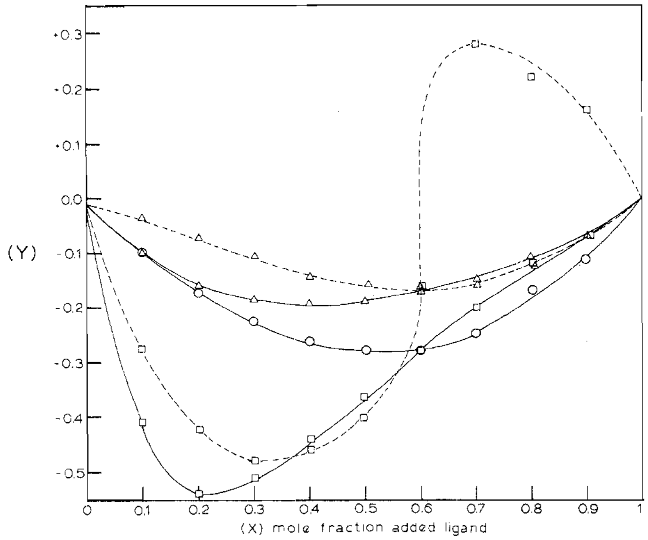

Figure 4. Job's law plots for $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ (- - -) and $[C_6H_5P(CH_3)_2]_2Pd(N_3)_2$ (——) with $(CH_3O)_3P$ (○), pyridine (△), and $(CH_3)_2PC_6H_5$ (□) in dichloromethane plotted as $Y = A - (1 - X)A_0$ *vs.* mole fraction of added ligand (X); measured at 30.5 kK for $[CH_3P(C_6H_5)_2]_2Pd(N_3)_2$ and at 31.3 kK for $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$.

formation of 2:1 electrolyte than of the 1:1 electrolyte. Similarly, there is less 1:1 electrolyte formation for $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ than for $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$ as would be expected for associative attack on a larger species.

Addition of all other bases gave only straight-line plots with slowly increasing conductivities (Figure 3). Several attempts at isolating the new species indicated here were made, but only the original complexes were obtained.

Electronic Spectral Studies. Another method which may be used to substantiate the presence of nonisolable species in solution is that of Job.[36] In this method, the deviation from Beer's law at a particular wavelength is plotted. If new species are formed in solution, significant deviations should be observed. The average number of added ligands, $\bar{n}$ can be calculated from the formula $\bar{n} = X/(1 - X)$ where X is the mole fraction of added ligand. This allows a somewhat quantitative view of the stoichiometry at maximum deviation from Beer's law. Typical plots are given in Figure 4. It should be noted that significant deviations occurred in every case. Additionally, it was observed that in all cases, as the concentration of the base increased, the wavelength of maximum absorbance changed, also indicating the formation of some new species in solution. The results of the conductometric titrations and Job's law studies are therefore complementary and both indicate the formation of new species upon addition of bases to solutions of the azido complexes.

Solid-State Structures. From the infrared and electronic spectral data presented in Table III and the nmr data presented in Table II it can be concluded that both $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$ and $[CH_3P(C_6H_5)_2]_2Pd(N_3)_2$ have the cis geometry in the solid state. These conclusions were made in the following manner. Each complex possesses two ν_{Pd-N} and two ν_{Pd-P} stretching vibrations in the solid and this supports a C_{2v} cis geometry. The D_{2h} trans geometry would give rise to only one ν_{Pd-N} and one ν_{Pd-P}. The solid-state electronic spectral data for each complex are very similar to the solution spectral data in solvents where the nmr data show that only the cis isomer is present. (For example, compare the solid electronic spectral results to the 1,1,1-trichloroethane solution results.) It should be stated that it is extremely difficult to assign geometries for these complexes on the basis of electronic spectral data alone. The fact that these complexes exist as cis isomers in the solid state and rapidly equilibrated mixtures of cis and trans isomers in solution shows that these complexes are kinetically labile and that there is a very small difference (Table II) in the thermodynamic stability of the two isomers.

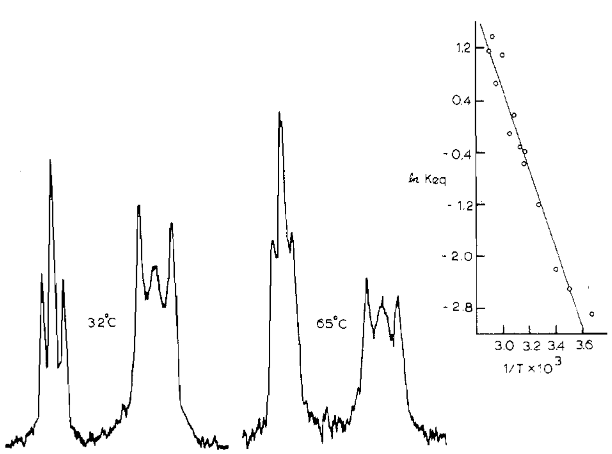

Figure 5. Typical line shapes as a function of temperature and a representative least-squares ln K *vs.* T^{-1} plot for the complex $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ in $CDCl_3$. The filled-in doublet is due to the cis isomer and the triplet is due to the trans isomer.

Discussion

Equilibrium Thermodynamics. The equilibrium thermodynamic data collected for these azido complexes is not as extensive as that collected for the analogous chloride complexes (Table II and Figure 5). This is primarily due to the fact that the azido complexes are often wholly cis in solution. The ^1H nmr spectra were recorded in 11 different solvents and variable-temperature studies were performed in most of these. In all cases where both cis and trans isomers exist in solution simultaneously, heating the solution results in an increase in the amount of the trans isomer at the expense of the cis isomer. Equilibration requires only a few minutes which is longer than the time required for the analogous chloro complexes to equilibrate. Additionally, the same trend of isomer population with change in dipole moment of the solvent that was noted previously for the chloro[6] and tetrazolato[7] complexes is found here for the azido complexes. The amount of the cis isomer increases as the dipole moment of the solvent increases. It seems that here also, the isomerization process is entropy controlled as ΔS_{eq} is several times larger than ΔH_{eq}. Another important observation is that in all cases where only the cis isomer is present in solution at room temperature, neither isomerization nor ligand exchange could be promoted by heating the solution.

As was previously argued,[6] there should be two major contributions to both ΔH_{eq} and ΔS_{eq}. For ΔH_{eq}, these are solvation effects and changes in internal bond strengths. Both of these effects favor the cis isomer. For ΔS_{eq}, the two major contributions are ΔS of solvation and changes in the internal degrees of freedom brought about by steric crowding. Since the azido complexes should have higher dipole moments than the chloro complexes and since they should also be less sterically hindered, both ΔH and ΔS of solvation should be greater for the azido complexes than for the chloro complexes. Moreover, the steric contributions should be rather small for the azido complexes since these complexes exhibit a greater amount of the cis isomer (the sterically more hindered) than do the chloro complexes. This would seem to suggest that ΔS of solvation is the major factor in ΔS_{eq}. Additionally, it is seen in Table II that $\Delta\Delta S_{eq}$ for the two azido complexes in $CDCl_3$ is 1.65 eu. For the chloro complexes $\Delta\Delta S_{eq}$ in $CDCl_3$ is 10.1 eu. For the complex $[C_6H_5P(CH_3)_2]_2PdCl_2$ $\Delta\Delta S_{eq}$ between the extremes of the solvent dipole moments is 11.2 eu,[6] while for $[(C_6H_5)_2PCH_3]_2PdCl_2$ the same $\Delta\Delta S_{eq}$ is 6.8 eu.[6] This suggests that ΔS for solvent effects and ΔS for steric effects have comparable magnitudes for the chloro complexes. $\Delta\Delta S_{eq}$ on changing solvents from $CDCl_3$ to *sym*-tetrachloroethane is 6.3 and −0.2 eu for $[(C_6H_5)_2PCH_3]_2PdCl_2$ and $[C_6H_5P(CH_3)_2]_2PdCl_2$, respectively. Here the change in ΔS seems to be larger for steric changes than for solvent changes. For the azido complexes $\Delta\Delta S_{eq}$ on changing phosphine is 1.65 eu in $CDCl_3$ and 11.3 eu in *sym*-tetrachloroethane. On balance, it seems that these two effects are not completely separable. When steric effects are small such that the solvent can effectively interact with the solute, solvent effects predominate in ΔS especially for high dipole moment solvents. On the other hand, when steric effects are large, solvent cannot effectively interact with solute and solvent effects are smaller. It seems, however, that throughout the azido complexes have greater contributions from solvent effects than the chloro complexes. This is probably due to the lesser steric requirements of the azide ion as compared to the chloride ion. Since ΔS seems to control the isomerization process and since solvation contributions to ΔS favor the trans isomer, the lesser steric effects and greater ΔH of solvation are probably the major reasons that the azido complexes exhibit a greater amount of the cis isomer than the chloro complexes.

Another important observation is the reversal of the order of increasing ΔH_{eq} from that found for the chloro complexes. For the chloro complexes, it was noted that the complex with the phosphine which is the weakest base had the largest ΔH_{eq} and it was argued that this was a manifestation of Pd–P π bonding.[6] For the azido complexes, however, ΔH_{eq} is larger for the better and smaller base $C_6H_5P(CH_3)_2$. This is probably a manifestation of a larger contribution of solvent effects to ΔH_{eq} for the azido complexes. For the analogous tetrazolato complexes,[7] however, it was shown that the reversal in the order of ΔH_{eq} over the chloro complexes was in fact an effect due to bond strength differences and that in turn σ bonding predominated. In any event, it appears that azide ion behaves differently from either chloride or tetrazolate, especially as no rapid ligand exchange or isomerization occurs when only the cis isomer is present. Thus, a subtle balance of metal–ligand bond strengths, steric effects, and solvent effects will determine the relative thermodynamic stabilities of isomeric square-planar palladium(II) complexes.

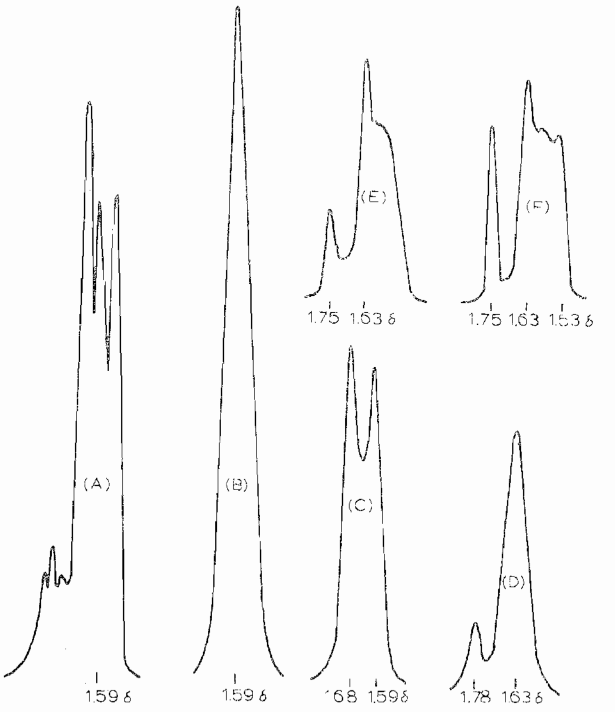

Figure 6. The 100-MHz ^1H nmr spectra in the methyl region for a solution of $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$ in $CDCl_3$ containing a trace of $(CH_3)_2PC_6H_5$ as a function of temperature and time: (A) no added phosphine; (B) trace of phosphine added, 23°; (C) more phosphine added, 23°; (D) solution C at 50°; (E) solution C after 3 days at 23°; (F) solution C after 5 days at 23°.

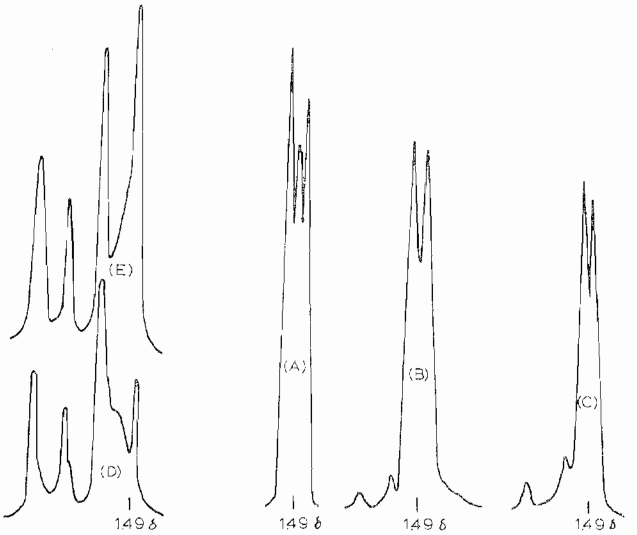

Figure 7. The 100-MHz ^1H nmr spectra in the methyl region for a solution of $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$ in CD_3NO_2 containing a trace of $(CH_3)_2PC_6H_5$ as a function of temperature and time: (A) no added phosphine; (B) trace of phosphine added, 23°; (C) solution B at 40°; (D) solution B at 108°; (E) solution B after 3 days at 23°.

Catalyzed Isomerization. In an attempt to determine if five- and six-coordinate species could be observed *via* ^1H nmr as was suggested by the Job's law and conductivity studies, small amounts of bases (*viz.*, $(CH_3O)_3P$ and $C_6H_5P(CH_3)_2$) were added to solutions of the complexes in $CDCl_3$ and CD_3NO_2. When $C_6H_5P(CH_3)_2$ (a catalytic amount) was added to a solution of $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ in $CDCl_3$, the triplet and filled-in doublet collapsed to a broad singlet. This behavior can be explained in terms of rapid free-coordinated ligand exchange (on the nmr time scale) and the same type of behavior has been reported for similar complexes.[5-7,11,45] This indicates that $\Delta G^{\ddagger}$ for isomerization has been lowered significantly, especially when even heating a solution of this complex to 140° in nitrobenzene did not initiate rapid exchange. Nitrobenzene is a polar solvent with moderate coordinating ability and it was found that rapid ligand exchange occurred[7] for the tetrazolate complexes in this solvent at or below 140°. When a small amount of $C_6H_5P(CH_3)_2$ was added to a solution of $[C_6H_5P(CH_3)_2]_2Pd(N_3)_2$ in $CDCl_3$, the solution changed from yellow-orange to orange-red and the original filled-in doublet and very small triplet collapsed to a singlet at δ 1.59 (Figure 6). When slightly more $C_6H_5P(CH_3)_2$ was added, the solution lightened in color and a new singlet appears at δ 1.68. These two resonances might arise from bis(phosphine) complex rapidly exchanging with free phosphine at δ 1.59 and five- or six-coordinate species undergoing rapid fluxional behavior (it cannot also be rapidly exchanging phosphine since only one signal would then be observed). When this solution is heated to 50°, the two singlets do collapse to one, but also a new resonance appears at δ 1.75. This spectrum remains the same even when cooled to room temperature. Over a period of time at room temperature this new resonance grows and is actually half of a doublet. At this point it is not possible to say much which is not speculation, but it seems quite reasonable that five-coordinate species are formed. The temperature and time dependencies of the spectra seem to indicate that the new species, whatever they are, have varied kinetic and thermodynamic stabilities. Similar behavior

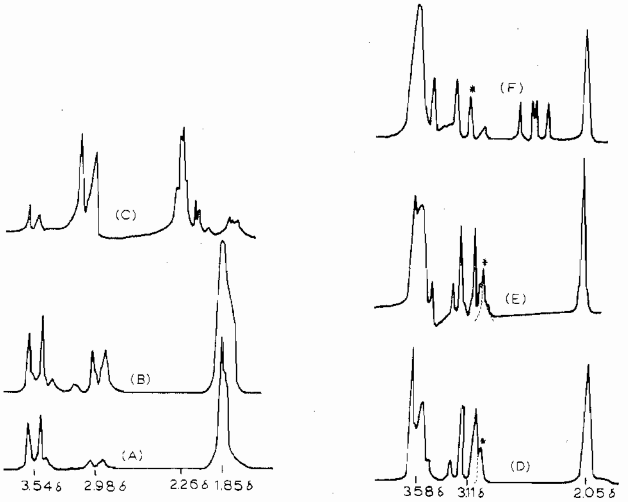

Figure 8. The 100-MHz ^1H nmr spectra in the methyl region for a solution of $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ in $CDCl_3$-containing $(CH_3O)_3P$, 0.2:1 phosphite:complex (A–C) and 1:1 phosphite:complex (D–F) mole ratios, as a function of time, at 23°: (A) and (D) initial; (B) after 1 hr at 23°; (C) after 2 days at 22°; (E) after 2 hr at 23°; (F) after 2 days at 23°. The starred resonance is due to an impurity in the phosphite.

is noted upon further addition of $C_6H_5P(CH_3)_2$ to $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ in $CDCl_3$ and for both complexes in CD_3NO_2 (Figure 7).

One difficulty in the above study was that the free phosphine and the coordinated phosphines have very similar chemical shifts. If there were a larger difference in chemical shifts between the added base and the coordinated phosphine, it might be possible to identify better the different species which are formed. Additionally, it should be easier to determine the time-dependent behavior of the new species if their resonances do not overlap. With this in mind, we added known quantities of $(CH_3O)_3P$ in $CDCl_3$ to known quantities of $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ in $CDCl_3$. We varied the mole ratios of the two components and followed the changes in the ^1H nmr spectrum with time. When the mole ratio is 0.2:1 = phosphite:complex, the initial spectrum shows the presence of free phosphite as a doublet at δ 3.54 (Figure 8) and the phosphine resonances have collapsed to a singlet, due to rapid exchange of free displaced phosphine with coordinated phosphine at δ 1.85. In this spectrum a small amount of a new species is evidenced by the appearance of a doublet at δ 2.98. Over a 2-hr period this doublet continues to increase in intensity with concurrent decrease in the intensity of the free phosphite resonance and a second new species is evidenced by the appearance of a doublet at δ 3.30. Over a 48-hr period, the doublet at δ 2.98 continues to increase and a new multiplet at δ 2.26 appears. This new multiplet has arisen at the expense of the original phosphine resonance, but by now the spectrum is too complicated to speculate beyond the presence of at least two new species.

When the molar ratio of phosphite to complex is 1:1 (Figure 8), two new doublets appear at δ 3.11 and 3.35 as were seen above. Over a 2-hr period, both of these increase in intensity and the doublet arising from free phosphite at δ 3.58 begins to collapse. The singlet arising from displaced phosphine exchanging with the original complex is shifting toward the phosphite resonances. After 48 hr, the appearance of the phosphite resonance indicates rapid exchange. A new doublet of doublets, or two doublets (indicating the formation of at least one new species), is also seen at δ 2.52 and 2.68. It appears that this solution contains at least five species. If this is the case, some must be five-coordinate and others mixed phosphine–phosphite complexes, but it is not possible to determine which is which.

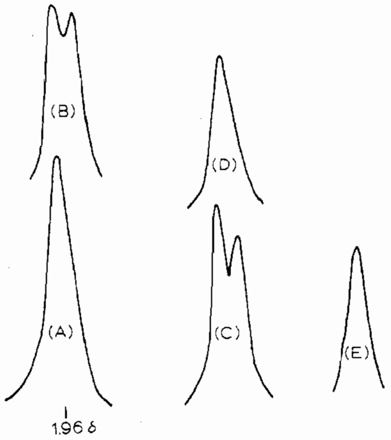

Figure 9. The 100-MHz ^1H nmr spectra in the methyl region for a solution of $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ in pyridine as a function of temperature: (A) 24°; (B) 50°; (C) 75°; (D) 95°; (E) return to 50°.

When the molar ratio of phosphite to complex exceeds 2:1, the two doublets at δ 3.11 and 3.55 are formed very rapidly, and over a 48-hr period the spectrum becomes very much the same as that seen after 48 hr for the 1:1 molar ratio solution.

From the data discussed above, it can be seen that five-coordinate species are formed in solution when a weak base is added to a solution of the $L_2Pd(N_3)_2$ complexes. These species show varied kinetic and thermodynamic stabilities. It would seem enticing to suggest that some of these are ionic in nature but the conductivity experiments mitigate somewhat against this suggestion. There could be intimate ion pairs formed which would go undetected by conductivity. Studies directed at identifying these species are currently in progress.

We have previously obtained seemingly anomalous behavior for these and similar complexes in pyridine and DMSO-d_6 solutions where the complexes seem to be undergoing some type of temperature-dependent phenomena which cannot be accounted for by isomerization. It now seems likely that these solvents are coordinating and perhaps even displacing phosphine ligands in these solutions. Examples of their behavior are seen in Figures 9 and 10. The doublet which is seen is either the result of intermediate exchange or ligating solvent which changes the magnitude of the coupling constants and consequently the line shape. In either case, the doublet normally collapses with an increase in temperature indicating rapid exchange or fluxional behavior. Rapid exchange was not observed for these azido complexes in any other solvent unless phosphine or phosphite were added. Therefore, it seems that pyridine and DMSO-d_6 are acting in much the same way as other bases and must be coordinating but they do not produce ionic species (*vide supra*). An attempt was made to extract and isolate a new complex from the pyridine solution, but even though the solution is orange-red, only the original yellow azido complex could be extracted.

If, as these data indicate, five-coordinate species are formed, which dissociate only slightly to ionic species, and rapid isomerization and/or ligand exchange occurs, the azido complexes would seem to follow the nonionic mechanism of isomerization (Figure 11). Since, at most, 10% of the five-coordinate complex dissociates to ionic species, then the rate of the ionic pathway must be 10 times faster than the rate of the nonionic pathway to be kinetically important. This seems unlikely.[46] It is known that the chloro complexes do isomerize *via* an ionic mechanism in combination with the nonionic mechanism,[6,11] and the tetrazolate complexes follow a nonionic mechanism when uncatalyzed and an ionic mechanism when catalyzed.[7] This indicates that both routes are viable possibilities for isomerization, and whichever mechanism will prevail depends intimately upon the nature of the phosphine,

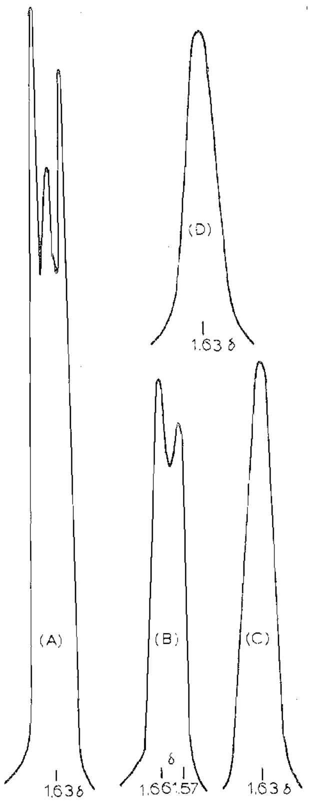

Figure 10. The 100-MHz ^1H nmr spectra in the methyl region for a solution of $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$ in DMSO-d_6 as a function of temperature: (A) 23°; (B) 53°; (C) 78°; (D) 98°.

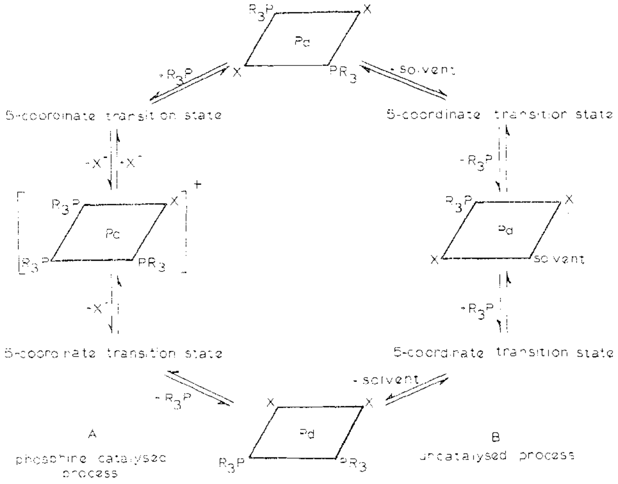

Figure 11. Isomerization mechanisms for the phosphine-catalyzed (process A) and the uncatalyzed (process B) cis-trans isomerizations of the complexes $(R_3P)_2PdX_2$. For the complexes studied here, *i.e.*, $X = N_3^-$, process B seems to occur in all cases. When a catalyst is added, solvent should be replaced by the catalyst in the mechanism. The geometry of the five-coordinate transition states is unknown but believed to be irregular (see "Inorganic Reaction Mechanisms," Vol. 2, The Chemical Society, London, 1972, pp 135-136).

the solvent, and the anion and the presence or absence of a catalyst.

We are currently attempting to identify and isolate these new species. Likewise we are also trying to determine their kinetic and thermodynamic stabilities.

Conclusions

Significant conclusions from four different areas can be drawn from the data presented herein. The first is that $^{13}C\{^1H\}$ nmr is useful in determining geometries of bis(phosphine) complexes. Additionally, it is shown that $^2J_{PP}$ in these types of complexes is a function of the anion (something which we are investigating further). The second conclusion is that it appears that the bond strengths in these azido complexes are dependent upon the σ-bonding abilities of the phosphine, such that the phosphine which is the stronger base has the strongest metal ligand bonds. The third conclusion is that it is conclusively shown that for the azido complexes addition of bases initiates formation of five-coordinate species in solution. Some of these are ionic, but it has recently been shown that in some cases $[ML_3X]^+ + X^-$ does not react at a fast enough rate to account for isomerization.[46] This, then, suggests that the mechanism of isomerization does not proceed primarily *via* an ionic pathway but rather through solvent or base association to produce five- and/or six-coordinate species which undergo fluxional behavior or ligand exchange to yield (with loss of associated base or solvent) the other isomer. The fact that none of these species are isolable seems to indicate that they are thermodynamically and kinetically unstable with respect to the four-coordinate species. The fourth conclusion is, that as might be expected, the isomerization and ligand substitution mechanisms of square-planar palladium(II) complexes are intimately related.[47,48]

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Registry No. *cis*-$[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$, 52881-91-1; *trans*-$[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$, 27285-41-2; *cis*-$[(C_6H_5)P(CH_3)_2]_2Pd(N_3)_2$, 52810-36-3; *trans*-$[(C_6H_5)P(CH_3)_2]_2Pd(N_3)_2$, 52881-92-2.

References and Notes

(1) (a) University of Nevada. (b) Stanford Research Institute.
(2) P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 4996 (1970).
(3) P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 5243 (1970).
(4) P. Haake and R. M. Pfeiffer, *Chem. Commun.*, 1330 (1969).
(5) D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, **95**, 1102 (1973).
(6) D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, **12**, 15 (1973).
(7) D. A. Redfield, J. H. Nelson, R. A. Henry, D. W. Moore, and H. B. Jonassen, *J. Amer. Chem. Soc.*, **96**, 6298 (1974).
(8) D. A. Redfield, L. W. Cary, and J. H. Nelson, submitted for publication.
(9) L. Cattalini and M. Martelli, *J. Amer. Chem. Soc.*, **91**, 312 (1969).
(10) J. R. Shapley and J. A. Osborn, *J. Amer. Chem. Soc.*, **92**, 6976 (1970).
(11) D. G. Cooper and J. Powell, *Can. J. Chem.*, **51**, 1684 (1973).
(12) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).
(13) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **12**, 991 (1973).
(14) A. J. Cheney and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 860 (1972).
(15) B. E. Mann, B. L. Shaw, and R. E. Stainbank, *J. Chem. Soc., Chem. Commun.*, 151 (1972).
(16) A. J. Cheney, B. E. Mann, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 431 (1971).
(17) D. F. Gill, B. E. Mann, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 311 (1973).
(18) D. E. Axelson and C. E. Holloway, *J. Chem. Soc., Chem. Commun.*, 455 (1973).
(19) M. Fild and W. Althoff, *J. Chem. Soc., Chem. Commun.*, 933 (1973).
(20) C. W. Haigh, *J. Chem. Soc. A*, 1682 (1970).
(21) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).
(22) J. G. Verkade, *Coord. Chem. Rev.*, **9**, 1 (1972/73).
(23) Z. Dori and R. F. Ziolo, *Chem. Rev.*, **73**, 247 (1973).
(24) W. Beck and M. Bauder, *Chem. Ber.*, **103**, 583 (1970).
(25) P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, **93**, 84 (1971).
(26) L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **92**, 5865 (1970).
(27) W. Beck, W. P. Fehlhammer, P. Pollman, and H. Schachl, *Chem. Ber.*, **102**, 1976 (1969).
(28) W. Beck in "Progress in Coordination Chemistry," M. Cais, Ed., American Elsevier, New York, N. Y., 1969.
(29) R. R. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **12**, 212 (1973).
(30) G. L'Abbe, *Chem. Rev.*, **69**, 345 (1969).
(31) P. Kreutzer, C. Weis, H. Boehme, T. Kemmerich, W. Beck, C. Spencer, and R. Mason, *Z. Naturforsch. B*, **27**, 745 (1972).
(32) W. E. Bull, S. K. Madan, and J. E. Willis, *Inorg. Chem.*, **2**, 303 (1963).
(33) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 1158 (1963).
(34) A. K. R. Unni, L. Elias, and H. F. Schiff, *J. Chem. Phys.*, **67**, 1216 (1963).

(35) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(36) R. J. Angelici, "Synthesis and Techniques in Inorganic Chemistry," W. B. Saunders Co., Philadelphia, Pa., 1969, pp 99–104.
(37) W. Beck, W. P. Fehlhammer, D. Pollman, E. Schuieuer, and K. Feldl, *Chem. Ber.*, **100**, 3335 (1967).
(38) K. Bowman and Z. Dori, *Inorg. Chem.*, **9**, 395 (1970).
(39) These statements could also be extended to octahedral complexes but there are known exceptions, *viz.*, complexes of Cr(0), Mo(0), W(0), and Mn(I); see *e.g.*, J. F. Nixon and A. Pidcock, *Annu. Rev. NMR* (*Nucl. Magn. Resonance*) *Spectrosc.*, **2**, 345 (1969); F. B. Oglivie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1916 (1970); P. K. Maples and C. S. Kraihanzel, *ibid.*, **90**, 6645 (1968).
(40) R. J. Goodfellow, M. J. Hardy, and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 2450 (1973).
(41) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
(42) A Ault, *J. Chem. Educ.*, **47**, 812 (1970).
(43) D. A. Redfield, J. H. Nelson, and L. W. Cary, *Inorg. Nucl. Chem. Lett.*, **10**, 727 (1974).
(44) P. Diehl, R. K. Harris, and R. G. Jones, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 37 (1967).
(45) J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, **91**, 1941 (1969); C. G. Grimes and R. G. Pearson, *Inorg. Chem.*, **13**, 970 (1974).
(46) W. J. Louw, *J. Chem. Soc., Chem. Commun.*, 353 (1974).
(47) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," Benjamin, New York, N. Y., 1965, pp 18–51.
(48) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968, pp 351–435.

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Alkoxalyl Complexes of Palladium(II) and Platinum(II)

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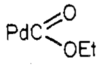
Alkoxalyl complexes of the general formula *trans*-$MCl(COCO_2R)L_2$, where M = Pt or Pd, R = CH_3 or C_2H_5, and L = $P(C_6H_5)_3$, $P(CH_3)(C_6H_5)_2$ or $P(C_2H_5)_3$, were prepared by oxidative-addition reactions of ML_4 with $ClCOCO_2R$. The C=O groups of the planar alkoxalyl ligand have an s-trans conformation in the solid state, but in solution $PtCl(COCO_2CH_3)L_2$ exists as two conformers as indicated by infrared studies. With Cl_2, $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ rapidly yields $ClCOCO_2CH_3$ and $PtCl_2[P(C_6H_5)_3]_2$. With C_2H_5OH and a trace of $C_2H_5O^-$, $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ is transesterified to give $PtCl(COCO_2C_2H_5)[P(C_6H_5)_3]_2$. While the platinum–alkoxalyl complexes are stable in solution, the palladium analogs readily undergo decarbonylation in solution to give the corresponding alkoxycarbonyl complexes ($PdCl(CO_2R)L_2$). This decarbonylation is greatly inhibited by adding phosphines (L) to the solutions. Attempts to prepare alkoxalyl complexes by CO insertion into alkoxycarbonyl complexes are also briefly described.

Palladium(II) chloride promotes the reaction of ethanol with CO and base to give diethyl carbonate[1]

$$2EtOH + CO + PdCl_2 + 2Na_2CO_3 \rightarrow (EtO)_2CO + Pd + 2NaCl + 2NaHCO_3 \qquad (1)$$

The reaction has been postulated to proceed through an ethoxycarbonyl intermediate

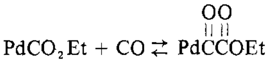


which is subsequently converted to the carbonate by ethoxide attack at the carbonyl carbon atom. The preparation and isolation[2-4] of related alkoxycarbonyl complexes, $PdCl(CO_2R)L_2$, stabilized by phosphine (L) ligands support this idea.

Under more vigorous conditions, $PdCl_2$ together with a cocatalyst such as $CuCl_2$ or $FeCl_3$ and a dehydrating agent catalyzes the reaction of ethyl alcohol, CO, and O_2 to give diethyl oxalate and smaller amounts of $(EtO)_2CO$[5]

$$2EtOH + 2CO + {}^1/_2O_2 \rightarrow EtO_2C\text{-}CO_2Et + H_2O \qquad (2)$$

This reaction is also postulated to involve the formation of an ethoxycarbonyl complex ($PdCO_2Et$), which is then converted to the oxalate ester. At the high CO pressures, this latter step could proceed *via* CO insertion into the Pd–C bond to give an ethoxalyl complex



$$PdCO_2Et + CO \rightleftarrows Pd\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OEt \qquad (3)$$

which would undergo OEt^- attack giving the product. The purpose of our investigation was to determine whether or not stable Pd(II) and Pt(II) complexes bearing the novel alkoxalyl ligand could be synthesized according to eq 3 as well as by other routes and, if so, to examine some of their reactions.

Experimental Section

Materials. The compounds PtL_4 (L = $P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$) were prepared as described in the literature.[6] The analogous PdL_4 complexes were prepared by adding L to a pentane solution of $(\pi\text{-}C_5H_5)Pd(\pi\text{-}C_3H_5)$.[7] Solutions of $Pd[P(C_2H_5)_3]_4$ were prepared by slowly adding $P(C_2H_5)_3$ to a pentane solution of $(\pi\text{-}C_5H_5)Pd(\pi\text{-}C_3H_5)$ until the color turned from red to yellow. This solution was used directly for subsequent oxidative-addition reactions. The $(\pi\text{-}C_5H_5)Pd(\pi\text{-}C_3H_5)$ was prepared either by the literature method[8] or by a more convenient modification using TlC_5H_5 instead of NaC_5H_5. This was done by stirring a solution of 1.94 g (5.3 mmol) of $[(\pi\text{-}C_3H_5)PdCl]_2$ and 2.87 g (10.7 mmol) of TlC_5H_5 in 25 ml of tetrahydrofuran (THF) under a nitrogen atmosphere at 25° for 5 min. After evaporating the solvent under vacuum, the residue was extracted with 50 ml of pentane. After filtering, the pentane was removed under vacuum leaving 1.89 g (85%) of the red crystalline product.

Alkoxycarbonyl Complexes by Oxidative-Addition Reactions. a. $PdCl(CO_2CH_3)[P(C_6H_5)_3]_2$. To a solution of 0.67 g (0.58 mmol) of $Pd[P(C_6H_5)_3]_4$ in 20 ml of benzene under N_2 was added 0.054 g (0.58 mmol) of $ClCO_2CH_3$. After stirring for 5 hr at 25°, the solvent was removed under vacuum and the remaining residue was washed with diethyl ether. Recrystallization from CH_2Cl_2–hexane gave the pale yellow crystalline product (0.34 g, 80% yield).

Anal. Calcd for $PdCl(CO_2CH_3)[P(C_6H_5)_3]_2$: C, 63.0; H, 4.56; Cl, 4.84. Found: C, 63.4; H, 4.83; Cl, 5.01.

b. $PtCl(CO_2CH_3)[P(C_6H_5)_3]_2$. Methyl chloroformate ($ClCO_2CH_3$) was added to a refluxing solution of 1.16 g (0.94 mmol) of $Pt[P(C_6H_5)_3]_4$ in 50 ml of benzene under an N_2 atmosphere until the yellow solution became pale yellow. Removal of benzene under vacuum yielded a white solid which was washed with ether and recrystallized from CH_2Cl_2–hexane to give 0.57 g (75%) of the product. Its ir and proton nmr spectra (Table I) were virtually identical with those reported for this compound prepared by a different method.[9] The analogous $Pt(Cl)(CO_2C_2H_5)[P(C_6H_5)_3]_2$ was prepared by refluxing a 20-ml toluene solution of 0.91 g (8.4 mmol) of $ClCO_2C_2H_5$ and 0.46 g (0.47 mmol) of $Pt[P(C_6H_5)_3]_3$[10] for 12 hr. Isolation as described above gave 0.21 g (54%) of the white product.[9]

Alkoxycarbonyl Complexes by Carbonylation of MCl_2L_2 Complexes. a. $PdCl(CO_2CH_3)[P(C_6H_5)_3]_2$. A suspension of 0.74 g (1.0 mmol) of *trans*-$PdCl_2[P(C_6H_5)_3]_2$ and 0.057 g (1.0 mmol) of $NaOCH_3$ in 50 ml of CH_3OH was stirred under CO (1 atm) for 5 hr at 25°. The resulting pale pink solid was collected by filtration and washed with H_2O, C_2H_5OH, and finally ether to give 0.67 g (88%) of $PdCl(CO_2CH_3)[P(C_6H_5)_3]_2$, whose spectra (Table I) were identical with those of this complex prepared by the oxidative-addition route. The platinum analog was prepared similarly from *cis*-$PtCl_2[P(C_6H_5)_3]_2$.