Lithium perchlorate was prepared from the carbonate and purified by recrystallization. Solutions of lithium thiocyanate were prepared from potassium thiocyanate and an excess (ca. 10%) of lithium perchlorate. The precipitated potassium perchlorate was filtered at 0 °C, and the filtrate was analyzed separately for [Li^+] and total thiocyanate, the latter by Volhard titration.

Induced Solvolysis. Solutions of chloromethylchromium(III) ion (typically 300 cm^3 of 10^{-3}–10^{-4} M $CrCH_2Cl^{2+}$ in 0.1 M H^+) were mixed at room temperature with solutions of mercuric nitrate. Both solutions had been made up to the same mole fraction of methanol, and the Hg(II) was added within 100 s of adding methanol to $CrCH_2Cl^{2+}$. The dealkylation reaction was allowed to proceed to completion; its progress was monitored spectrophotometrically as the rate was noticeably slower at higher methanol concentration. The slowest reaction required ca. 15 min to go to completion.

After dealkylation was complete, hydrochloric acid was added (to complex $HgCH_2Cl^+$ and excess Hg^{2+}), and the Cr(III) ions absorbed on a column of Dowex 50W-X8 cation exchange resin. The column was washed with 100 cm^3 of 0.1 M HCl followed by 100 cm^3 of 0.1 M $HClO_4$. The Cr(III) complexes were eluted with 4 M H_2SO_4. After 25 cm^3 of eluent had been collected, the column was allowed to stand for 3 h. Then the rest of the Cr(III) species were eluted. Recovery of Cr(III) was 96–100% complete in 100 cm^3 of eluent. The eluent solution was analyzed for methanol content (50-cm^3 portion) and for total chromium (5-cm^3 portion) by conversion to chromate (ϵ 4830 M^{-1} cm^{-1} at 372 nm). Analysis for methanol was accomplished by the procedure of Jayne and King.[21]

Equilibrium and Kinetic Data. The spectrophotometric data were obtained using a Cary Model 14 recording spectrophotometer with a specially thermostated (±0.1°) cell compartment. The kinetic data were evaluated by standard methods.

Registry No. $(H_2O)_5CrCH_2Cl^{2+}$, 17477-09-7; $(H_2O)_5CrCHCl_2^{2+}$, 17477-10-0; NCS^-, 302-04-5; *trans*-$(H_2O)_4Cr(NCS)(CH_2Cl)^+$, 63950-82-3; *trans*-$(H_2O)_4Cr(NCS)(CHCl_2)^+$, 63976-46-5.

References and Notes

(1) (a) Based in part on the Ph.D. thesis of W.R.B., Iowa State University, 1972. (b) Work performed for U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.

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Palladium(II) Complexes of Benzylphosphorus Ligands[1]

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Palladium(II) complexes and some platinum(II) complexes of the phosphorus ligands Bzl_nPPh_{3-n} (Bzl = $C_6H_5CH_2$, n = 1–3), $(BzlE)_nPPh_{3-n}$ (E = O, S), and $(Bzl_2N)_nPPh_{3-n}$ (n = 1–3) have been prepared and characterized. Characterizaton was achieved by physical data, conductance titrations, and infrared, electronic, and ^1H, $^{13}C\{^1H\}$, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$ nuclear magnetic resonance spectroscopy. The NMR spectra of the benzylphosphine oxides, sulfides, methiodides, benzyl chlorides, and phosphonium salts have been obtained. Most of the chloride complexes are trans in solution and probably trans in the solid state as well. The complex $[BzlPPh_2]_2PdCl_2$ undergoes reversible thermal isomerization while the complexes $[Bzl_nPPh_{3-n}]_2Pd(N_3)_2$ (n = 1, 2) undergo both reversible thermal and photochemical isomerization in solution. The complex $[Bzl_3P]_2Pd(N_3)_2$ is trans in solution and in the solid state as shown by a complete x-ray structure determination. Addition of excess ligand (L′) to solutions of any of the ML_2X_2 complexes causes ligand exchange and produces mixed-ligand complexes ($MLL'X_2$) but does not catalyze geometric isomerization. Conductance titrations demonstrate the absence of ionic species in all these solutions. Several coupling constant and chemical shift relationships are found and discussed. Computer simulations of the $[ABX]_2$, A, B = ^1H, X = ^{31}P, spin system which results for the intrinsically asymmetric methylenes in several of these compounds have been undertaken and compared with spectra obtained at various field strengths. General conclusions regarding line shapes in the NMR of compounds of this type are drawn.

Introduction

Palladium(II) and platinum(II) form many stable square-planar complexes of the type $(R_3P)_2MX_2$, where X represents a monodentate uninegative anion and R_3P a tertiary phosphine.[3] Complexes of this type have received considerable attention because they serve as model systems for square-planar substitution and isomerization reactions and because these reactions proceed at rates which are conveniently measured by conventional techniques.[4,5] There is currently considerable interest in complexes of sterically hindered phosphines,[6,7] stemming from the fact that many complexes containing sterically hindered phosphines undergo reactions, which, as a class, may be termed "internal-, cyclo-, or ortho-metalation reactions".[8] One of the primary reasons for this interest is that many of the complexes which undergo internal metalations are very good catalysts for homogeneous hydrogenations and isomerizations of unsaturated organic substrates at ambient temperature and pressure. More specifically, it has been shown that palladium(II) and platinum(II) complexes of a polymer containing benzyldiphenylphosphine catalyze the selective hydrogenation of polyolefins to monoolefins.[9]

Complexes of the type $(R_3P)_2MX_2$ and their reactions are made amenable to study by using phosphines which contain α-methyl or methylene groups since the gross geometry of the complexes can be determined from either their ^1H or their $^{13}C\{^1H\}$ NMR spectra.[10-13] The palladium(II) complexes, while being thermodynamically stable, are generally kinetically more labile to substitution and isomerization than the analogous platinum(II) complexes.[12] One indication of the greater lability of the palladium(II) complexes is the simultaneous appearance of both the cis and trans isomers in solution,[12,14] while only one isomer is usually observed in solutions of the platinum(II) complexes. Thus, while isomerization generally requires either a catalyst[15] or photolysis[16] for the platinum(II) complexes, the palladium(II) complexes often spontaneously isomerize at measurable rates.[17-19] All isomerization studies thus far reported have involved complexes of phosphines. No isomerization studies have been conducted with phosphites or aminophosphines and very few complexes of thiophosphites have been reported.

For these reasons, as well as the aforementioned parallels with catalysis and metalations, we have prepared a series of benzylphosphorus ligands and have studied some representative palladium(II) and platinum(II) complexes of them. Their characterization, magnetic resonance spectra (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^1H\{^{31}P\}$), and solution behavior are reported herein.

Experimental Section

A. Reagents and Physical Measurements. Chemicals used were reagent grade and commercially purchased. All solvents, when necessary, were dried by standard procedures and stored over Linde 3A molecular sieves for at least 2 days prior to use. All reactions involving organophosphorus compounds were conducted in a prepurified nitrogen atmosphere. Melting points were determined on Fischer-Johns and Mel-Temp melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., or Chemalytics, Inc., Tempe, Ariz.

Infrared spectra were recorded on a Beckman IR-8 or a Beckman IR-12 infrared spectrometer as $CHCl_3$ solutions and as Nujol mulls between CsBr plates. Samples of the phosphines were prepared under nitrogen in a glovebag and the sample holder was sealed with Teflon tape so as to minimize exposure to oxygen. The infrared spectra of the phosphines were compared with those of the phosphine oxides and no phosphorus–oxygen vibrations, notably $\nu_{P=O}$ in the 1100–1200-cm^{-1} region, were observed in the spectra of the phosphines.

Electronic spectra were recorded on a Cary 14 spectrophotometer as $CDCl_3$ or CH_2Cl_2 solutions or as Nujol mulls supported on Whatman No. 1 filter paper with Nujol-saturated filter paper as a reference.

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 nuclear magnetic resonance spectrometer equipped with a V-6040 variable-temperature controller, and at 220 and 300 MHz on Varian instruments at Varian Associates, Palo Alto, Calif. The $^{13}C\{^1H\}$ spectra were recorded at 25.2 MHz, the $^{31}P\{^1H\}$ spectra at 40.5 MHz, and the $^1H\{^{31}P\}$ spectra at 100 MHz on a Varian XL-100-15 NMR spectrometer in Fourier transform mode.[20] The ^{13}C–^1H and ^{31}P–^1H couplings were eliminated using broad-band ^1H noise-modulated decoupling for the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra and on-resonance single-frequency ^{31}P irradiation for the $^1H\{^{31}P\}$ spectra. The ^{13}C and ^1H chemical shifts are relative to internal TMS while the ^{31}P chemical shifts are relative to external H_3PO_4 (capillary). Downfield ^{31}P shifts are negative. Samples for NMR were prepared as previously described.[12] Computer simulations of spectra were obtained with Varian XL-100 computer software and also with a Nicolet 1180 computer using 0.8-Hz line widths. Since the six spin–spin systems studied form excellent test cases for the ability of the computers, some comments seem useful. The Varian 620L is a 12K computer which uses a six-spin program designated LSIM, line simulation, and called LXSPIN. The Nicolet 1180 is a 12K computer which uses a six-spin program called ITRCAL. Both the Varian and Nicolet programs use LOACN-3 as their basis but ITRCAL is capable of more iterations. LSIM is capable of performing six-spin calculations, but in the fitting process it will diagonalize a maximum of 1596 times. If convergence is not reached at this point, an amplitude error is indicated. ITRCAL can calculate an $[ABX]_2$ spin system which LSIM cannot properly perform. $[AX]_2$ spin simulations were performed on both computers as a check for internal accuracy. Some calculations were also performed with a modified version[21] of LAOCN-3 on a CDC 6400 computer.

Photolyses were performed by irradiating chloroform solutions in Pyrex or quartz vessels with an Illumination Industries Model LS-351Q 100-W mercury source.

Conductivity studies were performed at 25 ± 0.1 °C as previously described.[18,19]

B. Syntheses. 1. Ligands. These ligands are moderately to very air sensitive and consequently were prepared and handled under a nitrogen atmosphere. The phosphines were prepared by the reaction of benzylmagnesium chloride with the appropriate phosphorus halide.[22] Their derivatives were prepared by standard literature methods.[22,23] The benzyl phosphites,[24] benzyl thiophosphites,[25] and dibenzylaminophosphines[26] were prepared by solvolysis reactions of the appropriate phosphorus halide. The thiophosphites were used without further purification as NMR spectra showed them to be greater than 95% pure and because they underwent destructive distillation at pressures greater than 0.07 Torr. An example of the aminophosphine preparations follows as their isolation and purification differ from those of the other compounds.

Tris(dibenzylamino)phosphine $(Bzl_2N)_3P$. To a solution of 13.72 g (0.1 mol) of PCl_3 in 50 mL of diethyl ether cooled to −78 °C was added dropwise with stirring 118.2 g (0.6 mol) of dibenzylamine in 100 mL of diethyl ether over a 1-h period. The initial addition of the amine caused precipitation of dibenzylamine hydrochloride. Upon completion of the amine addition, the solution was allowed to warm to room temperature. The resultant slurry was gently warmed with a 40–45 °C water bath for 1 h with stirring. After cooling to room temperature, the solution was filtered and the amine hydrochloride was washed with 50 mL of diethyl ether. The combined filtrate and washings were reduced in volume on a flash evaporator. The resulting crude viscous aminophosphine was dissolved in a minimum volume of $CHCl_3$–CH_3OH (1:1) and placed into a separatory funnel to which distilled water was slowly added. The organic layer was separated, evaporated to near dryness, and triturated with a few drops of distilled water to yield 61.5 g (99%) of tris(dibenzylamino)phosphine (mp 99 °C). Similarly, bis(dibenzylamino)phenylphosphine (49.6 g, 99%; mp 78 °C) and (dibenzylamino)diphenylphosphine (37.7 g, 99%; mp 72 °C) were prepared. It is noteworthy that $(Bzl_2N)_2P(O)Ph$ could not be prepared from $PhP(O)Cl_2$ and dibenzylamine.[27]

2. Complexes. The chloride complexes were prepared by reaction of the phosphorus ligand with $(C_6H_5CN)_2MCl_2$ (M = Pd, Pt) in dichloromethane.[28] The azide complexes were prepared by metathesis[12] of the chloride complexes with sodium azide in methanol–chloroform solution. Attempts to prepare azides of the phosphite, aminophosphine, and thiophosphite complexes by this route were unsuccessful except for $[(Bzl_2N)_2PPh]_2Pd(N_3)_2$. Satisfactory elemental analysis were obtained for all the complexes.

Results and Discussion

Magnetic Resonance: The Phosphines and Their Organic Derivatives. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectral data for the organophosphorus compounds are presented in Tables I–III. ^1H NMR spectra of other benzylphosphines have been reported previously and it has been noted that the benzyl protons appear as doublets[29-32] with small $^2J_{PH}$ values (0–3 Hz) for the phosphines and with large $^2J_{PH}$ values (ca. 15 Hz) for their derivatives.[32,33]

The CH_2 ^1H NMR resonance of Bzl_3P in $CDCl_3$ is a doublet with $^2J_{PH}$ = 0.8 Hz, and in C_6D_6 $^2J_{PH}$ is 1.3 Hz. For Bzl_2PPh the CH_2 ^1H NMR resonance in $CDCl_3$ is a singlet, but in C_6D_6 it is a doublet with $^2J_{PH}$ = 1.1 Hz, while for $BzlPPh_2$ only a singlet is observed for the CH_2 resonance in

Table I. ^1H Nuclear Magnetic Resonance Data for the Benzylphosphines and Their Derivatives

		$(C_6H_5CH_2)_3P$			$(C_6H_5CH_2)_2P(C_6H_5)$			$(C_6H_5CH_2)P(C_6H_5)_2$		
Derivative	Solvent	δ, ppm	Line shape[a]	$^2J_{PH}$, Hz	δ, ppm	Line shape[a]	$^2J_{PH}$, Hz	δ, ppm	Line shape[a]	$^2J_{PH}$, Hz
Free phosphine	$CDCl_3$	2.74	d	0.8	3.10	s		3.42	s	
Free phosphine	C_6D_6	2.60	d	1.3	2.92	d	1.1	3.28	s	
Phosphine oxide	$CDCl_3$	3.00	d	14.0	3.37	d[h]	14.0	3.66	d	14.0
Phosphine sulfide	$CDCl_3$	3.18	d	12.7	3.51	dq	*b*	3.59	d	13.0
Phosphonium ion[c]	$CDCl_3$–CF_3COOH (4:1 v/v)	3.52	d	15.0	3.95	dq	14.5 (2.0)[d]	4.20	d	15.0
Methiodide[e]	$CDCl_3$	4.35	d	15.0	4.74	dq	*f, i*	4.97	d	16.0
Benzyl chloride[g]	$CDCl_3$	4.62	s		4.52	d	16.2	5.16	d	15.0

[a] d = doublet; dq = ABX doublet of quartets; s = singlet. [b] $\delta_A = 352.4$, $\delta_B = 350.8$ Hz at 100 MHz; $^2J_{HH} = 13.2$ Hz, $^2J_{PH_a} = 13.3$ Hz, $^2J_{PH_b} = 15.9$ Hz. [c] The P–H resonance was not observed. [d] $^2J_{PH}$ values given are line separations of the ABX spectra and are not actually $^2J_{PH}$; only four lines were observed. [e] The CH_3 chemical shifts and coupling constants are respectively: δ 1.91, $^2J_{PH} = 13.0$ Hz; δ 2.30, $^2J_{PH} = 13.0$ Hz; δ 2.72, $^2J_{PH} = 14.0$ Hz. [f] $\delta_A = 474$, $\delta_B = 475$ Hz at 100 MHz; $^2J_{HH} = 14.7$ Hz, $^2J_{PH_a} = 15.2$ Hz, $^2J_{PH_b} = 15.2$ Hz: F. Caesar and W.-D. Balzer, *Chem. Ber*, **102**, 1665 (1969). [g] For $[(C_6H_5CH_2)P(C_6H_5)_3]^+Cl^-$, the CH_2 resonances occurred at δ 5.38 with $^2J_{PH} = 14.0$ Hz. [h] Becomes a singlet with phosphorus decoupling. [i] Becomes an AB quartet with $J_{AB} = 15$ Hz with phosphorus decoupling.

Table II. ^1H and $^{31}P\{^1H\}$ Nuclear Magnetic Resonance Data for the Phosphorus Esters

Compd	$\delta(CH_2)$,[a] ppm	$^3J_{PH}$, Hz	δ(Ph), ppm	$\delta(^{31}P)$, ppm
$(C_6H_5CH_2O)_3P$	4.95 d	8.5	7.45 s	−124.8
$(C_6H_5CH_2O)_2PC_6H_5$	4.78 dq	*b*	7.43 s	−104.8
$C_6H_5CH_2OP(C_6H_5)_2$	5.00 d	9.5	7.48 m	−114.3
$(C_6H_5CH_2S)_3P$	3.90 d	8.5	7.26 s	−112.1
$(C_6H_5CH_2S)_2PC_6H_5$	3.87 dq	*c*	7.25 s	−75.5
$(C_6H_5CH_2S)P(C_6H_5)_2$	3.87 d	9.5	7.21 m	−42.8
$[(C_6H_5CH_2)_2N]_3P$	4.29 d	9.2	7.45 s	−140.3
$[(C_6H_5CH_2)_2N]_2P(C_6H_5)$	4.17 dq	*d*	7.32 s	−104.7
$[(C_6H_5CH_2)_2N]P(C_6H_5)_2$	4.25 d	9.5	7.58 m	−66.5

[a] d = doublet, q = quartet, s = singlet, m = complex multiplet, dq = ABX doublet of quartets. [b] $\delta_A = 5.07$, $\delta_B = 4.50$, $^2J_{HH} = 13$, $^2J_{PH_a} = 3.9$, $^2J_{PH_b} = 0.1$ Hz. [c] $\delta_A = 3.94$, $\delta_B = 3.80$, $^2J_{HH} = 13$, $^2J_{PH_a} = {}^2J_{PH_b} = 8.5$ Hz. [d] $\delta_A = 4.46$, $\delta_B = 3.87$, $^2J_{HH} = 14.5$, $^2J_{PH_a} = 10.95$, $^2J_{PH_b} = 9.05$ Hz.

either solvent. A solvent dependence of $^2J_{PH}$ has been previously observed and for benzene it is attributed to a specific solvent–solute interaction ascribed to a benzene "complex".[34]

It is noted for these three compounds (Table I) that $^2J_{PH}$ increases as the number of benzyl groups increases. This is opposite to the trend observed for the methyl(phenyl)phosphine series for which the magnitude of $^2J_{PH}$ decreases as the number of methyl groups increases.[35] It is concluded, from a plot of $\delta(^1H)$ vs. $^2J_{PH}$ for the CH_2 groups, that $^2J_{PH}$ for $BzlPPh_2$ in C_6D_6 should be finite but less than 0.5 Hz, the resolving power of the instrument.

It is known that $^2J_{PH}$ may be either positive or negative[35] and that the magnitude of $^2J_{PH}$ can change in two ways. First, $^2J_{PH}$ becomes less positive as the s character of the phosphorus bonding orbitals increases.[35] Second, the coupling becomes more positive as the s character of the carbon bonding orbitals increases.[35] Consequently, the change in $^2J_{PH}$ depends upon the hybridization of both the carbon and phosphorus atoms. If $^2J_{PH}$ is positive in the benzyl series, then the observed coupling constant trend could arise from either a decrease in the s character of the phosphorus bonding orbitals or an increase in the s character of the carbon bonding orbitals or both as the number of benzyl groups increases. A vicinal angle dependence has been found for $^2J_{PH}$ such that the $^2J_{PH}$ values could be of different sign and magnitude.[36] If so, free rotation about the P–C bond could average these values to zero.[32,36]

For the benzylphosphonium chlorides $[Bzl_{4-n}PPh_n]^+Cl^-$, $n = 1$–3, the value of $^2J_{PH}$ increases as the number of benzyl groups increases (Table I), and $^2J_{PH}$ and $\delta(^1H)$ are linearly related. In addition, $^2J_{PH}$ increases upon quaternization, and this increase has been attributed to an increase in the s character of the P–C bond.[10,32,33] Anomalous spectra were obtained for $[Bzl_4P]^+Cl^-$, where only a CH_2 singlet was observed and $\delta(^1H)$ is not consistent with the other compounds. The singlet could arise from rapid exchange of benzyl chloride (i.e., the reverse of the preparation of the compound) and would be consistent with observations that phosphines may be prepared by elimination of benzyl chloride from the appropriate salt.[37] This exchange is not supported by ^{13}C spectra which show normal J_{PC} coupling (Table III).

The CH_2 protons of Bzl_2PPh, all its derivatives, $(BzlO)_2PPh$, $(BzlS)_2PPh$, and $(Bzl_2N)_2PPh$ are intrinsically asymmetric[27,38] and should give rise to ABX doublets of quartets in their ^1H NMR spectra. This is the case except for Bzl_2PPh and $Bzl_2P(O)Ph$ where only doublets are observed and the intrinsic asymmetry is not manifested. This implies that for these two compounds the average environments of the individual benzyl protons are insufficiently dissimilar to observe the symmetry-required nonequivalence. Several studies[39] with *N*-benzylpiperidines have indicated that steric effects play an important role in the observability of nonequivalence for intrinsically asymmetric benzyl protons. Since the spectra of the phosphorus compounds are temperature invariant from −30 to +62 °C in $CDCl_3$, it is probably steric effects which make the nonequivalence observable for the phosphorus compounds as well.

For all the phosphine derivatives, except the sulfides and benzyl chlorides, $\delta(^1H)$ (Table I) of the benzyl protons is linearly related to the number of benzyl groups. This indicates, particularly since the slopes of these relationships are nearly the same, that there is a "benzyl group" contribution and that it acts in the same manner for each type of derivative. The ^{31}P chemical shifts (Tables II and III) are related to the number of benzyl groups for the phosphines, thiophosphites, and aminophosphines though not linearly. Group contributions to $\delta(^{31}P)$ have been noted elsewhere.[40]

The $\delta(^{13}C)$ values of the methylene carbons (Table III) are related to the number of benzyl groups and they correlate with $^1J_{PC}$ for the phosphines and phosphine oxides. As with $^2J_{PH}$, $^1J_{PC}$ is greater for the phosphine derivatives than for the phosphines themselves. This probably corresponds to an increase in the s character[41] in the C–P bond and parallels the results found for C–H coupling.[42]

Magnetic Resonance: The Complexes. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectral data for the complexes are presented in Tables IV and V. For the complexes $(Bzl_3P)_2MX_2$ ($X = Cl^-$, N_3^-; M = Pd, Pt), $[(BzlO)_3P]_2PdCl_2$, $[(BzlS)_3P]_2PdCl_2$, and $[(Bzl_2N)_3P]_2PdCl_2$ the ^1H and $^{13}C\{^1H\}$ spectra contained only 1:2:1 triplets for the methylene resonances and on this basis these complexes were assigned as wholly trans in solution.[43–55] Further a complete x-ray crystal structure (details

Table **III.** $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR Data of $CDCl_3$ Solutions of Benzylphenylphosphines and Derivatives[a]

Benzyls

Compd	δ(CH$_2$), ppm	J_{PC}, Hz	δ(C$_1$), ppm	J_{PC_1}, Hz	δ(C$_{2,6}$), ppm	$J_{PC_{2,6}}$, Hz	δ(C$_{3,5}$), ppm	$J_{PC_{3,5}}$, Hz	δ(C$_4$), ppm	J_{PC_4}, Hz
$BzlP(O)Ph_2$	38.14	66.6	130.27	0.0	131.76	2.4	128.26	0.0	126.76	3.0
$Bzl_2P(O)Ph$	37.43	63.5	131.65	0.0	129.98	4.9	128.45	0.0	126.80	3.0
$Bzl_3P{=}O$	35.43	61.6	131.73	17.3[b]	129.88	5.4	128.76	1.8	126.95	2.4
$BzlP(S)Ph_2$	40.98	50.7	130.59	0.0	131.41	0.0	127.90	3.0	127.10	3.0
$Bzl_2P(S)Ph$	40.67	48.2	131.34	0.0	131.23	5.0	128.11	3.1	127.08	3.7
$BzlP(CH_3)Ph_2{}^+I^-$	29.96	45.2	134.73	0.0	130.33	4.9	129.03	3.0	128.27	3.6
$BzlPPh_3{}^+Cl^-$	29.60	45.2	134.64	0.0	130.70	5.5	128.65	2.5	127.78	4.8
$Bzl_2PPh_2{}^+Cl^-$	28.14	45.2	134.59	0.0	130.72	5.4	129.18	2.4	128.37	3.1
Bzl_2PPh_2	37.51	15.6	138.80	8.0	131.0	6.9	130.00	0.0	127.18	0.0
Bzl_2PPh	35.65	17.4	138.35	6.81	130.8	6.5	130.00	0.0	127.4	0.0
Bzl_3P	34.09	19.1	137.60	5.5	129.13	6.1	128.31	0.0	125.75	1.8
$Bzl_4P^+Cl^-$	27.15	42.7	127.92	8.1	130.7	5.2	129.54	2.9	128.56	3.6

Phenyls

Compd	δ(PC$_1$), ppm	J_{PC_1}, Hz	δ(C$_{2,6}$), ppm	$J_{PC_{2,6}}$, Hz	δ(C$_{3,5}$), ppm	$J_{PC_{3,5}}$, Hz	δ(C$_4$), ppm	J_{PC_4}, Hz	δ(^{31}P), ppm
$BzlP(O)Ph_2$	130.27	0.0	131.18	9.2	128.54	8.0	130.06	0.0	−29.2
$Bzl_2P(O)Ph$	131.65	0.0	131.07	8.6	128.22	10.0	131.65	0.0	−34.8
$Bzl_3P{=}O$									−40.7
$BzlP(S)Ph_2$	130.39	0.0	131.59	9.0	128.43	12.1	127.07	0.0	−42.0
$Bzl_2P(S)Ph$	131.03	0.0	131.86	9.8	128.19	20.0	127.09	0.0	−45.2
$Bzl_3P{=}S$									−45.0
$BzlP(CH_3)Ph_2{}^+I^-$	130.76	0.0	132.86	9.1	129.24	20.0	127.99	9.2	−22.56
$BzlPPh_3{}^+Cl^-$	134.64	0.0	134.29	9.1	129.62	12.2	128.02	0.0	−21.2
$Bzl_2PPh_2{}^+Cl^-$	134.59	0.0	133.17	7.9	129.71	12.2	128.01	8.4	−27.2
$BzlPPh_2$	139.5	15.0	134.0	18.6	129.95	12.1	127.2	0.0	10.4
Bzl_2PPh	139.0	14.5	133.5	18.0	130.0	12.0	127.5	0.0	12.1
Bzl_3P									12.9
$Bzl_3PPh^+Cl^-$									−22.4
$Bzl_4P^+Cl^-$									−24.5
$Bzl_2P(CH_3)Ph^+I^-$									−26.6
$Bzl_3P(CH_3)^+I^-$									−26.93

[a] Bzl = $CH_2C_6H_5$; Ph = C_6H_5. [b] δ(CH$_3$) = 3.16 ppm; J_{PCH_3} = 56.8 Hz.

Table **IV.** ^{1}H (100 MHz) and ^{31}P Nuclear Magnetic Resonance Data for the Complexes L_2MX_2 in $CDCl_3$ Solution

L	δ(CH$_2$), ppm	"J",[a] Hz	Line shape[b]	Isomer	−δ(^{31}P),[c] ppm	−Δ(^{31}P),[d] ppm
			L_2PdCl_2			
Bzl_3P	3.34	7	t	Trans	13.3	23.7
Bzl_2PPh	3.58	8[e]	qt[e]	Trans	14.15	26.25
$BzlPPh_2$	3.95, 4.05	8.5, 11	t, d	Trans, cis	20.06, 30.27	30.22, 40.05
$(BzlO)_3P$	5.11	8.25	t	Trans	92.5	−32.3
$(BzlO)_2PPh$	4.92	8.0[f]	qt[f]	Trans	122.8	18
$BzlOPPh_2$	4.68	7.5	fd	Cis	110.6	−3.7
$(BzlS)_3P$	4.46	11.25	t	Trans	77.7	−34.4
$(BzlS)_2PPh$	4.07	9.4[g]	qt[g]	Trans	80.4	4.9
$BzlSPPh_2$	4.00	11.2	fd	Cis	78.5	35.7
$(Bzl_2N)_3P$	4.22	10.0	t	Trans	93.8	46.5
$(Bzl_2N)_2PPh$	4.52	10.0[h]	qt[h]	Trans	98.3	6.4
Bzl_2NPPh_2	4.50	11.2	fd	Cis	93.4	26.9
			$L_2Pd(N_3)_2$			
Bzl_3P	3.22	6.5	t	Trans	15.70	28.6
Bzl_2PPh	3.48, 3.25	5, 8[i]	q, fd[i]	Trans, cis	18.10, 31.20	30.20, 43.30
$BzlPPh_2$	3.81, 3.76	7.5, 15	t, d	Trans, cis	19.82, 29.65	30.22, 40.05
			L_2PtCl_2			
Bzl_3P[j]	3.42	8.4	3t	Trans	5.78	18.68
Bzl_2PPh[k]	3.47	10	3q	Trans	8.40	20.5
$BzlPPh_2$[l]	4.05	12	3d	Cis	9.88	20.28

[a] "J" = $|{}^nJ_{PH} + {}^{n+2}J_{PH}|$. [b] t = triplet, d = doublet, qt = quartet of triplets, fd = filled-in doublet, 3t = three triplets, 3q = three quartets, 3d = three doublets. [c] Negative chemical shifts are less shielded than 85% H_3PO_4. [d] Δ(^{31}P) = δ(^{31}P(complex)) − δ(^{31}P(free ligand)). [e] $^2J_{HH}$ = 15 Hz; becomes an AB quartet with phosphorus decoupling. [f] $^2J_{HH}$ = 11.5 Hz; becomes an AB quartet with phosphorus decoupling. [g] $^2J_{HH}$ = 12.5 Hz; becomes an AB quartet with phosphorus decoupling. [h] $^2J_{HH}$ = 16 Hz; becomes an AB quartet with phosphorus decoupling. [i] Becomes two singlets with phosphorus decoupling. [j] J_{Pt-H} = 21.4, J_{Pt-P} = 2460 Hz. [k] J_{Pt-P} = 2534 Hz. [l] J_{Pt-H} = 24, J_{Pt-H} = 3736 Hz.

will be presented elsewhere) showed that $(Bzl_3P)_2Pd(N_3)_2$ is trans in the solid state. The ^{1}H and $^{13}C\{^1H\}$ spectra of $(BzlPPh_2)_2PdCl_2$ contain a 1:2:1 triplet and a 1:1 doublet for the methylene resonances. Thus, both the cis and trans isomers are present in solution simultaneously.[43-55] The ratio of the integrated intensities of the triplet to the doublet (trans to cis) is >19:1.

The ^{1}H NMR spectra for the methylene groups of the

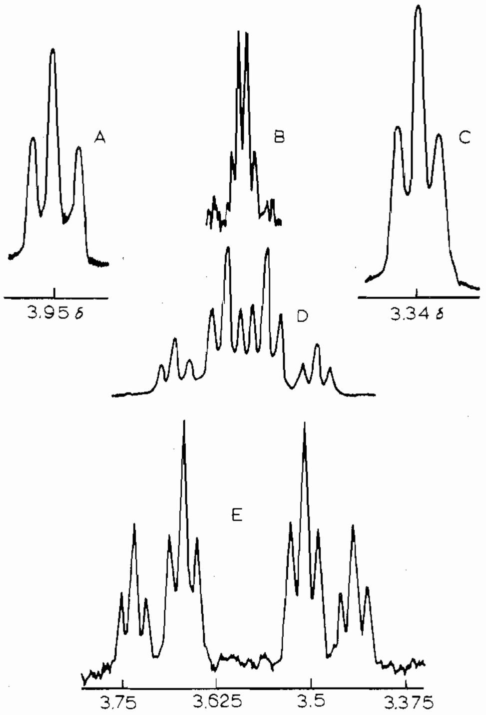

Figure 1. NMR spectra in the methylene region: (A) $[(C_6H_5CH_2)P(C_6H_5)_2]_2PdCl_2$ at 100 MHz, 180-Hz sweep width; (B) $[(C_6H_5CH_2)_2P(C_6H_5)]_2PdCl_2$ at 60 MHz, 500-Hz sweep width; (C) $[(C_6H_5CH_2)_3P]_2PdCl_2$, at 100 MHz, 180-Hz sweep width; (D) $[(C_6H_5CH_2)_2P(C_6H_5)]_2PdCl_2$, at 100 MHz, 180-Hz sweep width; (E) $[(C_6H_5H_2)_2P(C_6H_5)]_2PdCl_2$, at 220 MHz, 250-Hz sweep width; all in $CDCl_3$ at ambient temperature.

complexes $(Bzl_2PPh)_2MCl_2$ (M = Pd, Pt), $[(BzlO)_2PPh]_2PdCl_2$, $[(BzlS)_2PPh]_2PdCl_2$, and $[(Bzl_2N)_2PPh]_2PdCl_2$ at 60 MHz appear as poorly resolved quartets (Figure 1). At 100 MHz and at 220 MHz these quartets become quartets of triplets which are reproducible over long periods of time and over a temperature range of 20–70 °C in $CDCl_3$. With phosphorus decoupling these quartets of triplets each become AB quartets at 100 MHz (Table IV). The quartet of triplets is due to the magnetic nonequivalence of the methylene protons and virtual coupling resulting in $[ABX]_2$ spin systems.[38,54,55] In order to be certain that these multiplets were indicative of the trans geometry a complete computer analysis of the $[ABX]_2$ spin system was performed. The results of this analysis, exemplified in Figure 2, indicate that the line shapes for this spin system will parallel those for the $[X_nA]_2$ spin systems.[54] When $0 \leq {}^2J_{PP} \leq 3$ Hz, an ABX doublet of quartets will normally be observed. When $30 \leq {}^2J_{PP} \leq 70$ Hz, a quartet of "filled-in" doublets will be observed,[47] and when ${}^2J_{PP} \geq 100$ Hz, a quartet of triplets will be observed. These line shapes depend upon $\nu_A - \nu_B$ and J_{AB}, J_{AX}, and J_{BX} as well such that even with complete computer simulations it will not generally be possible to determine ${}^2J_{PP}$. As quartets of triplets are observed in each case for these complexes, ${}^2J_{PP} \geq 100$ Hz and these complexes are wholly trans in solution.[44]

The ^1H and $^{13}C\{^1H\}$ NMR spectra for the methylene groups of the complexes $(BzlOPPh_2)_2PdCl_2$, $(BzlSPPh_2)_2PdCl_2$, $[(Bzl_2N)PPh_2]_2PdCl_2$, and $(BzlPPh_2)_2PtCl_2$ exhibited resonances which are typical of cis complexes[47] and on this basis each complex is wholly cis in solution.

The NMR spectra of the complex $(Bzl_2PPh)_2Pd(N_3)_2$ are time dependent. Upon initial dissolution, the 60- and 100-MHz ^1H NMR spectra of the methylene groups appear as a filled-in doublet representing the cis isomer. Over a period of hours, the filled-in doublet decreases in intensity with the simultaneous appearance and increase in intensity of a quartet, representing the trans isomer. At 300 MHz the quartet is seen to be a quartet of triplets (Figure 3), as was observed for $(Bzl_2PPh)_2PdCl_2$, and the filled-in doublet becomes an AB

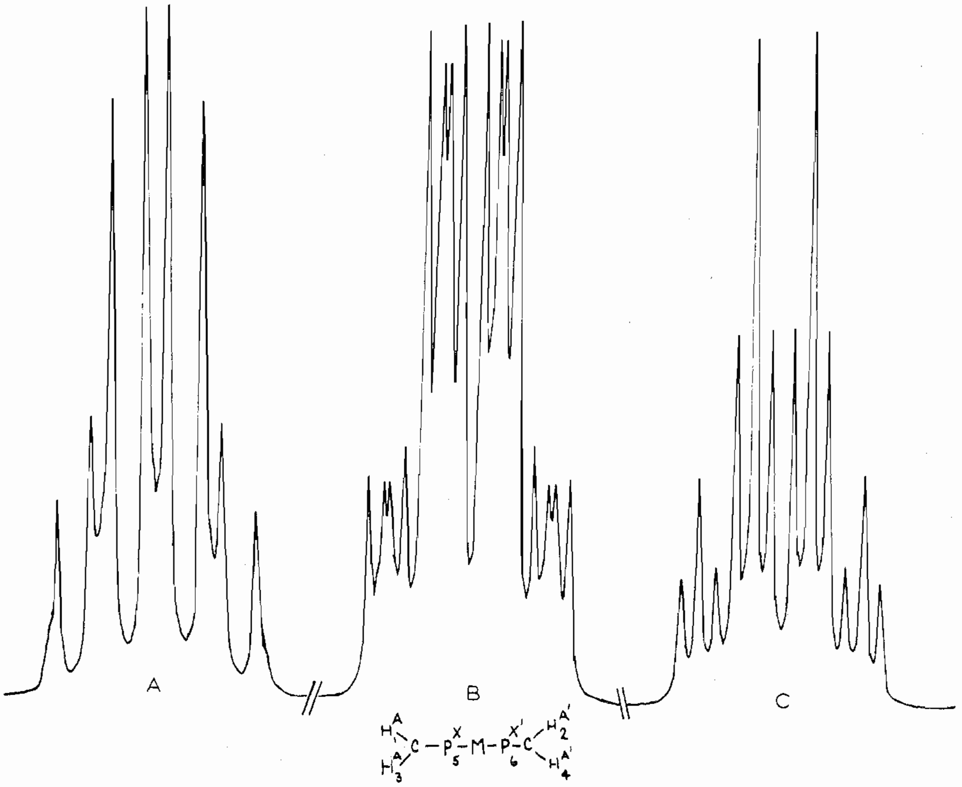

Figure 2. Calculated spectra for the $[ABX]_2$ spin system present in the complexes of dibenzyl ligands. $J_{12} = J_{14} = J_{23} = J_{34} = 0$; $J_{13} = J_{24} = 12.4$; $J_{15} = J_{26} = J_{46} = J_{35} = 10$; $J_{16} = J_{25} = J_{45} = J_{36} = -2.0$: (A) $J_{56} = 5$; (B) $J_{56} = 50$; (C) $J_{56} = 500$. $[ABX]_2$ spectra will always be symmetrical about the midpoint and these illustrations should be typical for (A) cis phosphine, (B) cis phosphite and (C) trans complexes.

Table V. ^{13}C Nuclear Magnetic Resonance Data for L_2PdCl_2 and Other Complexes[a,b]

Benzyls

L	$\delta(CH_2)$, ppm	“J_{PC}”, Hz	$\delta(C_1)$, ppm	“J_{PC_1}”, Hz	$\delta(C_{2,6})$, ppm	“$J_{PC_{2,6}}$”, Hz	$\delta(C_{3,5})$, ppm	“$J_{PC_{3,5}}$”, Hz	$\delta(C_4)$, ppm	“J_{PC_4}”, Hz
L_2PdCl_2										
Bzl_3P	28.74 t	22.2	133.72 s	0	130.31 s	0	128.61 s	0	126.80 s	0
Bzl_2PPh	27.88 t	23.9	132.91 s	0	130.47 s	0	128.33 s	0	126.80 s	0
$BzlPPh_2$	32.29 t, 39.29 “q”	22.2, 23	131.27 s	0	130.56 s	0	127.79 s	0	126.66 s	0
$(BzlO)_3P$	69.83 t	3.8	135.34 t	7.1	128.57 s	0	128.30 s	0	128.67 s	0
$(BzlO)_2PPh$	70.85 t	5.8	135.51 t	7.5	128.64 s	0	128.39 s	0	128.75 s	0
$(BzlO)PPh_2$	70.76 “t”	6.8	133.05 d	17	128.47 s	0	128.18 s	0	128.57 s	0
$(Bzl_2N)_3P$	52.49 t	12	136.31 s	0	130.33 s	0	129.14 s	0	127.92 s	0
$(Bzl_2N)_2PPh$	53.30 t	9	137.70 s	0	128.97 s	0	128.05 s	0	126.95 s	0
$(Bzl_2N)PPh_2$	52.90 d	10.8	134.02 s	0	129.14 s	0	128.28 s	0	126.95 s	0
$(BzlS)_3P$	39.46 t	11	131.31 s	0	130.52 s	0	129.44 s	0	127.42 s	0
$(BzlS)_2PPh$	39.95 t	10	132.68 d	3	129.52 s	0	128.53 s	0	126.79 s	0
$BzlSPPh_2$	39.71 d	10	131.83 s	0	131.11 s	0	128.85 s	0	128.21 s	0
$[Bzl_nPPh_{3n}]PtCl_2$										
Bzl_3P	27.61 “q”	28.5[c]	133.60 s	0	130.34 s	0	128.46 s	0	126.68 s	0
Bzl_2PPh	26.73 “q”	29.3[d]	133.08 s	0	130.56 s	0	128.22 s	0	126.71 s	0
$BzlPPh_2$	37.91 5L	38.1[e]	133.82 s	0	130.81 s	0	127.98 s	0	127.04 s	0
$[Bzl_nPPh_{3-n}]Pd(N_3)_2$										
Bzl_3P	28.49 t	20.6	133.05 s	0	130.03 s	0	128.94 s	0	127.10 s	0
Bzl_2PPh	31.65 5L, 28.76 t	24.9,[f] 22	132.26 s	0	130.07 s	0	128.46 s	0	127.12 s	0
$BzlPPh_2$	32.49 t, 35.97 “t”	23.3, 27.5	132.76 s	0	130.49 s	0	128.63 s	0	127.19 s	0

Phenyls

L	$\delta(C_1)$, ppm	“J_{PC_1}”, Hz	$\delta(C_{2,6})$, ppm	“$J_{PC_{2,6}}$”, Hz	$\delta(C_{3,5})$, ppm	“$J_{PC_{3,5}}$”, Hz	$\delta(C_4)$, ppm	“J_{PC_4}”, Hz
L_2PdCl_2								
Bzl_2PPh	133.15 t	11.2	130.57 s	0	128.33 s	0	126.80 s	0
$BzlPPh_2$	134.03 t	11.3	130.56 s	0	128.00 s	0	126.66 s	0
$(BzlO)_2PPh$	131.19 t	13.3	128.58 t	?	128.22 s	0	132.51 s	0
$(BzlO)PPh_2$	132.92 “t”	12.5	128.50 d	5.2	128.18 s	0	131.94 s	0
$(Bzl_2N)_2PPh$	134.0 t	12	134.28 t	10.4	134.00 t	5.7	130.56 s	0
$(Bzl_2N)PPh_2$	134.01	13.2	132.20 fd	16.5	127.47 d	5	130.33 s	0
$(BzlS)_2PPh$	131.59 fd	11	130.65 d	11.5	128.97 d	3	?	
$BzlSPPh_2$	135.36 d	10	131.88 d	9	128.83 d	8.7	129.37 s	0
$[Bzl_nPPh_{3-n}]_2PtCl_2$								
Bzl_2PPh	133.27	9.7[g]	130.56 s	0	128.22 s	0	126.71 s	0
$BzlPPh_2$	134.02 3t	9.8[h]	131.36 s	0	127.73 s	0	127.52 s	0
$[Bzl_nPPh_{3-n}]_2Pd(N_3)_2$								
Bzl_2PPh	132.55 t	12.1	130.44 s	0	128.46 s	0	126.84 s	0
$BzlPPh_2$	133.40 t	10.0	131.10 s	0	128.42 s	0	126.98 s	0

[a] t = triplet; s = singlet; fd = filled-in doublet; d = doublet; “q” = pseudo-quintet; “t” = non-1:2:1 triplet; 5L = five-line multiplet; 3t = three triplets. [b] “J” = $|^nJ_{PC} + {}^{n+2}J_{PC}|$. [c] $^2J_{Pt-C}$ = 28.5 Hz. [d] $^2J_{Pt-C}$ = 35 Hz. [e] $^1J_{PC}$ = 23.5, $^3J_{PC}$ = 14.6, $^2J_{PP}$ = 4.4, $^2J_{Pt-C}$ = 38.1 Hz. [f] $^1J_{PC}$ = 24.6, $^3J_{PC}$ = 0.3, $^2J_{PP}$ = 26 Hz. [g] $^2J_{Pt-C}$ = 20 Hz. [h] $^2J_{Pt-C}$ = 27 Hz.

quartet. This indicates that for both the cis and trans isomers of this complex there are two chemical shift nonequivalent sets of protons. With phosphorus decoupling two singlets are observed at 100 MHz. Thus, the chemical shift difference of the intrinsically asymmetric methylene protons is less than 0.3 Hz at 100 MHz. Like Bzl_2PPh and $Bzl_2P(O)Ph$ the average environments of the individual benzyl protons are insufficiently dissimilar to observe the symmetry-required nonequivalence for both the trans and the sterically more demanding cis isomer of $(Bzl_2PPh)_2Pd(N_3)_2$ at 100 MHz. This is most likely because the steric effect of the azide ion is less than that of the chloride ion since nonequivalence was observed for *trans*-$(Bzl_2PPh)_2MCl_2$ (M = Pd, Pt) at 100 MHz. For $(Bzl_2PPh)_2Pd(N_3)_2$ the ^{13}C{^{1}H} NMR shows that the benzyl carbons are chemical shift equivalent, and for the cis isomer a complete line shape analysis on the five-line multiplet was accomplished (Table V, Figure 3).

There is evidently a considerable increase in the magnitude of $^2J_{PP}$ when the anion is changed from chloride to azide,[12] as the cis isomer ^{1}H NMR CH_2 multiplet is a doublet for $(BzlPPh_2)_2PdCl_2$ and a filled-in doublet for $(BzlPPh_2)_2Pd(N_3)_2$. Likewise the ^{13}C{^{1}H}CH_2 resonance is a doublet for $(BzlPPh_2)_2PdCl_2$ and a non-1:2:1 triplet for $(BzlPPh_2)_2Pd(N_3)_2$. Equilibrium thermodynamics have been obtained for the isomerization of $[(Bzl_nPPh_{3-n})]_2Pd(N_3)_2$ (n = 1, 2) and reported elsewhere.[14]

The ^{13}C{^{1}H} spectra of the phenyl carbons, in contrast to the CH_2 carbons, seem to contain little information. From previous work it was expected that the phenyl carbons should be, via varying chemical shifts and P–C coupling constants, sensitive to changes in the number of benzyl groups, anion, and geometry.[56] Contrary to these expectations, there is often very little chemical shift difference between the phenyl carbons and benzyl carbons. In addition, there is often no observable P–C coupling. The absence of P–C coupling is due to the fortuitous cancelation of $^nJ_{PC}$ with $^{n+2}J_{PC}$ (they are equal in magnitude and opposite in sign).[12] Where coupling is observed, the line shapes indicate the same geometry as was deduced

Table VI. Electronic and Infrared Spectral Data for L_2PdCl_2

	Electronic spectral data				Infrared spectral data, cm^{-1}	
	Before photolysis		After photolysis			Other vibrations
L	λ, nm	log ε	λ, nm	log ε	ν_{Pd-Cl}	
$BzlOPPh_2$	315	3.73	316	3.73	295, 315	444, 471, 504, 526, 556, 590
$(BzlO)_2PPh$	315	3.76	314	3.77	320	276, 296, 388, 442, 470, 500, 548, 595
$(BzlO)_3P$	307	3.66	308	3.66	311	301, 418, 480, 534, 590
Bzl_2NPPh_2	346	4.30	346	4.30	295, 310	352, 385, 452, 479, 500, 534, 592
$(Bzl_2N)_2PPh$	387	4.11	389	4.12	302	287, 349, 416, 466, 477, 493, 535, 547, 592
$(Bzl_2N)_3P$	320	3.91	320	3.91	302	285, 349, 415, 435, 452, 466, 500, 535, 576, 598
$BzlSPPh_2$	323	4.25	323	4.26	298, 335	277, 375, 395, 431, 467, 520, 535
$(BzlS)_2PPh$	364	4.25	364	4.25	300	265, 352, 380, 395, 420, 467, 517, 539
$(BzlS)_3P$	348	4.17	348	4.17	313	260, 341, 430, 467, 522, 535, 562
Bzl_3P	330	4.08	330	4.08	350	280, 300, 310, 380, 455, 470
Bzl_2PPh	337	5.34	337	5.34	342	380, 430, 475, 485
$BzlPPh_2$	342	4.11	342	4.11	333	280, 455, 490

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

	IR data		Electronic data	
	Low-freq Nujol-mull ν, cm^{-1}	$CHCl_3$ soln ν_{N_3}(as), cm^{-1}	$CHCl_3$ soln λ, nm (log ε)	Solid-state Nujol-mull λ, nm
R_3P				
Bzl_3P	285, 309, 332, 344, 380, 408, 464, 480	2050 sh, 2042	338 (4.08)	330
Bzl_2PPh	284, 330, 338, 350, 380, 448, 468, 478, 486	2050, 2032 sh	260 (4.15), 333 (4.4)	265 sh, 355 vw
$BzlPPh_2$	282, 345, 360, 380, 425, 447, 477, 487	2050, 2040	335 (4.34)	335

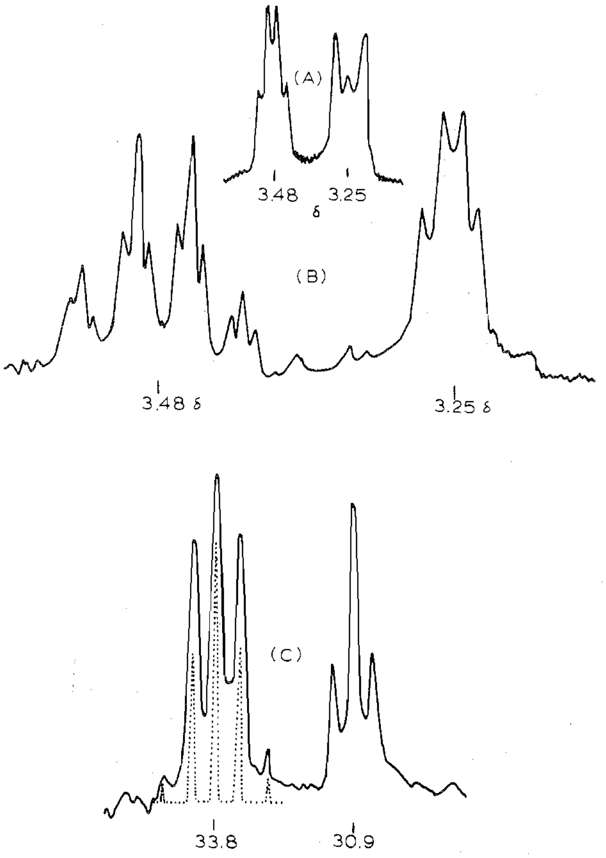

Figure 3. NMR spectra in the methylene region for $[(C_6H_5CH_2)_2P(C_6H_5)]_2Pd(N_3)_2$: (A) ^1H, 100 MHz, 450-Hz sweep width; (B) ^1H, 300 MHz, 100-Hz sweep width; (C) $^{13}C\{^1H\}$, 25.2 MHz, 250-Hz sweep width; (—) experimental data; (···) computer simulation using extracted coupling constants; all in $CDCl_3$. All chemical shifts relative to TMS internal standard.

from the methylene resonances.

The $^{31}P\{^1H\}$ NMR (Table IV) are straightforward and are consistent with the assignments based on ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In all cases where only one isomer was found via ^1H or $^{13}C\{^1H\}$ NMR only one singlet was observed in the $^{31}P\{^1H\}$ NMR spectrum. When the existence of two isomers is demonstrated via ^1H or $^{13}C\{^1H\}$ NMR, it is confirmed by the presence of two singlets in the $^{31}P\{^1H\}$ NMR spectra. One noteworthy observation is that in all cases, the cis $^{31}P\{^1H\}$ resonance is broader than the trans resonance. The ^{31}P coordination chemical shifts, Δ, are consistent with the geometry assignments.[57] The difference between the calculated[57] and observed coordination chemical shifts generally decreases as the number of benzyl groups decreases and the difference is generally larger for the chloro complexes than for the azido complexes. This is probably due to steric effects.[57] The ^{31}P chemical shifts are linearly related to the Pauling electronegativities of the heteroatoms for the $(BzlE)_2PPh$ and $BzlEPPh_2$ complexes (E = O, S, N) but not for the $(BzlE)_3P$ complexes. The lack of linearity in the tris complexes is probably due to the dominance of steric effects over electronic effects.

Table VIII. Infrared Spectral Data for the $(R_3P)_2PtCl_2$ Complexes (cm^{-1})

R_3P	νPt-Cl	Other vibrations
Bzl_3P	340	470, 460, 392, 374, 320
Bzl_2PPh	336	484, 470, 430, 416, 300
$BzlPPh_2$	325, 295	485, 450, 435, 360, 270

The ^1H, ^{31}P, and ^{13}C chemical shifts for the phosphine complexes change regularly as the number of benzyl groups change. It was previously shown that the ^1H CH_2 chemical shift of the phosphines changes as the number of benzyl groups changes (vide supra). Such changes have previously been noted and it is known that geometry and anion affect the chemical shifts as well. By plotting $\delta(^{31}P)$ vs. $\delta(^{13}C)$ or $\delta(^1H)$ vs. $\delta(^{13}C)$ or $\delta(^{31}P)$ vs. $\delta(^1H)$ it is possible to make comparisons of the various nuclei. Linear correlations are obtained for the trans azido complexes and nearly linear correlations are obtained for the trans chloro complexes. The chloro complexes are not as well behaved as the azido complexes. These correlations indicate that whatever is causing the chemical shift changes is occurring in a parallel manner for the three nuclei. Since it is known that the anion affects the chemical shifts, it is not surprising that the slopes of the lines are not the same for the chloro and azido complexes. The more linear behavior of the azido complexes seems to be a further manifestation of the lesser steric interactions in these complexes as compared to the chloro complexes.

Infrared Spectroscopy. Infrared data for the complexes are presented in Tables VI–VIII. From standard group theoretical analysis,[58,59,] it is concluded that if two Pd–P, Pd–N, or Pd–Cl bonds are mutually cis and the complex possesses C_{2v} symmetry, then two IR-active absorptions are expected for each type of bond. If the two bonds are mutually trans and the complex possesses D_{2h} symmetry, then only one IR-active stretching frequency should occur for each bond type. It is possible to assign the metal–ligand vibrations by comparing the low-frequency infrared spectra of the phosphines and the phosphine oxides to those of the corresponding complexes. These metal–ligand vibrations are usually of weak or medium intensity. In the solid state, it appears that most of the chloro complexes are trans since at most two new absorptions were found for each complex. The azido complexes except for $(Bzl_3P)_2Pd(N_3)_2$ appear to be cis in the solid state as more than two new absorptions were found for each complex. It may be possible to assign specific frequencies to ν_{Pd-P} and ν_{Pd-Cl} in the chloro complexes as ν_{Pd-Cl} normally occurs in the region of 350–360 cm^{-1} for trans palladium(II) bis(phosphine) complexes.[9,60,61] If this is true, then there is a linear correlation between ν_{Pd-Cl} and ν_{Pt-Cl} and the number of benzyl groups in the trans chlorophosphine complexes (viz., ν_{Pd-Cl} is at 350, 342, and 333 cm^{-1} for *trans*-$(Bzl_3P)_2PdCl_2$, *trans*-$(Bzl_2PPh)_2PdCl_2$, and *trans*-$(BzlPPh_2)_2PdCl_2$ and at 340 and 336 cm^{-1} for *trans*-$(Bzl_3P)_2PtCl_2$ and *trans*-$(Bzl_2PPh)_2PtCl_2$, respectively). This is the same order as the basicity of the phosphines and would seem to imply that the Pd–Cl and Pt–Cl bond strengths follow the basicity of the phosphines if the stretching force constants and bond strengths are linearly related. For the azido complexes specific assignments are precarious at best as ν_{Pd-N} and ν_{Pd-P} normally occur in the same region.

The N≡N stretching frequencies ν_{N_3}(as) are indicative of the azido complexes.[62] They are always found near[63] 2000 cm^{-1} and are reported in Table VIII. In each case this vibration is asymmetric. The asymmetry may be the result of the presence of more than one isomer as ν_{N_3}(as) changes for the complex $(Bzl_2PPh)_2Pd(N_3)_2$ as the ratio of the cis and trans isomers changes (Figure 4). Solid-state infrared spectra in this region exhibit a severe Christiansen effect[64] making absorption maxima extremely difficult to ascertain.

Electronic Spectroscopy. The electronic spectral data are listed in Tables VII and VIII. Both solution ($CHCl_3$) and solid-state electronic spectra were obtained, hopefully to compare the geometries in solution with those in the solid state. For these complexes it can be seen from the data in Tables VI and VII that the solution and solid-state spectra are virtually identical. This implies that the chloro complexes have the same geometry in the solid state and in solution. It has already been shown via ^{1}H, ^{13}C, and ^{31}P NMR that the complex $(Bzl_2PPh)_2Pd(N_3)_2$ is initially cis in solution and slowly isomerizes to an equilibrium mixture of the cis and trans isomers. This seems to indicate that the solid-state geometry is cis. The electronic spectrum of this complex in $CDCl_3$ exhibits two electronic transitions, one at 260 nm and one at 345 nm. The 260-nm transition decreases in intensity while the 345-nm transition increases in intensity as a function of time. These changes parallel the changes which occur in the various NMR spectra. The solid-state spectrum possesses transitions at 265 and 355 nm. Evidently both the cis and trans isomers have electronic transitions at very nearly the same wavelengths which differ only in intensity. It is believed that for most of these complexes the electronic transitions are masked by charge transfer and strong intraligand transitions of the phosphine such that electronic spectroscopy is not very useful for isomer characterization of these complexes. The solid-state electronic spectral data and infrared data are consistent; both suggest that most of the complexes are trans in the solid state. The difference in isomeric structure in the solid state could be a function of either crystal packing or thermodynamic stabilities. Thermodynamic data on other chloro and azido complexes consistently show that the cis isomer has greater thermodynamic stability for the azido complexes than for the chloro complexes.[12,19] However, the bulky benzyl ligands seem to stabilize the trans isomers sterically as the cone angle defined by Tolman[65] is crystallographically found to be about 180° for Bzl_3P in $(Bzl_3P)_2Pd(N_3)_2$.

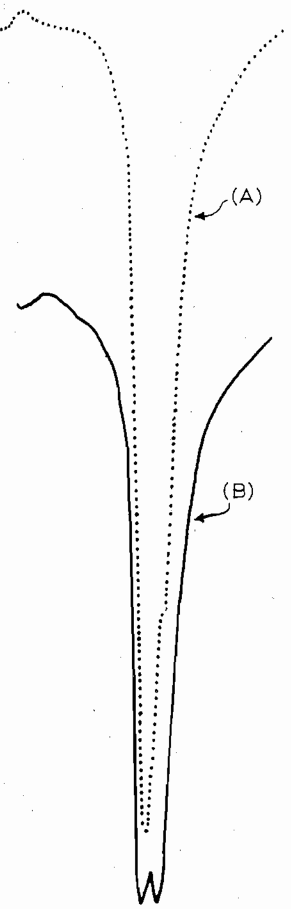

Figure 4. Infrared spectral changes in the ν_{N_3}(as) stretching region for a solution of $[(C_6H_5CH_2)_2PC_6H_5]_2Pd(N_3)_2$ in $CDCl_3$: (A) spectrum recorded immediately after solution preparation; (B) spectrum recorded 72 h later.

Attempted Catalyzed Isomerizations. Complexes of the type L_2MCl_2 have been shown[15–19] to undergo ligand-catalyzed isomerizations. The addition of dimethylphenylphosphine to a solution of $[(BzlO)_3P]_2PdCl_2$ immediately collapses the ^{1}H methylene triplet resonance to a singlet. Over a 3-h period this singlet broadens and eventually becomes a 1:1 doublet. Simultaneously the ^{1}H methyl singlet resonance of dimethylphenylphosphine becomes a 1:1 doublet. These two doublets represent the mixed-ligand complex *cis*-$[(CH_3)_2PPh][(BzlO)_3P]PdCl_2$. The addition of other phosphites and phosphines to a solution of $[(BzlO)_3P]_2PdCl_2$ similarly result in mixed-ligand complexes following rapid phosphite exchange. In no case does geometric isomerization occur. Similar behavior was found for all of the palladium complexes and in each case rapid ligand exchange occurs initially upon adding a catalytic amount of a phosphorus ligand. Each of these complexes forms mixed-ligand complexes[47] but in no case was geometric isomerization

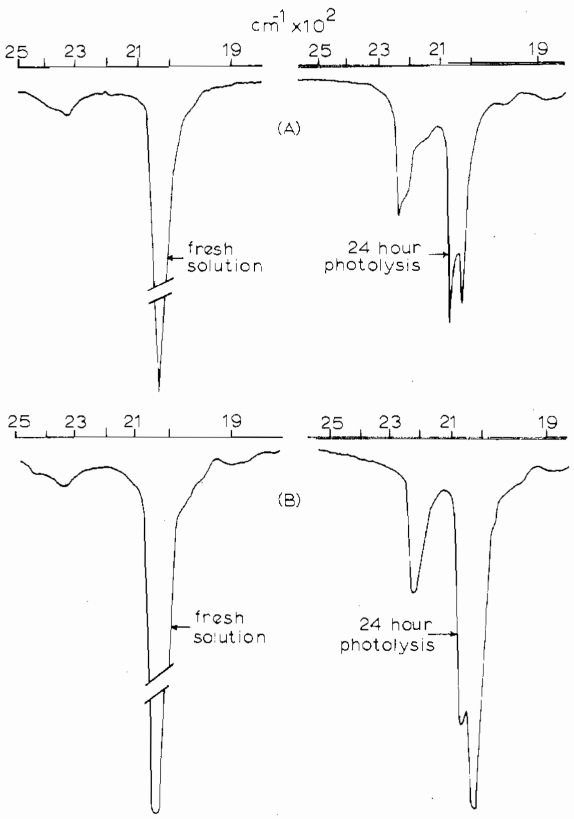

Figure 5. Infrared spectral changes in ν_{N_3}(as) of (A) $(Bzl_2PPh)_2Pd(N_3)_2$ and (B) $(BzlPPh_2)_2Pd(N_3)_2$ upon photolysis in $CDCl_3$ solution.

catalyzed. Equimolar solutions of these complexes and $[(CH_3)_2PPh]_2PdCl_2$ were prepared and in each case mixed-ligand complexes were formed[47]

Conductivity Studies. Since ionic species have been previously suggested[18,66] as isomerization intermediates, we wished to determine if ionic species could be formed with these complexes. Consequently, a known volume and concentration of the complexes were conductometrically titrated with their respective ligands in nitromethane to a 4:1 ligand to complex mole ratio. In addition they were similarly titrated with the smaller and more basic ligand $(CH_3O)_3P$. Plots of the volume-corrected conductance (range $(40-60) \times 10^{-6}$ mho) vs. moles of ligand were linear in every case. The conductance of the ligands alone in the same concentration range is $(35-45) \times 10^{-6}$ mho. Thus no ionic $[L_3PdX]^+X^-$ species were formed. Consequently, even though the consecutive ligand displacement isomerization mechanism to form $LL'PdX_2$ but not $[L_3PdX]^{+X^-}$ can occur for these complexes,[19] the cis isomer is usually so sterically unstable that it does not form.

Photochemical Behavior of the Azide Complexes. It was noted very early that the azide complexes darkened upon standing, changing from yellow to gold, yellow-orange, or red. It was determined that this behavior resulted from exposure to room light. This change in color normally requires several days except for $(Bzl_3P)_2Pd(N_3)_2$ where it occurs within 1 day but only on the exposed surfaces. Once the surface color change occurs, the complexes are apparently stable indefinitely. It is important to note that no palladium metal formed as the darker color is easily removed by recrystallization from $CHCl_3$ without noticeable loss of complex or palladium deposition on the filter papers through which the solutions were filtered. The color changes were also found to occur in $CHCl_3$ and CH_2Cl_2 solutions upon exposure to light.

Comparisons of IR spectra before and after photolysis indicate the presence of a new absorption near 2250 cm⁻¹ for solutions of the photolyzed complexes (Figure 5). The species giving rise to this absorption is unknown though absorptions arising from N≡O,[67] diazonium salts,[67] NCO,[63] and N_2O[67] are known to occur in this region. Additionally, Beck et al.[63] have shown that $(R_3P)_2Pd(N_3)_2$ complexes react with carbon monoxide to produce $(R_3P)_2Pd(NCO)_2$. The new IR absorption occurs for complexes photolyzed either in solution or in the solid state when open to the atmosphere. It is interesting to note that the absorption does not continue to increase in intensity indefinitely, and this may be linked to the aforementioned surface-only reaction (solid state) or some photostationary equilibrium (solution).

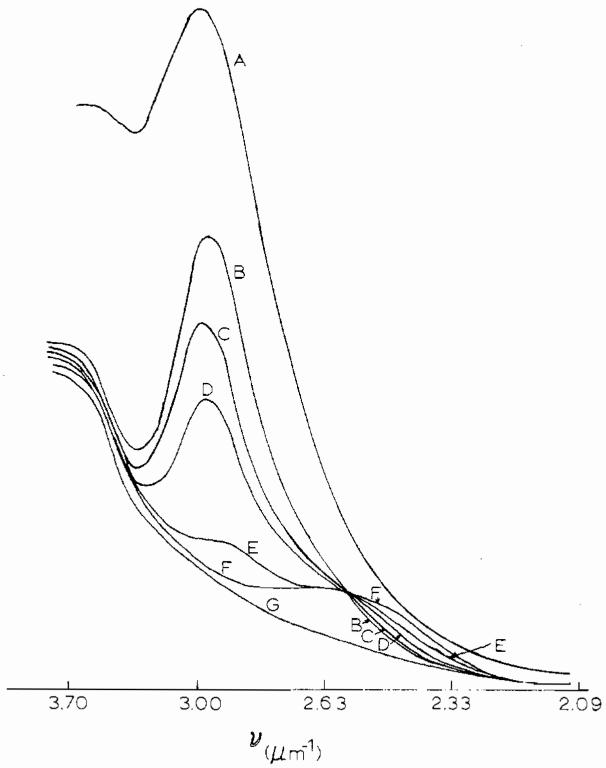

Figure 6. Behavior of $[(CH_3)_2PPh]_2Pd(N_3)_2$ upon photolysis: the electronic spectrum after (A) no photolysis, (B) 2 h, (C) 5 h, (D) 8 h, (E) 21.5 h, (F) 30.5 h, and (G) 70 h in CH_2Cl_2 in a degassed sealed quartz cell at 25 °C.

If photolysis is carried out in solution by irradiation from a quartz lamp, a white substance is found after many hours of photolysis on the side of the container toward the lamp. This occurs whether the solutions are open to the atmosphere or blanketed with nitrogen. It does not appear that the N_3 radical is generated as found by others[68] as addition of cyclohexene produced none of the radical adduct nor did the addition of KI to a solution followed by photolysis produce the expected I_2 color which would be indicative of the presence of radicals.

Solutions of $[(C_6H_5)P(CH_3)_2]_2Pd(N_3)_2$ were photolyzed in degassed sealed quartz UV cells under vacuum. The electronic spectral changes observed were recorded as a function of time (Figure 6). The loss of the isosbestic point coincided somewhat with the formation of the white substance on the wall of the cell. In a similar study on $(BzlPPh_2)_2Pd(N_3)_2$ it was found that an increase in the absorption at 30.2×10^3 cm⁻¹ was observed on photolysis which then decreases in intensity on sitting in the dark. This seems to be consistent with an increase in the concentration of the trans isomer on photolysis followed by a decrease in the trans isomer concentration upon sitting in the dark. Cis–trans isomerizations are known to occur on photolysis for similar complexes.[69] Photoisomerism also seems consistent with the IR data (Figure 5) where the fresh solution contains only one absorption near 2000 cm⁻¹, while, after photolysis, two absorptions near 2000 cm^{-1} were observed. Using the previously outlined arguments for interpretation of IR absorptions in terms of cis and trans geometries, it would seem that the fresh solution contains the cis isomer and on photolysis the trans isomer is formed. This would also be consistent with the changes observed for $(Bzl_2PPh)_2Pd(N_3)_2$ as a function of time, where cis → trans isomerization was found.

Since this work was completed, it was reported[70] that similar complexes formed from organic azides and $(R_3P)_2MX_2$ complexes are photosensitive and useful as photographic image formers.

None of the chloride complexes were found to be photosensitive in solution, as after 24 h of photolysis at 25 ± 0.1 °C with a mercury lamp the electronic spectra were identical with those obtained on aliquots of the same solutions which had not been photolyzed (Table VII).

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Registry No. Bzl_3P, 7650-89-7; $Bzl_3P{=}O$, 4538-55-0; $Bzl_3P{=}S$, 21187-15-5; Bzl_3PH^+, 63832-83-7; $Bzl_3P(CH_3)^+I^-$, 17586-68-4; $Bzl_4P^+Cl^-$, 15049-34-0; Bzl_2PPh, 7650-90-0; $Bzl_2P(O)Ph$, 24442-45-3; $Bzl_2P(S)Ph$, 13298-01-6; Bzl_2PPhH^+, 63832-84-8; $Bzl_2P(CH_3)Ph^+I^-$, 51290-74-5; $Bzl_3PPh^+Cl^-$, 63832-85-9; $BzlPPh_2$, 7650-91-1; $BzlP(O)Ph_2$, 2959-74-2; $BzlP(S)Ph_2$, 15367-75-6; $BzlPPh_2H^+$, 63832-86-0; $BzlP(CH_3)Ph_2{}^+I^-$, 63832-87-1; $Bzl_2PPh_2{}^+Cl^-$, 33417-24-2; $(C_6H_5CH_2O)_3P$, 15205-57-9; $(C_6H_5CH_2O)_2PC_6H_5$, 62292-07-3; $C_6H_5CH_2OP(C_6H_5)_2$, 53772-44-4; $(C_6H_5CH_2S)_3P$, 1656-65-1; $(C_6H_5CH_2S)_2PC_6H_5$, 63832-88-2; $(C_6H_5CH_2S)P(C_6H_5)_2$, 63832-89-3; $[(C_6H_5CH_2)_2N]_3P$, 59758-28-0; $[(C_6H_5CH_2)_2N]_2P(C_6H_5)$, 63057-80-7; $[(C_6H_5CH_2)_2N]P(C_6H_5)_2$, 27826-15-9; *trans*-$(Bzl_3P)_2PdCl_2$, 49607-85-4; *trans*-$(Bzl_2PPh)_2PdCl_2$, 49607-84-3; *cis*-$(BzlPPh_2)_2PdCl_2$, 55529-12-9; *trans*-$(BzlPPh_2)_2PdCl_2$, 49607-83-2; *trans*-$((BzlO)_3P)_2PdCl_2$, 63902-68-1; *trans*-$((BzlO)_2PPh)_2PdCl_2$, 63902-67-0; *cis*-$((BzlO)PPh_2)_2PdCl_2$, 55481-12-4; *trans*-$((BzlS)_3P)_2PdCl_2$, 63848-42-0; *trans*-$((BzlS)_2PPh)_2PdCl_2$, 63848-41-9; *cis*-$((BzlS)PPh_2)_2PdCl_2$, 63848-40-8; *trans*-$((Bzl_2N)_3P)_2PdCl_2$, 63848-39-5; *trans*-$((Bzl_2N)_2PPh)_2PdCl_2$, 63848-38-4; *cis*-$((Bzl_2N)PPh_2)_2PdCl_2$, 63848-37-3; *trans*-$(Bzl_3P)_2Pd(N_3)_2$, 58179-14-9; *cis*-$(Bzl_2PPh)_2Pd(N_3)_2$, 53554-39-5; *trans*-$(Bzl_2PPh)_2Pd(N_3)_2$, 53585-61-8; *cis*-$(BzlPPh_2)_2Pd(N_3)_2$, 53554-38-4; *trans*-$(BzlPPh_2)_2Pd(N_3)_2$, 53585-60-7; *trans*-$(Bzl_3P)_2PtCl_2$, 63902-66-9; *trans*-$(Bzl_2PPh)_2PtCl_2$, 63848-36-2; *cis*-$(BzlPPh_2)_2PtCl_2$, 61586-06-9; *cis*-$[(CH_3)_2PPh]_2Pd(N_3)_2$, 52810-36-3; *trans*-$[(CH_3)_2PPh]_2Pd(N_3)_2$, 52881-92-2; PCl_3, 7719-12-2; dibenzylamine, 103-49-1; ^{13}C, 14762-74-4; $BzPPh_3{}^+Cl^-$, 1100-88-5.

Supplementary Material Available: A table of analytical data and physical properties of the complexes (1 page). Ordering information is given on any current masthead page.

References and Notes

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Kinetics of the Disproportionation Reaction of Mercury(I) in Alkaline Solutions

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The kinetics of the disproportionation reaction of mercury(I) in alkaline solutions have been measured by the stopped-flow method. The rate law is given by $-d[Hg_2OH^+]/dt = k_1[Hg_2OH^+] + k_2[Hg_2OH^+][OH^-]$ in alkaline concentrations of 0.004 54–0.049 15 M. The values for k_1 and k_2 at 25 °C and $\mu = 0.1$ are estimated to be 9.0 ± 0.2 s^{-1} and $(2.8 \pm 0.1) \times 10^2$ M^{-1} s^{-1}, respectively. The activation parameters associated with k_1 and k_2 are $\Delta H_1^* = \Delta H_2^* = 12 \pm 1$ kcal mol^{-1}, $\Delta S_1^* = -14 \pm 4$ cal mol^{-1} deg^{-1}, and $\Delta S_2^* = -7.2 \pm 1.8$ cal mol^{-1} deg^{-1}. The proposed mechanism is as follows: $Hg_2^{2+} + OH^- \rightleftharpoons Hg_2OH^+$, rapid equilibrium; $Hg_2OH^+ \rightarrow Hg^0 + HgOH^+$, k_1; $Hg_2OH^+ + OH^- \rightarrow Hg^0 + Hg(OH)_2$, k_2. General discussions on the disproportionation mechanism of mercury(I) ions were made.

Introduction

In the presence of complexing ligands such as ammonia, cyanide ion, and hydroxide ion, disproportionation of mercury(I) ions occurs to give elemental mercury and the corresponding mercury(II) complexes, because of the relatively greater stability of the mercury(II) complexes.[1] One of the major problems in mercury(I) chemistry is the disproportionation of this ion which greatly depends on ligands attached to it.[2] However, there have been few data concerning the kinetics of the disproportionation reaction. The author has recently studied the kinetics with HCN and reported that $(Hg-Hg-CN)^+$ species, formed as an intermediate, weakens the Hg–Hg bond and leads to disproportionation.[3]

The compound claimed to be "mercurous oxide" by earlier investigators has been shown to be a mixture of metallic mercury and mercuric oxide.[4] It is worthwhile to study the kinetics in alkaline solutions. Moreover, it has been of interest to many investigators to determine the rate of disproportionation equilibrium of mercury(I), $Hg_2^{2+} \rightleftharpoons Hg^0 + Hg^{2+}$, which has been recognized to be rapidly established. For this purpose, the kinetic studies must be designed under simplified conditions, in which only OH^- ion is present and leads to disproportionation. The data obtained from this study will be available for consideration of the mechanism of mercury(I) disproportionation.

Experimental Section

Materials. Doubly distilled water free of carbon dioxide was used throughout this work. Mercurous perchlorate solutions in 0.05 M perchloric acid were prepared and the concentrations of Hg_2^{2+} and $HClO_4$ were standardized as described previously.[3] All kinetic data were obtained with $[Hg_2^{2+}]_0 = 2.5 \times 10^{-5}$ M. At higher or lower concentrations it proved to be difficult to follow absorbance changes, owing to occurrence of a grayish dark turbidity, probably mercuric oxide, or to lower absorbance change. Sodium hydroxide sample solutions, 0.06–0.15 M, were prepared by dilution with water from a NaOH stock solution (1 M), and their alkaline concentrations were determined titrimetrically with standard $HClO_4$ solution. Sodium perchlorate solutions (2 M) were added to maintain the ionic strength at $\mu = 0.1$.

Table I. Amount of Metallic Mercury Found with and without Reductant (25 °C, $\mu = 0.1$)

[NaOH], M	Amt of Hg_2^{2+} taken, 10^{-8} mol	Amt found, 10^{-8} mol	
		Hg^0	Hg^0_{Red}
0.03	0.50		0.85
0.03	1.0		2.0
0.03	1.5		2.6
0.03	2.0		4.2
0.005	2.0	1.8	
0.01	2.0	1.7	
0.03	2.0	2.2	
0.05	2.0	2.1	

Stoichiometric Measurements. Stoichiometry with regard to elemental mercury was measured by the cold-vapor atomic absorption method. The method was essentially similar to that of the previous paper.[3] Aliquots, 0.5–2 mL, of the mercurous solution (10^{-5} M) were added to reaction vessels containing 200 mL of various NaOH concentrations (0.005–0.05 M), and then the mixed solutions were aerated with and without reductant for 30 min into the permanganate–sulfuric acid absorbing solutions.

Kinetics. Rates of reaction were followed spectrophotometrically using an Aminco-Morrow stopped-flow apparatus attached to an Aminco DW-2 UV–visible spectrophotometer. The change in the transmittance was monitored at 235 nm (Figure 1, top). Triplicated experiments were conducted using freshly prepared Hg_2^{2+} and NaOH solutions. The rapid-scanning spectrum[5] for the reaction of Hg_2^{2+} with excess NaOH reveals that a new band appears at the lower wavelength region immediately after mixing (Figure 2). Then, the stopped-flow measurements were also made at 228 nm. The results obtained at this wavelength were, however, less reliable than those at 235 nm because of the higher noises of our instrument in the lower wavelength region. All other kinetic measurements were made in the same manner as described previously.[3]