Phospholes as Ligands: Palladium(II) Complexes of 1-Substituted 3.4-Dimethylphospholes. Structure and Properties¹

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A series of palladium(II) complexes of the type L_2PdX_2 (L = 1-R-3,4-dimethylphosphole; R = -CH₃, -n-C₄H₉, -t-C₄H₉, $-C_6H_5$, $-CH_2C_6H_5$; X = Cl⁻, Br⁻, N₃⁻) have been prepared and characterized by elemental analyses, physical properties, conductance measurements, infrared and electronic spectroscopy, and ¹H, ³¹C(¹H), and ³¹P(¹H) NMR spectroscopy. The complexes all appear to be cis in the solid state. Several isomerize at room temperature to equilibrium mixtures of cis and trans isomers in chloroform solution. The ³¹P coordination chemical shifts for the complexes behave in a fashion similar to that of phosphine complexes. The crystal structure of cis-dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II) was determined from three-dimensional X-ray diffraction techniques. The molecule crystallizes in the monoclinic space group Cc in a unit cell of dimensions a = 10.427 (4) Å, b = 15.070 (6) Å, c = 15.910 (6) Å, $\beta = 92.88$ (2)°, $\rho_{calcd} = 1.48$ g/cm^3 , and $\rho_{obsd} = 1.48$ (1) g/cm^3 . Least-squares refinement converged at final values of R = 0.042 and $R_w = 0.047$. The phosphole ring is planar, indicating the existence of some intracyclic electron delocalization within the complexed phosphole. Short Pd-P (2.241 Å average) and Pd-Cl (2.353 Å average) bond distances indicate strong Pd-P bonds containing some π component. All the data suggest that Pd-phosphole bond strengths are somewhat greater than the Pd-P bond strengths in structurally similar Pd-phosphine complexes. Palladium-phosphole bonds are strong due to three contributing factors: (a) the phosphole does not undergo structural reorganization upon coordination, (b) phospholes are sterically undemanding, and (c) phospholes have a moderate π -acceptor capacity.

Introduction

Tertiary phosphine complexes of transition metals have been well studied, and during the last decade or so a large body of information has been compiled on the coordination chemistry of cyclic phosphines and their derivatives.² The chemical and structural character of several of these cyclic compounds has allowed the formation of many interesting organometallic complexes, some having unusual structures and uncommon coordination numbers.^{3,4} In addition, some transition-metal complexes of these cyclic phosphines have been shown to be active homogeneous catalysts for the hydrogenation of alkenes.⁵

The phosphole ring system (I) is theoretically quite inter-



esting.^{2,6} There is considerable controversy as to the amount of $(2p-3p) \pi$ -type interaction within the phosphole ring. In particular, the question of whether the interaction of the cis-butadiene moiety and the substituted phosphorus atom is stabilizing or destabilizing is somewhat unsettled.⁷ Superficially, phosphole (I, $\mathbf{R} = \mathbf{R'} = \mathbf{H}$) is very similar to pyrrole, which is regarded as an aromatic system due to π delocalization of the nitrogen lone pair over the entire ring.⁸ Studies regarding the possible aromatic character of the phospholes

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have been reviewed elsewhere.⁹ The possible interaction of the phosphorus lone pair with the ring π system would clearly affect the donor character of the phosphorus atom toward transition metals. If there is considerable lone-pair delocalization within the ring, the phospholes should be weak bases and should not readily coordinate to transition metals. This is the case with 1-substituted phospholes (I, R' = H; R = alkylor aryl); compare the pK_a of 1-methylphosphole¹⁰ ($pK_a = 0.5$) to those of regular phosphines $(pK_a = 7-8)$. However, it has been shown that the donor character of the phosphole system depends to a large extent upon the substitution pattern around the phosphole ring,⁶ and therefore studies of such donor properties are of interest. The effect of substituents at carbons 3 and 4 on the electronic characteristics of the phosphole ring poses an interesting question, which has been studied to some degree.⁹ In addition, the presence of the butadiene moiety in these molecules offers the possibility of π coordination to transition metals, which has in fact been realized.¹¹

With these ideas in mind, we have prepared and characterized a series of palladium(II) complexes of the type L₂PdX₂ (L = 1-R-3,4-dimethylphosphole; $R = -CH_3$, $-n-C_4H_9$, -t- C_4H_9 , $-C_6H_5$, $-CH_2CH_6H_5$; X = Cl⁻, Br⁻, N₃⁻) and have investigated their solution behavior.

Experimental Section

A. Reagents and Physical Measurements. Chemicals were reagent grade and were used as received or synthesized as described below. All solvents were dried when necessary by standard procedures and stored over Linde 4-Å molecular sieves. Melting points were determined on a Meltemp apparatus and are uncorrected. Elemental analyses were performed by Chemalytics Inc., Tempe, AZ 85282, and are listed in Table I.

Conductivity studies were carried out at 25 ± 0.1 °C. Temperature regulation was achieved with a Brinkman Lauda K-2/R temperature controller. Conductance measurements were made by using a Yellow Springs Instruments conductivity cell, Model No. 3403, and measured with an Industrial Instruments conductivity bridge, Model RC16B2, which was adapted for use with a Tektronix Type 310 oscilloscope. Conductance ranges for electrolytes were taken from published values.¹²

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Table I.	Physical	Properties of	` (1-R-3, <u>'</u>	4-dimethy	lphosphole) ₂ Pd	X_2
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						ana	ıl.
				electronic spectra		% C	% H
R	Х	color	mp, °C	CHCl ₃ soln λ , nm (log ϵ)	Nujol mull λ , nm	calcd found	calcd found
CH ₃	a	yellow	130	235 (4.50), 251 (4.40), 262 (4.33), 343 (3.70)	227, 377	39.16 38.90	5.16 5.27
$n - C_4 H_9$	Cl	yellow	134	238 (4.76), 250 (4.64), 349 (4.04)	227, 343	46.79 46.31	6.67 6.28
$t-C_4H_9$	Cl	yellow	dec above 260	238 (4.54), 250 (4.37), 259 (4.35), 274 (4.25), 353 (3.77)	234, 340	46.79 46.87	6.67 6.87
$C_6 H_5$	C1	yellow	206	237 (4.47), 248 (4.35), 259 (4.26), 360 (3.58)	237, 397	52.08 51.98	4.73 4.81
CH ₂ C ₆ H ₅	Cl	yellow	192	244 (4.52), 262 (457), 349 (3.60)	241, 373	53.70 53.42	5.20 5.37
CH ₃	Br	yellow-orange	262	249 (4.36), 261 (4.34), 273 (4.24), 371 (3.83)	376	32.44 32.04	4.24 4.30
<i>n</i> -C ₄ H ₉	Br	yellow-orange	110	235 (4.49), 249 (4.23), 262 (4.17), 287 (3.88), 370 (3.61)	262, 385	39.88 40.05	5.64 5.59
t-C ₄ H ₉	Br	orange	dec at 260	236 (4.48), 248 (4.46), 262 (4.30), 284 (3.91), 387 (4.19)	259, 324, 391	39.88 39.65	5.64 5.55
$C_6 H_5$	Br	orange	235	239 (4.58), 249 (4.48), 289 (4.14), 386 (3.88)	213, 264, 399	44.87 44.62	4.05 4.21
$CH_2C_6H_5$	Br	orange	208	not available	not available	46.58 46.32	4.47 4.19
CH ₃	N ₃	yellow	113	243 (4.25), 325 (4.07)	244, 280, 377, 427	38.00 37.89	4.97 4.69
<i>t</i> -C ₄ H ₉	N ₃	yellow	dec at 206	247 (4.21), 340 (4.05)	210, 360, 419 sh	45.62 45.27	6.46 6.61
$C_6 H_5$	N_3	orange	148	231 (4.33), 246 (4.21), 336 (3.95)	218, 238, 281, 389, 453	50.87 50.79	4.59 4.72
$CH_2C_6H_5$	N_3	yellow-orange	144	not available	218, 264, 286, 357, 436	52.54 52.26	5.05 5.24

The complexes are nonelectrolytes in both $CHCl_3$ and CH_3NO_2 solutions in the absence of excess ligand.

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer as Nujol mulls between CsBr plates and, in addition, as $CHCl_3$ solutions in NaCl cells for the azide complexes.

Electronic spectra were recorded on a Cary 14 spectrophotometer as $CHCl_3$ solutions in 1-cm quartz cells and as Nujol mulls suspended on Whatman No. 1 filter paper with Nujol-saturated filter paper as reference. The physical properties and electronic spectral data are listed in Table I.

The ¹H, ¹³C(¹H), and ³¹P(¹H) NMR spectra were recorded at 99.54, 25.00, and 40.26 MHz, respectively, on a JEOL FX-100 spectrometer in FT mode. Proton and carbon chemical shifts are downfield relative to internal Me₄Si, while the phosphorus chemical shifts are relative to P(OCH₃)₃ and corrected to 85% H₃PO₄. The trimethyl phosphite was dissolved in CDCl₃ and placed in a 5-mm NMR tube and supported concentrically in a 10-mm NMR tube containing the dissolved complex. The positive signs on the δ ³¹P chemical shifts indicate a downfield position relative to H₃PO₄. Solvents were spectroscopic grade and were used as received from the manufacturer. Preparation of samples for NMR analyses has been previously described.¹³

Computer simulations of spectra were obtained with the JEOL FX-100 computer software, using 0.75-Hz resolution and 1.5-Hz line widths, which approximated the nominal ${}^{13}C{}^{1}H{}$ spectral conditions.

B. X-ray Data Collection. A crystal of approximate dimensions $0.18 \times 0.18 \times 0.32$ mm was selected for data collection, mounted on the end of a glass fiber, and transferred to an Enraf-Nonius CAD4 diffractometer. Indexing of 12 reflections obtained by automatic peak search and centering routines produced a triclinic cell of approximate dimensions a = 9.16 Å, b = 9.15 Å, c = 15.91 Å, $\alpha = 91.7^{\circ}$, $\beta =$ 91.7°, and $\gamma = 110.6^{\circ}$. A Delaunay reduction indicated the true crystal system to be monoclinic. Transformation of the cell by the matrix $(110/\overline{1}10/001)$, followed by the least-squares refinement of the setting angles of 12 high-angle reflections, yielded a C-centered cell of dimensions a = 10.427 (4) Å, b = 15.070 (6) Å, c = 15.910(6) Å, and $\beta = 92.88$ (2)°, based on graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.70930$ Å). The calculated density for 4 molecules per unit cell is 1.48 g/cm⁻³, compared to an experimental density of 1.48 (1) g/cm^{-3} determined by flotation in ethanol/carbon tetrachloride.

Data $(h,k,\pm l)$ were collected by using $\theta - 2\theta$ scans and graphitemonochromatized Mo K α radiation to $\theta = 30^{\circ}$. The scan range was calculated according to the formula $\theta = (0.90 + 0.35 \tan \theta)^{\circ}$ and was extended by 25% on each end of the scan range for background measurement. The scan rate, based on a fast prescan, was computed such that, if possible, 5×10^3 counts were to be obtained in a maximum allowed time of 90 s. An aperture with a height of 4.0 mm and variable width of $(3.5 + 2.11 \tan \theta)$ mm was placed in front of the counter 173 mm from the crystal. The intensities of three standard reflections, measured after every 50 reflections, showed no significant variation over the course of data collection. A total of 2971 reflections were collected, of which 131 were collected twice. These were averaged to give a set of 2722 unique reflections, of which 2217 were judged to be observed by the criterion $F^2 \ge 2.5\sigma(F^2)$. The data were corrected for Lp and absorption effects. The transmission coefficients ranged between 0.82 and 0.89 based on a linear transmission coefficient μ = 10.83 cm⁻¹.

Analysis of the systematic absences hkl, $(h + k) \neq 2n$, and h0l, $l \neq 2n$, indicated the space group to be Cc or C2/c. The intensity statistics strongly indicated Cc,¹⁴ a choice substantiated by the subsequent solution and refinement of the structure. The Pd atom position was obtained from a Patterson map. The remainder of the structure was obtained from successive difference maps. Refinement of all non-H atom positions and isotropic temperature parameters converged at R = 0.099 and $R_w = 0.110$. At this point anisotropic thermal parameters of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl]$ + $2B_{23}kl$)] were assigned to the Pd, P, Cl, and phosphole carbon atoms. In addition, phenyl H atoms were placed in calculated positions and assigned isotropic temperature factors 1.0 Å² greater than that of the carbon atom to which it is attached. Refinement converged at R =0.042 and $R_w = 0.047$ based on 111 variables and 2217 observations. The error in an observation of unit weight was computed to be 1.35. Since not all of the nonphenyl H atoms could be located, none were included in the final refinement. Scattering factors for the neutral atoms were taken from ref 15. Corrections for anomalous scattering were applied to those of the Pd, P, and Cl atoms.¹⁶ During the final cycle of refinement, no parameter varied by more than 0.02 in its standard deviation. Computer programs used have been described previously.¹⁷ A table of observed and calculated structure factor

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Table II. ¹H NMR Data for the 1-R-3,4-dimethylphospholes and Their Complexes L₂PdX₂ at 30°C^a.

· · · · · · · · · · · · · · · · · · ·			δ (¹ H), line shape, J_{PH} in Hz						
	R	x	phosphole ring CH ₃	ring H	t-Bu CH ₃	P-CH ₃	benzyl CH ₂		
	CH,	free ligand	2.03, dd, 2.75	6.40, d, 37.7		1.21, d, 1.7			
	CH	Cl	2.03, s	6.32, d, 33.0	1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -	1.65, d, 12.0			
	CH	Br	2.05, s	6.47, d, 31.0	and the second second	1.67, c			
	CH	Ν,	2.12, s	6.28, d, 32.0		1.57, d, 10.0			
	<i>n</i> -Bu	free ligand	2.04, dd, 2.60	6.37, d, 37.7					
	n-Bu	C1	2.06, s	6.34, d, 33.0					
	n-Bu	Br	2.05, s	6.41, d, t, 33.0					
	t-Bu	free ligand	2.07, dd, 2.54	6.26, d, 37.7	1.10, d, 13.3				
	t-Bu	CI	2.00, s	6.42, t, 30.0	1.33, t, 15.0				
				6.55, d, 31.0					
	t-Bu	Br	2.02, s	6.55, d, t, 30.0	1.31, t, 15.5				
	t-Bu	N ₃	2.11, s	6.36, d, t, 32.0	1.13, d, 16.0				
					1.33, t, 15.0				
	Ph	free ligand	2.07, dd, 3.12	6.49, d, 37.7	and the second second				
	Ph	Cl	1.97, s	6.42, d, 33.0					
	Ph	Br	2.05, s	6.72, d, 33.0					
	Ph	N ₃	2.04, s	6.27, d, 33.0					
	Bzl	free ligand	1.96, d, 3.00	6.31, d, 37.2			2.97, s		
	Bzl	Cl di	1.87, s	6.05, d, 32.0			3.36, d, 13.0		
	Bzl	Br	1.85, s	6.19, d, 32.8			3.49, d, 12.5		
	Bzl	N ₃	1.89, s	5.93, d, 32.0			3.19, d, 11.0		

 $a_{s} = singlet$, d = doublet, t = triplet, dd = doublet of doublets, c = collapsed multiplet.

amplitudes is listed in the supplementary material.

The quantity minimized in the full-matrix least-squares refinement is $\sum w(|F_0| - |F_c|)^2$, where F_0 and F_c are the observed and calculated structure factor amplitudes. The weights, w, were taken as $4F_0^2/$ $\sigma^2(F_0^2)$. The discrepancy indices are defined as $R = \sum ||F_0| - |F_0|$

 $|F_c|| \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 \sum wF_o)^{1/2}$. C. Syntheses. 1. Phospholes. The phospholes are moderately air sensitive and were handled and allowed to react with other chemicals in a nitrogen atmosphere. All of the phospholes were prepared by previously described methods.18

2. Bis(phosphole)palladium(II) Complexes. The chloride complexes were prepared by reacting the appropriate phosphole with dichlorobis(benzonitrile)palladium(II). The bromide and azide complexes were in turn prepared by metathesis of the chloride complex. Representative examples are described below. The physical properties of the complexes are given in Table I.

(a) Dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II). To 2.10 g (5.47 \times 10⁻³ mol) of dichlorobis(benzonitrile)palladium(II) in 100 mL of benzene was added, under a nitrogen atmosphere, 2.06 g (1.09 \times 10⁻² mol) of 1-phenyl-3,4-dimethylphosphole. After 1 h of stirring, the resulting yellow solution was filtered to remove any palladium metal, and its volume was reduced to approximately 15 mL on a rotary evaporator. The solution was allowed to stand, and after a time, yellow needles appeared which were filtered off, washed with cold pentane, and finally recrystallized from hot methanol solution. A 1.94 g (64%) sample of the complex was recovered.

(b) Dibromobis(1-n-butyl-3,4-dimethylphosphole)palladium(II). To 0.5 g (9.7 \times 10⁻⁴ mol) of the chloride complex dissolved in CHCl₃ (30 mL) was added 0.2 g (1.9×10^{-3} mol) of NaBr in 25 mL of methanol. The solution was stirred for approximately 30 min with gentle heating. The solution was then stripped of all solvent and the residue extracted with hot chloroform. After being filtered, the chloroform solution was slowly evaporated to yield 0.42 g (72% yield) of orange crystals.

c) Diazidobis(1,3,4-trimethylphosphole)palladium(II). To 0.5 g $(1.16 \times 10^{-3} \text{ mol})$ of the chloride complex in CHCl₃ was added 0.15 g (2.23 \times 10⁻³ mol) of NaN₃ in 25 mL of methanol. The solution was stirred with gentle heating for 30 min and then stripped of all solvent on a rotary evaporator. The resulting solid was extracted with hot CHCl, which, after filtering, was slowly evaporated to yield 0.39 g (76% yield) of orange crystals.

Results

Elemental analyses, spectroscopic data, and the lack of solution conductance indicate that 1-substituted 3,4-dimethylphospholes react with (PhCN)₂PdCl₂ to produce typical square-planar complexes which do not ionize or readily dissociate in solution. Contrary to the observations of Hughes et al.,¹⁹ the resulting L_2PdX_2 complexes (L = 1-substituted 3,4-dimethylphosphole) give well-resolved proton NMR spectra which, in conjunction with other spectral data, are useful in the elucidation of structure. Hughes' inability to obtain well-resolved proton NMR spectra could be due to the adventitious presence of excess ligand, which has been shown²⁰ to promote ligand exchange, resulting in broad ill-defined proton NMR spectra.

A. ¹H NMR Spectra. The geometry of most square-planar bis(phosphine) transition-metal complexes can be determined via ¹H NMR if the phosphine ligands contain α -methyl or α -methylene groups,²¹ since these groups exhibit the phenomenon of virtual coupling. In trans complexes, where ${}^{2}J_{PP}$ is usually on the order of hundreds of Hertz,²² the α -methyl or α -methylene resonances appear as 1:2:1 triplets. When the complexes are cis, ${}^{2}J_{PP}$ is usually less than 20 Hz,²² and these proton resonances usually appear as 1:1 doublets. In the 3,4-dimethylphosphole molecules, the ring protons on the carbons adjacent to phosphorus fall into this category and upon initial examination would be considered a structural probe in addition to the exocyclic substituent on phosphorus, which can also contain α -methyl or α -methylene protons (e.g., -CH₃, $-n-C_4H_9$, $-CH_2C_6H_5$).

The phosphole ring proton resonance (Table II) appears as a doublet in the majority of the complexes studied in CDCl₃ solution at room temperature, indicating the presence of primarily the cis isomer. Upon further inspection, one finds that there are certain disadvantages in the exclusive use of these proton resonances for structure elucidation (Figure 1). The peak intensities are relatively weak, and, in addition, there

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Figure 1. 99.54-MHz ¹H NMR spectra of phosphole ring secondary proton exhibiting (A) clearly one isomer, (B) clearly two isomers, and (C) ambiguous assignments.

is a small coupling of this proton to the phosphole ring methyl protons ($J_{\rm HH} \simeq 0.5$ -1.0 Hz). Furthermore, when one takes into consideration the line shapes of other proton resonances, it becomes apparent that proton NMR is not in itself conclusive in assigning absolute geometry for these complexes. The employment of ³¹P{¹H} and ¹³C{¹H} NMR is necessary for conclusive structural assignments for the majority of the phosphole complexes.

A further examination of Table II reveals certain changes in chemical shift and in ${}^{n}J_{PH}$ of the phosphole ring protons upon coordination to the metal. In most cases the chemical shift for these protons moves downfield roughly in the order $Br^- \ge Cl^- > N_3^-$. This order roughly correlates with the trans influence parameters of Gofman and Nefedov,23 which may reflect the relative strength of the palladium-phosphole bond via inductive effects. ${}^{n}J_{PH}$ for these protons decreases upon coordination, however, following no clear trend. One should note that ${}^{n}J_{PH}$ increases upon coordination for the protons on exocyclic substituents.

An interesting aside concerns the 1-tert-butyl-3,4-dimethylphosphole complexes. Shaw and co-workers²⁴ have suggested that the proton resonances of the tert-butyl methyl groups could be used to distinguish between cis and trans isomers through virtual coupling. The phosphole chloride and azide complexes, which were shown to contain a mixture of isomers in CDCl₃ solutions by ³¹P{¹H} NMR (vide infra), yield ambiguous results with respect to the tert-butyl methyl proton resonance. The chloride complex shows only a triplet, while the azide complex gives the expected doublet and triplet. In a similar manner, the 1,3,4-trimethylphosphole bromide complex, which is actually a mixture of isomers in CDCl₃ solution, also yields ambiguous information with respect to the p-methyl proton resonance, which appears as a collapsing triplet. These results tend to underline the potential ambiguities of ¹H NMR in the conclusive assignment of geometry.

B. ¹³C{¹H} NMR Spectra. Carbon-13 NMR of these phosphole complexes (Table III) affords a clearer picture of the isomers present in solution than does ¹H NMR. It has been shown²⁵ that for cis isomers, the ¹³C resonance for carbons



Figure 2. 25.00-MHz ¹³C¹H NMR spectra showing five-line multiplets and computer simulations.

adjacent to phosphorus may appear as a five-line multiplet, a non-1:2:1 triplet, a doublet of doublets, or a doublet. For trans isomers these resonances have appeared as 1:2:1 triplets in every case studied thus far. Figure 2 shows some representative five-line multiplets and computer simulations, for these compounds.

The coupling constants for the various carbon resonances usually cannot be obtained directly from a spectrum, as the observed splitting represents $|{}^{n}J_{PC} + {}^{n+2}J_{PC}|$. However, five-line multiplets (Table III) were observed for one or more of the carbon resonances, allowing the calculation²⁶ of all coupling constants for each cis complex. These coupling constants were verified by a satisfactory computer simulation of all line shapes. In the case of the trans isomers, where only $|{}^{n}J_{PC} + {}^{n+2}J_{PC}|$ is readily accessible, ${}^{n}J_{PC}$ was assumed to be similar to that of a cis isomer, leaving only two possibilities (one positive and one negative) for ${}^{n+2}J_{PC}$. These possible values were studied by computer simulation, varying the value of ${}^{2}J_{PP}$ until a satisfactory fit with the actual spectrum was obtained.

From past studies,^{22,27} computer simulations and actual spectral data, one can make the following statements concerning the various coupling constants for the 1-substituted 3,4-dimethylphosphole complexes: for the cis complexes, ${}^{2}J_{PP}$ = <6-10 Hz for the chlorides, 10-12 Hz for the bromides, and 21-37 Hz for the azides. The anion effect seems to indicate that the s character of the Pd-P bonds increases in the order $Cl \leq Br < N_3$ ²⁸ which is the same as that observed for phosphine complexes.²⁹ Irrespective of anion, " J_{PC} for a particular carbon atom approaches the value (~90%) of $|^{n}J_{PC}$

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Phospholes as Ligands

²J_{PP}, Hz 6.1 10.3 >150 >150 >150 NA^d >150 9.8 11.7 >150 36.6 J_{PP}, Hz 9.1 8.99 NA >150 36.3 21.4 % 13.5 s 13.6, s 13.6, s n-Bu 8 benzyl methylene C 29.6, d, 7.3 25.9, s^b 27.6, s^b 34.3, d, 28.7 35.6, d, 29.3 31.9, t, 24.5 33.2, d, 18.6 *n*-Bu γ 24.1, d, 7.3 23.9, f, 14.7 23.9, d, 14.6 131.7, s 132.9, t, 2.9 131.5, t, 2.3 131.8, s 138.1, d, 2.2 133.7, d, 7.5 134.0, f, 7.3 129.3, s^b ø n-Bu Ph C ŝ 128.7, d NA = not available. 23.6, d, 14.7 27.5, d, 12.2 27.4, d, 14.6 27.7, t, 31.9 129.2, d, 25.6 128.8, f, 11.8 128.7, f, 12.2 128.6, t, 10.9 129.0, t, 11.0 127.7, d, 1.7 128.1, d, 3.5 17.9, s^b n-Bu α^{c} Ph C_{3,5} ¹³C NMR Data for the 1-R-3,4-dimethylphospholes and Their Complexes L_2 PdX₂: δ ⁽¹³C), Line Shape, $|^n J_{PC} + {}^{n+2}J_{PC}|$ in Hz^a 29.4, t, 9.8 28.9, t, 11.2 29.6, s^b 28.6, t, 12.2 29.2, d, 11.0 t-Bu prim C 28.2, t, 11.6 e P-Ca-Cb-CY-Cb. 133.0, f, 12.4 133.3, f, 12.9 133.2, t, 13.6 132.8, t, 12.2 128.2, d, 4.9 129.6, d, 5.8 129.5, f, 6.1 133.1, s^b 33.1, d, 18. C2,6 Ē 32.7, d, 8.6 36.7, f, 26.4 35.1, t, 22.9 35.1, t, 22.9 35.1, t, 23.2 37.0, t, 25.6 35.6, t, 23.0 t-Bu tert C $nJ_{PC} = -n^{+2}J_{PC}$. 132.2, d, 12.2 125.2, d, 56.7 126.1, d, 58.7 125.0, t, 51.3 125.0, d, 56.0 125.3, d, 2.2 126.7, d, 4.2 126.7, f, 2.9 126.5, s^b υ 11.9, f, 34.3 13.2, d, 35.4 9.6, t, 27.4 9.4, t, 30.5 £ 7.1, d, 18.3 P-CH, Fortuitous cancelation: 17.7, f, 13.9 17.8, t, 13.4 17.6, t, 14.6 17.7, t, 13.4 17.7, d, 13.4 17.7, d, 13.6 17.7, d, 13.6 17.6, f, 13.4 17.7, t, 12.2 d, 3.7 ring CH₃ 17.8, f, 13.3 17.7, d, t, 14.7 17.7, d, 2.4 17.6, d, t, 12.4 7.7, d, t, 13.4 17.8, t, 11.0 18.0, t, 11.5 17.7, t, 11.8 17.5, d, 3.7 17.7, f, 12.2 ring CH₃ l 7.6, d, 3.7 17.6, 17.8 s^b 128.3, d, 7.3 124.3, d, 58.1 125.9, d, 62.9 126.8, t, 63.0 122.3, f, 54.9 122.3, f, 54.9 123.7, d, 52.9 123.7, d, 52.1 125.2, f, 53.3 121.2, f, 51.3 q ring sec C t, 53.7 $a_{s} = singlet, d = doublet, t = triplet, f = five-line multiplet.$ 125.6, f, 56.2 126.8, f, 53.3 125.6, t, 50.7 123.7, f, 53.1 129.2, d, 3.7 129.4, 4.4.8 124.1, t, 44.8 124.1, t, 44.4 125.0, f, 50.4 122.8, t, 44.4 122.8, t, 44.6 119.3, t, 41.5 ring sec C 131.4, d, 3.7 148.8, d, 8.5 153.7, f, 12.4 153.3, f, 12.2 152.7, t, 14.7 154.6, t, 10.1 149.7, d, 6.8 153.2, d, 10.9 152.7, f, 11.0 153.7, t, 8.6 ring tert C 152.4, d, 13.0 152.1, t, 13.2 153.6, s^b 152.8, f, 11.3 152.6, f, 11.0 152.5, t, 11.6 148.7, d, 6.1 152.7, t, 9.7 152.3, t, 11.6 152.2, t, 11.0 154.3, t, 11.2 f, 12.4 [47.8, d, 7.3 147.6, d, 7.3 ring tert C 53.7, t, 8.9 52.6, 1 N₃ free ligand Br N₃ free ligand free ligand CI ligand ligand × × D H free B C te

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Table III.

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Table IV. ³¹	P NMR	. Data fo	r the	Complexe	s L, PdX.
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							Δδ (³¹ P)	
		K_{eq}	δ ³¹ P)			ca	alcd ^a	found ^b	
R	X	trans:cis	free ligand	cis	trans	cis	trans	cis	trans
CH ₃	Cl	all cis	-20.2	18.88		39.83		39.08	
<i>n</i> -Bu	Cl	all cis	-6.5	30.11		34.59		36.61	
t-Bu	Cl	3.92	27.5	48.97	43.59	21.61	18.43	21.47	16.09
Ph	Cl	all cis	-2.5	26.36		33.07		28.86	
Bzl	C1	all cis	-3.0	33.31		33.26		36.31	
CH,	Br	0.549	-20.2	16.48	8.74	37.46	28.83	36.68	28.94
<i>n</i> -Bu	Br	0.472	-6.5	28.15	19.93	31.17	24.14	34.65	26.43
t-Bu	Br	all trans	27.5		40.39		12.52		12.89
Ph	Br	0.565	-2.5	24.15	17.50	29.34	22.78	26.65	19.99
Bzl	\mathbf{Br}	0.0052	-3.0	30.98	20.32	29.57	22.95	33.98	23.32
CH.	Ν.	all cis	-20.2	17.03		37.21		37.22	20102
t-Bu	N,	0.61	27.5	49.11	46.28	21.56	13.76	21.61	18.78
Ph	N,	all cis	-2.5	26.18		31.40		28.68	10.70
Bzl	N,	all cis	-3.0	31.21		51.56		34.21	

^{*a*} $\Delta\delta({}^{31}P(\text{ligand})) + B$ (see Table VI). ^{*b*} $\Delta\delta({}^{31}P) = \delta({}^{31}P(\text{complex}) - \delta({}^{31}P(\text{ligand})).$

+ $^{n+2}J_{PC}$, and $^{n+2}J_{PC}$ is very small. For the trans complexes, ${}^{2}J_{PP}$ is greater than 150 Hz irrespective of ligand or anion. In addition, the values of ${}^{n}J_{PC}$ and ${}^{n+2}J_{PC}$ follow those for the cis complexes; that is, ${}^{n}J_{PC}$ is positive and large compared to $^{n+2}J_{PC}$, which is very small and either positive or negative. The changes in ${}^{2}J_{PP}$ from cis to trans can be rationalized in terms of a trans influence,^{23,30} and the trends for ${}^{n}J_{PC}$ and ${}^{n+2}J_{PC}$ have been previously noted²⁹ for phosphine complexes.

Examination of Table III yields some interesting information regarding chemical shift trends. Upon coordination, the phosphole ring tertiary carbon (carbons 3,4) chemical shift moves downfield with a concurrent small increase in coupling. The ring secondary carbon (carbons 2,5) chemical shift, however, moves upfield in every case, and the coupling increases greatly. These trends may very well result from $(2p-3d) \pi$ interaction between the phosphorus and the ring butadiene moiety. Support for this statement comes from the observation that the secondary and tertiary carbons of exocyclic *n*-butyl and *tert*-butyl phosphorus substituents do not experience as great (if any) a chemical shift change as do the phosphole ring carbons, and upon coordination ${}^{2}J_{PC}$ increases for exocyclic carbons. It would seem that there is some electron delocalization in the phosphole ring, even for the coordinated phosphole. Quantum mechanics and photoelectron spectroscopy⁷ have indicated the presence of delocalization in the free phosphole ligands.

The chemical shifts for the remaining carbon atoms seem to be much less sensitive to coordination. In most cases coordination to palladium brings increases in P-C coupling for all carbons, falling roughly in the order Br \approx Cl > \dot{N}_3 . This also has been noted for phosphine complexes.²⁹

The assignment of the C_{α} and C_{β} resonances of the 1-*n*butyl-3,4-dimethylphosphole chloride and bromide complexes could not be conclusively made even with selectively decoupled ¹³C{¹H} and "J-scaling"³¹ experiments. Our assignments for these resonances agree with previous assignments³² for butyl phosphine complexes in terms of chemical shifts. The C_y and C_b assignments are unequivocal from ¹³C{¹H} selective decoupling and "J-scaling" experiments. C. ³¹P{¹H} NMR Spectra. The ³¹P{¹H} NMR data (Table

IV) resolve several ambiguities not cleared up by proton and carbon-13 NMR spectroscopy. In most cases where only one isomer is indicated by ¹H or ¹³C¹H NMR, one singlet is

Table	v.	Calculated	and	Observed	δ (³¹ P)	for	the
1-R-3,	4-di	methylpho	spho	les			

R	group contribn ^a	$\delta(^{31}P(calcd))$	δ (³¹ P(exptl))
CH,	-21	-20.2	-20.2
n-Bu	-11	-10.2	-6.5
t-Bu	23	23.8	27.5
Ph	-3	-2.2	-2.5
Bz1	-4	-3.2	-3.0

^{*a*} 3,4-Dimethylphospholyl group contribution is +0.8.

Table VI. Coordination Chemical Shift Equations: $\Delta \delta$ (³¹P) = $A\delta$ (³¹P(Free Ligand)) + B

compd	A	В	r ² a
L = all phospholes	· · · · · · · · · · · · · · · · · · ·		
cis-L ₂ PdCl ₂	0.382	32.11	0.85
cis-L ₂ PdBr ₂	0.459	28.19	0.65
trans-L ₂ PdBr ₂	0.342	21.92	0.92
$cis - L_2 Pd(N_3)_2$	0.328	30.58	0.90
L = phosphines			
cis-L ₂ PdCl ₂	0.212	38.63	0.61-0.91
trans- L_2 PdCl ₂	0.304	26.79	0.69-0.96
$cis-L_2Pd(N_3)_2$	0.440	28.25	0.65-0.98
$trans-L_2Pd(N_3)_2$	0.353	23.47	0.83-0.98

^a The correlation coefficients.

observed in the ${}^{31}P{}^{1}H$ spectrum, while the existence of two isomers gives two singlets. It is noted that the cis resonances are broader than the trans resonances and appear downfield of the trans resonances when both isomers are present in solution. This line-width difference has been observed for phosphine complexes as well.^{33,34} Since ${}^{2}J_{PP}$ for a trans complex is greater than that for a cis complex, it is likely that the trans isomer ³¹P relaxation rate is slower than the cis isomer relaxation rate. Scalar coupling could be an important contributor to the relaxation process,³⁵ and work is in progress to test this hypothesis.

The chemical shifts of the free phospholes ($\delta(^{31}P)$) resemble those of ordinary phosphines at first glance. However, it is unwise to conclude from this that phospholes are like ordinary phosphines. The $\delta(^{31}P)$ of free phospholes are generally shifted downfield¹⁰ relative to normal phosphines. Nonetheless, since

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Table VII. Infrared Spectral Data^{*a*} for $(1-R-3,4-dimethylphosphole)_2 PdX_2$ ($\tilde{\nu}$, cm⁻¹)

				vas ^c	
R	Х	ν_{PdX}	ν_{PdP}	(N ₃)	other vibrations
CH ₃	Cl	294, 338	397, 436		313, 443, 511, 531
n-Bu	Cl	305, 283	396, 466		355, 368, 481, 528, 553
t-Bu	C1	303, 298	385, 418		328, 352, 375, 400, 458,
Ph	Cl	285.310	378.400		411, 475, 495, 536, 555
Bzl	Cl	290, 310	336, 405		489, 519, 532, 567
CH_3	N ₃	334, 532	373, 440	2031, 2043	356, 512, 595, 638
t-Bu	N ₃	363, 540	395, 432	2032, 2045	276, 458, 559, 593 sh, 607
Ph	N ₃	296, 535	380, 404	2032, 2041	271, 357, 389, 475, 497, 554, 595, 616
Bz1	N_3	330, 532	370, 489?	2033, 2044	521, 570, 594, 619
CH3	Br	b	394, 437		330, 375, 403, 488 sh, 510, 529, 600 sh, 615
<i>n</i> -Bu	Br	<i>b</i> .	395, 466		350, 365, 480 sh, 526, 549, 577 sh, 613
t-Bu	Br	b	387,429		279, 363, 458, 536, 603
Ph	Br	Ь	373, 405		273, 456, 473, 495, 534
Bz1	Br	b	396, 404		256, 334, 487, 516, 529, 568, 613 sh, 620

^a Assignments were made consistent with those of D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, J. Chem. Soc. A, 545 (1970); P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, J. Chem. Soc., Dalton Trans., 1298 (1972). ^b These vibrations would occur at or below 200 cm⁻¹, the lower limit of our instrument, and were therefore not observed. ^c Nujol mull and CHCl₃ solution.

the 3,4-dimethyl substitution induces shielding¹⁸ of phosphorus, the resulting ³¹P chemical shifts of 1-substituted 3,4-dimethylphospholes lie nearer to those of ordinary phosphines.

Using the group contributions of Grim et al.²⁷ and taking into account the 3,4-dimethylphospholyl³⁶ group contribution of $+\delta$ 0.8, we predicted the δ (³¹P) for 1-substituted 3,4-dimethylphospholes with good accuracy (Table V). This suggests that the exocyclic phosphorus substituents on these phospholes affect the phosphorus electron density as in normal phosphines.

The ³¹P coordination chemical shifts ($\Delta\delta$ (³¹P)) are also at first glance like those expected for normal phosphine complexes. There have been recent efforts^{24,27,37} to correlate $\Delta\delta$ (³¹P) with δ (³¹P) for a variety of complexes. From these studies a correlation equation of the form $\Delta_{calcd} = A\delta_{free} + B$ was obtained. For the phospholes and their palladium complexes, new values of A and B were calculated (Table VI). The results parallel those of normal phosphine complexes. The full meaning of these observations will be pursued in the Discussion.

The cis:trans ratio, K_{eq} (Table IV), was established by means of ³¹P spectral integration. The phosphorus substituent has a small effect on the isomer population. Note, however, that the chlorides and azides are all cis with the exception of the *tert*-butyl complexes, which are mixtures of isomers. The bromides are also isomeric mixtures with the cis isomer predominating. The *tert*-butyl bromide complex is all trans in solution; however, apparently the enhancement of the trans isomer population for the *tert*-butyl complexes is steric in nature.

Equilibrium energetics of isomerization are presently being investigated and will be reported at a later date.

D. Infrared and Electronic Spectroscopy. The infrared data are given in Table VII. Each of the complexes exhibit two

 Table VIII.
 Interatomic Distances (A) and Angles (Deg) in cis-Dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II)

	Bond D	vistances	
Pd-Cl(1)	2.350 (3)	Pd-P(1) 2	.243 (3)
Pd-Cl(2)	2.356 (3)	Pd-P(2) 2	.238 (2)
P(1) C(11)	1 700 (0)	C(12) - C(13) = 1	441 (15)
P(1) = C(11)	1.733(3)	C(12) - C(15) = 1	556 (14)
P(1) = C(14)	1,791(9) 1,915(0)	C(12) = C(13) = 1 C(12) = C(14) = 1	330(14)
P(1)=C(1A)	1,013 (9)	C(13) - C(14) = 1	5/1(15)
C(11) - C(12)	1.353 (15)	C(13) = C(16) = 1	.511 (10)
P(2)-C(21)	1.793 (1)	C(22)-C(23) 1	.494 (15)
P(2)-C(24)	1.790 (9)	C(22)-C(25) = 1	.495 (15)
P(2)-C(2A)	1.796 (11)	C(23)-C(24) = 1	.334 (15)
C(21)-C(22)	1.338 (14)	C(23) - C(26) = 1	.517 (15)
	Bond	Angles	
Cl(1)-Pd- $Cl(2)$	91.3 (1)	Cl(2)-Pd-P(1)	178.6 (1)
CI(1)-Pd-P(1)	88.90 (9)	Cl(2)-Pd-P(2)	86.0 (1)
C1(1)-Pd-P(2)	172.3 (1)	P(1)-Pd-P(2)	93.43 (9)
$Pd_{-}P(1) - C(11)$	114.8 (3)	C(1) = C(12) = C(13)	116.1 (8)
Pd-P(1)-C(14)	121.6 (3)	C(11)-C(12)-C(15)	121.9 (10)
$Pd_P(1) = C(1 A)$	109.7(3)	C(13)-C(12)-C(15)	122.0(10)
C(11) = P(1) = C(14)	927(5)	C(12) = C(12) = C(14)	114 1 (9)
C(11) = P(1) = C(14)	1075(4)	C(12) = C(13) = C(16)	127(9)
C(14) = P(1) = C(1A)		C(12) = C(13) = C(16)	1212(9)
P(1) C(11) C(12)	109.0(7)	C(14) = C(13) = C(10) C(12) = C(14) = D(1)	1088(7)
F(1)=C(11)=C(12)	100.2 (7)	C(13) - C(14) - I(1)	100.0 (7)
Pd-P(2)-C(21)	121.5 (3)	C(21)-C(22)-C(23)	112.6 (9)
Pd-P(2)-C(24)	109.2 (3)	C(21)-C(22)-C(25)	124.9 (10)
Pd-P(2)-C(2A)	114.1 (4)	C(23)-C(22)-C(25)	122.5 (9)
C(21)-P(2)-C(24)	91.8 (5)	C(22)-C(23)-C(24)	115.0 (8)
C(21)-P(2)-C(2A)	107.2 (5)	C(22)-C(23)-C(26)	121.5 (10)
C(24)-P(2)-C(2A)	110.7 (5)	C(24)-C(23)-C(26)	123.5 (11)
P(2)-C(21)-C(22)	110.6 (7)	C(23)-C(24)-P(2)	109.4 (7)

Pd-P stretching frequencies.³⁸ The chloride and azide complexes exhibit two Pd-X stretches³⁸ (ν_{Pd-Br} occurs below the lower limit of our spectrometer), and the azide complexes exhibit two ν_{as} N₃ vibrations. The observation of two bands for each of these vibrations suggests that all the complexes are cis in the solid state. The Pd-P stretching frequencies occur at the same energy as or higher energy than those observed for similar phosphine complexes, suggesting that the palladium-phosphine bond is as strong if not stronger than palladium-phosphine bonds on the assumption that force constants are linearly related to bond strengths. Similarly, the Pd-X bond energies in the phosphole and similar phosphine complexes are essentially the same, as ν_{Pd-X} is essentially the same for both types of complexes.

The electronic spectral data (Table I) show that the solid state spectra are different than the solution spectra, supporting other spectroscopic data which indicate that geometry changes occur upon dissolution for most of the complexes. However, no clear pattern is evident which would allow the assignment of individual transitions to a particular geometry. Consistent with past experience²⁹ electronic spectra are not very useful for geometry assignment. It was hoped that intraligand π - π * transitions could be used as an indicator of electronic interactions within the phosphole ring and between the phosphole and palladium, but these transitions cannot be assigned with certainty.

E. Description of the Structure of Dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II). The material crystallizes in space group Cc with four discrete molecules per unit cell. There is no crystallographic symmetry imposed on the molecules. A perspective drawing of the complex, depicting the atom numbering scheme, is illustrated in Figure 3. Intramolecular geometric parameters are listed in Table VIII. Atomic positional and thermal parameters for $C_{24}H_{26}P_2PdCl_2$ are listed in Table IX.

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Table IX.	Atomic	Positional	and	Thermal	Parameters	for	C24H2	6P2	PdCl	2,1	D
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atom	x	у	Z	β_{11}^{c}	β	22	β ₃₃	β_{12}	β_{13}	β ₂₃
Pd	0	6074 (1)	2500	82 (1)	30	(1)	21(1)	6 (1)	11(1)	1 (1)
P(1)	-544 (2)	6345 (2)	1142 (2)	59 (2)	30	(1)	23 (1)	8 (1)	3 (1)	0 (1)
P(2)	944 (2)	4777 (2)	2233 (2)	78 (2)	27	(1)	24 (1)	8(1)	3 (1)	0(1)
Cl(1)	-712 (3)	7506 (2)	2831 (2)	143 (3)	35	(1)	34 (1)	25 (2)	20 (2)	-5(1)
Cl(2)	524 (3)	5770 (2)	3928 (2)	175 (4)	48	(1)	19(1)	14 (2)	7(1)	4(1)
C(11)	-1930 (9)	7044 (6)	966 (6)	68 (9)	45	(5)	34 (4)	13 (5)	2 (5)	4 (4)
C(12)	-2782 (9)	6613 (7)	442(7)	77 (9)	51	(6)	44 (5)	28 (6)	10(6)	21 (4)
C(13)	-2390 (9)	5754 (7)	152(6)	76 (9)	48	(5)	30 (4)	-12(6)	5 (5)	9 (4)
C(14)	-1196 (9)	5495 (6)	460 (6)	76 (9)	45	(5)	27 (4)	3 (6)	5 (5)	-1 (3)
C(15)	-4113 (10)	7019 (9)	176 (9)	76 (12) 88	(9)	76 (8)	41 (8)	-19 (8)	10(7)
C(16)	-3177 (12)	5176 (9)	-454 (9)	91 (13) 76	(8)	56 (7)	-12 (8)	-28 (8)	3 (6)
C(21)	1510 (9)	4528 (6)	1214 (5)	103 (11) 43	(5)	19 (4)	21 (6)	3 (5)	-1 (3)
C(22)	2794 (9)	4552 (7)	1230 (7)	85 (10) 41	(5)	43 (5)	12(6)	11 (6)	6 (4)
C(23)	3380 (9)	4711 (6)	2094 (7)	74 (10) 34	(5)	55 (6)	6 (5)	-6 (6)	0 (4)
C(24)	2543 (9)	4781 (6)	2697 (7)	98 (11) 30	(4)	41 (5)	10 (5)	-17 (6)	-4 (3)
C(25)	3583 (12)	4446 (9)	478 (9)	107 (15) 85	(9)	57 (7)	11 (9)	32 (8)	5 (6)
C(26)	4821 (11)	4800 (8)	2251 (11)	57 (11) 59	(7)	103 (11)	-3 (7)	-12 (8)	-9 (6)
atom	x	у	Z	<i>B</i> , Å ²	atom		x	у	Z	<i>B</i> , Å ²
C(1A)	787 (8)	6874 (6)	646 (5)	2.7 (1)	C(2A)	,	74 (13)	3823 (5)	2568 (9)	3.3 (2)
C(1B)	1159 (12)	6620 (8)	-136 (8)	5.2 (2)	C(2B)	-11°	78 (11)	3882 (8)	2808 (8)	5.1 (2)
C(1C)	2204 (13)	7042 (9)	-487 (9)	5.6 (3)	C(2C)	-18	64 (13)	3134 (8)	3041 (9)	5.9 (3)
C(1D)	2800 (10)	7714 (8)	-92 (8)	4.5 (2)	C(2D)	-120	64 (15)	2330 (10)	3042 (10)	7.0 (3)
C(1E)	2444 (14)	7979 (10)	674 (10)	6.9 (4)	C(2E)	10	05 (17)	2254 (11)	2805 (10)	7.6 (4)
C(1F)	1437 (12)	7530 (8)	1072 (8)	5.5 (3)	C(2F)	6	15 (12)	2985 (9)	2562 (8)	5.8 (3)

^a Atoms are labeled as indicated in Figure 3. ^b Standard deviations in the least significant figure are given in parentheses. Except for B, the isotropic temperature factor, all values are $\times 10^4$. ^c The form of the anisotropic thermal ellipsoids is given in the text.





Figure 3. Perspective drawing of *cis*-dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II).

The coordination sphere around the Pd atom is somewhat distorted from ideal square planar, as indicated by a dihedral angle of 7.2° between the planes defined by P(1)-Pd-P(2) and Cl(1)-Pd-Cl(2). This tetrahedral distortion is somewhat less than that of the structurally similar dimethylphenylphosphine complex,³⁹ which exhibits an angle of 8.7° between the analogous planes. The deviations (in Å) of the coordinated atoms from the plane defined by P₂PdCl₂ are as follows: P(1), -0.07; P(2), 0.10; Cl(1), 0.10; Cl(2), -0.07.

The Pd-P bond lengths of 2.238 (3) and 2.243 (3) Å are slightly shorter than that of 2.260 (2) Å found for $(Me_2PhP)_2PdCl_2^{39}$ and are generally somewhat shorter than those in similar phosphorus-containing Pd complexes.⁴⁰ In spite of this, the P(1)-Pd-P(2) angle of 93.93 (9)° in the phosphole complex is slightly less than the value of 97.85 (9)° found for the phosphine complex, indicating that the phosphole ligand is slightly less sterically demanding than the phosphine

Figure 4. Arrangements of palladium and its ligands in dichlorobis(dimethylphenylphosphine)palladium(II) and dichlorobis(1phenyl-3,4-dimethylphosphole)palladium(II).

ligand, which has a cone angle⁴¹ of 122°.

The phenyl and phosphole rings are all planar within experimental error. In addition, the methyl groups on the phosphole ligand lie in the plane of the phosphole ring. The dihedral angle between the phenyl and phosphole rings on P(1) is 70.6° while that on P(2) is 88.5°. The dihedral angle between the phenyl ring on P(1) and the phosphole ring on P(2) is 44.8°, indicating little if any charge transfer between these ligand substituents.

Discussion

We began our study of the coordination behavior of 1substituted 3,4-dimethylphospholes with the idea that they would be poor ligands toward palladium. Previous workers⁴² had shown that 1-methylphosphole and 1-benzylphosphole did not form complexes with divalent nickel. As was mentioned earlier, considerable phosphorus electron delocalization within the phosphole ring should decrease the basicity and therefore the coordinating ability of the phospholes. There is NMR¹⁰ and crystallographic⁴³ data for 1-substituted phospholes which

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is consistent with this interpretation. On the other hand, 1-benzyl-3,4-dimethylphosphole does form a complex⁴² of the type L₂NiCl₂. While we were preparing this paper, Hughes' work¹⁹ appeared with a brief description of nickel(II), palladium(II), and platinum(II) chloride complexes of 1-phenyl-3-methylphosphole and 1-phenyl-3,4-dimethylphosphole. In addition, our present work indicates that, in general, 1-substituted 3,4-dimethylphospholes form stable L_2MX_2 complexes with palladium. It is apparent that substituents on the 3 and 4 positions of the phosphole ring play an important role in phosphole coordination behavior. Substituent effects on the properties of free phospholes have been previously noted.⁶ The effects could be steric² in nature, with the substituents disrupting the ring π system, adversely affecting the electron delocalization in the phosphole ring, and thereby enhancing the availability of the phosphorus lone pair for donation to the metal. This does not explain the fact that 1-substituted 3methylphospholes, which would experience little steric strain in the ring, coordinate to transition metals. Furthermore, the X-ray crystal structure of cis-dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II) shows the ring methyl carbons to be in the same plane as the phosphole ring itself, even though the methyl groups are well within van der Waals radii of each other (2.0 Å calculated for methyl groups⁴⁴ and 1.55 Å radius measured for methyls in this complex). More likely, the enhanced basicity of the phosphorus in these ligands is due to variation of the relative energies of molecular orbitals⁷ (due to ring substitution) which is inductive in nature and would affect the energy of the highest occupied molecular orbital, which is the donor orbital.

Electron delocalization in the phosphole ring would tend to make phospholes poorer bases than normal phosphines. Lack of phosphorus rehybridization upon coordination would make phospholes better bases than phosphines, which do rehybridize. An X-ray structure of 1-benzylphosphole⁴³ shows the molecule to possess a geometry which would enable coordination without phosphorus rehybridization. This tenet is supported by structures^{45,46} of the related dibenzophospholes and their complexes, as well as ¹³C{¹H} NMR⁴⁷ and theoretical studies.⁴⁸

The mean endocyclic P-C bond length in cis-dichlorobis-(1-phenyl-3,4-dimethylphosphole)palladium(II) (1.798 Å) is shorter than the calculated⁴³ P-C sp² single bond length (1.84 Å) and indicates that stabilizing interactions between the phosphorus atom and the butadiene moiety still exist in the coordinated phosphole. (Table X relates some structural features of various phospholes and phosphole complexes to possible aromatic character.) Consequently, donation of the phosphorus lone pair upon coordination should be manifested by a large downfield $\Delta \delta(^{31}P)$. One might also expect to find the effects of exocyclic phosphorus substituents and those of anions on $\Delta\delta(^{31}P)$ of phospholes to be similar to those of phosphines, for which these effects are predominantly inductive. We find that for 1-substituted 3,4-dimethylphosphole complexes of palladium, the latter seems to be the case while the former is not. This apparent discrepancy, as well as other differences in coordination behavior between phospholes and phosphines, can be rationalized through closer inspection of the NMR data.

The ³¹P chemical shifts of the phospholes and their complexes are generally downfield from their phosphine counterparts, which reflects the presence of the electronegative

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Table X. Structural Features of the Phosphole Ring Related to Possible Aromaticity

Compound - by	a (mean) d		Comments	Reference
H V V CH ₂ Ph	1.783	1.858	0.075	Aromatic	43
PhC ₂ Ph Ph Ph	1.809	1.845	0.036	Reduced Aromaticity due to Benzo-Annelation	58
Me Me p PdC12	1,795 1,792	1.815 1.796	0.020 0.004	Weak Residual Aromaticity	This Work
Ph Ph Ph Ph OP Ph	1.810	1.796	0.014	No Aromaticity	56
	c	b (mean)	c-b†	Comments	Reference
Fe	1,414	1.405	0.009	High Aromaticity- Friedel-Crafts C-acylations are possible	55
$\langle \sum_{\substack{n \\ \mu}} \rangle$	1.417	1.382	0.035	5 "	57
↓ CH₂Ph	1.438	1.343	0.095	Weak Aromaticity- No Friedel-Crafts	43
Me Me PdCl ₂	1,441' 1,444	1.362 1.336	0.079 0.108	9 Residual Aromaticity 3	This Work
CH2	1.469	1.342	0.123	No Aromaticity	59
Ph Ph	1.505	1.355	0.150) "	56

For a fully aromatic system, c-b is close to 0. The validity of this structural criterion has been discussed in ref. 43 for heterocyclopentadienes. The authors conclude that this is the best possible criterion.

butadiene moiety. In addition, the further downfield the free phosphole $\delta(^{31}P)$, the smaller the coordination chemical shift $\Delta\delta(^{31}P)$. This observation is consistent with the effects of ligand bulkiness on $\delta(^{31}P)$ and $\Delta\delta(^{31}P)$ as put forth by Tolman.⁴¹ Less bulky ligands within the phospholes series exhibit a higher field $\delta(^{31}P)$, and the magnitude of $\Delta\delta(^{31}P)$ tends to be greater for the smaller ligands than for the larger ones. The data in Table IV substantiate this to a great extent. Also, the slopes of $\Delta\delta(^{31}P)$ vs. $\delta(^{31}P)$ correlations (Table VI) have similar magnitudes for the phosphole and phosphine complexes. This suggests that, toward palladium, the 1-substituted 3,4-dimethylphospholes have Lewis base strengths comparable to those of phosphines.

The ³¹P coordination chemical shift is a measure of the electron-density change about phosphorus upon coordination and for phospholes is among the smallest yet found for phosphorus-containing complexes. Phospholes possess empty antibonding orbitals with the proper symmetry to interact with occupied d_{xy} , d_{xz} , and d_{yz} orbitals on palladium through metal-to-ligand π back-donation. These molecular orbitals are admixtures of the two highest energy butadiene antibonding orbitals and phosphorus d orbitals. If π back-donation is occurring in these complexes, it should strengthen the metal-phosphorus bond, increase electron density on phosphorus relative to no π back-donation, and increase electron density on the phosphole ring α -carbons while having little effect on the remaining carbons in the system. Indeed, the mean palladium-phosphorus bond length in cis-dichlorobis-(1-phenyl-3,4-dimethylphosphole)palladium(II) is 0.0195 Å shorter than that³⁹ in *cis*-dichlorobis(dimethylphenylphosphine)palladium(II). Also, the ¹³C chemical shift of the complexed phosphole ring α -carbons reflects their enhanced

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electron density. Consequently, since $\Delta\delta(^{31}P)$ is much smaller than expected, it would seem likely that some degree of metal-to-ligand π interaction is operative. However, we feel that its contribution to the overall stability of the phosphole complexes is relatively small.

The ¹³C¹H and ¹H NMR data for the phosphole exocyclic substituents do not differ substantially from those for substituents on ordinary phosphines. If phosphole rehybridization is minimal upon coordination, the exocyclic carbon and proton chemical shifts and coupling constants would result primarily from inductive and not steric effects. Since ordinary phosphines do rehybridize⁴¹ upon coordination (except for $\hat{P}F_{3}$,⁴⁹ which contains highly electronegative fluorine in analogy to the electronegative butadiene moiety of phospholes) and exhibit similar carbon and proton chemical shifts and coupling constant trends relative to exocyclic phosphole carbons and protons, this would tend to support Verkade²⁸ in his interpretation that the main effect upon $\delta({}^{31}\text{P})$ as well as upon $\delta({}^{13}\text{C})$ and $\delta(^{1}H)$ is inductive for phosphines.

In light of the data presented here, we feel that the predominant metal-ligand interaction in the palladium phosphole system is a σ bond; however, some π back-bonding is also present. If σ -bonding effects predominate in a strong metal-phosphorus bond, one would expect to see a lengthened metal-chlorine bond in phosphole complexes relative to phosphine complexes.⁵⁰ If π -bonding effects predominate, just the opposite would be expected. The palladium-chlorine bond of cis-dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II) is 0.01 Å shorter than that³⁹ in *cis*-dichlorobis-(dimethylphenylphosphine)palladium(II). Clearly, σ bonding does not, in itself, accurately describe the palladium-phosphole bonding mode.

It has been previously shown^{13,27,29,33,34,51} that cis-L₂PdX₂ complexes are thermodynamically more stable than trans- L_2PdX_2 complexes in cases where L is not bulky; ligands with large steric bulk tend to stabilize the trans isomer. In the case of dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II) (and most likely for the majority of L_2PdX_2 complexes where L = 1-substituted 3,4-dimethylphosphole), the palladium center is most stable in the cis square-planar form (in the solid state). This is most likely due to electronic and not steric effects. Figure 3 illustrates that 1-substituted 3,4-dimethylphospholes may very well be sterically less demanding than their $RP(CH_3)_2$ phosphine analogues, as indicated by the smaller P_1 -Pd- P_2 angle in the phosphole complex. The dihedral angle (between the planes containing P_1 -Pd- P_2 and $Cl_1-Pd-Cl_2$) in the phosphole complex (7.2°) is also smaller than for the $PhP(CH_3)_2$ phosphine complex (8.7°). This suggests that in L_2PdX_2 complexes, the coordination geometry is determined mainly by electronic factors, and relief from steric interaction results in pseudotetrahedrality (an unstable⁵² electronic arrangement for palladium) rather than in the trans isomer, unless the steric interactions are substantial.

It was thought that there might be a stabilizing intraligand charge-transfer interaction between the two phosphole ligands. There is precedence⁴⁶ for this in dibenzophosphole complexes. Analysis of the crystal structure of *cis*-dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II) rules out such an interaction, as the plane of the phenyl group of one ligand is oriented at 44.8° relative to the plane of the phosphole ring of the second ligand.

In conclusion, the data indicate that the palladium-phosphorus bond in 1-substituted 3,4-dimethylphosphole complexes is as strong if not stronger than the Pd-P bond in phosphine complexes. We attribute this to three factors (in order of their importance): (a) there is little or no electronic reorganization of the phosphole phosphorus upon coordination, (b) the phospholes are sterically less demanding than analogous phosphines, and (c) there is a greater possibility of metalphosphorus π back-donation in these phosphole complexes than in phosphine complexes. This last factor is supported by Hall's⁵³ photoelectron spectroscopy studies and Fenske-Hall MO calculations for phosphorus donors possessing electronegative substituents. In addition, there is evidence that some degree of electron delocalization in the phosphole ring is still extant in these coordinated phospholes, but see ref 54.

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Registry No. cis-(1-CH₃-3,4-dimethylphosphole)₂PdCl₂, 72402-81-4; cis-(1-n-Bu-3,4-dimethylphosphole)₂PdCl₂, 72402-82-5; cis-(1-t-Bu-3,4-dimethylphosphole)₂PdCl₂, 72402-83-6; trans-(1-t-Bu-3,4-dimethylphosphole)₂PdCl₂, 72442-15-0; cis-(1-Ph-3,4-dimethylphosphole)₂PdCl₂, 66368-11-4; *cis*-(1-Bzl-3,4-dimethyl-phosphole)₂PdCl₂, 72402-84-7; *cis*-(1-CH₃-3,4-dimethylphosphole)₂PdCl₂, 72402-84-7; $cis-(1-CH_3-3,4-dimethyl-phosphole)_2PdBr_2$, 72402-85-8; $trans-(1-CH_3-3,4-dimethyl-phosphole)_2PdBr_2$ phosphole)₂PdBr₂, 72442-16-1; cis-(1-n-Bu-3,4-dimethylphosphole)₂PdBr₂, 72402-86-9; trans-(1-n-Bu-3,4-dimethylphosphole)₂PdBr₂, 72442-17-2; cis-(1-t-Bu-3,4-dimethylphosphole)₂PdBr₂, 72402-87-0; trans-(1-t-Bu-3,4-dimethylphosphole)₂PdBr₂, 72442-18-3; cis-(1-Ph-3,4-dimethylphosphole)2PdBr2, 72402-88-1; trans-(1-Ph-3,4-dimethylphosphole)₂PdBr₂, 72442-19-4; cis-(1-Bzl-3,4-dimethylphosphole)₂PdBr₂, 72402-89-2; *trans*-(1-Bzl-3,4-dimethylphosphole)₂PdBr₂, 72442-20-7; cis-(1-CH₃-3,4-dimethylphosphole)₂Pd(N_3)₂, 72402-90-5; *cis*(1-*t*-Bu-3,4-dimethyl-phosphole)₂Pd(N_3)₂, 72402-91-6; *trans*-(1-*t*-Bu-3,4-dimethylphosphole) $_2$ Pd(N₃)₂, 72442-21-8; *cis*-(1-Ph-3,4-dimethyl-phosphole) $_2$ Pd(N₃)₂, 72402-92-7; *cis*-(1-Bzl-3,4-dimethyl-phosphole)Pd(N₃)₂, 72402-93-8; 1-CH₃-3,4-dimethylphosphole, 37739-99-4; 1-n-Bu-3,4-dimethylphosphole, 30540-39-7; 1-t-Bu-3,4dimethylphosphole, 38066-25-0; 1-Ph-3,4-dimethylphosphole, 30540-36-4; 1-Bzl-3,4-dimethylphosphole, 38864-30-1; dichlorobis-(benzonitrile)palladium(II), 14220-64-5.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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