containing one heteroatom. The 2-D ^{11}B COSY spectrum shows a cross peak between the resonance at 12.3 ppm (area 1, B(12)) and the resonance at −6.7 ppm (thus assigned to B(7–11)).

The antipodal effect for nido and closo boron cage compounds has been well documented.[12] In general, it is observed, for a given periodic table group (e.g., P, As, Sb, Bi) of hetero boranes, that the more electronegative the heteroatom, the more shielded is the antipodal boron atom of the icosahedral structure. The ^{11}B chemical shift values for the antipodal boron atoms of the As-$B_{11}H_{11}^-$, $SbB_{11}H_{11}^-$, and $BiB_{11}H_{11}^-$ ions are +7.9, +9.4, and +12.3 ppm, respectively, in accord with this generality. For hetero-boranes from different periodic groups, the shielding of the antipodal atom (with the limited data available) appears to decrease in the order group 13 > group 14 > group 15 > group 16. A more detailed discussion on the chemical shift trends of group 14–16

icosahedral heteroatom boranes will be published in the near future.

Thermal Properties. In the solid state, none of the compounds melts up to 500 °C. **2** starts darkening above 250 °C, while **1** and **3–5** darken above 350 °C. Thus, these compounds are much more stable thermally than known lead-containing carboranes[5,6] but not as thermally stable as group-15 boranes containing one or two group-15 atoms other than bismuth in the cage. With the exception of **2**, however, they are surprisingly heat stable.

Contribution from the Departments of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2, and Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Phosphoranimine Phosphines and Arsines as Heterodifunctional Coordinating Ligands. Synthesis and Characterization of New Palladium(II) Metallacycles $\overline{RN=PPh_2(CH_2)_nEPh_2}PdCl_2$ (R = SiMe₃, GeMe₃, H; *n* = 1, 2; E = P, As) and the Crystal and Molecular Structure of $\overline{HN=PPh_2CH_2PPh_2}PdCl_2$, the First Structural Example of a Phosphoranimine Phosphine Complex

K. V. Katti,[†] R. J. Batchelor,[‡] F. W. B. Einstein,[‡] and R. G. Cavell[*,†]

Reaction of the *N*-(trimethylsilyl)- or *N*-(trimethylgermyl)phosphoranimine phosphines Me₃ENPPh₂CH₂PPh₂ (E = Si, Ge) or the *N*-(trimethylsilyl)phosphoranimine arsine Me₃SiNPPh₂CH₂CH₂AsPh₂ with PdCl₂(PhCN)₂ gave metallacyclic Pd^{II} derivatives $\overline{Me_3ENPPh_2(CH_2)_nQPh_2}PdCl_2$ (Q = P, *n* = 1, E = Si or Ge; Q = As, *n* = 2, E = Si). Water reacts with Me₃Si-$\overline{NPPh_2CH_2PPh_2}PdCl_2$ to form the parent imine complex $\overline{HNPPh_2CH_2PPh_2}PdCl_2$ (**12**), the structure of which has been determined. (Crystal data for **12** (as a 1:1 adduct with CH₂Cl₂): monoclinic $P2_1/n$ (No. 14), *a* = 8.953 (3) Å, *b* = 21.151 (4) Å, *c* = 14.773 (2) Å, β = 93.98 (2)°, *Z* = 4, final *R*(F) = 0.034, R_w(F) = 0.037.) The imine ligand adopts an "envelope" five-membered chelate ring configuration bonded at N and P. The Pd—N (2.021 (6) Å) and N═P (1.599 (6) Å) bond lengths are in accord with expectations for Pd—N single and P═N double bonds. The nitrogen atom is pyramidal. **12** is also formed by reaction of Me₃SiNPPh₂CH₂PPh₂ with K₂PdCl₄ in the presence of water. Activated fluoroaromatics (e.g. pentafluorobenzonitrile) replace Me₃Si or Me₃Ge groups on the ligand framework by elimination of Me₃SiF and attachment of the fluoroaromatic exclusively at the para position. Full spectral characterization of all complexes is given. The Me₃Ge phosphoranimine phosphine shows conformational behavior similar to that of the Me₃Si analogue reported earlier. All conformers in the mixture however give a metal complex with only one conformation. We also describe a more efficient synthesis of Me₃GeN₃, which was developed in the course of the study.

Introduction

Synthesis of appropriate heterodifunctional ligands for development of homogeneous catalyst applications[1] is often the major barrier to progress; frequently the synthesis of ligands with chemically diverse donating (or bonding) atoms requires multistep manipulations with concomitantly poor yields or difficult separations. An example is the partial oxidation of dppm to the catalytically useful ligand Ph₂PCH₂P(O)Ph₂, which involves a multistep sequence of reactions employing organolithium or Grignard reagents.[2] Additional advantages would be provided by the possibility of easily making modifications to the reactivity of the ligand by systematic alteration of its substituents, a flexibility that could strongly influence the design of catalytic complexes with appropriate chemical selectivity and stereoselectivity.
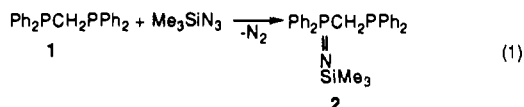
We recently reported a new approach to the preparation of heterodifunctional ligands based on the partial oxidation of di-phosphines such as dppm (**1**) by means of a Staudinger reaction with Me₃SiN₃ (eq 1).[3a] This reaction represents the first example

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‡ Simon Fraser University.

(1) For leading references illustrating the catalytic potential of different types of heteroatomic chelated transition-metal compounds, see: (a) Kraft, M. E.; Wilson, L. J.; Onan, K. D. *Organometallics* **1988**, *7*, 2528. (b) Anderson, M. P.; Casalnuovo, A. L.; Johnson, B. J.; Mattson, B. M.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 1649. (c) Wang, H. H.; Casalnuovo, A. L.; Johnson, B. J.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 325. (d) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167. (e) Wegman, R. W.; Abatjoglou, A. G.; Harrison, A. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1891. (f) Bonnet, M. C.; Stitou, B.; Tkatchenko, I. *J. Organomet. Chem.* **1985**, *279*, C1. (g) Brunner, H.; Rahman, A. F. M. M. *Chem. Ber.* **1984**, *117*, 710. (h) Organ, G. J.; Cooper, M. K.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1984**, 2377. (i) Breque, A.; Santini, C. C.; Mathey, F.; Fischer, J.; Mitschler, A. *Inorg. Chem.* **1984**, *23*, 3463. (j) Roundhill, D. M.; Bechtold, R. A.; Roundhill, S. G. N. *Inorg. Chem.* **1980**, *19*, 284.
(2) (a) Grim, S. O.; Satek, L. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1975**, *14*, 656. (b) Carr, S. W.; Colton, R. *Aust. J. Chem.* **1981**, *34*, 35. (c) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982.

$$Ph_2PCH_2PPh_2 + Me_3SiN_3 \xrightarrow{-N_2} Ph_2PCH_2PPh_2$$

$$\underset{\mathbf{1}}{} \qquad\qquad \underset{\mathbf{2}}{\begin{array}{c} \| \\ N \\ SiMe_3 \end{array}} \tag{1}$$
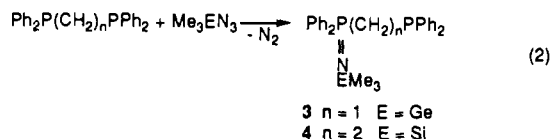
of the partial oxidation of an alkane diphosphine with a nitrogen base. The reaction is also applicable to the selective oxidation of phosphorus in the mixed arsenophosphine ARPHOS and to diphosphines of various alkane chain lengths.[4,5] In addition, a reactive functionality, e.g. the $SiMe_3$ group, remains on the phosphoranimine nitrogen in the product and is available for additional transformations.

Our initial studies[3a,6] with this ligand system have demonstrated its versatility toward forming M–N σ bonds to both "early" and "late" transition metals and binding to metals in both high and low oxidation states. Replacement of the Me_3Si group with active fluoroaromatics can be easily accomplished to introduce a dimension of basicity control that cannot be attained with the existing partially oxidized dppm type derivatives Ph_2PCH_2P-$(Z)PPh_2$ (Z = O, S, Se) and related ligands.[7]

Herein we report extensions of the system with the synthesis of new phosphoranimine phosphines (Q = P) and arsines (Q = As) of the general form $RN=PPh_2(CH_2)_nQPh_2$ and the preparation of a series of Pd(II) complexes of these ligands. The crystal and molecular structure of one new complex, $HN=PPh_2CH_2PPh_2PdCl_2$, representing the first example of a structurally characterized phosphoranimine–phosphine chelate, is reported.

Results

Reaction of bis(diphenylphosphino)methane (1) with azidotrimethylgermane in the absence of solvents at the melting point temperature of the former gave 3 in almost quantitative yields (eq 2; n = 1, E = Ge). The procedure is similar to that used

$$Ph_2P(CH_2)_nPPh_2 + Me_3EN_3 \xrightarrow{-N_2} \underset{\begin{array}{c} \| \\ N \\ EMe_3 \end{array}}{Ph_2P(CH_2)_nPPh_2} \tag{2}$$

$$\begin{array}{l} \mathbf{3}\ n=1\ E=Ge \\ \mathbf{4}\ n=2\ E=Si \end{array}$$

previously for the silyl analogue.[3a] The synthesis of the germyl compound was aided by the development of an improved synthetic route to Me_3GeN_3: the reaction of NaN_3 with Me_3GeCl in hexamethylphosphoramide (HMPA) followed by reduced-pressure distillation gave much improved yields of the azide compared to the previously reported[8] procedure, which involved an aqueous workup step.

Similar synthetic procedures with trimethylsilyl azide and bis(diphenylphosphino)ethane gave 4 (eq 2; n = 2, E = Si). The arsenic analogue $Me_3SiN=PPh_2CH_2CH_2AsPh_2$ (5) was prepared via an analogous reaction described earlier.[4] The new heterodifunctional ligands 3 and 4 are air-stable crystalline solids and are monomeric in solution. Their composition was established by mass spectrometric and C, H, and N analytical data.

Spectroscopic data are given in Table I. The ^{31}P NMR data, which show the essential P^{III}, P^V construction of the ligand, are discussed in more detail below. The ^{29}Si (INEPT) spectra of ligands 2, 4, and 5 consist of doublets centered around −11 to −13 ppm showing a $^2J_{PSi}$ of 19–20 Hz with the iminato phosphorus.
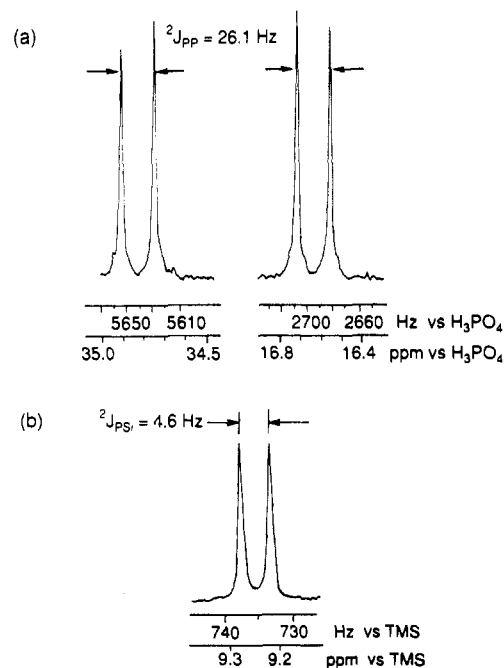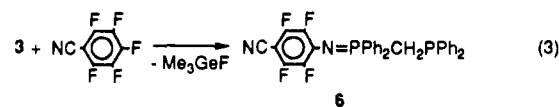
(3) (a) Katti, K. V.; Cavell, R. G. *Inorg. Chem.* **1989**, *28*, 413. (b) Related methylene-bridged phosphoraniminato phosphines with phenyl, methyl, and trifluoromethoxy substituents on phosphorus have been prepared via deprotonation of CH_3 on P followed by treatment with Ph_2PCl: Roy, A. K.; Neilson, R. H.; Wisian-Nelson, P. *Organometallics* **1987**, *6*, 378.
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(7) (a) Reference 1. (b) Higgins, S. J.; Taylor, R.; Shaw, B. L. *J. Organomet. Chem.* **1987**, *325*, 285. (c) Belgroune, F.; Braunstein, F.; Grandejean, D.; Matt, D.; Novel, D. *Inorg. Chem.* **1988**, *27*, 3320.
(8) Thayer, J. S.; West, R. *Inorg. Chem.* **1964**, *3*, 889.

Figure 1. (a) $^{31}P\{^1H\}$ NMR (161.98-MHz) spectrum of 7 in $CDCl_3$. (b) ^{29}Si INEPT NMR (79.5-MHz) spectrum of 7 in $CDCl_3$.

Scheme I
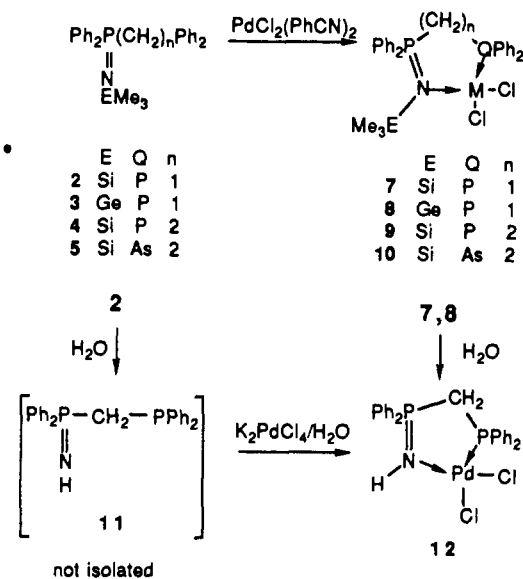
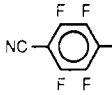No long-range couplings with the trivalent phosphorus were observed.

The smooth replacement of the $SiMe_3$ functionality in the silylphosphoranimines demonstrated earlier[4] also occurs for the $GeMe_3$ series of ligands. Thus, reaction of 3 with pentafluorobenzonitrile gave 6 in virtually quantitative yield:

$$\mathbf{3} + NC\underset{F\ F}{\overset{F\ F}{\bigcirc}}F \xrightarrow{-Me_3GeF} NC\underset{F\ F}{\overset{F\ F}{\bigcirc}}N=PPh_2CH_2PPh_2 \tag{3}$$

$$\mathbf{6}$$

Reactivity of 2–5 with $PdCl_2(PhCN)_2$: Formation of Pd(II) Heteroatomic Metallacyclic Chelates. The heterodifunctional ligands 2–5 react cleanly with $PdCl_2(PhCN)_2$ in dichloromethane to afford new heteroatomic Pd(II) metallacyclic chelates in almost quantitative yields (Scheme I). The new metallacycles 7–10 are air-stable crystalline compounds that are monomeric in solution. Their composition was established by C, H, and N analytical and multinuclear NMR spectroscopic data (Table I). The $^{31}P\{^1H\}$ NMR spectra of 7–9 (spectrum of 7 is shown in Figure 1a) consisted of doublets of an AX spin system with the phospho-

Table I. Phosphorus-31[a] and Silicon-29[b,c] NMR Spectroscopic Data for Phosphoranimine Phosphines and Their Metal Complexes

	σ_{PIII}	σ_{PV}	$^2J_{PP}$, Hz	σ_{Si}	$^2J_{PSi}$, Hz	$^3J_{PSi}$, Hz
Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$ (2)[d]	−28.20	−1.38	57.7	−12.78	21.8	
Me$_3$GeN=PPh$_2$CH$_2$PPh$_2$ (3)	−27.55, −27.78, −28.08	6.08, 6.04	57.0			
Me$_3$SiN=PPh$_2$(CH$_2$)$_2$PPh$_2$ (4)	−11.96	3.50	48.6	−11.33	19.6	
Me$_3$SiN=PPh$_2$(CH$_2$)$_2$AsPh$_2$ (5)[e]		1.83		−13.21	20.2	
NC–⟨◯⟩–N=PPh$_2$CH$_2$PPh$_2$ (6)[c] (F,F / F,F)	−30.12	13.04	53.6			
Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$PdCl$_2$ (7)	16.64	34.81	26.2	9.28	4.6	
Me$_3$GeN=PPh$_2$CH$_2$PPh$_2$PdCl$_2$ (8)	17.89	36.56	29.2			
Me$_3$SiN=PPh$_2$(CH$_2$)$_2$PPh$_2$PdCl$_2$ (9)	20.67	31.51	11.6	10.07	4.7	
Me$_3$SiN=PPh$_2$(CH$_2$)$_2$AsPh$_2$PdCl$_2$ (10)		32.84		10.15	5.1	
HN=PPh$_2$CH$_2$PPh$_2$ (11)	−28.25	21.45	57.2			
HN=PPh$_2$CH$_2$PPh$_2$PdCl$_2$ (12)	25.18	53.80	30.0			
Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$Rh(CO)Cl (13)[f]	37.4	24.36	31.1	6.04	5.2	
Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$W(CO)$_4$ (14)[e]	18.17	40.02	48.9	4.26	7.1	3.9
Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$Mo(CO)$_4$ (15)[e]	27.22	33.29	50.8	2.26	6.9	3.1

[a] All spectra in CDCl$_3$; ppm vs 85% H$_3$PO$_4$. Values quoted are those determined at normal probe temperatures. [b] All spectra in CDCl$_3$; ppm vs SiMe$_4$. [c] Spectra recorded by using INEPT technique. [d] Data from ref 3a; shift values for the recrystallized material are given. [e] Data from ref 4. [f] Data from ref 5.

raninimine units resonating at low fields (31–36 ppm) compared to the phosphine centers (17–20 ppm) Table I). The chemical shift of the phosphoranimine phosphorus (32.84 ppm), which is the only phosphorus center in **10**, agrees well with the chemical shifts of similar functionalities in **7–9**. The ^{29}Si NMR spectra in the silicon-containing complexes **7, 9,** and **10** (the spectrum of **7** is shown in Figure 1b) consisted of a deshielded doublet signal due to the coupling with the phosphine phosphorus (–PPh$_2$) across two bonds (Table I).

Reaction of **2** in a mixed aqueous/organic solvent system with Pd(II) salts presumably proceeds with the initial hydrolysis of the silylated compound to form the free imine **11**, which then complexes in situ with the metal to form the imine complex **12** as the only product (Scheme I). The ^{31}P{^{1}H} NMR spectrum of the reaction mixture recorded immediately after the complete addition of **2** to an aqueous solution of K$_2$PdCl$_4$ consisted of two sets of doublet of doublet signals of an AX spin pattern centered at 25.18, 53.80 ppm ($^2J_{PP}$ = 30 Hz) and −28.25, 21.45 ppm ($^2J_{PP}$ = 57 Hz), respectively. The former AX set of signals can be assigned to the Pd(II) metallocycle **12**, and the latter can be assigned to the free phosphoranimine HN=PPh$_2$CH$_2$PPh$_2$ (**11**) generated from the hydrolysis of the N–Si bond in **2**, an assignment confirmed by independent hydrolysis experiments on **2**. ^{31}P{^{1}H} spectroscopic analysis of aliquots extracted at different times during the reaction of **2** with K$_2$PdCl$_4$ confirmed that **2** is hydrolyzed to the free imine prior to its coordination with Pd(II). For an alternative route, the silyl and germyl complexes **7** and **8** were smoothly converted to **12** by means of aqueous hydrolysis.

The imine complex **12** represents the first example of a compound containing a phosphoranimine phosphine ligand. The composition was established by satisfactory C, H, and N analyses. Molecular weight determinations indicated that the complex was monomeric in solution. The presence of the N–H functionality was clearly indicated by the IR peak (ν_{NH}) at 3340 cm^{-1}. The ^{31}P NMR spectrum of **12** consisted of two doublets of an AX spin system centered at 53.80 and 25.18 ppm, assigned to the pentavalent and trivalent phosphorus atoms, respectively.

Crystal and Molecular Structure of 12. The structure comprises the neutral monomeric complex HNPPh$_2$CH$_2$PPh$_2$PdCl$_2$ and cocrystallized molecules of methylene chloride (crystal data) are in Table II). The complex, shown in Figure 2, contains Pd in a typical square-planar environment with the (NHPPh$_2$CH$_2$PPh$_2$) ligand chelating in a cis fashion via N and P(1) to form a five-membered ring. Only disordered sites (see Experimental Section) are involved in intermolecular distances apparently less than van der Waals distances.
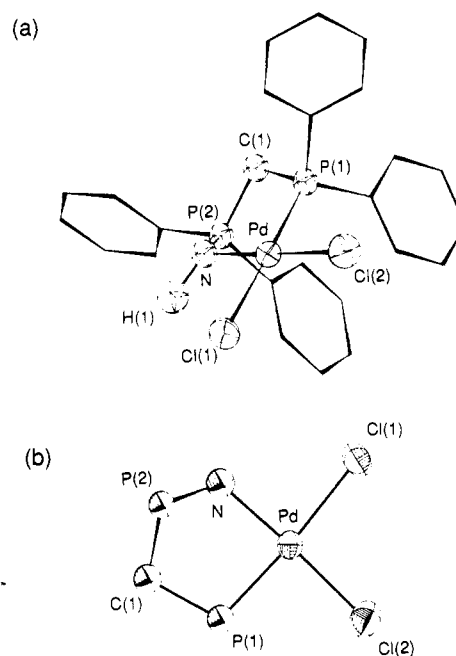
(a)

(b)

Figure 2. (a) Molecular structure of **12**, showing the central atoms and numbering scheme of the complex. All atoms are shown on this SNOOPI diagram as 20% ellipsoids except substituent phenyl rings, which are shown in stylized hexagons. (b) View of the central fragments of the molecule. All atoms shown except P(2), which forms the "flap" of an envelope, are essentially coplanar. (Cl(1) shows a small out-of-plane bend toward H(1) (see text).)

Table II. Crystallographic Data for **12**

chem formula	PdCl$_4$P$_2$NC$_{26}$H$_{25}$	space group	$P2_1/n$ (No. 14)
a, Å	8.953 (3)	λ, Å	0.710 69
b, Å	21.151 (4)	ρ_{calcd}, g cm^{-3}	1.575
c, Å	14.773 (2)	μ(Mo Kα), cm^{-1}	11.72
β, deg	93.98 (2)	transm	0.748–0.862
V, Å^3	2790.7	$R(F_o)^a$	0.034
Z	4	$R_w(F_o)^b$	0.037
fw	661.6		

[a] $R(F_o) = \sum(|F_o| - |F_c|)/\sum|F_o|$ for 2296 observed data ($F_o \geq s\sigma(F_o)$). [b] $R_w(F_o) = [\sum(w(F_o - F_c)^2)/\sum(wF_o^2)]^{1/2}$.

Least-squares plane analysis shows that Pd, N, Cl(2), P(1), and C(1) are coplanar. The maximum deviation from the plane calculated for these five atoms is 0.001 Å. P(2) deviates from

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for [Cl$_2$PdP(C$_6$H$_5$)$_2$CH$_2$P(C$_6$H$_5$)$_2$NH]·CH$_2$Cl$_2$

Distances			
Pd–Cl(1)	2.375 (2)	Pd–Cl(2)	2.319 (2)
Pd–P(1)	2.224 (2)	Pd–N	2.021 (6)
P(1)–C(1)	1.842 (7)	P(1)–C(11)	1.802 (7)
P(1)–C(21)	1.797 (8)	P(2)–N	1.599 (6)
P(2)–C(1)	1.805 (7)	P(2)–C(31)	1.800 (7)
P(2)–C(41)	1.790 (7)	N–H(1)	0.76 (7)

Angles			
Cl(2)–Pd–Cl(1)	94.61 (7)	P(1)–Pd–Cl(1)	175.35 (8)
P(1)–Pd–Cl(2)	89.94 (8)	N–Pd–Cl(1)	88.4 (2)
N–Pd–Cl(2)	177.0 (2)	N–Pd–P(1)	87.1 (2)
C(1)–P(1)–Pd	105.5 (2)	C(11)–P(1)–Pd	115.8 (2)
C(11)–P(1)–C(1)	103.5 (3)	C(21)–P(1)–Pd	116.3 (2)
C(21)–P(1)–C(1)	105.2 (3)	C(21)–P(1)–C(11)	109.1 (3)
C(1)–P(2)–N	100.7 (3)	C(31)–P(2)–N	116.2 (3)
C(31)–P(2)–C(1)	107.9 (3)	C(41)–P(2)–N	111.1 (3)
C(41)–P(2)–C(1)	112.2 (3)	C(41)–P(2)–C(31)	108.5 (3)
P(2)–N–Pd	115.4 (3)	H(1)–N–Pd	111 (1)
H(1)–N–P(2)	114 (1)	P(2)–C(1)–P(1)	105.1 (3)
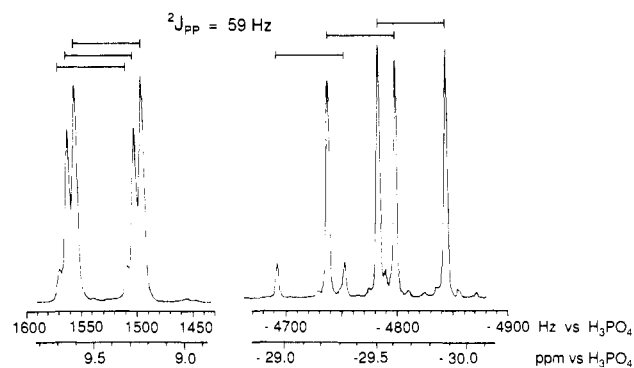
Figure 3. ^{31}P{^{1}H} NMR (161.98-MHz) spectrum of **3** prepared at 140 °C and dissolved in CDCl$_3$. The spectrum was measured at –40 °C in order to sharpen the lines of the P^{III} region signals. The chemical shift scale has not been corrected for temperature-dependent shifts of reference and lock signals.

this plane by 0.792 Å, forming the "envelope flap" of the five-membered ring. Interestingly, Cl(1) also deviates from the plane by 0.052 Å. The reason for this might be an attractive interaction between Cl(1) and H(1) (2.80 (7) Å) and/or a repulsive interaction between Cl(1) and H(34)' (bound to C(34)) (2.86 Å; prime indicates equivalent position $^1/_2 + x$, $^1/_2 - y$, $-^1/_2 + z$). The H(1)–N–Pd–Cl(1) torsion angle is 14°. The geometry about N is pyramidal rather than planar, as shown by the deviation of H(1) from the Pd–N–P(2) plane by 0.54 Å.

Important bond lengths and angles are listed in Table III, and positional parameters, in Table IV.

Discussion

Conformations of Phosphoranimine Phosphines Me$_3$EN= PPh$_2$CH$_2$PPh$_2$ (E = Si, Ge). The previous proposal that **2** as prepared exists as a mixture of conformational isomers[3a] is further reinforced by the comparable behavior of **3**. The ^{31}P NMR spectrum of a solution of **3** prepared from the raw product (Figure 3) consisted of closely spaced doublet structures within each major region arising from the P(V) and P(III) centers. The correspondence of relative intensity and coupling constants of these doublets in the A and X regions confirms that the P–C–P unit has been preserved in all cases. As is similar to the situation for **2**[3a] the P(V) chemical shift differences between the various conformers of **3** were very small whereas larger differences exist within the P(III) sets. Also, parallel to the situation with **2** the relative proportions of the conformers are dependent on the temperature of the preparation reaction. Four different conformers were identifiable throughout the temperature range evaluated (140–200 °C), and in Figure 4 the comparison of the 140 and 180 °C distribution shows the difference in relative intensities typical of the system. The conformational distribution is dictated by the

Table IV. Atomic Coordinates (×10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 × 10^4) for [Cl$_2$PdP(C$_6$H$_5$)$_2$CH$_2$P(C$_6$H$_5$)$_2$NH]·CH$_2$Cl$_2$^{a}

atom	x/a	y/b	z/c	U(iso)
Pd	477.9 (6)	1300.5 (3)	2111.8 (4)	362
Cl(1)	2910 (2)	1754 (1)	2235 (1)	535
Cl(2)	1250 (2)	331 (1)	2709 (1)	602
Cl(3)^b	5892 (9)	1202 (6)	7180 (8)	1348
Cl(4)^b	7715 (22)	1481 (6)	8709 (11)	1764
Cl(5)^c	6059 (17)	1255 (9)	7010 (11)	1282
Cl(6)^c	8195 (28)	1505 (7)	8495 (16)	1452
P(1)	–1873 (2)	954.9 (9)	1983 (1)	387 (4)
P(2)	–1951 (2)	2320.0 (9)	1850 (1)	357 (4)
N	–308 (7)	2128 (3)	1588 (4)	430 (16)
C(1)	–2989 (7)	1620 (3)	1499 (5)	409 (17)
C(11)	–2708 (7)	794 (3)	3034 (4)	368 (16)
C(12)	–4220 (8)	639 (4)	3035 (5)	503 (19)
C(13)	–4868 (9)	572 (4)	3849 (5)	596 (22)
C(14)	–4048 (9)	668 (4)	4656 (6)	593 (22)
C(15)	–2550 (8)	810 (4)	4662 (5)	540 (21)
C(16)	–1881 (8)	869 (3)	3852 (5)	481 (19)
C(21)	–2256 (7)	307 (3)	1216 (4)	516 (20)
C(22)^d	–2757 (10)	–272 (4)	1512 (8)	757
C(23)^d	–2927 (11)	–770 (6)	914 (8)	901
C(24)^d	–2614 (9)	–711 (6)	27 (9)	798 (35)
C(25)^d	–2085 (11)	–139 (5)	–244 (9)	901
C(26)^d	–1903 (10)	369 (5)	341 (6)	757
C(52)^e	–3614 (20)	298 (14)	679 (12)	894 (89)
C(53)^e	–4067 (34)	–142 (11)	19 (15)	848 (87)
C(54)^e	–3074 (29)	–615 (14)	–127 (18)	798 (35)
C(55)^e	–1687 (31)	–657 (13)	349 (14)	848 (87)
C(56)^e	–1349 (29)	–191 (7)	999 (16)	894 (89)
C(31)	–2179 (7)	2442 (3)	3039 (4)	367 (16)
C(32)	–923 (8)	2517 (3)	3627 (5)	465 (18)
C(33)	–1068 (9)	2594 (4)	4545 (5)	582 (22)
C(34)	–2454 (9)	2586 (4)	4871 (6)	654 (24)
C(35)	–3719 (10)	2499 (4)	4309 (6)	661 (23)
C(36)	–3589 (9)	2425 (4)	3381 (5)	549 (21)
C(41)	–2609 (7)	3008 (3)	1241 (4)	396 (17)
C(42)	–2441 (8)	3025 (4)	311 (5)	491 (19)
C(43)	–2845 (8)	3569 (4)	–172 (5)	588 (22)
C(44)	–3400 (9)	4075 (4)	242 (5)	601 (22)
C(45)	–3594 (9)	4064 (4)	1150 (6)	666 (24)
C(46)	–3183 (8)	3523 (4)	1653 (5)	550 (21)
C(2)^b	7785 (9)	1363 (10)	7527 (10)	1117 (53)
C(3)^c	6754 (28)	983 (12)	8092 (12)	1117 (53)
H(1)	264 (74)	2390 (33)	1665 (44)	530 (16)

^{a} Hydrogen atoms other than H(1) given as supplementary material in Table S1. ^{b} Site occupancy 0.601 (13). ^{c} Site occupancy 0.399 (13). ^{d} Site occupancy 0.725 (9). ^{e} Site occupancy 0.275 (9).
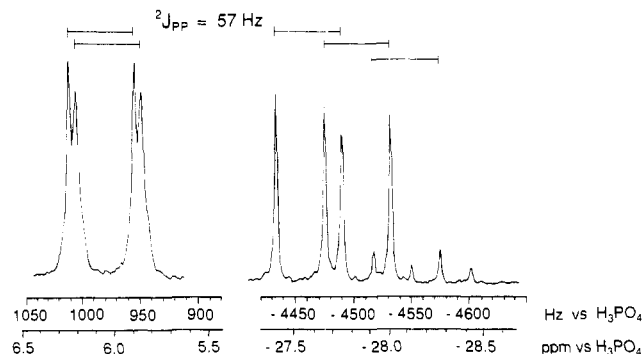
Figure 4. ^{31}P{^{1}H} (161.98-MHz) NMR spectrum of **3** obtained by heating the sample to 180 °C during the preparation step. The spectrum was measured on a CDCl$_3$ solution at normal probe temperature (~30 °C).

highest temperature reached during the synthesis, and the distribution is preserved on dissolution in the NMR solvent but not after recrystallization, and so the barriers to interchange must be fairly large.

We surmise that the conformational distribution of rotamers existing in these products (e.g., Figure 5) arises because of a
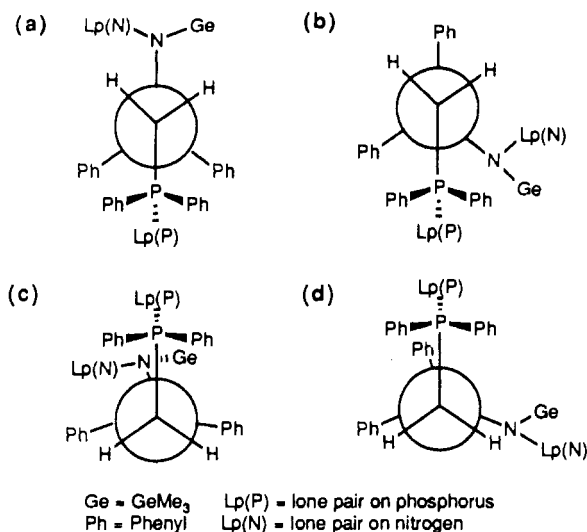
(a)

Lp(N) N Ge

H H

Ph Ph

Ph P Ph

Lp(P)

(b)

Ph

H H

Ph

Lp(N)

Ph P Ph Ge

Lp(P)

(c)

Lp(P)

Ph P Ph

Lp(N) N Ge

Ph Ph

H H

(d)

Lp(P)

Ph P Ph

Ph

Ph Ge

H H N

Lp(N)

Ge = GeMe₃   Lp(P) = lone pair on phosphorus
Ph = Phenyl   Lp(N) = lone pair on nitrogen

Figure 5. Modified Newman projections illustrating some possible conformations of **3**.

restricted rotation about the backbone of the molecule.

In contrast to the case for **2**,[3a] where stirring in acetonitrile was sufficient, the conversion to a single conformation was not easily accomplished for **3** by either thermal or solvent (THF, CH₃CN, toluene) treatment. However like **2**, the conformer mixture **3** reacted with Pd(II) salts to yield a product that apparently exists in only one conformation. Likewise, conversion of the conformer mixture **3** to **6** gave, according to the NMR spectra, a product with only one conformational isomer.

Phosphoranimine Phosphine Complexes of Pd[II]. Phosphineimides of the type [:NPR₂R′]⁻, which are isoelectronic with phosphine oxides, OPR₃, have been extensively utilized in recent years as 1-, 2-, or 4-electron donors to "early" or "late" transition metals and also to actinides.[3a,9–13]

The phosphoranimine phosphines **2–4** and the arsine **5** react readily with PdCl₂(PhCN)₂ to form the complexes **7–10**, which demonstrate the bifunctionality of the ligand by the formation of chelate complexes. These chelates show, in the ³¹P NMR spectra, a more pronounced deshielding of the P(V) unit compared to the P(III) center, presumably as a consequence of the greater electron donation to the metal from the P(V) center via the imine nitrogen. Parallel behavior has been previously recorded[4–6] in a number of related metallocycles. Significant deshielding of the SiMe₃ signals is also apparent in the silylated complexes (**7, 9, 10**), and this is accompanied by a marked decrease of ²J_PSi relative to that the free ligands. Although the Pd(II) center is two bonds removed from both the Me₃Si substituent and the P(V) atom, it seems to exert a profound influence on these centers in terms of significant withdrawal of electron density through the Si—N—Pd[II] and Ph₂P=N—Pd[II] frameworks. Comparison of ²⁹Si NMR shifts of these Pd(II) complexes with data obtained for a Rh(I) complex[5] (in **13**) shows that the parameters are essentially identical. Significant differences arise when metallacycles of the early transition metals such as W(0) (**14**) or Mo(0) (**15**) (see Table I)[4] are compared with the late-metal complexes. These metallacycles of the early transition metals also showed a unique Si–P coupling with the diphenylphosphide (PPh₂) unit across three bonds via the metal centers that did not occur in complexes of the late transition metals. This difference may be rationalized

by invoking an easier delocalization of electron density through the Si–N–M–PPh₂ framework, which is possible with the electron-poor Mo(0) or W(0) centers compared to the electron-rich Pd(II) or Rh(I) late transition metals, where the electron density is more likely to be localized on the metal centers. Such heteronuclear coupling interactions across the metal centers may provide a useful insight into bonding interactions in metallacyclic systems, however, more detailed study is required before definitive conclusions can be reached.

Very marked deshielding is noted for both the P(III) and P(V) centers in **12**, wherein the substituent on N is only a H atom. This may be rationalized by the higher basicity of the nitrogen in this case, which assists the delocalization of electron density toward the metal. A similar effect is expected in **5** or **8**, however, the ability of the Si or Ge substituents to participate in π bonding may moderate the delocalization toward the Pd(II) center. Schweizer et al.[14] have postulated similar models to account for ¹³C NMR behavior of a large number of phosphoranimines. Intriguing possibilities arise from the reactivity of the NH functionality in **12**. Notable, early-transition-metal halides such as CpTiCl₃ eliminate HCl with the formation of a Ti–N σ bond.[17] Further details on this aspect of the reactivity of NH in **12** with the metal and non-metal halides are presently being studied.

The longer Pd–Cl(1) (Table III) bond length compared to Pd–Cl(2) is consistent with the greater trans influence of P compared to N. The Pd–N bond length (2.021 (6) Å) is reasonable for a single coordinate-covalent bond. The structure of the phosphineimide can be represented as a resonance hybrid of the double-bond form (A) and the dipolar form (B). The N–P(2)

—P = N   ⟷   —P⁻δ⁺ — N⁻δ⁻

A   **B**
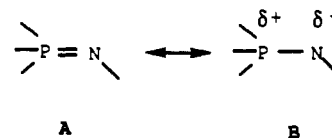
bond length in **12** (1.599 (6) Å) is within the range of values for covalent radii (1.64 Å)[15a] for a double bond and is not significantly different from those of [N(PPh₃)₂]⁺ (1.60 Å),[15b] Ph₂FP=NMe (1.64 Å),[15c] and Ph₃P=NC₆H₄Br-p (1.567 Å).[15d] Therefore, the value of the N–P(2) bond length observed in **12** indicates a large contribution from the double-bond form (A) and little or no contribution from the dipolar form (B). The P–C bond lengths fall within the normal range for single covalent bonds. The P(1)–C(1) bond length is slightly but significantly longer than the others, as might well be expected with sp³ hybridization for both of these atoms. The Pd–P bond length for **12** is in the range found for (dppm)PdCl₂,[16] (dppe)PdCl₂,[16] and (dppp)PdCl₂[16] complexes. The cis geometry of the NHPPh₂CH₂PPh₂ ligand around the square-planar Pd(II) center found in **12** is similar to that reported for the Rh(I) complex[1e] of a phosphine oxide phosphine ligand, Ph₂PCH₂P(O)Ph₂, which is isoelectronic to our phosphoranimine phosphine ligand in **12**.

Experimental Section

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^{1}H, ^{31}P, and ^{29}Si NMR spectra were obtained on a Bruker WH400 instrument (operating at 400.13, 161.97, and 79.50 MHz, respectively) using SiMe$_4$, 85% H$_3$PO$_4$, and SiMe$_4$, respectively, as the external standards. An INEPT sequence was employed to enhance signals in the ^{29}Si NMR spectra.[19] In all the spectroscopic studies CDCl$_3$ was used as the solvent and as an internal lock. Positive shifts lie downfield of the standard in all cases. Solution molecular weight measurements were performed in dibromomethane solution with a Mechrolab 301A vapor-phase osmometer.

Modified Synthesis of Azidotrimethylgermane, N$_3$GeMe$_3$. A fine powder of sodium azide (5.0 g; 76.92 mmol) was introduced into a three-necked, round-bottomed flask containing HMPA (50 mL) and equipped with a dropping funnel and water-cooled reflux condenser. Trimethylchlorogermane (10 g, 65.33 mmol) was added to the powdered azide dropwise over a period of 30 min with stirring at room temperature. At the end of 3 h, the reaction flask was arranged for distillation at reduced pressure. Trimethylgermanium azide distilled as a colorless liquid at 30 °C (0.15 mmHg). Repeated distillation of this crude product gave pure Me$_3$GeN$_3$ (yield 9.25 g, 88%). Anal. Calcd for C$_3$H$_9$N$_3$Ge: C, 22.56; H, 5.68; N, 26.30. Found: C, 22.52; H, 5.65; N, 26.31.

Synthesis of Me$_3$GeN=PPh$_2$CH$_2$PPh$_2$ (3). A slurry of dppm (5.00 g; 13.00 mmol) in Me$_3$GeN$_3$ (2.18 g; 13.65 mmol) placed in a 100-mL round-bottomed flask was heated with stirring in an oil bath maintained at 140 °C. After 8 h of heating, the clear melt was cooled to give a waxy material, which, when dissolved in CH$_3$CN and cooled to 0 °C, gave crude 3. Repeated recrystallization from dry CH$_3$CN gave analytically pure 3 (yield 5.15 g, 76%; white microcrystalline; mp 76 °C). Anal. Calcd for C$_{28}$H$_{31}$NP$_2$Ge: C, 65.11; H, 6.00; N, 2.71. Found: C, 65.10; H, 5.95; N, 2.69. ^{1}H NMR (CDCl$_3$): phenyl rings, δ 7.30, 7.55, 7.80 (m, 20 H); PCH$_2$P methylene, δ 3.06, 3.08 (d, 2 H, $^2J_{P^VH}$ = 13.0, 13.15 Hz). MS (EI, m/z): 516 (M$^+$, 100%). Solution mol wt: calcd, 516; found, 521.

Synthesis of Me$_3$SiN=PPh$_2$(CH$_2$)$_2$PPh$_2$ (4). A slurry of dppe (3.510 g; 8.81 mmol) in Me$_3$SiN$_3$ (1.063 g; 9.24 mmol) placed in a 100-mL round-bottomed flask was heated with stirring in an oil bath maintained at 150 °C. After 8 h of heating, the clear melt was cooled to give a viscous oil, which, when dissolved in CH$_3$CN and cooled to 0 °C, gave crude 4. Repeated recrystallization from CH$_3$CN produced pure 4 (yield 3.35 g, 78%; white microcrystalline; mp 85 °C). Anal. Calcd for C$_{29}$H$_{33}$NP$_2$Si: C, 71.69; H, 6.79; N, 2.88. Found: C, 71.50; H, 6.82; N, 2.85. ^{1}H NMR (CDCl$_3$): phenyl rings, δ 7.31, 7.60, 7.82 (m, 20 H); PCH$_2$CH$_2$P, δ 2.22 (m, 2 H), 2.35 (m, 2 H); Si(CH$_3$)$_3$, 0.05 (s, 9 H). MS (EI, m/z): 485 (M$^+$, 100%). Solution mol wt: calcd, 485.40; found, 490.

Reaction of 3 with Pentafluorobenzonitrile. Pentafluorobenzonitrile (0.220 g; 11.39 mmol) was added, via a syringe, to a solution of 3 (0.560 g; 10.85 mmol) in dry toluene (50 mL). The reaction mixture was refluxed for 12 h, and then the solvent was removed in vacuo to leave a pale yellow solid. The crude product was crystallized from acetonitrile to give pure 6 (yield 65%; pale yellow needle-shaped crystals; mp 188 °C). Anal. Calcd for C$_{32}$H$_{22}$F$_4$N$_2$P$_2$: C, 67.10; H, 3.84; N, 4.89. Found: C, 67.05; H, 3.80; N, 4.87. MS (EI, m/z): 572 (M$^+$). The ^{1}H and ^{19}F NMR spectroscopic and the analytical data are in full agreement with an authentic sample of 6 obtained by us[4] from the reaction of Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$ (2) with pentafluorobenzonitrile.

Synthesis of Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$PdCl$_2$ (7). A solution of 2 (2.255 g; 4.78 mmol) in dry dichloromethane (50 mL) was added drop-wise at 25 °C to a solution of PdCl$_2$(PhCN)$_2$ (1.835 g; 4.78 mmol) also in dichloromethane (20 mL). The mixture was stirred for 4 h, after which the solvent was removed in vacuo to yield a pale yellow crystalline solid, 7. This crude compound was crystallized from CH$_2$Cl$_2$-hexane (2:1) to obtain the analytically pure dichloromethane adduct of 7 (yield 2.97 g, 84%; pale yellow cubic crystals; mp 220 °C dec). Anal. Calcd for C$_{29}$H$_{33}$NP$_2$Cl$_4$PdSi: C, 47.46; H, 4.50; N, 1.90; Cl, 19.33. Found: C, 47.39; H, 4.42; N, 1.93; Cl, 19.31. ^{1}H NMR (CDCl$_3$): phenyl rings, δ 7.30, 7.57, 7.80 (m, 20 H); PCH$_2$P methylene, δ 3.77 (t, 2 H, $^2J_{PH}$ = 11.00 Hz); Si(CH$_3$)$_3$ δ 0.03 (s, 9 H).

The metallacycles 8–10 were prepared by a procedure similar to that described above for 7.

Me$_3$GeN=PPh$_2$CH$_2$PPh$_2$PdCl$_2$ (8). Recrystallization of the crude material was achieved from a CH$_2$Cl$_2$-hexane (2:1) mixture to obtain pure 5·CH$_2$Cl$_2$ (yield 1.75 g, 76%; brown microcrystalline; mp 205 °C dec). Anal. Calcd for C$_{29}$H$_{33}$Cl$_4$GeNP$_2$Pd: C, 44.71; H, 4.24; N, 1.79; Cl, 18.22. Found: C, 44.40; H, 4.11; N, 1.74; Cl, 18.17. ^{1}H NMR

(CDCl$_3$): phenyl rings, δ 7.25, 7.60, 7.85 (m, 20 H); PCH$_2$P methylene, δ 3.75 (t, 2 H, $^2J_{PH}$ = 10.75 Hz); Ge(CH$_3$)$_3$, δ 0.05 (s, 9 H).

Me$_3$SiN=PPh$_2$(CH$_2$)$_2$PPh$_2$PdCl$_2$ (9). A mixture of CH$_2$Cl$_2$-hexane (2:1) was used to obtain a microcrystalline analytically pure dichloromethane solvate of 9 (yield 1.41 g, 76%; dark brown microcrystalline; mp 195 °C dec). Anal. Calcd for C$_{30}$H$_{35}$Cl$_4$NP$_2$PdSi: C, 54.49; H, 5.29; N, 2.11; Cl, 21.46. Found: C, 54.36; H, 5.33; N, 2.14; Cl, 21.70. ^{1}H NMR (CDCl$_3$): phenyl rings, δ 7.30, 7.62, 7.87 (m, 20 H); PCH$_2$CH$_2$P, δ 2.20 (m, 2 H), 2.65 (m, 2 H); Si(CH$_3$)$_3$ δ 0.04 (s, 9 H).

Me$_3$SiN=PPh$_2$(CH$_2$)$_2$AsPh$_2$PdCl$_2$ (10). The crude product was purified by crystallization from CH$_2$Cl$_2$-hexane (2:1), which gave an analytically pure dichloromethane solvate of 10 (yield 2.01 g, 77%; pale yellow microcrystalline; mp 190 °C dec). Anal. Calcd for C$_{30}$H$_{35}$Cl$_4$NAsPPdSi: C, 45.50; H, 4.42; N, 1.76; Cl, 17.92. Found: C, 45.44; H, 4.39; N, 1.69; Cl, 17.87. ^{1}H NMR (CDCl$_3$): phenyl rings, δ 7.29, 7.55, 7.85 (m, 20 H); PCH$_2$CH$_2$As, δ 2.20 (m, 2 H), 2.62 (m, 2 H); Si(CH$_3$)$_3$, 0.03 (s, 9 H).

Synthesis of HN=PPh$_2$CH$_2$PPh$_2$PdCl$_2$ (12). A solution of 2 (2.750 g; 5.83 mmol) in dry acetonitrile (25 mL) was added dropwise to a solution of K$_2$PdCl$_4$ (1.905 g; 5.83 mmol) in distilled water (5 mL). The reaction mixture turned turbid after an addition of a few drops of 2, but after most of 2 was added the solution became clear and homogeneous. The solution was stirred for 1 h, and then the solvents were removed in vacuo to obtain a pale yellow residue, which was then extracted with dichloromethane (3 × 25 mL). Removal of dichloromethane from the combined extracts in vacuo yielded pale yellow crystalline 12. The crude 12 was recrystallized from CH$_2$Cl$_2$-hexane (3:1) to give an analytically pure dichloromethane solvate of 12 (yield 2.50 g, 64%; pale yellow cubic crystals; mp 310 °C dec). Anal. Calcd for C$_{26}$H$_{25}$Cl$_4$NP$_2$Pd: C, 47.18; H, 3.78; N, 2.11; Cl, 21.44. Found: C, 47.09; H, 3.69; N, 2.09; Cl, 21.37. ^{1}H NMR (CDCl$_3$): phenyl rings, δ 7.31, 7.56, 7.82 (m, 20 H); PCH$_2$P methylene, δ 3.55 (ddd, 2 H; $^2J_{P^VH}$ = 11.91 Hz; $^2J_{P^{III}H}$ = 9.77 Hz; $^4J_{HH}$ = 1.79 Hz (NH–CH)). A procedure similar to that described above was used to obtain 12 from 3 and K$_2$PdCl$_4$. Yield of 12:57%. The analytical and spectroscopic data for this product were the same as given above.

Preparation of HN=PPh$_2$CH$_2$PPh$_2$PdCl$_2$ (12) from the Hydrolysis of Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$PdCl$_2$ (7) or Me$_3$GeN= PPh$_2$CH$_2$PPh$_2$PdCl$_2$ (8). Almost quantitative yields of 12 were obtained by allowing solutions of 7 or 8 in acetonitrile to interact with methanol at room temperature. Typically, distilled methanol (20 mL) was added to a solution of 7 (1.50 g; 2.04 mmol) in acetonitrile (25 mL) and the solution was stirred at room temperature for 4 h before the solvent was then removed in vacuo to give analytically pure 12 in almost quantitative yield. The analytical and spectroscopic data of the product as obtained were in full agreement with those listed above for 12.

Crystal Structure Determination of 12. A crystal (0.15 × 0.23 × 0.26 mm) of PdCl$_2$(P(C$_6$H$_5$)$_2$CH$_2$P(C$_6$H$_5$)$_2$NH)·CH$_2$Cl$_2$ was mounted on a Pyrex filament with 5-min epoxy resin. Intensity data were collected with an Enraf Nonius CAD-4F diffractometer using graphite-monochromated Mo Kα radiation. The unit cell was determined from 25 well-centered reflections (16.1° ≤ θ ≤ 19.2°). Two intensity standards were measured every 1.33 h of acquisition time. These showed no significant deviations during the course of data acquisition. The data (2° ≤ 2θ ≤ 45°) were corrected analytically for absorption.[20] Data reduction was performed, including intensity scaling and Lorentz and polarization corrections.

The position of the Pd atom was determined from the Patterson map, and most of the remaining non-hydrogen atoms were found from a subsequent Fourier synthesis, showing positional disorder of the methylene chloride molecule. An electron density difference synthesis also revealed disorder of one of the phenyl groups. Both this phenyl group and the methylene chloride molecule were modeled with two orientations having refined occupancies the sum of which was constrained to 1 in each case (see Table IV). C–Cl and Cl–Cl distance restraints for the methylene chloride molecule as well as C–C distance restraints and planarity restraints for each disordered orientation of the phenyl group were applied to the coordinate shifts from the least-squares refinement. Anisotropic thermal parameters were refined for the Pd and Cl atoms. Further electron density difference synthesis revealed many but not all of the H atoms as well as peaks indicative of more complex disorder in the phenyl group mentioned above. Anisotropic thermal parameter refinement for the meta and ortho carbon atoms of the phenyl orientation having the higher occupancy effectively removed the latter peaks. The two ortho carbon atoms were assigned a single set of refined anisotropic thermal parameters, as were the pair of meta carbon atoms. The difference

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between the mean-squared displacements of the meta and ortho C atoms was restrained to 0 along their bond. While the anisotropic thermal parameters for these carbon atoms, as well as those of the chlorine atoms of the methylene chloride, model the actual electron density rather well, their magnitudes and extreme anisotropies suggest unresolved disorder rather than normal thermal motion. The disorder of the phenyl group involves different rotational conformations about the P(1)–C(21) bond. More complex models were considered.

The hydrogen atoms were, in general, placed in calculated positions, and the shifts of their coordinates during least-squares refinement were linked to those of the carbon atoms to which they were bonded. The one exception to this was H(1) (bonded to N), which was refined independently. A single isotropic thermal parameter was refined for the two H atoms of the methylene bridge in the chelate (H(2) and H(3)), another for the H atom sites of the methylene chloride (H(4)–H(7)), and one for all the H atoms of the phenyl groups. The root mean square |shift/esd| was 0.01, while the largest |shift/esd| was 0.08, for the final full-matrix least-squares refinement of 215 parameters for 2296 observations ($F_o \leq 5.0\sigma(F_o)$) and 32 restraints. The largest peak in the final difference map was 0.4 (4) e Å^{-3}. With unit weights, $w(|F_o| - |F_c|)^2$ was near constant as a function of both $|F_o|$ and $(\sin\theta)/\lambda$.

Complex scattering factors for neutral atoms[21] were used in the calculation of structure factors. The programs used for data reduction, structure solution and refinement were from ref 22. The program suite CRYSTALS[23] was employed in the final stages of refinement involving the use of restraints. Diagrams were generated with the program SNOOPI.[24] All computations were carried out on a MicroVAX-II computer.

Listings of full experimental details, coordinates and temperature factors for the hydrogen atoms, other than H(1), anisotropic temperature

factors, and observed and calculated structure factors are deposited as supplementary material.

Summary and Conclusion

One phosphorus atom of bis(diphenylphosphino)methane and its ethane homologue can be cleanly oxidized with trimethylsilyl or trimethylgermyl azide. As prepared, the resultant methylene-bridged phosphoranimine phosphines appear to exist as conformational isomers in the case of the Me₃Si and Me₃Ge derivatives, but only one form was shown by the fluoroaromatic derivative (readily obtained from the reaction of the silyl or germyl precursors with an activated fluoroaromatic) and the free imine (obtained by mild hydrolysis of the original silyl and germyl ligands). These new ligands readily formed P,N chelate complexes with Pd(II), and regardless of the conformational complexity of the ligand, only one complex was formed. Conducting the complexation reaction in water (or hydrolysis of the Me₃Si- or Me₃Ge-containing complexes of Pd(II)) gives the Pd(II) complex of the parent imine. The structural characterization of this complex showed a chelate with normal bonding features.

This work demonstrates that the heterodifunctional ligand system formed by controlled oxidation of the one phosphorus center in a diphosphine readily forms stable chelate complexes with the prototypical late-transition-metal Pd(II) center. A variety of substitutional changes can be made to the ligand that allow basicity at nitrogen to be modified. In addition, parallel chemistry can be developed by the higher homologue and by the related phosphoranimine arsine. Further extensions to the chemistry of this versatile system are in progress.

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Syntheses and Properties of [Cu{B₂H₄·2P(CH₃)₃}₂]X (X = Cl, I) and X-ray Crystal Structure of the Iodide

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Chloride and iodide salts of bis{bis(trimethylphosphine)tetrahydrodiboron-H^1,H^2}copper(I), [Cu{B₂H₄·2P(CH₃)₃}₂]X (X = Cl, I), were prepared by the reactions of B₂H₄·2P(CH₃)₃ with the copper(I) halides. X-ray crystal structure analysis of the iodide shows that each ligand is coordinated to the copper atom through two vicinal hydrogen atoms and the copper atom is ligated with four hydrogen atoms tetrahedrally. Crystal data: monoclinic with the space group $I2/a$, $a = 13.003$ (1) Å, $b = 16.257$ (2) Å, $c = 12.974$ (3) Å, $\beta = 92.63$ (1)°, $V = 2739.7$ (8) Å³, $Z = 4$, and $R(F_o) = 0.057$ for 1676 reflections with $|F_o| > 3\sigma(F_o)$.

Introduction

Although quite a large number of metallaboranes or metal complexes of boron hydrides have been reported,[1-4] most of them are neutral or anionic, and only a small number of cationic boron hydride complexes are known, i.e. [Fe(CO)₃(B₅H₁₀)]⁺,[5] [Co-

(CO)₃(B₅H₉)]⁺,[5] [Cu₂(PPh₃)₄(BH₄)]⁺,[6] and [NiL(BH₄)]⁺ (L = cyclic tetramine or noncyclic quadridentate Schiff base).[7] This is due to the fact that only anionic boron hydrides are known to be good ligands and is parallel to the scarcity of cationic boron hydrides[8] in contrast to the abundance of neutral and anionic boron hydrides.

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