the N- and CH-bridged complexes show no such asymmetry in solution. This may well be a steric effect, and the molecular mechanics calculations[15] will hopefully provide information on this unusual observation.

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Registry No. 1, 114378-75-5; **2**, 114378-78-8; **3**, 114378-72-2; PCl_3, 7719-12-2; $[Ru(DMF)_6](tos)_2$, 114378-79-9; tris(2-pyridyl)methane, 77429-58-4; bis(2-pyridyl)methane, 1132-37-2; 2-bromopyridine, 109-04-6; tris(2-pyridyl)phosphine, 26437-48-9; $[Ru\{(2\text{-}py)_3N\}_2](tos)_2$, 114466-50-1.

Supplementary Material Available: Tables S1–S12, listing thermal parameters, the derived hydrogen positions, and bond distances and angles for **1–3** (12 pages); Tables S13–S15, listing calculated and observed structure factors for **1–3** (44 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Unusual Bonding in the Secondary Aminophosphine $[HP\{N(SiMe_3)_2\}_2]_2$: X-ray Structures and NMR and IR Studies of the Main Group V Amino Compounds $HE(NR_2)_2$ ($E = P, As, R = SiMe_3; E = P, R = Ph$)

Marilyn M. Olmstead, Philip P. Power,* and Gary A. Sigel

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Crystal structures of the secondary aminophosphines and -arsines $[HP\{N(SiMe_3)_2\}_2]_2$ (**1**), $HAs\{N(SiMe_3)_2\}_2$ (**2**), and $HP(NPh_2)_2$ (**3**) are described. In addition, the synthesis of $HP\{N(C_6H_{11})_2\}_2$ (**4**) is given, along with spectroscopic data for **2–4**. The dimeric structure of **1** features a unique, planar, P_2H_2 core with hydrogen bridging of the P atoms. Each phosphorus atom has a distorted-tetrahedral geometry with P–H distances averaging 1.73 Å and P–N bond lengths averaging 1.818 Å. In contrast, compound **2**, the arsenic analogue of **1**, is monomeric. The As–N distances are 1.879 (3) and 1.874 (4) Å; N–As–N is 106.5 (1)°. Complex **3** is also monomeric, with no short intermolecular contacts. Crystallographic data with Mo Kα radiation ($\lambda = 0.71069$ Å) at 130 K: (**1**) $a = 13.629$ (13) Å, $b = 18.210$ (7) Å, $c = 17.755$ (14) Å, $\beta = 91.84$ (7)°, monoclinic, space group $P2_1$, $Z = 4$, $R = 0.049$; (**2**) $a = 8.805$ (8) Å, $b = 11.252$ (10) Å, $c = 12.944$ (10) Å, $\alpha = 66.73$ (6)°, $\beta = 85.34$ (7)°, $\gamma = 69.63$ (6)°, $Z = 2$, triclinic, space group $P\bar{1}$, $R = 0.047$; (**3**) $a = 9.925$ (6) Å, $b = 38.632$ (18) Å, $c = 10.368$ (5) Å, orthorhombic, space group *F2dd*, $Z = 8$, $R = 0.036$.

Introduction

Primary and secondary aminophosphines are often unstable under ambient conditions due to amine elimination and formation of ill-characterized phosphorus polymeric species. However, kinetic stabilization of these compounds can be achieved by using bulky amino substituents.[1-6] Thus, the compounds $HP(NR_2)_2$, R = *i*-Pr, Ph, or $SiMe_3$, have been synthesized in relatively good yield by the reduction of the $ClP(NR_2)_2$ precursor by $LiAlH_4$.[2-6] Detailed structural information on transition-metal complexes of some aminophosphines has been provided by King and co-workers.[7,8] However, no structures are currently available for the ligands themselves. Previously, we reported that $HP\{CH(SiMe_3)_2\}_2$ (isoelectronic with $HP\{N(SiMe_3)_2\}_2$) underwent an unusual rearrangement in its reaction with $Rh(\eta^4\text{-}1,5\text{-cyclooctadiene})(\eta^3\text{-}2\text{-Me-}C_3H_4)$.[9] Similar work on $HP\{N(SiMe_3)_2\}_2$ (**1**) was in progress when large crystals were observed growing from the samples of the ligand as neat liquid. An X-ray structure determination of a crystal of **1** showed that it had a unique dimeric structure. This prompted us to investigate its arsenic analogue **2** and the aryl derivative $HP(NPh_2)_2$ (**3**). In this paper the first structural characterizations of secondary aminophosphine and -arseine complexes are described for **1–3**. Also reported are spectroscopic data and additional information on a related compound $HP\{N(C_6H_{11})_2\}_2$ (**4**).

Experimental Section

General Procedures. All reactions were performed with modified Schlenk techniques under an inert atmosphere of N_2. Solvents were freshly distilled from drying agents and degassed before use. The compound $HP\{N(SiMe_3)_2\}_2$ (**4**) and the precursors $ClAs\{N(SiMe_3)_2\}_2$[10] and $ClP(NPh_2)_2$[11] were synthesized by published procedures.

Physical Methods. Infrared spectra were recorded on an IBM IR/32 spectrometer. ^{31}P NMR spectra were obtained on an NT-200 FT NMR spectrometer operating at 81 MHz. All values are reported in ppm relative to an external standard of 85% H_3PO_4 or TMS.

$[HP\{N(SiMe_3)_2\}_2]_2$ (1). After distillation of **1**, slow cooling afforded colorless crystals suitable for X-ray diffraction studies. Spectroscopic data have been previously reported.[2,4]

$HAs\{N(SiMe_3)_2\}_2$ (2). $ClAs\{N(SiMe_3)_2\}_2$ (27 g, 62.5 mmol) in Et_2O (200 mL) was added dropwise to a slurry of $LiAlH_4$ (1.18 g, 31.25 mmol) in Et_2O (10 mL) at −78 °C. The solution was allowed to warm to room temperature overnight and stirred for a further 24 h. Filtration to remove the brown precipitate, followed by removal of the solvent under reduced pressure, produced a yellow oil. The oil was extracted into *n*-hexane (50 mL) and filtered. Removal of the solvent, followed by distillation under reduced pressure (bp 74–84 °C/0.1 mm), afforded a colorless oil (13.1 g, 53% yield). Slow cooling of the oil to −20 °C gave colorless crystals suitable for X-ray diffraction studies. ^1H NMR (neat): δ 0.3 (36 H, $SiMe_3$), 7.2 (1 H). IR (As–H): 2041, 1928 cm^{-1}. Analogous to the

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preparation of **2**, reduction of $ClAs\{N(SiMe_3)_2\}_2$ with $LiAlD_4$ in ether afforded $DAs\{N(SiMe_3)_2\}_2$ (**5**). ^1H NMR (neat): δ 0.3. IR (As–D): 1465 cm^{-1}.

$HP(NPh_2)_2$ (3). Although the preparation of $ClP(NPh_2)_2$ has been previously described,[11] we report an alternative method via metal–halogen exchange. Addition of PCl_3 (3.43 g, 25 mmol) in Et_2O (20 mL) to $LiNPh_2$ (60 mmol, from 10 g of $HNPh_2$ and 37.5 mL of 1.6 M *n*-BuLi in hexane in Et_2O (100 mL) gave an immediate reaction, shown by the formation of LiCl. The solution was stirred overnight and filtered. The solvent was removed under reduced pressure and the material extracted into *n*-hexane (50 mL) and refiltered. Removal of the solvent under reduced pressure afforded the crude product, $ClP(NPh_2)_2$ (3.0 g, 30% yield). ^{31}P NMR: δ 123.8. $LiAlH_4$ (0.27 g, 7.2 mmol) was added to $ClP(NPh_2)_2$ (3 g, 7.5 mmol) in Et_2O (70 mL) at −78 °C. The solution was allowed to warm slowly to room temperature and then filtered. Removal of the solvent under reduced pressure, followed by extraction into *n*-hexane (50 mL), gave a yellow solution. A reduction in volume of 50% under reduced pressure and filtration, followed by slow cooling to −20 °C, yielded colorless crystals (0.56 g, 21% yield (6.3% overall)). ^{31}P NMR: δ 69.14 (J_{P-H} = 256 Hz).

$HP\{N(C_6H_{11})_2\}_2$ (4). $ClP\{N(C_6H_{11})_2\}_2$ was prepared by dropwise addition of PCl_3 (5.27 mL, 60 mmol) in Et_2O (10 mL) to a stirred solution of $LiN(C_6H_{11})_2$ (from $HN(C_6H_{11})_2$ (21.0 g, 120 mmol) and *n*-BuLi (72.1 mL)) in Et_2O (100 mL) at −78 °C. After warming to room temperature, the solution was refluxed for 30 min. Filtration and the removal of solvent under reduced pressure, followed by extraction with hexane and another filtration, gave an amber solution. Removal of *n*-hexane under reduced pressure gave crude $ClP\{N(C_6H_{11})_2\}_2$ as an amber oil (26.45 g, 62% yield). ^{31}P -NMR: δ 144. At −78 °C, $LiAlH_4$ (1.42 g, 37.56 mmol) was added in portions to $ClP\{N(C_6H_{11})_2\}_2$ (16.45 g, 37.56 mmol) in Et_2O (70 mL). After the mixture was stirred for 3 days, the Et_2O was removed under reduced pressure at 0 °C to yield a yellow material. Extraction into *n*-hexane (10 mL), filtration, and then cooling of the resulting light orange solution yielded the product as colorless crystals (4.5 g, 30% yield). ^{31}P NMR: δ 126.0 (J_{P-H} = 251 Hz).

X-ray Crystallographic Studies. All X-ray data were collected with a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 device. Calculations were carried out on a Data General Eclipse computer using the SHELXTL programs, version 4. The atom form factors and corrections for anomalous scattering were from ref 12.

Colorless prisms of $[HP\{N(SiMe_3)_2\}_2]_2$ (**1**) were obtained as described and protected from air by a layer of hydrocarbon oil. A crystal was selected and placed in 5-min epoxy resin (Devcon) without hardener, attached to a glass fiber on a mounting pin, and immediately placed in the low-temperature N_2 stream. The space group was determined to be either $P2_1$ or $P2_1/m$ by the condition $0k0$, $k = 2n$. Attempts to solve the structure by direct methods in both space groups led to the successful solution and refinement of **1** in $P2_1$ and not $P2_1/m$. There are two crystallographically independent dimers in the asymmetric unit. The data were corrected for absorption effects.[13] Handedness was not determined. In the final cycles of refinement, phosphorus and silicon atoms were refined anisotropically. All hydrogen atoms except those on phosphorus were included at calculated positions with a riding model. Isotropic thermal parameters were fixed at 1.2 times that of the bonded carbon, and the C–H distance was fixed at 0.96 Å. The hydrogen atoms on phosphorus were located in the final difference map. They appear among the 10 largest features in the difference map at heights of 0.5 e $Å^{-3}$. Other peaks in this size range correspond to methyl hydrogens, which could not be included due to the 200-atom restriction of SHELXTL. Further details of data collection and refinement are given in Table I.

Colorless needles of $HAs\{N(SiMe_3)_2\}_2$ (**2**) were obtained by slow cooling of the neat liquid to −20 °C. Crystals were kept at −20 °C and transferred to a precooled hydrocarbon oil. A crystal was selected, attached to glass fiber on a mounting pin, and immediately placed in the low-temperature N_2 stream. The structure was solved by the Patterson technique. In the final cycles of refinement, all non-hydrogen atoms were refined anisotropically. Hydrogens except those on arsenic were included by using the riding model described for **1**. The hydrogen bonded to arsenic was located on a difference map, and its coordinates were fixed in the final cycles of refinement. Further details of data collection and refinement are in Table I.

X-ray data on $HP(NPh_2)_2$ (**3**) were obtained in a manner identical with that for **2**. The structure was solved by direct methods in the orthorhombic space group $F2dd$. The phosphorus atom lies on a crystallographic 2-fold axis. All hydrogens except that on phosphorus were included at calculated positions with the riding model described for **1**. The hydrogen atom on phosphorus was located on a difference map and found to be statistically disordered between two symmetry-related sites, thereby requiring an occupancy of 0.5. Its positional and thermal parameters were allowed to refine. Further details are given in Table I. The atomic coordinates and isotropic temperature factors for complexes **1** and **3** are given in Table II.

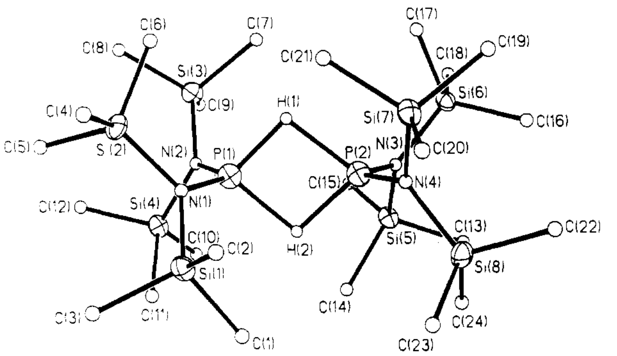

Figure 1. Computer-generated drawing (probability level of thermal ellipsoids 50%) of **1**, showing one of the two molecules in the asymmetric unit. Carbon, nitrogen, and hydrogen atoms have been given an arbitrary size.

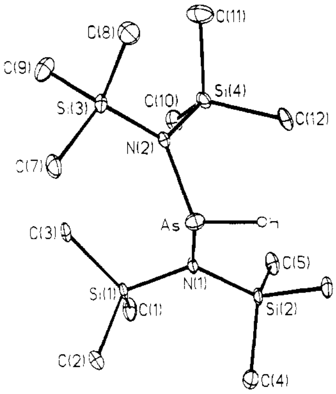

Figure 2. Computer-generated drawing (probability level 35%) of **2**. Hydrogen is drawn at an arbitrary size.

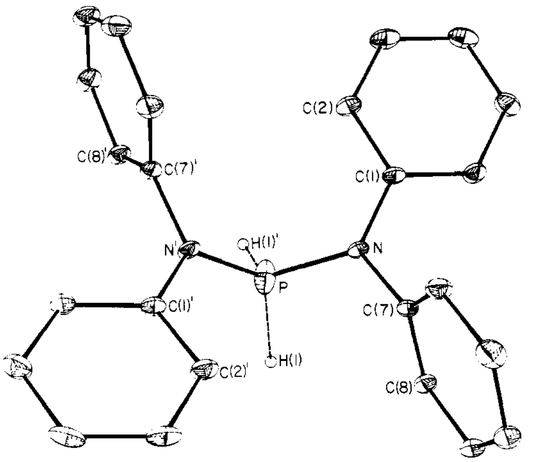

Figure 3. Computer-generated thermal ellipsoid drawing (probability level 35%) of **3**. The hydrogen atom is disordered between the two positions shown.

Results and Discussion

Structural Studies. Complexes **1**–**3** illustrated in Figures 1–3 are the first X-ray structural characterizations of uncomplexed secondary aminophosphine and -arsine compounds. Selected bond lengths and angles for these compounds are given in Table III. In **1**, the overall structure is dimeric with nearly D_{2h} symmetry for the $P_2H_2N_4$ array. Each phosphorus atom is in a distorted-tetrahedral environment and is bonded to two bridging hydrogens and two amide $N(SiMe_3)_2$ groups. In contrast to **1**, the arsenic

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(12) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(13) Program XABS written by H. Hope and B. Moezzi. The program obtains an absorption tensor from $F_o - F_c$ differences.

Table I. Crystallographic Data and Summary of Data Collection and Refinement[a]

	1	2	3
formula	$C_{24}H_{74}N_4Si_8P_2$	$C_{12}H_{37}N_2Si_4As$	$C_{24}H_{21}N_2P$
fw	705.52	396.42	368.48
cryst system	monoclinic	triclinic	orthorhombic
space group	$P2_1$	$P\bar{1}$	$F2dd$
conditions	$0k0$: $k = 2n$		hkl: $h + k, h + l, k + l = 2n$ $hk0$: $k + h = 4n$ $h0l$: $h + l = 4n$
cryst dimens, mm	0.18 × 0.18 × 0.40	0.19 × 0.19 × 1.13	0.6 × 0.75 × 1.00
cryst color and habit	colorless prisms	colorless needles	colorless needles
temp, K	140	130	130
a, Å	13.629 (13)	8.805 (8)	9.925 (6)
b, Å	18.210 (7)	11.252 (10)	38.632 (18)
c, Å	17.755 (14)	12.994 (10)	10.368 (5)
α, deg		66.73 (6)	
β, deg	91.84 (7)	85.34 (7)	
γ, deg		69.63 (6)	
Z	4	2	8
V, Å^3	4404 (6)	1106 (2)	3975 (4)
d_{calcd}, g/cm^3	1.06	1.19	1.23
linear abs coeff, cm^{-1}	3.3	18.2	1.5
scan speed, deg min^{-1}	30	30	15
scan width, deg	1	1.1	1
max 2θ, deg	45	55	55
ω offset for bkgd, deg	1	1	1
range of abs factors	1.05–1.13	1.34–5.37	1.08–1.17
octants	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,+l$
no. of variables	417	208	120
data/variable ratio	11.3	19.2	10.1
check reflcns	(1,0,6), (2,0,4)	(2,1,2), (1,3,5)	(4,4,0), (2,8,2)
no. of reflcns collcd	6349	5103	1346
R(merge)	0.039	0	0.0219
no. of unique data	5994	5050	1207
no. of data used in refinemt	4713 ($I > 3\epsilon(I)$)	3991 ($I > 2\sigma(I)$)	1062 ($I > 3\sigma(I)$)
$R(F)$	0.049	0.047	0.036
$R_w(F)$	0.053	0.051	0.039
weighting scheme, w	$[\sigma^2(F_0)]^{-1}$	$[\sigma^2(F_0)]^{-1}$	$[\sigma^2(F_0) + 0.00058F_0]^{-1}$
largest Δ/σ	0.047	0.001	0.010
largest feature of final diff map, e Å^{-3}	0.50	1.0	0.17
location of feature	bridging H	near As	near P

[a] All data were taken with Mo Kα radiation with $\lambda = 0.71069$ Å by using the ω-scan technique. $R = \sum ||F_o| - |F_c|| / |F_o|$ and $R_w = \sum |(|F_o| - |F_c|)w^{1/2}|$ with weighting scheme as listed above.

analogue **2** is monomeric and has a pyramidal geometry at the arsenic atom. In the case of **3**, the overall structure is monomeric with no close hydrogen interactions.

The most interesting feature of **1** is its existence as a hydrogen-bridged dimer. To our knowledge there are no other reports of phosphines displaying this mode of hydrogen bonding. Hydrogen bonding between hydrogen and halogen is, however, proposed in compounds of the type $[PH_4X]$ (X = Cl, Br, I). Microwave studies (X = Cl, Br) suggest a dimeric structure with doubly bridging P–H···X hydrogen bonds.[14] Neutron diffraction studies have shown that PH_4I is monomeric with weak P–H···I interactions. Here the P–H bond length is 1.418 (8) Å, and the closest hydrogen contact is to the iodide atom (2.87 Å).[15] There is an uncommon similarity between **1** and the lithium-bridged dimer $[LiP(CHSiMe_3)_2]_2$, which has a Li–P bond length of 2.48 Å and a long P···P separation of ca. 4.0 Å.[16] In **1**, the P–H distances as taken from the difference map range from 1.58 to 1.85 Å and average 1.73 Å. Unfortunately, the data do not warrant a statement as to whether the bridging is symmetrical or not. P···P distances are 2.645 (4) Å.

The average P–N bond length of 1.818 Å is somewhat longer than those reported for other P–N compounds. This could be due to the higher coordination at phosphorus in **1**. For comparison the three-coordinate aminophosphines $P(\overline{NCH_2CH_2})_3$ and $P(NMe_2)_3$ were reported to have P–N bond lengths of 1.75 and 1.70 Å, respectively.[17] Further reduction in the coordination number of the phosphorus atom gives rise to an even shorter P–N single bond distance, as seen in the two-coordinate compound $(Me_3Si)_2NPNSiMe_3$.[18]

Complex **2**, illustrated in Figure 2 is the first secondary aminoarsine compound to be reported. Angles at the arsenic atom are larger than those usually found for tertiary arsines.[15] The values found in **2** are HAsN(1) = 110 (4)°, HAsN(2) = 114 (4)°, and N(1)AsN(2) = 106.5 (1)°. The As–H bond length is 1.5 (1) Å, with no close hydrogen contacts between molecules. In comparison to the dimeric nature of **1**, the monomeric nature of **2** may be due to weaker bonding (as a result of poorer overlap) between the arsenic and hydrogen orbitals. This is not an unreasonable assumption, considering the differences in As–H versus P–H bond energies in the compounds AsH_3 and PH_3.[20] The As–H bond distances (average 1.877 (3) Å) are somewhat shorter than the predicted sum of the covalent radii (1.92 Å).[21] It is likely that N–As pπ–dπ bonding accounts for the short As–N bond lengths. A similar As–N distance of 1.864 (4) Å has been noted for the As(I) complex $[[Cr(CO)_5]_2AsN(SiMe_3)]$.[22]

The structure of **3** (Figure 3) in many respects is similar to that

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **1–3**

	x	*y*	*z*	U^a		*x*	*y*	*z*	U^a
Compound **1**									
P(1)	6765 (2)	3651 (1)	1169 (1)	24 (1)*	C(11)	5397 (6)	2940 (5)	−149 (5)	25 (2)
P(2)	8243 (2)	4553 (1)	928 (1)	24 (1)*	C(12)	3581 (7)	3267 (5)	700 (5)	30 (2)
P(51)	1780 (2)	9535 (1)	4070 (1)	24 (1)*	C(13)	7926 (7)	6402 (5)	−759 (5)	28 (2)
P(52)	3148 (2)	8552 (1)	3784 (1)	25 (1)*	C(14)	6986 (7)	4917 (5)	−819 (5)	28 (2)
Si(1)	7714 (2)	2099 (1)	835 (1)	22 (1)*	C(15)	6015 (7)	6114 (6)	24 (6)	36 (2)
Si(2)	6594 (2)	2383 (1)	2240 (1)	23 (1)*	C(16)	9628 (6)	6423 (5)	944 (5)	26 (2)
Si(3)	4975 (2)	4565 (2)	1781 (1)	23 (1)*	C(17)	8448 (7)	5856 (5)	2221 (5)	28 (2)
Si(4)	4750 (2)	3672 (1)	367 (1)	20 (1)*	C(18)	7614 (7)	7025 (5)	1244 (5)	32 (2)
Si(5)	7242 (2)	5710 (1)	−188 (1)	20 (1)*	C(19)	10759 (7)	4838 (5)	2731 (5)	36 (2)
Si(6)	8385 (2)	6171 (1)	1221 (1)	19 (1)*	C(20)	11016 (7)	3271 (6)	1875 (6)	40 (3)
Si(7)	10067 (2)	4026 (1)	1936 (1)	22 (1)*	C(21)	9141 (7)	3690 (5)	2618 (5)	28 (2)
Si(8)	10259 (2)	4233 (1)	275 (1)	23 (1)*	C(22)	11404 (7)	4753 (6)	443 (5)	36 (2)
Si(51)	2907 (2)	11023 (1)	3743 (1)	20 (1)*	C(23)	10596 (7)	3282 (5)	−35 (5)	34 (2)
Si(52)	1861 (2)	10763 (1)	5193 (1)	20 (1)*	C(24)	9623 (7)	4654 (6)	−560 (5)	37 (2)
Si(53)	−82 (2)	8737 (1)	4724 (1)	20 (1)*	C(51)	3043 (7)	10673 (5)	2760 (5)	34 (2)
Si(54)	−269 (2)	9662 (1)	3333 (1)	23 (1)*	C(52)	4186 (6)	11133 (5)	4124 (5)	23 (2)
Si(55)	1912 (2)	7459 (1)	2733 (1)	20 (1)*	C(53)	2304 (7)	11957 (5)	3656 (5)	33 (2)
Si(56)	3098 (2)	6920 (1)	4078 (1)	20 (1)*	C(54)	2744 (7)	11426 (5)	5667 (5)	29 (2)
Si(57)	5072 (2)	8973 (1)	4739 (1)	23 (1)*	C(55)	637 (7)	11195 (5)	5103 (5)	32 (2)
Si(58)	5132 (2)	8799 (1)	3057 (1)	25 (1)*	C(56)	1800 (7)	9985 (5)	5886 (5)	25 (2)
N(1)	7089 (5)	2714 (4)	1405 (4)	17 (2)	C(57)	790 (6)	8069 (5)	5157 (5)	26 (2)
N(2)	5509 (5)	4006 (4)	1104 (4)	19 (2)	C(58)	−642 (7)	9308 (5)	5490 (5)	26 (2)
N(3)	7898 (5)	5476 (4)	648 (4)	16 (2)	C(59)	−1148 (6)	8198 (5)	4331 (5)	25 (2)
N(4)	9497 (5)	4235 (4)	1051 (4)	15 (2)	C(60)	−811 (7)	8994 (5)	2645 (5)	30 (2)
N(51)	2227 (5)	10440 (4)	4315 (4)	21 (2)	C(61)	443 (7)	10323 (5)	2783 (5)	34 (2)
N(52)	487 (5)	9268 (4)	4043 (4)	16 (2)	C(62)	−1313 (7)	10181 (5)	3728 (5)	29 (2)
N(53)	2682 (5)	7652 (4)	3509 (4)	17 (2)	C(63)	2439 (7)	6711 (5)	2142 (5)	27 (2)
N(54)	4446 (5)	8810 (4)	3870 (4)	17 (2)	C(64)	1701 (6)	8267 (5)	2100 (5)	23 (2)
C(1)	7982 (7)	2482 (6)	−105 (5)	35 (2)	C(65)	655 (6)	7168 (5)	3028 (5)	29 (2)
C(2)	8918 (7)	1818 (5)	1263 (5)	33 (2)	C(66)	4293 (7)	6552 (6)	3748 (5)	33 (2)
C(3)	6981 (7)	1250 (5)	642 (6)	34 (2)	C(67)	3287 (7)	7241 (5)	5077 (5)	26 (2)
C(4)	7311 (7)	1615 (6)	2692 (6)	40 (3)	C(68)	2217 (7)	6136 (6)	4133 (5)	34 (2)
C(5)	5309 (7)	2043 (6)	2069 (6)	37 (3)	C(69)	5679 (7)	8109 (6)	5142 (5)	36 (2)
C(6)	6598 (7)	3118 (5)	2954 (5)	31 (2)	C(70)	6119 (7)	9635 (6)	4653 (5)	35 (2)
C(7)	5926 (6)	5147 (5)	2289 (5)	28 (2)	C(71)	4231 (6)	9366 (5)	5443 (5)	26 (2)
C(8)	4290 (7)	4044 (5)	2497 (5)	33 (2)	C(72)	6233 (8)	8169 (6)	3131 (6)	40 (3)
C(9)	4068 (7)	5227 (5)	1349 (6)	36 (2)	C(73)	5615 (7)	9728 (6)	2780 (6)	40 (3)
C10)	4375 (7)	4369 (5)	−353 (5)	26 (2)	C(74)	4340 (7)	8473 (6)	2248 (6)	38 (3)
Hydrogen Coordinates ($\times 10^3$) from Final Difference Map									
H(1)	750	419	170		H(51)	253	892	442	
H(2)	752	394	43		H(52)	247	918	332	
Compound **2**									
As	2817 (1)	709 (1)	3831 (1)	24 (1)*	C(4)	939 (5)	5023 (4)	3572 (4)	33 (2)*
Si(1)	3715 (1)	3198 (1)	2155 (1)	20 (1)*	C(5)	−1071 (5)	4698 (4)	1965 (4)	33 (2)*
Si(2)	444 (1)	3739 (1)	3207 (1)	20 (1)*	C(6)	−557 (5)	2862 (4)	4455 (3)	27 (2)*
Si(3)	4723 (1)	−1567 (1)	2927 (1)	20 (1)*	C(7)	6476 (5)	−1655 (4)	3722 (4)	30 (2)*
Si(4)	1193 (1)	276 (1)	2040 (1)	22 (1)*	C(8)	4437 (6)	−3266 (4)	3687 (4)	33 (2)*
N(1)	2200 (4)	2600 (3)	2925 (2)	18 (1)*	C(9)	5366 (6)	−1421 (4)	1488 (4)	38 (2)*
N(2)	2962 (4)	−192 (3)	2864 (3)	18 (1)*	C(10)	1070 (5)	1734 (4)	672 (3)	32 (2)*
C(1)	2811 (5)	4971 (4)	1040 (4)	34 (2)*	C(11)	1083 (7)	−1196 (5)	1754 (5)	46 (2)*
C(2)	5165 (5)	3216 (5)	3114 (4)	33 (2)*	C(12)	−663 (5)	791 (5)	2788 (4)	33 (2)*
C(3)	4893 (5)	2107 (4)	1392 (3)	26 (2)*					
Compound **3**									
P	2000	2500	2500	38 (1)*	C(6)	520 (3)	2229 (1)	−902 (2)	26 (1)*
N	1019 (2)	2515 (1)	1138 (2)	22 (1)*	C(7)	632 (3)	2845 (1)	618 (2)	21 (1)*
C(1)	616 (3)	2214 (1)	445 (2)	21 (1)*	C(8)	1617 (3)	3079 (1)	247 (2)	24 (1)*
C(2)	346 (3)	1901 (1)	1070 (2)	26 (1)*	C(9)	1233 (3)	3409 (1)	−186 (2)	29 (1)*
C(3)	18 (3)	1609 (1)	349 (3)	31 (1)*	C(10)	−113 (3)	3496 (1)	−273 (3)	31 (1)*
C(4)	−68 (3)	1622 (1)	−1983 (3)	31 (1)*	C(11)	−1094 (3)	3257 (1)	76 (3)	32 (1)*
C(5)	183 (3)	1936 (1)	−1607 (3)	30 (1)*	C(12)	−724 (3)	2931 (1)	520 (2)	26 (1)*

[a] Asterisk indicates equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

of **2**. Details of bond distances and angles are given in Table III. The compound is monomeric with the phosphorus atom in a regular pyramidal environment. The angles at phosphorus are wide, having the values HPN = 117 (4)°, HPN′ = 117 (4)°, and NPN = 110.9 (1)°. The P–H bond length is 1.5 (1) Å. The P–N bond length is a normal 1.716 (2) Å. The geometry at the nitrogen atom is planar, a common feature for most phosphorus compounds containing the $-NR_2$ moiety.[23-25]

Spectroscopic Studies. The IR spectrum of neat $HP\{N(SiMe_3)_2\}_2$ shows two absorptions at 2305 and 2226 cm^{-1} that do not differ substantially from literature values (2300 and 2220 cm^{-1}).[4] However, a slight shift to a higher wavenumber is observed in one of the IR bands of solid **1**, which is unexpected. These absorptions appear at 2333 and 2227 cm^{-1}.

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Table III. Selected Bond Lengths (Å) and Angles (deg) for **1**–**3**

	Complex **1**		
P(1)–H(1)	1.81 (9)	P(1)–N(1)	1.809 (7)
P(1)–H(2)	1.77 (9)	P(1)–N(2)	1.829 (7)
P(2)–H(1)	1.85 (9)	P(2)–N(3)	1.810 (7)
P(2)–H(2)	1.72 (9)	P(2)–N(4)	1.811 (7)
N(1)–Si(1)	1.748 (7)	N(1)–Si(2)	1.761 (7)
P(1)···P(2)	2.646 (4)		
H(1)–P(1)–H(2)	84 (2)	P(1)–H(1)–P(2)	97 (2)
H(1)–P(2)–H(2)	80 (2)	P(1)–H(2)–P(2)	99 (2)
N(1)–P(1)–N(2)	124.7 (3)	N(3)–P(2)–N(4)	124.5 (3)
N(1)–P(1)–H(1)	107 (2)	N(2)–P(1)–H(1)	112 (2)
N(1)–P(1)–H(2)	108 (2)	N(2)–P(1)–H(2)	114 (2)
N(3)–P(2)–H(1)	113 (2)	N(4)–P(2)–H(1)	109 (2)
N(3)–P(2)–H(2)	109 (2)	N(4)–P(2)–H(2)	112 (2)
P(1)–N(1)–Si(1)	126.1 (4)	Si(1)–N(1)–Si(2)	118.5 (4)
P(1)–N(1)–Si(2)	114.9 (4)		
P(51)–H(51)	1.63 (9)	P(51)–N(51)	1.805 (7)
P(51)–H(52)	1.78 (9)	P(51)–N(52)	1.827 (7)
P(52)–H(51)	1.58 (9)	P(52)–N(53)	1.819 (7)
P(52)–H(52)	1.67 (9)	P(52)–N(54)	1.832 (7)
N(51)–Si(51)	1.755 (7)	N(51)–Si(52)	1.753 (7)
P(51)···P(52)	2.645 (4)		
H(51)–P(51)–H(52)	72 (2)	P(51)–H(51)–P(52)	111 (2)
H(51)–P(52)–H(52)	76 (3)	P(51)–H(52)–P(52)	100 (2)
N(51)–P(51)–N(52)	124.6 (3)	N(53)–P(52)–N(54)	125.5 (3)
N(51)–P(51)–H(51)	109 (2)	N(52)–P(51)–H(51)	115 (2)
N(51)–P(51)–H(52)	109 (2)	N(52)–P(51)–H(52)	115 (2)
N(53)–P(52)–H(51)	113 (2)	N(54)–P(52)–H(51)	111 (2)
N(53)–P(52)–H(52)	108 (2)	N(54)–P(52)–H(52)	112 (2)
P(51)–N(51)–Si(51)	126.4 (4)	Si(51)–N(51)–Si(52)	118 (4)
P(51)–N(51)–Si(52)	114.6 (4)		
	Complex **2**		
As–H	1.5 (1)	N(1)–Si(1)	1.763 (3)
As–N(1)	1.879 (3)	N(1)–Si(2)	1.750 (3)
As–N(2)	1.874 (4)		
H-As-N(1)	110 (4)	As–N(1)–Si(1)	117 (1)
H-As-N(2)	114 (4)	As–N(1)–Si(2)	118.9 (2)
N(1)–As–N(2)	106.5 (1)	Si(1)–N(1)–Si(2)	120.7 (2)
	Complex **3**		
P–H(1)	1.5 (1)	N–C(1)	1.422 (3)
P–N	1.716 (2)	N–C(2)	1.439 (3)
N–P–H(1)	106 (4)	C(1)–N–C(7)	117.4 (2)
N–P–H(1)′	117 (4)	P–N–C(7)	119.3 (2)
N–P–N′	110.9 (1)		
P–N–C(1)	123.2 (2)		

The ^{31}P NMR spectrum of $HP\{N(SiMe_3)_2\}_2$ (dissolved in toluene (1:3 v/v)) in the range of room temperature to −80 °C showed no indication of P–H–P bonding. However, broadening of the doublet (J_{P-H} = 207 Hz) was observed at −80 °C.

Spectroscopic evidence for the As–H bond in **2** comes from IR and ^1H NMR studies. In the infrared spectrum, two As–H absorptions are observed at 2041 and 1928 cm^{-1} that are significantly lower than the P–H stretching frequencies in **1**. This shift is expected due to the heavier arsenic atom and the weaker As–H bond relative to P–H. These assignments are confirmed by the synthesis of the deuterium analogue $DAs\{N(SiMe_3)_2\}_2$ (**5**), which displays an As–D absorption at 1465 cm^{-1} (other absorptions are probably obscured by bands at 1400 and 1437 cm^{-1}). The ^1H NMR spectrum of neat **2** consists of a singlet at 0.2 ppm for the $SiMe_3$ groups and a singlet at 7.2 ppm for the hydrogen directly bonded to arsenic. Unambiguous assignment of this resonance comes from the deuterium analogue **5**, which displays only one singlet at 0.2 ppm for the $SiMe_3$ groups. In contrast, the hydrogen signal of **1** has been reported to appear at 6.61 ppm. The downfield shift for the proton resonance of **2** relative to that of **1** can be explained in terms of electronegativity, since the more electronegative arsenic deshields the hydrogen atom more effectively than does phosphorus.

Table IV. ^{31}P NMR Data[a]

compd	^{31}P shift	J_{P-H}, Hz
$[HP\{N(SiMe_3)_2\}_2]$ (**1**)	59.6[b]	207
$[HP(NPh_2)_2]$ (**3**)	69.1	256
$[HP\{N(C_6H_{11})_2\}_2]$ (**4**)	126.0	251

[a] All values are given in ppm relative to H_3PO_4. Positive values designate downfield chemical shifts. [b] Reference 4.

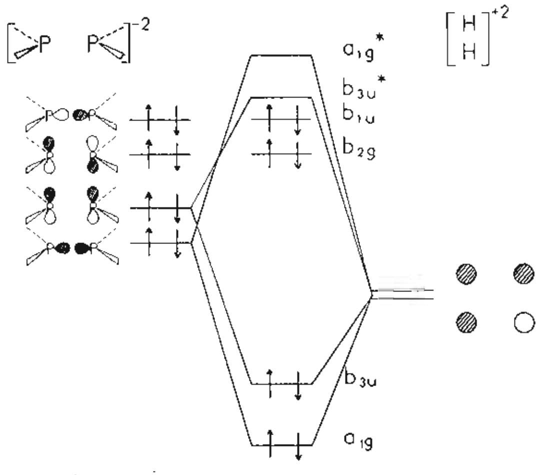

Figure 4. Schematic molecular orbital energy diagram for the bridging orbitals of **1**. A local point-group symmetry of D_{2h} was assumed for the $P_2H_2N_4$ array.

Spectroscopic evidence for the P–H bond in **3** and **4**, $[HP\{N(C_6H_{11})_2\}_2]$, comes from ^{31}P NMR studies. A summary of ^{31}P NMR data is given in Table IV. The ^{31}P NMR spectrum of **3** in ether solution shows a doublet at 69.1 ppm with a large J_{P-H} coupling constant of 256 Hz (251 Hz for **4**). The large coupling constants of **3** and **4** probably arise from electronic effects of the neighboring lone pair on nitrogen. Normally, dialkyl- and diarylphosphines exhibit J_{P-H} in the range of 180–200 Hz. The smaller J_{P-H} value for **1** may be due to the competition between silicon and phosphorus for the nitrogen lone pair.

Conclusion

In summary, the first structural characterization of a unique, associated phosphine has been described. However, the phenomenon of aggregation does not, at present, appear to be widespread among other phosphines or the analogous arsenic compounds. The association seems to be quite weak, and there is no evidence that it extends to the solution phase. The feeble nature of the association is also suggested by a qualitative molecular orbital diagram (Figure 4). This shows two occupied, strongly bonding MO's with the remaining two lone pairs in nonbonding or weakly antibonding MO's. Obviously, this arrangement does not offer a much greater stabilization advantage than two separate $HP(NR_2)_2$ species. Another possible qualitative account of the dimerization concerns the reduction of electron density on the nitrogens by the p–d π-bonding $SiMe_3$ substituents. This probably weakens any N–P, p–d π-bonding and leads to less electron density in the phosphorus d orbitals. Thus, there is a greater likelihood of P–H bridging to these more electron-poor orbitals. It must, however, be said that, in the MO diagram (Figure 4), d orbitals are unnecessary to account for the observed bonding. Clearly, rigorous and quantitative calculations are required to account for the observed dimerization.

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Registry No. **1**, 81072-86-8; **2**, 114397-70-5; **3**, 114397-71-6; **4**, 114397-72-7; $ClAs\{N(SiMe_3)_2\}_2$, 63429-89-0; $ClP(NPh_2)_2$, 58521-13-4; PCl_3, 7719-12-2; $LiNPh_2$, 5856-89-3; $ClP\{N(C_6H_{11})_2\}$, 114397-73-8; $LiN(C_6H_{11})_2$, 4111-55-1; $LiAlH_4$, 16853-85-3.

Supplementary Material Available: Full listings of bond distances and angles (Tables S1a–c and S2a–c), anisotropic thermal parameters (Table S3a–c), and hydrogen coordinates (Table S4a–c) (12 pages); listings of structure factors (59 pages). Ordering information is given on any current masthead page.