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Syntheses and Structures of *P*-Anilino-*P*-chalcogeno- and *P*-Anilino-*P*-iminodiazasilaphosphetidines and Their Group 12 and 13 Metal Compounds

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The *P*-anilino-*P*-chalcogeno(imino)diazasilaphosphetidines $[Me_2Si(\mu\text{-N}^tBu)_2P{=}E(NHPh)]$ (E = O (**3**), S (**4**), Se (**5**), N-*p*-tolyl (**6**)) were synthesized by oxidizing the *P*-anilinodiazasilaphosphetidine $[Me_2Si(N^tBu)_2P(NHPh)]$ (**2**) with cumene hydroperoxide, sulfur, selenium, and *p*-tolyl azide, respectively. The lithium salt of **4** reacted with thallium monochloride to produce $\{[Me_2Si(\mu\text{-N}^tBu)_2P{=}S(NPh)\text{-}\kappa N\text{-}\kappa S]Tl\}$ (**7**), which features a two-coordinate thallium atom. Treatment of **4**–**6** with $AlMe_3$ gave the monoligand dimethylaluminum complexes $\{[Me_2Si(\mu\text{-N}^tBu)_2P{=}E(NPh)\text{-}\kappa N\text{-}\kappa E]AlMe_2\}$ (E = S (**8**), Se (**9**), N-*p*-tolyl (**10**)), respectively. In these complexes the aluminum atom is tetrahedrally coordinated by one chelating ligand and two methyl groups, as a single-crystal X-ray analysis of **8** showed. A 2 equiv amount of **4**–**6** reacted with diethylzinc to produce the homoleptic diligand complexes $\{[Me_2Si(\mu\text{-N}^tBu)_2P{=}E(NPh)\text{-}\kappa N\text{-}\kappa E]_2Zn\}$ (E = S (**11**), Se (**12**), N-*p*-tolyl (**13**)). A crystal-structure analysis of **11** revealed a linear tetraspirocycle with a tetrahedrally coordinated, central zinc atom.

Introduction

Amino(imino)- and amino(chalcogeno)phosphoranes (**A**; Chart 1) are tetrasubstituted monophosphorus(V) compounds with an established chemistry.[1-3] The ready availability of these molecules has contributed much to their popularity as ligands, leading to numerous metal derivatives of chelating *N*,*N* or *N*,*E* phosphoranes with desirable functions and structures.[4-11]

Bis(1°-amino)cyclodiphosph(V)azanes (**B**, **C**) are heterocyclic molecules with two tetrasubstituted phosphorus(V) atoms, each having an environment similar to that in **A**. As ligands for main-group and transition metals,[12-16] these diphosphorus compounds have exhibited remarkable coordinative flexibility by being able to chelate metal atoms either as bis(amido) or as bis(chalcogenophosphoryl) ligands.[17-20] The most common coordination mode for bis(amino)cyclo-

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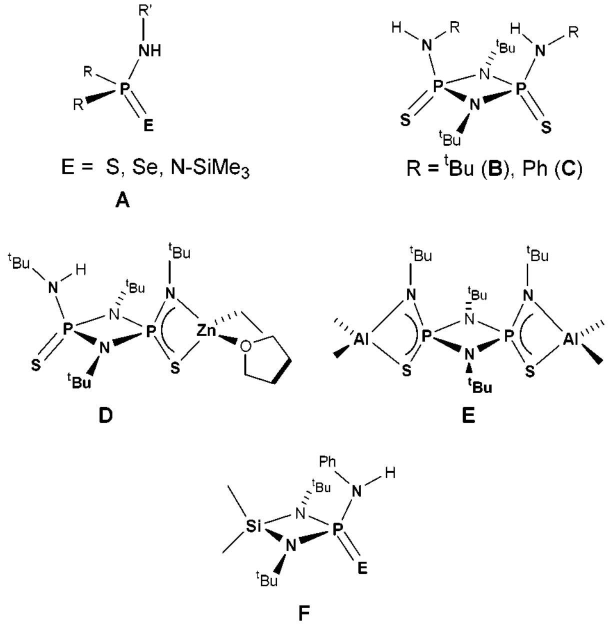
Chart 1



diphosph(V)azanes appears to be one in which they chelate metal atoms laterally, similar to aminophosphoranes (**A**).[18−20] The inclusion of the P(V) atoms in a heterocycle renders both, the ligands more compact and the phosphorus atoms more electron rich than those in acyclic aminophosphoranes, because the imido lone-pair electrons are now perfectly aligned with the empty d-orbitals of the phosphorus atoms.

Due to their bifunctionality bis(amino)cyclodiphosphazanes may coordinate either one (**D**) or two (**E**) metal fragments, thereby allowing the syntheses of monomeric mono- and dinuclear species and of extended structures. As with most ligands the coordination number can, to some degree, be controlled by the ligand's bulk. Structure control by steric bulk has limits, however, and to prevent bilateral coordination of bis(amino)cyclodiphosphazanes we have capped one end of the heterocycle with an unreactive dimethylsilyl group. This modification leads to *P*-aminodiazasilaphosphetidines (**F**),[21−31] which are monofunctional analogues of **B** and **C** and heterocyclic analogues of aminophosphoranes. Having only one chelation site, they are unable to form dinuclear and polymeric species and should therefore have a much simpler reaction and coordination chemistry than bis(amino)cyclodiphosph(V)azanes. Herein we report syntheses and structures of new *P*-anilinodiazasilaphosphetidines and their metal complexes.

Results and Discussion

Diazasilaphosphetidines may be synthesized in a variety of ways, the most unusual synthesis being the metal chloride-induced cyclization of bis(bis(trimethylsilyl)amino)thiophosphoryl chlorides.[31] This method, however, leads to mixtures of diazasilaphosphetidines and azathiasilaphosphetidines, the former being the thermodynamic product. The interactions of dimethyldichlorosilane with dilithiobis(amido)phosphines and of aminodichlorophosphines with dilithiobis(amido)dimethylsilanes are conceptually cleaner routes to the phosphorus(III) heterocycles.[28−30] In our hands even these reactions led to product mixtures, requiring additional separation steps. The previously reported displacement of $PbCl_2$ by PCl_3 from the diazasilaplumbetidine $[Me_2Si(\mu\text{-}N^tBu)_2Pb]$ is a much cleaner synthesis for the *P*-chlorodiazasilaphosphetidine $[Me_2Si(\mu\text{-}N^tBu)_2PCl]$ (**1**), which serves as the starting material for the title compounds.[27]

Many reported acyclic aminophosphoranes bear reactive (trimethylsilyl)amino groups which cannot be tuned sterically. Because steric variability is particularly easy to introduce with aryl groups, we treated **1** with lithium anilide to obtain quantitatively the *P*-anilinophosphetidine **2** (Scheme 1). The straightforward oxidations of **2** with chalcogens and tolyl azide (Scheme 1) then furnished the corresponding P(V) molecules $[Me_2Si(\mu\text{-}N^tBu)_2P{=}E(NHPh)]$, E = O (**3**), S (**4**), Se (**5**), and N-*p*-tolyl (**6**), in crystalline form. Their NMR spectra (^{1}H, ^{13}C, ^{31}P, ^{29}Si) are unremarkable and characteristic of molecules with time-averaged C_s symmetry.

Three of these (**3**, **4**, and **6**) were analyzed X-ray crystallographically, and their solid-state structures are shown in Figures 1 and 2. Data collection and selected bond parameters of **3**, **4**, and **6** are listed in Tables 1 and 2, respectively. The crystal structures consist of hydrogen-bonded dimers, arranged about either inversion centers (**3** and **4**) or 2-fold rotation axes (**6**) of their space groups. Possibly due to the intermolecular hydrogen bonding, the phenyl ring is canted toward the heterocycle and rotated out of the Si−P−N(anilido) plane. The differences between these molecules are limited to the exocyclic phosphorus substituents, allowing their structures to be discussed collectively below.

Compounds **4**−**6** are almost planar $Si(\mu\text{-}N)_2P$ heterocycles of tetrahedral silicon and phosphorus(V) atoms, connected by trigonal-planar *tert*-butylimido groups. The silicon−nitrogen (1.731(5)−1.745(2) Å), the endocyclic phosphorus−nitrogen (1.652(4)−1.674(3) Å), and the phosphorus−aniline

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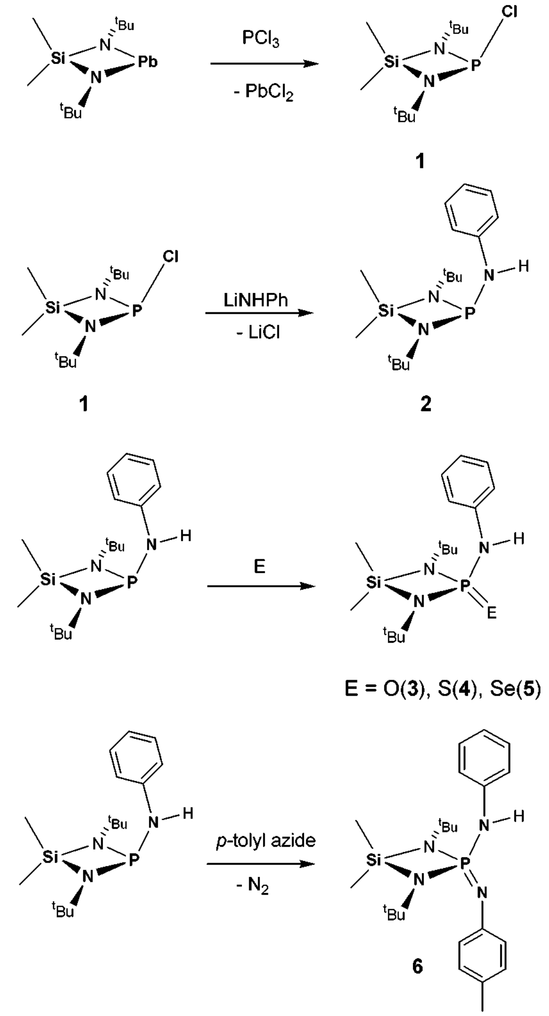
Scheme 1



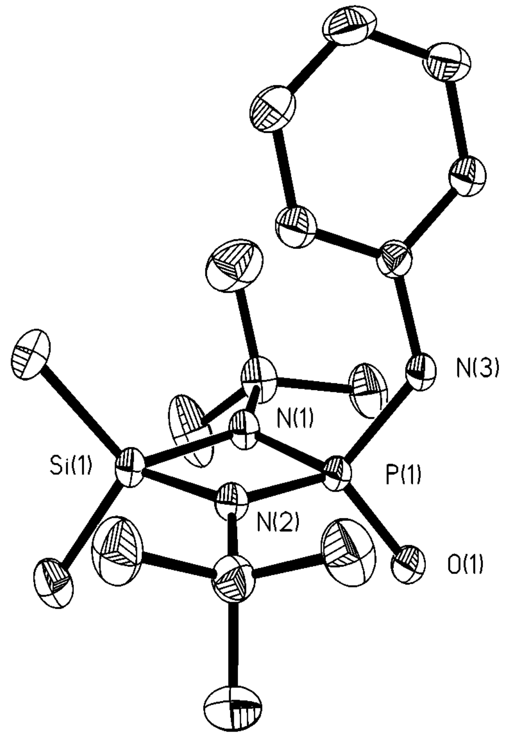


Figure 1. Solid-state structure of **3** (35% probability thermal ellipsoids). The sulfur analogue (**4**) has the same structure.

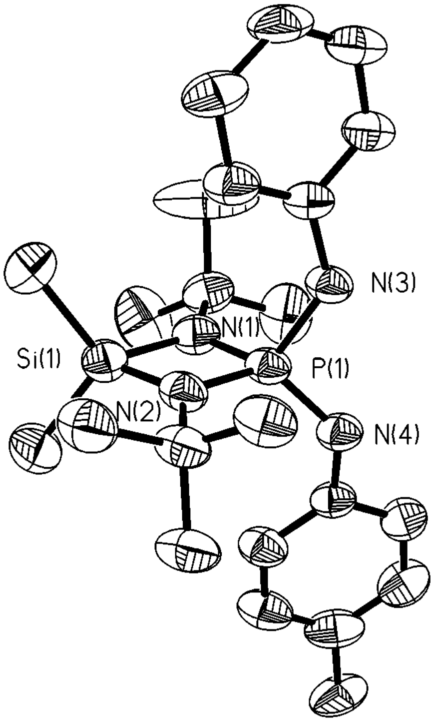


Figure 2. Solid-state structure of **6** (30% probability thermal ellipsoids). The solvent molecule (toluene) is not shown.

bonds (1.644(5)−1.658(2) Å) of **3**, **4**, and **6** are equidistant, while the P═O (1.4767(18) Å), P═S (1.938(2) Å), and P═N bonds (1.561(3) Å) show the expected lengths and variations. The very similar exocyclic phosphorus substituents of **6** (anilino and *p*-tolylimino) render the molecule almost C_{2v} symmetric, leading to a statistical disorder in the solid state, which caused somewhat larger uncertainties in the bond lengths and the thermal parameters of the affected atoms. The exocyclic N−P−E bite angles in **3** and **4** are identical but ca. 6° larger than the corresponding N−P−N angle in **6**.

The sulfur derivative **4** is particularly suitable for a structural comparison with **C** because the phosphorus environments in both compounds are formally identical. For example, the P═S bonds (1.938(2) Å in **4** and 1.9240(10) Å in **C**), the P−N(anilino) bonds (1.644(5) and 1.648(2) Å), and the P−N(imino) bonds (1.684(2) and 1.685(2) Å) are all equidistant within experimental error. Even the somewhat larger endocyclic N−P−N angle of **4** (87.0(2)° versus 83.60(1)° in **C**) does little to detract from the suitability of the silicon−phosphorus ligands as analogues.

Although Lewis acid−base adduct of diazasilaphosphetidines with group 13 metal chlorides are known,[31] complexes in which these molecules function as chelating *N,E* ligands and their solid-state structures have to our knowledge not been reported. To test the chelating ability of these ligands we synthesized simple complexes of diamagnetic mono-, di-, and trivalent metals. True to the model character of this study we chose metals for which bis(amido)cyclodiphosphazane derivatives were known, with particular emphasis on catalysis and the modeling of solid-state phosphates.

Table 1. Crystal Data for Compounds **3**, **4**, **6**−**8**, and **11**

param	**3**	**4**	**6**	**7**	**8**	**11**
chem formula	$C_{16}H_{30}N_3OPSi$	$C_{16}H_{30}N_3PSSi$	$C_{26.5}H_{41}N_4PSi$	$C_{16}H_{29}N_3PSSiTl$	$C_{18}H_{35}N_3AlPSSi$	$C_{32}H_{58}N_6P_2S_2Si_2Zn$
fw	339.49	355.55	474.65	558.91	411.59	774.45
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2/n$ (No. 13)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
T (°C)	21	22	21	−60	22	−60
a, Å	9.1646(9)	10.3241(19)	15.297(6)	13.5033(7)	16.916(2)	38.0(2)
b, Å	9.3112(10)	13.803(2)	9.486(3)	9.4370(4)	8.8658(8)	14.72(8)
c, Å	11.6963(13)	14.806(4)	20.172(9)	17.6696(9)	18.1264(16)	17.16(10)
α, deg	85.713(2)					
β, deg	88.744(2)	93.964(18)	93.66(3)	109.0550(10)	115.131(6)	116.07(11)
γ, deg	78.111(2)					
V, Å^3	990.57(18)	2105.0(7)	2921(2)	2128.27(18)	2461.4(4)	8630(88)
Z	2	4	4	4	4	8
ρ_{calc}, g cm^{-1}	1.138	1.122	1.080	1.744	1.111	1.192
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ, cm^{-1}	2.05	2.88	1.55	78.21	2.87	8.24
R(F)^a [$I > 2\sigma(I)$]	0.0512	0.0613	0.0608	0.0240	0.0429	0.0376
wR2(F^2)^b (all data)	0.1506	0.1671	0.1847	0.0634	0.1279	0.1088

^{a} $R = \sum|F_o - F_c|/\sum|F_o|$. ^{b} $R_w = \{[\sum w(F_o^2 - F_c)^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**, **4**, and **6**

	3	**4**	**6**
	Bond Lengths		
P═E	1.4767(18)	1.938(2)	1.561(3)
P(1)−N(3)	1.658(2)	1.644(5)	1.653(3)
P(1)−N(1)	1.655(2)	1.653(4)	1.666(3)
P(1)−N(2)	1.663(2)	1.652(4)	1.674(3)
Si(1)−N(1)	1.743(2)	1.741(4)	1.741(3)
Si(1)−N(2)	1.755(2)	1.731(5)	1.736(4)
Si(1)−Me(av)	1.848(3)	1.854(6)	1.860(4)
	Bond Angles		
N(3)−P(1)−E	106.03(10)	106.9(2)	100.07(16)
N(1)−P(1)−N(2)	87.85(11)	87.0(2)	86.33(16)
N(1)−Si(1)−N(2)	82.29(10)	81.9(2)	82.16(14)
Me−Si(1)−Me	108.34(15)	109.6(3)	107.2(2)
P(1)−N(1)−Si(1)	95.03(12)	95.0(2)	95.80(15)
P(1)−N(2)−Si(1)	94.27(11)	95.4(2)	95.68(15)

Scheme 2

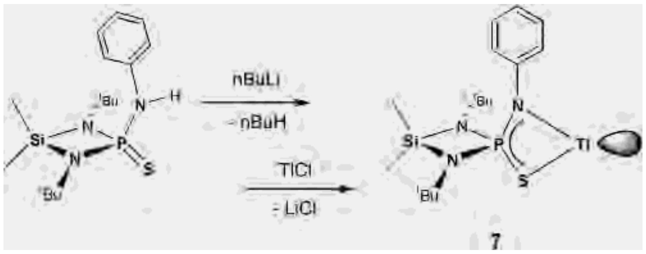


Table 3. Selected Bond Lengths (Å) and Angles (deg) for **7** and **8**

	7	**8**
	Bond Lengths	
M(1)−S	2.8861(9)	2.3518(10)
M(1)−N(3)	2.534(3)	1.9117(19)
Al−C(3)		1.958(3)
Al−C(4)		1.953(4)
P−S	2.0017(12)	2.0192(8)
P(1)−N(3)	1.609(3)	1.6198(18)
P(1)−N(1)	1.683(3)	1.6546(19)
P(1)−N(2)	1.682(3)	1.6545(18)
Si(1)−N(1)	1.737(3)	1.7515(19)
Si(1)−N(2)	1.739(3)	1.752(2)
Si(1)−Me(av)	1.857(4)	1.848(3)
	Bond Angles	
C(3)−Al−C(4)		116.25(17)
N(3)−M(1)−S(1)	63.44(6)	80.17(6)
M(1)−N(3)−P(1)	104.6(7)	103.16(9)
M(1)−S(1)−P(1)	84.55(4)	78.34(3)
N(3)−P(1)−S	105.84(14)	98.34(7)
N(1)−P(1)−N(2)	86.13(14)	88.02(10)
N(1)−Si(1)−N(2)	82.75(13)	82.04(9)
Me−Si(1)−Me	108.57(18)	110.09(14)
P(1)−N(1)−Si(1)	95.13(13)	94.68(9)
P(1)−N(2)−Si(1)	95.23(14)	94.68(10)

Amidodiazasilaphosphetidines are most conveniently introduced in the form of their lithium salts, but the tendency of such salts to coordinate donor solvents causes analytical problems. Related alkali-metal salts of acyclic phosphoranes, for example, were invariably isolated as THF adducts or ate complexes.[4] Thallium(I) derivatives are good analogues of alkali-metal salts, with the added advantage that they do not form etherates and are hydrolytically more stable than alkali-metal compounds; cf. TlC_5H_5 and NaC_5H_5.

When **4** was treated with *n*-butyllithium, followed by thallium monochloride (Scheme 2), crystalline {[$Me_2Si(\mu\text{-}N^tBu)_2P{=}S(NPh)$-$\kappa N$-$\kappa S$]Tl} (**7**) formed. Like cyclopentadienylthallium, but in stark contrast to the extremely air-sensitive dithallium bis(amido)cyclodiphosph(III)azane [$P(\mu\text{-}N^tBu)_2P(^tBuN\text{-}\kappa N^3Tl)_2$],[32] this colorless compound is surprisingly air stable in the solid state, showing decomposition only after lengthy exposure to the atmosphere. Although its lack of reactivity gave some indication that **7** might be an oligomer, the high solubility suggested a monomeric derivative.

A single-crystal X-ray diffraction study confirmed the spectroscopic findings. Crystal data and bond parameters for **7** are collected in Tables 1 and 3, respectively, and its solid-state structure is depicted in Figure 3. The crystal structure consists of zigzag chains of molecules, loosely connected by weak intermolecular thallium−sulfur bonds (3.599(2) Å). This spirocyclic thallium compound, with its central P(V) atom, is terminated by a dimethylsilyl group on one end and a highly exposed thallium(I) atom on the other. While the $Si(\mu\text{-}N)_2P$ ring is almost planar, the P−N−Tl−S metallacycle exhibits extensive puckering due to the incorporation of the large thallium atom. Heavy main-group elements are known for their ability to support small bond angles, but the N−Tl−S bond angle (63.44(6)°) is small even for thallium. The thallium−nitrogen (2.534(3) Å) and thallium−sulfur

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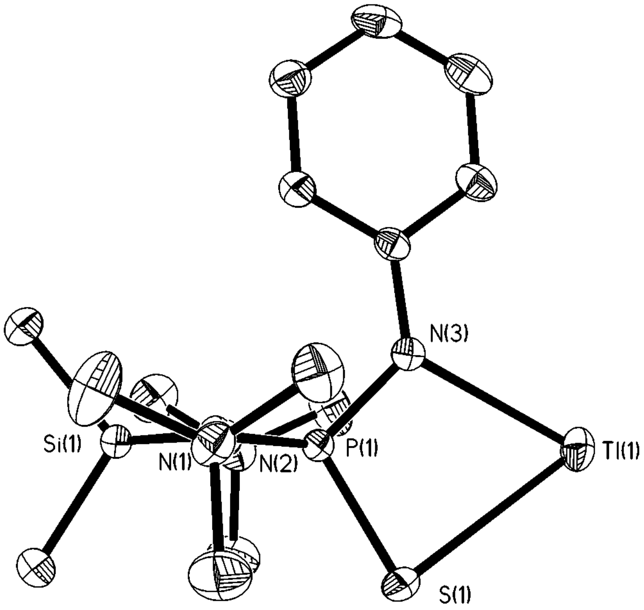


Figure 3. Solid-state structure of **7** (35% probability thermal ellipsoids).

(2.8861(9) Å) bonds are similar to those in related compounds.[33−49] Thus for example, the four Tl−N bonds in the heterocubic $[P(\mu\text{-}N^tBu)_2P(^tBuN\text{-}\kappa N^3Tl)_2]$ range from 2.559(3) to 2.587(3) Å,[32] while the Tl−S bonds in thallium dithiocarbamate dimers of the formula $\{[(C_3H_7)_2NCS_2\text{-}\kappa S^2]Tl]\}_2$, due to the higher coordination number (4), vary from 2.88(1) to 3.12(1) Å.[33,34]

The low dimensionality of **7** is surprising, because, as the disubstituted zinc compounds **11**−**13** show (see below), the ligand is not particularly bulky and one might, therefore, have expected stronger intermolecular interactions, possibly even between thallium atoms. The exposedness of the thallium atom and consequently that of its lone pair of electrons suggest that this compound may have ligand properties toward low-valent transition metals.

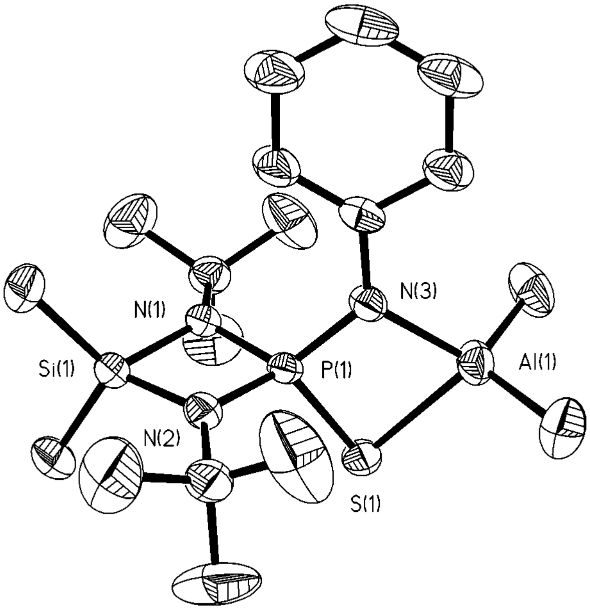
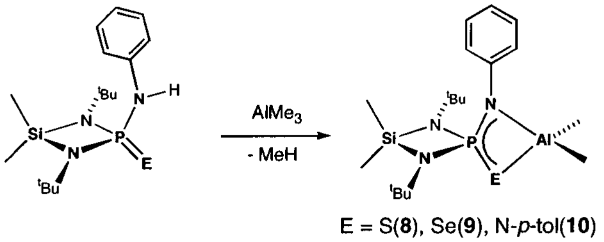


Figure 4. Solid-state structure of **8** (35% probability thermal ellipsoids).

Scheme 3



While the thallium(I) salt **7** is mainly of structural interest, the aluminum dialkyl derivatives of **3**−**6**, suitably activated, may polymerize ethylene to high polymers, as had been demonstrated for the structurally related dimethylaluminum−amidinates and −guanidinates.[50−54] In bimetallic **E** the presence of two aluminum atoms had introduced complications in mechanistic studies, which are not expected for similar monoaluminum complexes. When the monofunctional **4**−**6** were treated with 1 equiv of $AlMe_3$ (Scheme 3), the corresponding dimethylaluminum complexes **8**−**10** formed.

Of these, one (**8**) was subjected to an X-ray structure analysis. Its crystal and data collection parameters, as well as selected bond lengths and angles, are listed in Tables 1 and 3, respectively. A thermal-ellipsoid plot (Figure 4) shows that the aluminum atom is tetrahedrally coordinated by the N−P−S moiety of the chelating ligand and its remaining two methyl groups. The structural similarity of this compound with **E** is reflected in almost identical bond parameters. The coordination environment about aluminum is

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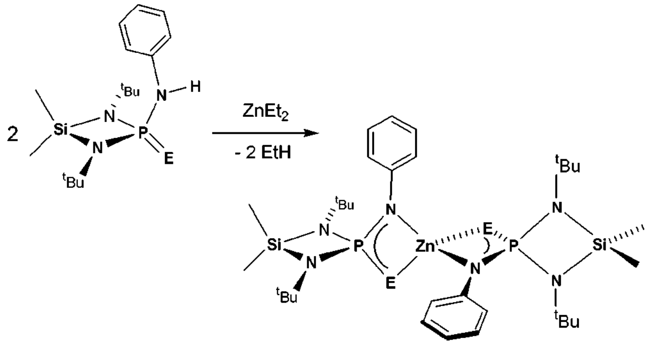
Scheme 4



E = S(**11**), Se(**12**), N-*p*-tol(**13**)

distorted tetrahedral, with an acute N−Al−S bond angle of 80.17(6)° and a more normal tetrahedral Me−Al−Me angle of 116.25(17)°. The aluminum−methyl bonds are equidistant (1.955(4) Å), while the Al−N (1.9117(19) Å) and Al−S (2.3518(10) Å) bonds are comparatively short and long, respectively, similar to those in **E**.

Sterically encumbered zinc amides are efficient polymerization catalysts for lactides and related monomers.[55−58] Although mono(ethylzinc) complexes, like **D**, may have catalytic properties, here we were interested solely in the structural aspects of these zinc amidodiazasilaphosphetidines.

Because NR and NR_2 are isoelectronic with O and O^-, respectively, bis(amino)cyclodiphosph(V)azanes may be considered hydrocarbon-soluble analogues of diphosphates. We had attempted to connect bis(amido)cyclodiphosph(V)azanes to one-dimensional metallapolyphosph(V)azanes, or *quasi*-polymetallaphosphates, using divalent metal ions. Zinc and magnesium are the most obvious metals for this purpose, because of their size, diamagnetism, and the commercial availability of their dialkyls.

In the course of these studies we discovered that bis(anilino)dithiacyclodiphosph(V)azane **C** reacts with 1 equiv of diethylzinc to form a precipitate, whose lack of solubility made its structure elucidation impossible.

To gain insight into the coordination environment about zinc in such polymeric species, we treated the identically substituted, but monofunctional, *P*-anilino-*P*-thiodiazasilaphosphetidine (**4**) with diethylzinc. As expected, and in distinct contrast to the monosubstitution of trimethylaluminum, diethylzinc reacted with 2 equiv of **4** (Scheme 4) to give a colorless product (**11**). The NMR spectra revealed unambiguously the loss of both ethyl groups, and this disubstitution could be prevented neither by lowering the reaction temperature nor by using ligands bearing the larger selenium (**5**) or tolylimino (**6**) phosphorus substituents. Thus the addition of **4**−**6** to $ZnEt_2$, both at low (−78 °C) and ambient temperatures, yielded analogous diligand complexes.

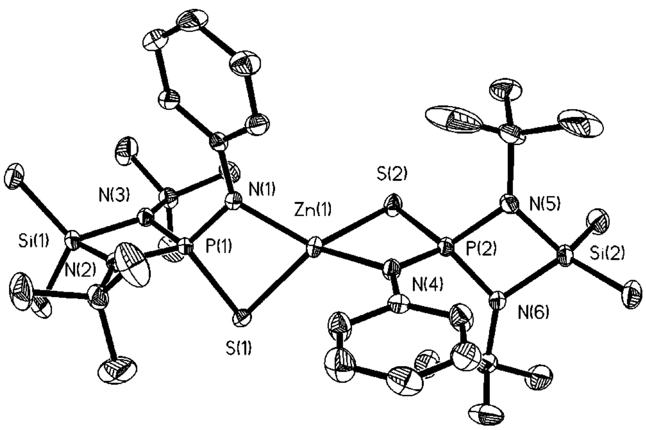


Figure 5. Solid-state structure of **11** (35% probability thermal ellipsoids).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **11**

	Bond Lengths		
Zn−S(av)	2.408(12)	P−imido(av)	1.694(8)
Zn−N(av)	2.020(9)	Si−N(av)	1.777(8)
P−S(av)	2.068(10)	Si−Me(av)	1.888(9)
P−anilido(av)	1.638(8)		
	Bond Angles		
S(1)−Zn−S(2)	120.6(4)	S(2)−Zn−N(4)	80.6(3)
N(1)−Zn−N(4)	131.7(3)	N−P−S(av)	101.5(2)
S(1)−Zn−N(1)	80.9(3)	N−P−N(endoc)	87.9(2)
S(1)−Zn−N(4)	125.8(3)	N−Si−N(av)	82.9(2)
S(2)−Zn−N(1)	123.1(4)	P−N−Si(av)	94.3(3)

These reactions are similar to those of acyclic amino(chalcogeno)phosphoranes with zinc reagents, where treatment of $[R_2P{=}E(NHR')]$ with $Zn[N(SiMe_3)_2]_2$ or $ZnEt_2$ had yielded complexes of the type $\{[R_2P(S)NR']_2Zn\}$.[59,60]

The crystal data and selected bond metrics of **11** are collected in Tables 1 and 4, respectively. As Figure 5 shows, the molecule is a linear tetraspirocycle, having a central zinc atom, flanked by two *P*-anilido-*P*-thiodiazasilaphosphetidines. This compound is structurally related to the bis(aminophosphoranate) complexes $\{Et_2P{=}E(NMe)\text{-}\kappa N\text{-}\kappa E]_2Zn\}$ and $\{[{}^tBu_2P{=}E(N^iPr)\text{-}\kappa N\text{-}\kappa E]_2Zn\}$,[59,60] E = S and Se, discussed above. In **11** the coordination geometry about zinc is distorted tetrahedral, with large N−Zn−N, N−Zn−S, and S−Zn−S angles (120.6(4)−131.7(3)°) between donor atoms from different ligands but small N−Zn−S angles (80.8(3)°) between donor atoms from the same ligand. None of the bond lengths of the Si(μ-N)$_2$P ligand changed significantly upon coordination, but the phosphorus−sulfur bond lengthened from 1.938(2) Å in **4** to 2.068(10) Å in the complex.

While the monothallium compound **7** is the only plausible stoichiometric product of the title ligands, diethylzinc and trimethylaluminum can react with up to 2 or 3 equiv of these diazasilaphosphetidines, respectively. The differing reactivity of alkylaluminum and -zinc reagents—strictly monoligand complexes for the former but diligand complexes for the latter—therefore deserves an additional comment. The reluctance of aluminum to coordinate more than one ligand is likely due to its smaller size and higher valence, because an

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aluminum complex bearing two chelating ligands would be five-coordinate. Given the size of these ligands, this coordination number apparently cannot be attained.

In summary, *P*-anilino-*P*-chalcogenodiazasilaphosphetidines combine the predictable coordination chemistry of aminophosphoranes with the steric and electronic advantages of bis(amino)cyclodiphosph(V)azanes. Because the utility of aminophosphoranes stems, in part, from their electron-richness, the cyclic species **3**−**6** should be even better ligands, since each phosphorus atom has not one or two but three (or four) nitrogen substituents. Although these synthetic and structural studies were limited to group 12 and 13 metals, they show that the bite angles of these ligands are sufficiently flexible to accommodate metals ranging in size from 1.18 to 1.48 Å, and one can therefore expect an extensive a coordination chemistry of *P*-aminodiazasilaphosphetidines.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of purified nitrogen or argon, using standard Schlenk techniques. Solvents were dried and freed of molecular oxygen by distillation under an atmosphere of nitrogen from sodium or potassium benzophenone ketyl immediately before use. NMR spectra were recorded on a Bruker Avance-500 NMR spectrometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra are referenced relative to C_6D_5H (7.15 ppm), C_6D_6 (128.0 ppm), and $P(OEt)_3$ (137.0 ppm), respectively. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by E and R Microanalytical Services, Parsipanny, NJ.

Trimethylaluminum was used as 2.0 M heptanes (Aldrich) and 2.4 M hexanes (Acros) solutions. Diethylzinc was purchased from Acros and diluted to 0.91 M in hexanes. Both $[Me_2Si(\mu\text{-N}^tBu)_2PCl]$ (**1**)[27] and *p*-tolyl azide[61] were synthesized by published procedures.

Syntheses. $[Me_2Si(\mu\text{-N}^tBu)_2P(NHPh)]$ (2) (1,3-Di-*tert*-butyl-2,2-dimethyl-4-anilino-1,3,2,4-diazasilaphosphetidine). A cold (0 °C) solution of aniline (7.30 mL, 80.1 mmol) in 25 mL of THF was treated dropwise with ^{n}BuLi (1.6 M in hexanes, 80.0 mmol), refluxed for 1 h, and then added dropwise at −78 °C to a solution of **1** (21.4 g, 80.0 mmol) in 25 mL of toluene. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. After all liquids had been removed in vacuo, the remaining solid was extracted with 50 mL of toluene, and the extract was filtered through a medium-porosity frit. The clear filtrate was concentrated in vacuo and stored at −21 °C until the syrupy liquid had solidified. Yield: 23.4 g (90.3%).

Mp: 45−47 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ = 7.12 (t, 2 H, J_{HH} = 7.9 Hz), 7.00 (dt, 2 H, J_{HH} = 8.5, 1.2 Hz), 6.76 (tt, 1 H, J_{HH} = 7.3, 2.1 Hz), 4.35 (s, 1 H), 1.16 (s, 18 H), 0.34 (s, 3 H), 0.33 (s, 3 H). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ = 145.5 (d, J_{PC} = 11.1 Hz), 129.5 (s), 119.5 (s), 116.9 (d, J_{PC} = 12.3 Hz), 50.3 (d, J_{PC} = 10.5), 32.7 (d, J_{PC} = 6.8 Hz), 8.5 (d, J_{PC} = 2.5 Hz), 5.3 (s). ^{31}P{^{1}H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ = 135.8 (s). ^{29}Si NMR (99.35 MHz, benzene-d_6, 26 °C): δ = 9.7 (s). Anal. Calcd for $C_{16}H_{30}N_3PSi$: C, 59.41; H, 9.35; N, 12.99. Found: C, 59.33; H, 9.64; N, 13.12.

$[Me_2Si(\mu\text{-N}^tBu)_2P{=}O(NHPh)]$ (3) (1,3-Di-*tert*-butyl-2,2-dimethyl-4-anilino-4-oxo-1,3,2,4-diazasilaphosphetidine). At 0 °C, a solution of **2** (0.490 g, 1.52 mmol) in 15 mL of toluene was treated with cumene hydroperoxide (0.29 mL, 1.5 mmol), and the mixture was allowed to stir at room temperature for 18 h. The tan-colored solution was concentrated in vacuo and stored at −21 °C until clear, colorless crystals had precipitated. These were redissolved in hot hexanes, and the flask was left to cool at room temperature until clear, colorless plates had formed. Yield: 0.394 g, 77%.

Mp: 200−202 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ = 9.15 (s, 1 H), 7.60 (d, 2 H, J_{HH} = 8.0 Hz), 7.18 (t, 2 H, J_{HH} = 7.8 Hz), 6.83 (t, 1 H, J_{HH} = 7.3 Hz), 1.30 (s, 18 H), 0.38 (s, 3 H), 0.35 (s, 3 H). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ = 144.0 (s); 128.8 (s), 120.4 (s), 118.6 (d, J_{PC} = 6.8 Hz), 51.9 (s), 31.9 (d, J_{PC} = 6.1 Hz), 4.0 (s), 2.1 (d, J_{PC} = 6.4 Hz). ^{31}P{^{1}H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ = 3.1 (d, J_{PH} = 5.5 Hz). ^{29}Si NMR (99.35, benzene-d_6, 26 °C): δ = −2.2 (s). Anal. Calcd for $C_{16}H_{30}N_3OPSi$: C, 55.61; H, 8.91; N, 12.38. Found: C, 55.63; H, 9.08; N, 12.43.

$[Me_2Si(\mu\text{-N}^tBu)_2P{=}S(NHPh)]$ (4) (1,3-Di-*tert*-butyl-2,2-dimethyl-4-anilino-4-thio-1,3,2,4-diazasilaphosphetidine). A mixture of sublimed sulfur (0.600 g, 18.7 mmol) and **2** (6.05 g, 18.7 mmol) in 60 mL of toluene was stirred for 18 h at 50 °C, concentrated in vacuo, and then stored at −21 °C. Several fractions of white crystals yielded 6.34 g (95.3%) of product.

Mp: 184−185 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ = 7.05 (t, 2 H, J_{HH} = 7.9 Hz), 6.83 (d, 2 H, J_{HH} = 7.8 Hz), 6.80 (t, 1 H, J_{HH} = 7.4 Hz), 5.70 (d, 1 H, J_{PH} = 12.1 Hz), 1.30 (s, 18 H), 0.35 (s, 3 H), 0.31 (s, 3 H). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ = 142.0 (d, J_{PC} = 5.8 Hz), 129.0 (s), 121.7 (s), 118.6 (d, J_{PC} = 5.8 Hz), 52.9 (s), 31.3 (d, J_{PC} = 6.2 Hz), 3.5 (s), 3.3 (d, J_{PC} = 4.5 Hz). ^{31}P{^{1}H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ = 64.1 (d, J_{PH} = 12.2 Hz). ^{29}Si NMR (99.35 MHz, benzene-d_6, 26 °C): δ = 2.6 (s). Anal. Calcd for $C_{16}H_{30}N_3PSSi$: C, 54.05; H, 8.50; N, 11.82. Found: C, 54.15; H, 8.58; N, 11.80.

$[Me_2Si(\mu\text{-N}^tBu)_2P{=}Se(NHPh)]$ (5) (1,3-Di-*tert*-butyl-2,2-dimethyl-4-anilino-4-seleno-1,3,2,4-diazasilaphosphetidine). A suspension of gray selenium (0.305 g, 3.86 mmol) in toluene was treated dropwise at room temperature with a toluene solution of **2** (1.25 g, 3.86 mmol). The mixture was stirred at reflux until it became clear (18 h) and concentrated in vacuo until a solid precipitated. This solid was redissolved, and the colorless solution was stored at −21 °C to afford a white powder (1.44 g, 92.5%).

Mp: 184−186 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ = 7.03 (t, 2 H, J_{HH} = 7.8 Hz), 6.79 (t, 1 H, J_{HH} = 7.6 Hz), 6.77 (d, 2 H, J_{HH} = 7.7 Hz), 5.80 (d, 1 H, J_{PH} = 14.6), 1.31 (s, 18 H), 0.35 (s, 3 H), 0.29 (s, 3 H). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ = 141.8 (d, J_{PC} = 8.5 Hz), 129.0 (s), 122.0 (s), 118.7 (d, J_{PC} = 5.9 Hz); 53.3 (s), 31.3 (d, J_{PC} = 5.9 Hz), 4.1 (d, J_{PC} = 3.0 Hz), 3.3 (s). ^{31}P{^{1}H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ = 35.9 (d, J_{PH} = 14.7 Hz). ^{29}Si NMR (99.35 MHz, benzene-d_6, 26 °C): δ = 4.0 (s). Anal. Calcd for $C_{16}H_{30}N_3PSeSi$: C, 47.75; H, 7.51; N, 10.44. Found: C, 47.69; H, 7.52; N, 10.42.

$\{[Me_2Si(\mu\text{-N}^tBu)_2P{=}(N\text{-}p\text{-tolyl})(NHPh)]\cdot 0.5C_6H_5Me\}$ (6) (1,3-Di-*tert*-butyl-2,2-dimethyl-4-anilino-4-(*p*-tolylimino)-1,3,2,4-diazasilaphosphetidine−Hemitoluene). A solution of **2** (6.18 g, 19.1 mmol) in 40 mL of toluene was treated with 2.80 g (21.0 mmol) of *p*-tolyl azide, dissolved in 10 mL of toluene. The reaction mixture, which evolved gas, was stirred for 18 h at room temperature and then refluxed for 2 h, while it became orange-red. Following two recrystallizations at −21 °C, colorless crystals (6.87 g, 75.8%) were recovered.

Mp: 134−135 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ = 7.51 (s, 1 H), 7.31 (d, 2 H, J_{HH} = 7.7 Hz), 7.24 (t, 2 H, J_{HH} = 7.4 Hz), 7.14 (d, 2 H, J_{HH} = 7.0 Hz), 6.95 (d, 2 H, J_{HH} = 7.9 Hz), 6.85 (t, 1 H, J_{HH} = 7.2 Hz), 2.13 (s, 3 H), 1.17 (s, 18 H), 0.47 (s, 3 H), 0.46 (s, 3 H). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6,

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26 °C): $\delta = 148.2$ (d, $J_{PC} = 1.6$ Hz), 143.3 (d, $J_{PC} = 2.9$ Hz), 129.4 (s), 128.8 (s), 128.5 (s), 122.4 (d, $J_{PC} = 14.0$ Hz), 121.1 (d, $J_{PC} = 11.1$ Hz), 119.2 (s), 52.0 (s), 31.9 (d, $J_{PC} = 5.5$ Hz), 20.7 (s), 3.5 (d, $J_{PC} = 2.9$ Hz), 3.4 (d, $J_{PC} = 2.8$ Hz). $^{31}P\{^1H\}$ NMR (202.46 MHz, benzene-d_6, 26 °C): $\delta = 12.0$ (s). ^{29}Si NMR (99.35 MHz, benzene-d_6, 26 °C): $\delta = -3.1$ (s). Anal. Calcd for $C_{26.5}H_{41}N_4PSi$: C, 67.05; H, 8.71; N, 11.80. Found: C, 67.12; H, 8.84; N, 11.85.

{[$Me_2Si(\mu$-N^{t}Bu$)_2$P=S(NPh)-κN-κS]Tl} (7) ((1,3-Di-*tert*-butyl-2,2-dimethyl-4-anilino-4-thio-1,3,2,4-diazasilaphosphetidinyl-κN-κS)thallium(I)). A cold solution of **4** (0.356 g, 1.00 mmol) in 10 mL of toluene was treated dropwise with 0.40 mL of ^{n}BuLi. After gas evolution had ceased, the reaction mixture was refluxed for 1 h and then added dropwise to a cold (0 °C) suspension of TlCl (0.240 g, 1.00 mmol) in 10 mL of THF. The mixture was stirred at room temperature for 18 h, taken to dryness in vacuo, and finally extracted with 10 mL of toluene. The extract was filtered through a medium-porosity frit, and the clear filtrate was concentrated in vacuo to ca. 5 mL and stored at −21 °C. Several fractions of thin, colorless plates afforded 0.391 g of product. Yield: 70%.

Mp: 201−203 °C (dec). ^1H NMR (500.13 MHz, benzene-d_6, 26 °C): $\delta = 7.32$ (t, 2 H, $J_{HH} = 7.5$ Hz), 7.15 (d, 2 H, $J = 7.4$ Hz), 6.92 (td, 1 H, $J_{HH} = 7.2$ Hz, 0.8 Hz), 1.34 (s, 18 H), 0.41 (s, 3 H), 0.39 (s, 3 H). $^{13}C\{^1H\}$ NMR (125.76 MHz, benzene-d_6, 26 °C): $\delta = 149.3$ (d, $J_{PC} = 8.6$ Hz), 128.0 (s); 121.9 (d, $J_{PC} = 16.3$ Hz), 119.6 (s), 52.7 (s), 31.8 (d, $J_{PC} = 5.3$ Hz); 4.1 (s), 3.6 (d, $J_{PC} = 3.8$ Hz). $^{31}P\{^1H\}$ NMR (202.46 MHz, benzene-d_6, 26 °C): $\delta = 38.3$ (s). ^{29}Si NMR (99.4 MHz, benzene-d_6, 26 °C): $\delta = -1.4$ (s). Anal. Calcd for $C_{16}H_{29}N_3PSSiTl$: C, 34.38; H, 5.23; N, 7.52. Found: C, 34.49; H, 5.40; N, 7.74.

{$Me_2Si(\mu$-N^{t}Bu$)_2$P=S(NPh)-κN-κS]AlMe$_2$} (8) ((1,3-Di-*tert*-butyl-2,2-dimethyl-4-anilino-4-thio-1,3,2,4-diazasilaphosphetidinyl-κN-κS)dimethylaluminum). To a cold (0 °C) solution of **4** (0.704 g, 1.98 mmol) in 20 mL of hexanes was added dropwise 1.00 mL of $AlMe_3$ in heptanes. The colorless solution was allowed to slowly warm to room temperature and kept at that temperature for 18 h. It was concentrated in vacuo and stored at −21 °C to afford 0.722 g of colorless needles. Yield: 89%.

Mp: 164−166 °C. ^1H NMR (500.13 MHz, benzene-d_6, 26 °C): $\delta = 7.25$ (d, 2 H, $J_{HH} = 7.6$ Hz), 7.13 (t, 2 H, $J_{HH} = 7.5$ Hz), 6.85 (t, 1 H, $J_{HH} = 7.4$ Hz), 1.18 (s, 18 H), 0.29 (s, 3 H), 0.20 (s, 3 H), −0.02 (s, 6 H). $^{13}C\{^1H\}$ NMR (125.76 MHz, benzene-d_6, 26 °C): $\delta = 145.9$ (d, $J_{PC} = 8.8$ Hz), 129.4 (s), 121.6 (s), 120.3 (d, $J_{PC} = 14.4$ Hz), 53.3 (s), 31.4 (d, $J_{PC} = 6.0$ Hz), 3.1 (s), 3.1 (s), −7.0 (s). $^{31}P\{^1H\}$ NMR (202.5 MHz, benzene-d_6, 26 °C): $\delta = 35.8$ (s). ^{29}Si NMR (99.35 MHz, benzene-d_6, 26 °C): $\delta = 3.1$ (s). Anal. Calcd for $C_{18}H_{35}N_3AlPSSi$: 52.53; H, 8.57; N, 10.21. Found: C, 52.13; H, 8.92; N, 10.28.

{[$Me_2Si(\mu$-N^{t}Bu$)_2$P=Se(NPh)-κN-κSe]AlMe$_2$} (9) ((1,3-Di-*tert*-butyl-2,2-dimethyl-4-anilino-4-seleno-1,3,2,4-diazasilaphosphetidinyl-κN-κS)dimethylaluminum). To a cooled (0 °C) toluene solution of $AlMe_3$ (1.00 mmol) was added a toluene solution of **5** (0.400 g, 0.993 mmol). The reaction mixture, which remained colorless and clear, was stirred at room temperature until all gas evolution had ceased (ca. 18 h). It was concentrated in vacuo and stored at −21 °C to produce 0.385 g of colorless needles. Yield: 84%.

Mp: 164−166 °C. ^1H NMR (500.13 MHz, benzene-d_6, 26 °C): $\delta = 7.31$ (d, 2 H, $J_{HH} = 8.5$ Hz), 7.13 (t, 2 H, $J_{HH} = 7.6$ Hz), 6.85 (t, 1 H, $J_{HH} = 7.4$ Hz), 1.19 (s, 18 H), 0.25 (s, 3 H), 0.18 (s, 3 H); 0.06 (s, 6 H). $^{13}C\ \{^1H\}$ NMR (125.76 MHz, benzene-d_6, 26 °C): $\delta = 146.7$ (d, $J_{PC} = 10.8$ Hz), 129.4 (s), 121.8 (s), 120.5 (d, $J_{PC} = 14.4$ Hz), 53.6 (s), 31.3 (d, $J_{PC} = 5.9$ Hz), 3.6 (d, $J_{PC} = 3.1$ Hz), 3.0 (s), −6.6 (s). $^{31}P\{^1H\}$ NMR (202.46 MHz, benzene-d_6, 26 °C): $\delta = 19.7$ (s). ^{29}Si NMR (99.35 MHz, benzene-d_6, 26 °C): $\delta = 3.9$ (s). Anal. Calcd for $C_{18}H_{35}N_3AlPSeSi_2$: C, 47.15; H, 7.69; N, 9.16. Found: C, 47.25; H, 7.73; N, 9.14.

{[$Me_2Si(\mu$-N^{t}Bu$)_2$P=(N-*p*-tolyl)(NPh)-κN^2]AlMe$_2$} (10) ((1,3-Di-*tert*-butyl-2,2-dimethyl-4-anilino-4-(*p*-tolylimino)-1,3,2,4-diazasilaphosphetidinyl-κN^2)dimethylaluminum). The addition of 0.46 mL of $AlMe_3$ to **6** (0.453 g, 1.01 mmol), dissolved in 10 mL of cold (0 °C) toluene, caused a rapid gas evolution. After the clear, colorless solution had been stirred at room temperature for 18 h, it was concentrated in vacuo and stored at −21 °C. Yield: 0.457 g, 92.9%, of colorless crystals.

Mp: 170−171 °C. ^1H NMR (500.13 MHz, benzene-d_6, 26 °C): $\delta = 7.23$−7.17 (m, 4 H), 7.12 (d, 2 H, $J_{HH} = 8.2$ Hz), 6.96 (d, 2 H, $J_{HH} = 8.3$ Hz), 6.85 (tt, 1 H, $J_{HH} = 6.9$, 1.5 Hz), 2.15 (s, 3 H), 1.04 (s, 18 H), 0.41 (s, 3 H), 0.40 (s, 3 H), 0.01 (s, 6 H). $^{13}C\{^1H\}$ NMR (125.76 MHz, benzene-d_6, 26 °C): $\delta = 145.8$ (s), 143.0 (s), 129.9 (s), 129.3 (s), 129.2 (s), 120.5 (s), 120.4 (s), 120.3 (s), 52.7 (s), 31.7 (d, $J_{PC} = 5.5$ Hz), 20.7 (s), 3.0 (dd, $J_{PC} = 4.8$, 2.9 Hz), −8.5 (s). $^{31}P\{^1H\}$ NMR (202.46 MHz, benzene-d_6, 26 °C): $\delta = 6.3$ (s). ^{29}Si NMR (99.35 MHz, benzene-d_6, 26 °C): $\delta = -1.1$ (s). Anal. Calcd for $C_{25}H_{42}N_4AlPSi$: C, 61.95; H, 8.73; N, 11.56. Found: C, 61.57; H, 8.94; N, 11.63.

{[$Me_2Si(\mu$-N^{t}Bu$)_2$P=S(NPh)-κN-κS]$_2$Zn} (11) (Bis(1,3-di-*tert*-butyl-2,2-dimethyl-4-anilino-4-thio-1,3,2,4-diazasilaphosphetidinyl-κN-κS)zinc). To a sample of **4** (0.352 g, 0.990 mmol), dissolved in 20 mL of cold (0 °C) toluene, was added dropwise 0.55 mL of the diethylzinc solution. The ice bath was removed, and the clear, colorless reaction mixture was stirred for 18 h at room temperature. It was then concentrated in vacuo and kept at rom temperature until 0.311 g of colorless plates had formed. Yield: 81%.

Mp: 302−304 °C. ^1H NMR (500.13 MHz, benzene-d_6, 26 °C): $\delta = 7.54$ (d, 2 H, $J_{HH} = 8.5$ Hz), 7.26 (t, 2 H, $J_{HH} = 7.4$ Hz), 6.92 (t, 1 H, $J_{HH} = 7.3$ Hz), 1.33 (s, 18 H), 0.34 (s, 3 H); 0.25 (s, 3 H). $^{13}C\{^1H\}$ NMR (125.76 MHz, benzene-d_6, 26 °C): $\delta = 149.0$ (d, $J_{PC} = 10.6$ Hz), 129.0 (s), 122.0 (d, $J_{PC} = 15.6$ Hz), 120.3 (s), 53.0 (s), 31.7 (d, $J_{PC} = 5.7$ Hz), 3.3 (d, $J_{PC} = 3.9$ Hz), 2.9 (s). $^{31}P\{^1H\}$ NMR (202.46 MHz, benzene-d_6, 26 °C): $\delta = 48.2$ (s). ^{29}Si NMR (99.35 MHz, benzene-d_6, 26 °C): $\delta = 1.3$ (s). Anal. Calcd for $C_{32}H_{58}N_6P_2S_2Si_2Zn$: C, 49.63; H, 7.55; N, 10.85. Found: C, 49.67; H, 7.73; N, 10.98.

{[$Me_2Si(\mu$-N^{t}Bu$)_2$P=Se(NPh)-κN-κSe]$_2$Zn} (12) (Bis(1,3-di-*tert*-butyl-2,2-dimethyl-4-anilino-4-seleno-1,3,2,4-diazasilaphosphetidinyl-κN-κSe)zinc). To a sample of **5** (0.402 g, 1.00 mmol), dissolved in 10 mL of cold (0 °C) toluene, was added dropwise 0.55 mL of the diethylzinc solution. The clear, colorless reaction mixture, which evolved ethane, was allowed to warm to room temperature and stirred for an additional 18 h. It was then concentrated in vacuo and stored at −21 °C until 0.398 g of colorless crystals had formed. Yield: 92%.

Mp: 306−308 °C. ^1H NMR (500.13 MHz, benzene-d_6, 26 °C): $\delta = 7.60$ (d, 2 H, $J_{HH} = 8.0$ Hz); 7.24 (t, 2 H, $J_{HH} = 7.5$ Hz); 6.91 (t, 1 H, $J_{HH} = 7.3$ Hz); 1.34 (s, 18 H); 0.32 (s, 3 H); 0.25 (s, 3H). $^{13}C\{^1H\}$ NMR (125.76 MHz, benzene-d_6, 26 °C): $\delta = 149.8$ (d, $J_{PC} = 13.6$ Hz), 129.0 (s), 122.2 (d, $J_{PC} = 16.0$ Hz), 120.5 (s), 53.3 (s), 31.6 (d, $J_{PC} = 5.4$ Hz), 3.9 (d, $J_{PC} = 2.8$ Hz), 2.8 (s). $^{31}P\{^1H\}$ NMR (202.46 MHz, benzene-d_6, 26 °C): $\delta = 32.3$ (s). ^{29}Si NMR (99.4 MHz, benzene-d_6, 26 °C): $\delta = 2.2$ (s). Anal. Calcd for $C_{32}H_{58}N_6P_2Se_2Si_2Zn$: C, 44.27; H, 6.73; N, 9.68. Found: C, 44.38; H, 6.81; N, 9.62.

{[$Me_2Si(\mu$-N^{t}Bu$)_2$P=(N-*p*-tolyl)(NPh)-κN^2]$_2$Zn} (13) (Bis(1,3-di-*tert*-butyl-2,2-dimethyl-4-anilino-4-(*p*-tolylimino)-1,3,2,4-di-

azasilaphosphetidinyl-κN^2)zinc). In a manner strictly identical with that used for the syntheses of **7** and **8**, a sample of **6** (0.428 g, 0.999 mmol) and 0.55 mL of the diethylzinc stock solution were allowed to react. Several fractions of a white powder yielded 0.395 g of product. Overall yield: 86%.

Mp: 320−322 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): $\delta = 7.43$ (d, 2 H, $J_{HH} = 8.0$ Hz), 7.34 (d, 2 H, $J_{HH} = 8.2$ Hz), 7.24 (t, 2 H, $J_{HH} = 7.7$ Hz), 7.03 (d, 2 H, $J_{HH} = 8.2$ Hz), 6.88 (t, 1H, $J_{HH} = 7.3$ Hz), 2.22 (s, 3 H), 1.22 (s, 18 H), 0.53 (s, 3 H), 0.52 (s, 3 H). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): $\delta = 149.2$ (s), 146.4 (s), 129.4 (s), 128.8 (s), 127.6 (s), 122.5 (d, $J_{PC} = 14.4$ Hz), 122.3 (d, $J_{PC} = 14.1$ Hz), 119.0 (s), 52.2 (d, $J_{PC} = 2.6$ Hz), 32.2 (d, $J_{PC} = 5.2$ Hz), 20.8 (s), 3.5 (m). ^{31}P{^{1}H} NMR (202.46 MHz, benzene-d_6, 26 °C): $\delta = 13.2$ (s). ^{29}Si NMR (99.4 MHz, benzene-d_6, 26 °C): $\delta = -3.5$ (s). Anal. Calcd for $C_{46}H_{72}N_8Si_2P_2$-Zn: C, 60.01; H, 7.88; N, 12.17. Found: C, 60.14; H, 7.96; N, 12.28.

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Supporting Information Available: Six X-ray crystallographic files for structures **3**, **4**, **6**−**8**, and **11** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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