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# Syntheses and Structures of Group 14 1,3-Dimetallacyclobutanes

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Metalation of 2,6-lutidine-functionalized bis(phosphoranimines) $(\mathrm{Me_3SiN{=}PPr^{\mathit{i}}_2CH_2})_2\mathrm{C_5H_3N}$-2,6 (**2**) using $\mathrm{MgBu_2}$ in THF yielded the magnesium compound $[\mathrm{Mg\{(Me_3SiN{=}PPr^{\mathit{i}}_2CH)_2C_5H_3N\text{-}2,6\}THF}]$ (**3**). Further reaction of **3** with 1 equiv of $\mathrm{SnCl_2}$ afforded the tin(II) compound $[\{2\text{-}\{\mathrm{Sn\{C(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}}\}\text{-}6\text{-}\{\mathrm{Sn\{CH(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}Cl}\}\}\mathrm{C_5H_3N}]_2$ (**4**). Treatment of **2** with 2 equiv of $\mathrm{Pb\{N(SiMe_3)_2\}_2}$ afforded the lead(II) compound $[\{2\text{-}\{\mathrm{Pb\{C(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}}\}\text{-}6\text{-}\{\mathrm{Pb\{CH(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}N(SiMe_3)_2}\}\}\mathrm{C_5H_3N}]_2$ (**5**). X-ray structural analysis revealed that **4** and **5** consist of a 1,3-dimetallacyclobutane and two metal(II) alkyl moieties. Similar reaction of **3** with 1 equiv of $\mathrm{GeCl_2}$(dioxane), however, yielded the germanium(II) compound $[\{2\text{-}\mathrm{CH(Pr^{\mathit{i}}_2P{=}NSiMe_3)}\text{-}6\text{-}\overline{\mathrm{CH(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}C_5H_3NGe\{2\text{-}\{C(Pr^{\mathit{i}}_2P{=}NSiMe_3)Ge}}\}\text{-}6\text{-}\mathrm{CH_2(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}C_5H_3N}]$ (**6**) without forming a similar 1,3-digermacyclobutane ring.

## Introduction

Phosphoranimines have been used as supporting ligands in the synthesis of metal complexes. For example, neutral P−N type ligands such as $\mathrm{Me_3SiN{=}PPh_2CH_2PPh_2}$,[1,2] 5-F,2,4-$(\mathrm{NO_2})_2\mathrm{C_6H_2N{=}PPh_2CH_2PPh_2}$,[3] $(\mathrm{Me_3SiN{=}PPh_2})_2\mathrm{CH_2}$,[4] and $\mathrm{CH_2(PPh_2{=}S)(PPh_2{=}NR)}$ (R = *p*-tolyl, *p*-anisyl)[5] and anionic P−N type ligands such as $[\mathrm{Li(PhNPPh_2)(Et_2O)}]_2$,[6] $[\mathrm{M\{HC(Ph_2P{=}NSiMe_3)_2}\text{-}\kappa N, \kappa N'\}(\mathrm{THF})_2]$ (M = Na, K),[7] and $[\overline{\mathrm{K\{P(Ph)C(Bu^{\mathit{t}}){=}C(H)P(Ph_2){=}N}}\mathrm{SiMe_3}\}]_\infty$[8] have been reported. Transition metal and lanthanide metal methandiide complexes based on the phosphoranimine ligands have been investigated.[9−11] We have communicated the synthesis of bigermavinylidene and group 14 1,3-dimetallacyclobutanes derived from different phosphoranimines.[12,13] In this paper, we report the use of a novel 2,6-lutidine-functionalized bis(phosphoranimine) **2**, as the ligand used in the synthesis of a series of group 14 metal compounds. The magnesium complex derived from **2** has been used both as the ligand transfer reagent and as the base to facilitate further dehydrochlorination.

## Results and Discussion

Bis(phosphoranimine) **2** was prepared by the reaction of $(\mathrm{Pr^{\mathit{i}}_2PCH_2})_2\mathrm{C_5H_3N}$-2,6 (**1**)[14] with $\mathrm{Me_3SiN_3}$, and the product obtained was purified by vacuum distillation (Scheme 1). Metalation of **2** using $\mathrm{MgBu_2}$ in THF afforded bright yellow crystalline solids of $[\mathrm{Mg\{(Me_3SiN{=}PPr^{\mathit{i}}_2CH)_2C_5H_3N\text{-}2,6\}THF}]$ (**3**) in 89% yield (step ii). Compound **3** reacted with 1 equiv of $\mathrm{SnCl_2}$ to yield the 1,3-distannacyclobutane $[\{2\text{-}\{\mathrm{Sn\{C(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}}\}\text{-}6\text{-}\{\mathrm{Sn\{CH(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}Cl}\}\}\mathrm{C_5H_3N}]_2$ (**4**) in 60% yield (step iii). In contrast, using $\mathrm{GeCl_2}$(dioxane), the germanium(II) compound $[\{2\text{-}\mathrm{CH(Pr^{\mathit{i}}_2P{=}NSiMe_3)}\text{-}6\text{-}\overline{\mathrm{CH(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}C_5H_3NGe\{2\text{-}\{C(Pr^{\mathit{i}}_2P{=}N{-}SiMe_3)Ge}}\}\text{-}6\text{-}\mathrm{CH_2(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}C_5H_3N}]$ (**6**) was obtained in 57% yield (step v). Treatment of **2** with 2 equiv of $\mathrm{Pb\{N(SiMe_3)_2\}_2}$ afforded the 1,3-diplumbacyclobutane $[\{2\text{-}\{\mathrm{Pb\{C(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}}\}\text{-}6\text{-}\{\mathrm{Pb\{CH(Pr^{\mathit{i}}_2P{=}NSiMe_3)\}N(SiMe_3)_2}\}\}\mathrm{C_5H_3N}]_2$ (**5**) in 29% yield (step iv).

On the basis of the structure of compound **4**, a possible mechanism has been proposed in Scheme 2. Compound **3** was first reacted with 2 equiv of $\mathrm{SnCl_2}$ to form an intermediate bischlorotin(II) alkyl complex, $\{\mathrm{Sn(Me_3SiN{=}PPr^{\mathit{i}}_2CH)Cl}\}_2\mathrm{C_5H_3N}$-2,6 (**3a**) (step i). It then further reacted with the remaining 1 equiv of compound **3** to undergo dehydrochlorination accompanied by the elimination of $\mathrm{MgCl_2}$ and **2** to form the unstable intermediate stannavinylidene (**3b**) (step ii). Subsequently, by “head-to-tail” cyclodimerization of the two stannavinylidene intermediates, the 1,3-distannacy-

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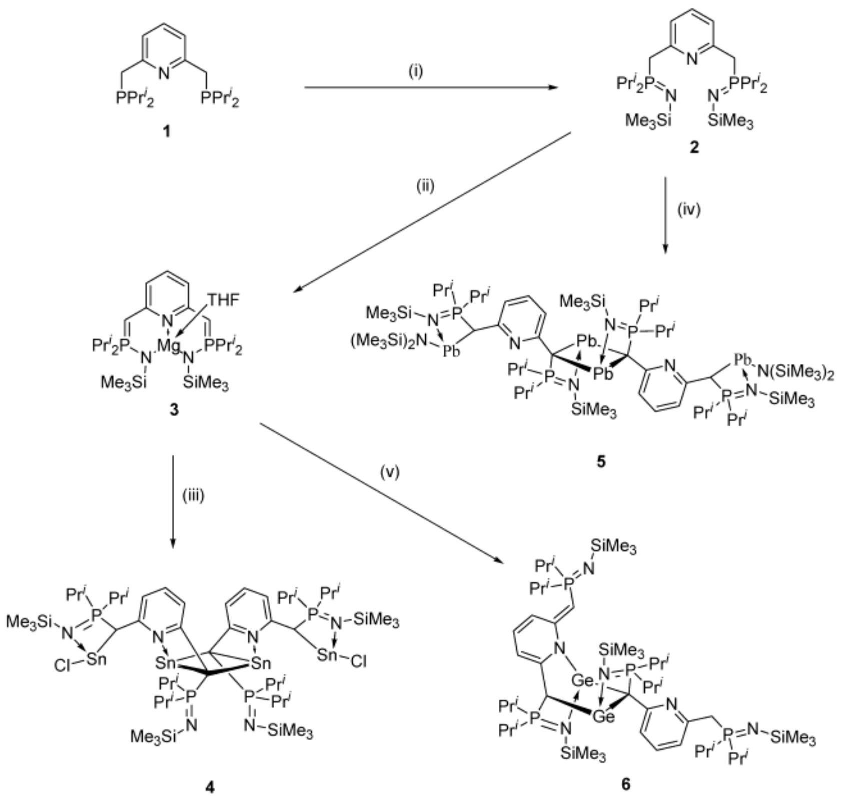
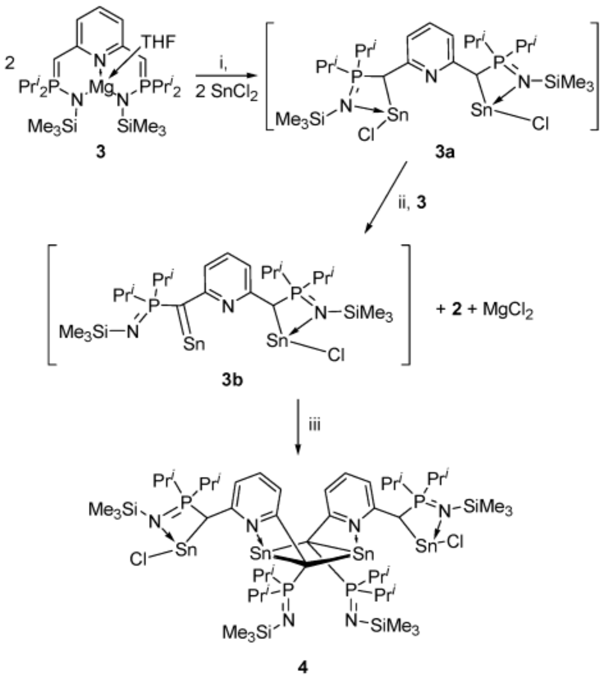
**Scheme 1. Syntheses of Compounds 2−6**[a]



[a] Reagents: (i) 2 $Me_3SiN_3$, toluene; (ii) $MgBu_2$, THF; (iii) $SnCl_2$, $Et_2O$; (iv) 2 $Pb\{N(SiMe_3)_2\}_2$, $Et_2O$; (v) $GeCl_2$(dioxane), $Et_2O$.

**Scheme 2. Proposed Mechanism for Compound 4**



clobutane ring of compound **4** was formed (step iii). The other chlorotin(II) alkyl within the same ligand remained unchanged. It is suggested that the magnesium compound **3** acts not only as the ligand transfer reagent but also as the strong base for dehydrochlorination. Compound **5** is presumably reacted in a mechanism similar to that proposed for compound **4**. No digermacyclobutane can be produced in compound **6**, possibly due to a smaller atomic size of the Ge(II) atom preventing the approach of the sterically crowded carbon atom. Similar group 14 1,3-dimetallacyclobutanes 1,3-[$M\{C(Pr^i{}_2P{=}NSiMe_3)(2\text{-}Py)\}]_2$ (M = Ge, Sn, and Pb), [$M\{\mu^2\text{-}C(Ph_2P{=}NSiMe_3)_2\}]_2$ (M = Sn and Pb), and a mixed-metal 1,3-stannapumbacyclobutane [1-$Sn\{C(Pr^i{}_2P{=}NSiMe_3)(2\text{-}Py)\}$-3-$Pb\{C(Pr^i{}_2P{=}NSiMe_3)(2\text{-}Py)\}$] have been reported.[12,13] Furthermore, group 4 metal "pincer" carbene complexes [$Zr\{CPh_2P{=}NR\}_2\text{-}\kappa^3C,N,N'](CH_2Ph)_2$] (R = adamantyl or $SiMe_3$) and group 13 metal alkylidene complex [$(AlMe_2)_2\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,C',N,N'\}$] synthesized through the methandiide ligands from double deprotonation of the methylene center of the phosphoraimines have also been reported [15,16]

The magnesium compound **3** is a yellow crystalline solid soluble in $Et_2O$, THF, and toluene. The $^1H$ NMR spectrum of **3** showed a doublet signal at $\delta$ 2.55 ppm ($J_{P-H} = 16.8$ Hz) that is due to the coupling of a methine proton to the phosphorus nucleus. The $^{13}C$ NMR spectrum was consistent with the solid-state structure determined. The $^{31}P$ NMR spectrum displayed one singlet at a lower field, $\delta$ 57.71 ppm, relative to the parent bis(phosphoranimine) ($\delta$ 34.42 ppm). In all the spectra, one set of signals due to the ligand was observed, suggesting that the ligands within the molecule are equivalent in solution. Compounds **4** and **5** are orange crystals soluble in $Et_2O$ and THF. The $^1H$ and $^{13}C$ NMR spectra of **4** exhibited two sets of signals due to the ligands, indicating that the ligands adopt two different environments. The $^{31}P$ NMR spectrum of **4** showed two sharp singlets at $\delta$ 43.44 and 70.06 ppm

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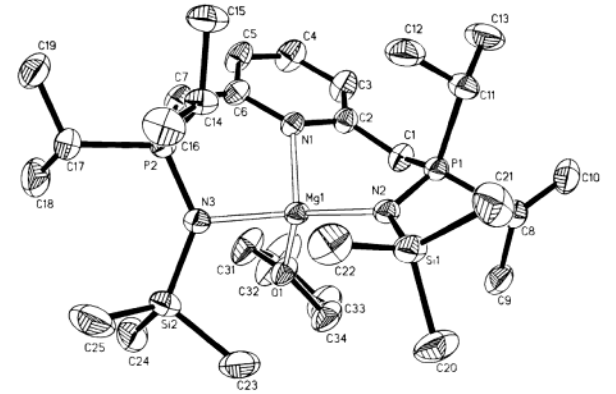

**Figure 1.** ORTEP drawing of **3**; hydrogen atoms are omitted for clarity.

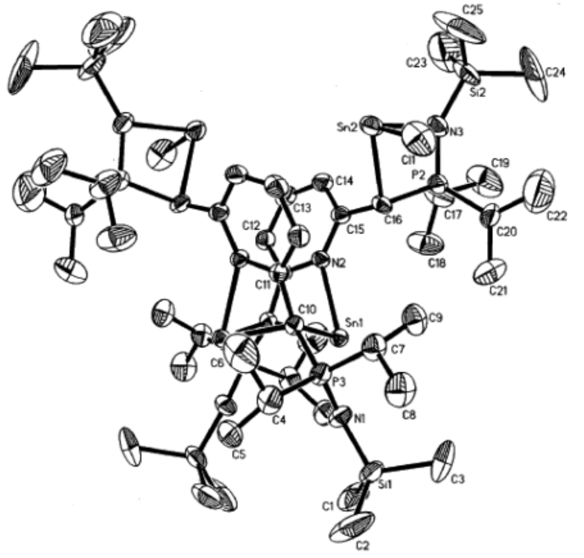

**Figure 2.** ORTEP drawing of **4**; hydrogen atoms are omitted for clarity.

due to the two different phosphorus environments. The $^{119}$Sn NMR spectrum of **4** displayed two doublets at $\delta$ $-72.23$ and $-10.96$ ppm due to the chlorotin(II) alkyl moieties and the 1,3-distannacyclobutane, respectively. They are assigned to the two different tin environments with $^{31}$P$-^{119}$Sn couplings of 140.4 and 157.2 Hz, respectively. The solution of compound **5** turned black slowly at room temperature when exposed to light; it can be characterized only by $^1$H NMR spectroscopy and X-ray crystallography. The $^1$H NMR spectrum of **5** also exhibited two sets of signals, indicating the presence of two different environments. Compound **6** is a bright orange crystalline solid soluble in $Et_2O$ and THF. The $^1$H and $^{13}$C NMR spectra of **6** exhibited four singlets due to the four different $SiMe_3$ groups, showing that the four ligand backbones are chemically nonequivalent. The methine proton signal at $\delta$ 4.62 ppm showed a significant downfield shift, and the aromatic ring protons showed upfield shifts, suggesting the existence of enamido coordination.

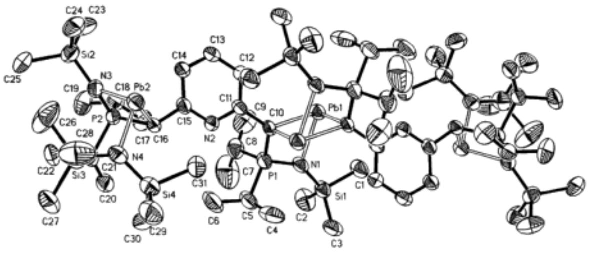

**Figure 3.** ORTEP drawing of **5**; hydrogen atoms are omitted for clarity.

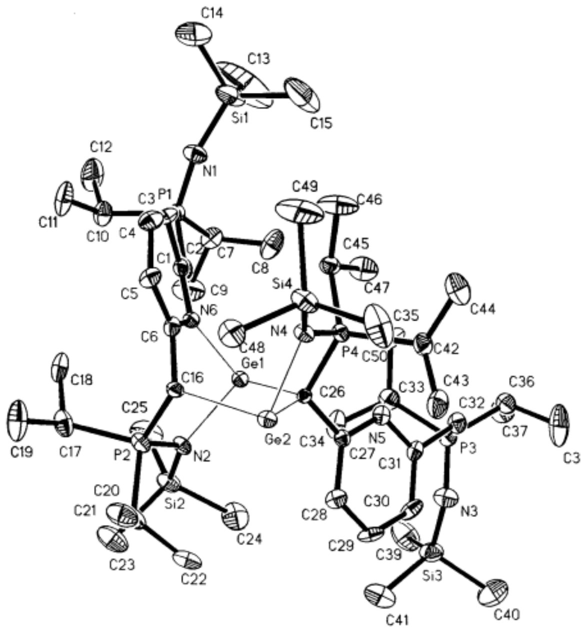

**Figure 4.** ORTEP drawing of **6**; hydrogen atoms are omitted for clarity.

**Table 1. Selected Bond Distances (Å) and Angles (deg) for Compound 3**

| | | | |
|---|---|---|---|
| Mg(1)−N(1) | 2.061(19) | Mg(1)−O(1) | 2.046(17) |
| Mg(1)−N(2) | 2.076(18) | Mg(1)−N(3) | 2.097(2) |
| P(1)−C(1) | 1.707(2) | P(2)−C(7) | 1.722(2) |
| P(1)−N(2) | 1.630(2) | P(2)−N(3) | 1.620(19) |
| C(1)−C(2) | 1.440(3) | C(6)−C(7) | 1.397(3) |
| C(2)−C(3) | 1.399(3) | C(3)−C(4) | 1.385(4) |
| C(4)−C(5) | 1.360(4) | C(5)−C(6) | 1.419(3) |
| N(1)−C(2) | 1.365(3) | N(1)−C(6) | 1.382(3) |
| O(1)−Mg(1)−N(1) | 99.83(8) | O(1)−Mg(1)−N(2) | 123.52(8) |
| O(1)−Mg(1)−N(3) | 98.44(7) | N(1)−Mg(1)−N(2) | 105.58(8) |
| N(1)−Mg(1)−N(3) | 101.25(8) | N(2)−Mg(1)−N(3) | 123.87(8) |
| C(2)−N(1)−Mg(1) | 107.61(14) | C(6)−N(1)−Mg(1) | 125.43(15) |
| N(2)−P(1)−C(1) | 113.05(11) | N(3)−P(2)−C(7) | 115.29(11) |
| C(2)−C(1)−P(1) | 126.15(19) | C(6)−C(7)−P(2) | 127.72(18) |
| N(1)−C(2)−C(1) | 117.7(2) | N(1)−C(6)−C(7) | 119.9(2) |
| C(2)−N(1)−C(6) | 120.78(19) | | |

The molecular structures of **3**−**6** are shown in Figures 1−4, respectively. Selected bond distances and angles are listed in Tables 1−4, respectively. The magnesium compound **3** is monomeric in the solid state. The coordination sphere of the magnesium atom is four-coordinate, being *N*,*N*′,*N*′-chelated by the ligand and coordinated to one THF molecule, and adopts a distorted tetrahedral geometry. Mg(1) is bonded to the two imino nitrogen atoms of the dianionic ligand at distances of 2.076(18) and 2.097(2) Å and to the neutral pyridyl nitrogen atom at a distance of 2.061(19) Å. The Mg(1)−N(pyridyl) bond distance of 2.061(19) Å is shorter than the Mg(1)−N(imino) bond distances of 2.076(18) and 2.097(2) Å. It is believed that the twisting of the chelating sidearms pushes the magnesium atom forward to the pyridyl nitrogen.

The tin(II) compound **4** and lead(II) compound **5** are dimeric in the solid state. Their structures are com-

**Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 4**

| | | | |
|---|---|---|---|
| Sn(1)−C(10) | 2.287(6) | Sn(1)−C(10′) | 2.362(7) |
| Sn(1)−N(2) | 2.316(5) | Sn(1′)−C(10) | 2.362(6) |
| Sn(2)−C(16) | 2.329(7) | Sn(2)−N(3) | 2.256(6) |
| Sn(2)−P(2) | 2.919(2) | Sn(2)−Cl(1) | 2.444(3) |
| P(3)−N(1) | 1.562(7) | P(2)−N(3) | 1.606(7) |
| P(3)−C(10) | 1.766(7) | P(2)−C(16) | 1.787(7) |
| C(10)−C(11′) | 1.444(9) | C(15)−C(16) | 1.455(10) |
| C(11)−C(12) | 1.413(9) | C(12)−C(13) | 1.389(10) |
| C(13)−C(14) | 1.378(11) | C(14)−C(15) | 1.400(10) |
| N(2)−C(11) | 1.381(8) | N(2)−C(15) | 1.351(8) |
| C(10)−Sn(1)−C(10′) | 88.0(2) | N(2)−Sn(1)−C(10) | 88.4(2) |
| N(2)−Sn(1)−C(10′) | 59.8(2) | Sn(1)−C(10)−Sn(1′) | 88.6(2) |
| C(11′)−C(10)−P(3) | 129.7(5) | C(11′)−C(10)−Sn(1) | 117.5(4) |
| Sn(1)−C(10)−P(3) | 100.7(3) | C(11′)−C(10)−Sn(1′) | 91.6(4) |
| Sn(1′)−C(10)−P(3) | 122.3(3) | N(3)−Sn(2)−Cl(1) | 96.7(2) |
| N(3)−Sn(2)−C(16) | 70.5(2) | C(16)−Sn(2)−Cl(1) | 98.2(2) |
| N(3)−P(2)−C(16) | 102.4(3) | P(2)−N(3)−Sn(2) | 96.7(3) |
| P(2)−C(16)−Sn(2) | 89.4(3) | P(2)−C(16)−C(15) | 120.8(5) |
| Sn(2)−C(16)−C(15) | 109.2(5) | | |

**Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 5**

| | | | |
|---|---|---|---|
| Pb(1)−C(10) | 2.363(10) | Pb(1)−C(10′) | 2.426(13) |
| Pb(1)−N(1) | 2.406(10) | Pb(1′)−C(10) | 2.426(13) |
| Pb(2)−C(16) | 2.427(12) | Pb(2)−N(3) | 2.524(11) |
| Pb(2)−P(2) | 3.045(4) | Pb(2)−N(4) | 2.283(11) |
| P(1)−N(1) | 1.614(10) | P(2)−N(3) | 1.611(11) |
| P(1)−C(10) | 1.749(12) | P(2)−C(16) | 1.785(13) |
| C(10)−C(11) | 1.489(16) | C(15)−C(16) | 1.490(14) |
| C(11)−C(12) | 1.424(17) | C(12)−C(13) | 1.425(17) |
| C(13)−C(14) | 1.370(17) | C(14)−C(15) | 1.459(18) |
| N(2)−C(11) | 1.350(14) | N(2)−C(15) | 1.340(14) |
| C(10)−Pb(1)−C(10′) | 86.6(4) | N(1)−Pb(1)−C(10) | 66.0(4) |
| N(1)−Pb(1)−C(10′) | 97.8(4) | Pb(1)−C(10)−Pb(1′) | 93.4(4) |
| C(11)−C(10)−P(1) | 118.9(8) | C(11)−C(10)−Pb(1) | 128.0(8) |
| Pb(1)−C(10)−P(1) | 92.8(5) | C(11)−C(10)−Pb(1′) | 106.9(8) |
| Pb(1′)−C(10)−P(1) | 114.5(6) | N(3)−Pb(2)−N(4) | 107.8(4) |
| N(3)−Pb(2)−C(16) | 66.3(4) | C(16)−Pb(2)−N(4) | 96.0(4) |
| N(3)−P(2)−C(16) | 105.7(6) | P(2)−N(3)−Pb(2) | 92.1(5) |
| P(2)−C(16)−Pb(2) | 91.3(4) | P(2)−C(16)−C(15) | 120.7(9) |
| Pb(2)−C(16)−C(15) | 106.0(8) | | |

**Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 6**

| | | | |
|---|---|---|---|
| Ge(1)−C(26) | 2.090(5) | Ge(1)−N(2) | 2.045(4) |
| Ge(1)−N(6) | 2.007(4) | Ge(2)−C(16) | 2.126(5) |
| Ge(2)−C(26) | 2.064(5) | Ge(2)−N(4) | 2.042(4) |
| P(1)−N(1) | 1.537(4) | P(2)−N(2) | 1.620(4) |
| P(1)−C(1) | 1.757(5) | P(2)−C(16) | 1.784(5) |
| C(1)−C(2) | 1.359(6) | C(6)−C(16) | 1.484(6) |
| C(2)−C(3) | 1.435(7) | C(3)−C(4) | 1.341(6) |
| C(4)−C(5) | 1.406(7) | C(5)−C(6) | 1.357(7) |
| N(6)−C(2) | 1.404(6) | N(6)−C(6) | 1.385(6) |
| P(3)−N(3) | 1.527(5) | P(4)−N(4) | 1.627(4) |
| P(3)−C(32) | 1.825(5) | P(4)−C(26) | 1.778(5) |
| C(31)−C(32) | 1.496(7) | C(26)−C(27) | 1.486(7) |
| C(27)−C(28) | 1.386(7) | C(28)−C(29) | 1.366(7) |
| C(29)−C(30) | 1.376(7) | C(30)−C(31) | 1.379(7) |
| N(5)−C(27) | 1.352(6) | N(5)−C(31) | 1.348(6) |
| N(2)−Ge(1)−C(26) | 99.37(17) | N(6)−Ge(1)−C(26) | 98.41(18) |
| N(2)−Ge(1)−N(6) | 92.69(16) | C(16)−Ge(2)−C(26) | 96.78(19) |
| N(4)−Ge(2)−C(16) | 96.62(18) | N(4)−Ge(2)−C(26) | 77.25(17) |
| Ge(1)−C(26)−Ge(2) | 112.7(2) | Ge(1)−C(26)−P(4) | 117.6(2) |
| Ge(1)−C(26)−C(27) | 101.0(3) | Ge(2)−C(26)−P(4) | 88.9(2) |
| C(27)−C(26)−Ge(2) | 120.3(3) | C(27)−C(26)−P(4) | 117.5(4) |
| C(6)−C(16)−P(2) | 112.6(3) | C(6)−C(16)−Ge(2) | 114.8(3) |
| P(2)−C(16)−Ge(2) | 109.8(3) | C(2)−C(1)−P(1) | 129.2(4) |
| C(31)−C(32)−P(3) | 116.3(4) | | |

prised of the 1,3-dimetallacyclobutanes and the chlorotin(II) or bis(trimethylsilyl)amido lead(II) alkyl moieties linked by the pyridyl ring at 2,6 positions. The two M(1) atoms are bonded to the two methandiide carbon centers, forming the 1,3-dimetallacyclobutane ring. With the coordination from the imino nitrogen atoms, the geometries at the two M(2) atoms in the chloro or bis(trimethylsilyl)amido M(II) alkyl moieties are trigonal pyramidal. In **4**, the $Sn_2C_2$ four-membered ring is folded along the C−C axis with a dihedral angle of 28°. The two pyridyl nitrogen atoms of the ligand coordinate to the trigonal pyramidal metal centers to form the SnCC(py)N(py) four-membered rings. These four-membered rings form an "open-box"-like structure framework. However, the molecular structure of **5** is slightly different from that of **4**. The $Pb_2C_2$ ring is planar, and the geometry of the three-coordinate lead atom is trigonal pyramidal. The two imino nitrogen atoms rather than the pyridyl nitrogen atom of the ligand coordinate to the Pb(II) centers, forming two PbCPN(imino) four-membered rings. These three four-membered rings form a "step-like" structure framework.

The average M−C distances of 2.337 Å (M = Sn) and 2.405 Å (M = Pb) in the dimetallacyclobutanes are similar to those of 2.322 Å (M = Sn) and 2.411 Å (M = Pb) in 1,3-$[M\{C(Pr^i_2P{=}NSiMe_3)(2\text{-}Py)\}]_2$[13] and 2.376 Å (M = Sn) and 2.477 Å (M = Pb) in $[M\{\mu^2\text{-}C(Ph_2P{=}NSiMe_3)_2\}]_2$.[12] M(2) is bonded to the carbon atom at distances of 2.329(7) Å (M = Sn) and 2.427(12) (M = Pb) and coordinated to the imino nitrogen atom at distances of 2.256(6) Å (M = Sn) and 2.524(11) Å (M = Pb). The average Sn−C distance of 2.337 Å in the distannacyclobutane and Sn(2)−C(16) distance of 2.329(7) in the chlorotin(II) alkyl moiety of **4** are longer than the Sn−C distance of 2.025(4) Å in stannene $[\{(Me_3Si)_2CH\}_2Sn{=}C\{(BBu^t)_2C(SiMe_3)_2\}]$.[17] The average bond distance of Pb−C (2.405 Å) in the diplumbacyclobutane and that of Pb(2)−C(16) (2.427(12) Å) in the bis(trimethylsilyl)amido lead(II) alkyl moiety of **5** are longer than the Pb−C distance of 2.336(3) Å in $[Pb\{CH(SiMe_3)(C_9H_6N\text{-}8)\}_2]$.[18] The M−M distances in **4** and **5** are too long to consider the existence of bonding interactions.

The germanium(II) compound **6** is a dimer in the solid state. The molecular structure shows that one of the anionic ligands is bonded to the Ge(1) via the pyridyl nitrogen N(6) rather than the α-carbon C(16). Since the charge is largely localized at the nitrogen atom, the C(1)−C(2) bond distance of 1.359(6) Å becomes shortened and exhibits the presence of an exocyclic double bond when compared with compounds **3**−**5**. The comparatively short C(3)−C(4) and C(5)−C(6) bond distances and long C(2)−C(3) and C(4)−C(5) bond distances within the pyridyl ring suggest that it has localized single and double C−C bonds and becomes nonaromatic due to the charge redistribution. The enamido types of alkali-metal complexes have been studied and reported.[19,20] The covalent Ge(1)−N(6) distance of 2.007(4) Å is only slightly shorter than the dative Ge−N distances of 2.044 Å, presumably due to the repulsion between the Ge(1) and the bulky ligands. The geometry at Ge(2) is trigonal pyramidal. Ge(2) is

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bonded to the methandiide carbon C(26) and the methine carbon C(16) and coordinated to the imino nitrogen.

## Conclusion

We have prepared low-valent tin(II) and lead(II) compounds containing 1,3-dimetallacyclobutanes and chloro or bis(trimethylsilyl)amido metal(II) alkyl moieties by the metathesis reaction of the bis(phosphoranoimido) magnesium salt with $\mathrm{SnCl_2}$ or by the metalation reaction of the neutral bis(phosphoranimine) with $\mathrm{Pb\{N(SiMe_3)_2\}_2}$. The chloro or bis(trimethylsilyl)amido metal(II) alkyl moieties suggest that the reaction proceeded through the metallavinylidene intermediate followed by "head-to-tail" cyclodimerization to produce the 1,3-dimetallacyclobutane moiety. Surprisingly, the germanium(II) compound obtained in a similar reaction has shown that one of the anionic ligands acts as the amide rather than the alkyl ligand to form the germanium(II) enamido and alkyl compound.

## Experimental Section

**General Procedures.** All manipulations were performed under nitrogen using standard Schlenk and vacuum line techniques. Solvents were dried over and distilled from sodium/benzophenone (diethyl ether and tetrahydrofuran) or sodium/potassium alloy (toluene). 2,6-Lutidine, $\mathrm{Bu}^n$Li, TMEDA, $\mathrm{Pr}^i{}_2$PCl, $\mathrm{Me_3SiN_3}$, $\mathrm{MgBu_2}$, and $\mathrm{SnCl_2}$ were purchased from Aldrich Chemical and were used without further purification. The $^1$H and $^{13}$C NMR spectra were measured at 300 and 75.5 MHz, respectively, using a Bruker dpx-300 spectrometer in sealed tubes at ambient probe temperature. $(\mathrm{Pr}^i{}_2\mathrm{PCH_2})_2\mathrm{C_5H_3N}$-2,6 was prepared according to the literature with some modifications.[14] The $^1$H chemical shifts were referenced to internal $\mathrm{CDCl_3}$ ($\delta$ = 7.24 ppm) or $\mathrm{C_6D_5H}$ ($\delta$ = 7.15 ppm) and $^{13}$C resonances to $\mathrm{CDCl_3}$ ($\delta$ = 77.0 ppm) or $\mathrm{C_6D_6}$ ($\delta$ = 128.0 ppm). $^{31}$P and $^{119}$Sn NMR spectra were recorded at 161.9 and 149.1 MHz, respectively, by using an INOVA Varian 400 spectrometer; the chemical shifts were quoted relative to external $\mathrm{SnMe_4}$ and 85% $\mathrm{H_3PO_4}$, respectively. Elemental analyses were carried out by Medac Ltd. (Brunel University, UK).

**$(\mathbf{Pr}^{\boldsymbol{i}}{}_2\mathbf{PCH_2})_2\mathbf{C_5H_3N}$-2,6 (1).** To a mixture of 2,6-lutidine (5.0 mL, 42.93 mmol), TMEDA (13.0 mL, 86.14 mmol), and diethyl ether (100 mL) was added dropwisely a solution of $\mathrm{Bu}^n$Li (54.0 mL, 86.40 mmol) at 0 °C with stirring. The orange mixture was stirred at ambient temperature for 4 h and added dropwisely to a cooled (−90 °C) solution of $\mathrm{Pr}^i{}_2$PCl (13.7 mL, 86.09 mmol) in diethyl ether (100 mL). The reaction mixture was stirred for 30 min at −90 °C and then at room temperature for a further 15 h. Filtration and removal of the solvent in a vacuum afforded a yellow oil. Purification by distillation at reduced pressure gave a pale yellow oil of the title compound (10.34 g, 71.0%), bp = 110−120 °C/ 0.01 mmHg. $^1$H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta$ (ppm) 1.14−1.22 (m, 24H, C$Me_2$), 1.87−1.97 (m, 4H, C$H$Me$_2$), 3.08 (d, $J_{\mathrm{P-H}}$ = 3.0 Hz, 4H, C$H_2$), 7.23 (d, $J$ = 6.0 Hz, 2H, $m$-C$_5H_3$N), 7.57 (t, $J$ = 6.0 Hz, 1H, $p$-C$_5H_3$N). $^{13}$C{$^1$H} NMR (75.5 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta$ (ppm) 18.84−19.75 (CH$Me_2$), 23.45 ($C$HMe$_2$), 32.37 ($C$H$_2$), 120.40, 136.18, 159.82 ($C_5$H$_3$N). $^{31}$P{$^1$H} NMR (161.9 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta$ (ppm) 24.33.

**$(\mathbf{Me_3SiN{=}PPr}^{\boldsymbol{i}}{}_2\mathbf{CH_2})_2\mathbf{C_5H_3N}$-2,6 (2).** A mixture of $(\mathrm{Pr}^i{}_2\mathrm{PCH_2})_2\mathrm{C_5H_3N}$-2,6 (10.30 g, 30.34 mmol) and $\mathrm{Me_3SiN_3}$ (8.9 mL, 67.05 mmol) in toluene (50 mL) was heated at 110−130 °C for 10 h with stirring. After cooling to room temperature, volatiles were removed in a vacuum and the residue was distilled at reduced pressure. A pale yellow oil of the title compound (14.49 g, 92.9%) was obtained, bp = 150−160 °C/ 0.01 mmHg. $^1$H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta$ (ppm) −0.05 (s, 18H, Si$Me_3$), 0.98−1.07 (m, 15.0 Hz, 24H, C$Me_2$), 1.86−1.94 (m, 4H, C$H$Me$_2$), 3.10 (d, $J_{\mathrm{P-H}}$ = 12.0 Hz, 4H, C$H_2$), 7.23 (d, $J$ = 9.0 Hz, 2H, $m$-C$_5H_3$N), 7.44 (t, $J$ = 9.0 Hz, 1H, $p$-C$_5H_3$N). $^{13}$C{$^1$H} NMR (75.5 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta$ (ppm) 4.75 (Si$Me_3$), 16.56 (d, CH$Me_2$), 27.19 (d, $C$HMe$_2$), 36.88 (d, $C$H$_2$), 122.85, 136.22, 154.96 ($C_5$H$_3$N). $^{31}$P{$^1$H} NMR (161.9 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta$ (ppm) 34.42.

**$[\mathbf{Mg\{(Me_3SiN{=}PPr}^{\boldsymbol{i}}{}_2\mathbf{CH)_2C_5H_3N}$-2,6$\}$THF] (3).** To a solution of **2** (1.85 g, 3.60 mmol) in THF (40 mL) at −78 °C was added dropwisely a solution of $\mathrm{MgBu_2}$ (3.7 mL, 1.0 M solution in heptane, 3.70 mmol). The reaction mixture was warmed to room temperature and stirred for 9 h. Filtration and concentration of the filtrate gave bright yellow crystals of the title compound (1.95 g, 89.1%), mp = 223.8−224.3 °C. Anal. Calcd (%) for $\mathrm{C_{25}H_{51}MgN_3P_2Si_2}$ (**3**−THF): C 56.01, H 9.59, N 7.84. Found: C 55.87, H 9.99, N 7.09. $^1$H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta$ (ppm) 0.35 (s, 18H, Si$Me_3$), 1.10−1.26 (m, 24H, C$Me_2$), 1.33−1.37 (m, 4H, THF), 2.01−2.04 (m, 4H, C$H$Me$_2$), 2.55 (d, $J_{\mathrm{P-H}}$ = 16.8 Hz, 2H, C$H$), 3.77−3.81 (m, 4H, THF), 5.82 (d, $J$ = 7.5 Hz, 2H, $m$-C$_5H_3$N), 6.86 (t, $J$ = 8.0 Hz, 1H, $p$-C$_5H_3$N). $^{13}$C{$^1$H} NMR (75.5 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta$ (ppm) 6.28 (Si$Me_3$), 18.59 (d, CH$Me_2$), 24.82 (s, THF), 30.23 (d, $C$HMe$_2$), 41.32 (d, $C$H), 69.87 (s, THF), 101.91, 135.93, 166.52 ($C_5$H$_3$N). $^{31}$P{$^1$H} NMR (161.9 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta$ (ppm) 57.71.

**$[\{2\text{-}\{\mathbf{Sn\{C(Pr}^{\boldsymbol{i}}{}_2\mathbf{P{=}NSiMe_3)\}}\}\text{-}6\text{-}\{\mathbf{Sn\{CH(Pr}^{\boldsymbol{i}}{}_2\mathbf{P{=}NSiMe_3)\}Cl}\}\}\mathbf{C_5H_3N}]_2$ (4).** To a suspension of $\mathrm{SnCl_2}$ (0.24 g, 1.27 mmol) in $\mathrm{Et_2O}$ (10 mL) at 0 °C was added a solution of **3** (0.76 g, 1.25 mmol) in $\mathrm{Et_2O}$ (20 mL) with stirring. The mixture was warmed to room temperature and stirred for 48 h and then filtered. Solvent was removed under vacuum, and the residue was extracted with THF. The solution was concentrated to ca. 5 mL. After standing for 1 day, **4** was obtained as bright orange crystals (0.59 g, 60.2%). Anal. Calcd (%) for $\mathrm{C_{50}H_{100}Cl_2N_6P_4Si_4Sn_4}$: C 38.32, H 6.43, N 5.36. Found: C 38.50, H 6.47, N 5.34. $^1$H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta$ (ppm) 0.18 (s, 18H, Si$Me_3$), 0.55 (s, 18H, Si$Me_3$), 0.91−1.47 (m, 48H, C$Me_2$), 2.01−2.22, 2.62−2.69 (m, 8H, C$H$Me$_2$), 6.12 (d, $J$ = 6.0 Hz, 2H, $m$-C$_5H_3$N), 6.56 (d, $J$ = 6.0 Hz, 2H, $m$-C$_5H_3$N), 7.60 (t, $J$ = 9.0 Hz, 1H, $p$-C$_5H_3$N). $^{13}$C{$^1$H} NMR (75.5 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta$ (ppm) 3.00 (Si$Me_3$), 5.72 (Si$Me_3$), 15.03−17.77 (m, CH$Me_2$), 25.62−33.64 (m, $C$HMe$_2$), 109.73, 118.43, 122.61, 137.98, 154.37, 164.21 ($C_5$H$_3$N). $^{31}$P{$^1$H} NMR (161.9 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta$ (ppm) 43.44, 70.06. $^{119}$Sn{$^1$H} NMR (149.1 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta$ (ppm) −72.23 (d, $J$ = 140.4 Hz), −10.96 (d, $J$ = 157.2 Hz).

**$[\{2\text{-}\{\mathbf{Pb\{C(Pr}^{\boldsymbol{i}}{}_2\mathbf{P{=}NSiMe_3)\}}\}\text{-}6\text{-}\{\mathbf{Pb\{CH(Pr}^{\boldsymbol{i}}{}_2\mathbf{P{=}NSiMe_3)\}N(SiMe_3)_2}\}\}\mathbf{C_5H_3N}]_2$ (5).** A solution of **2** (1.83 g, 3.56 mmol) in $\mathrm{Et_2O}$ (20 mL) was added to a solution of $\mathrm{Pb\{N(SiMe_3)_2\}_2}$ (3.79 g, 7.22 mmol) in $\mathrm{Et_2O}$ (20 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min and then at room temperature for 2 days. The resulting orange solution was concentrated and cooled to yield **5** as orange crystals (2.21 g, 28.6%). $^1$H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta$ (ppm) −0.04 (s, 18H, Si$Me_3$), 0.28 (s, 18H, Si$Me_3$), 0.40 (s, 36H, Si$Me_3$), 0.91−1.30 (m, 48H, C$Me_2$), 1.64−2.03 (m, 8H, C$H$Me$_2$), 6.31 (d, $J$ = 6.0 Hz, 2H, $m$-C$_5H_3$N), 6.49 (d, $J$ = 6.0 Hz, 2H, $m$-C$_5H_3$N), 7.41−7.46 (m, 2H, $p$-C$_5H_3$N).

**Preparation of $[\{2\text{-}\mathbf{CH(Pr}^{\boldsymbol{i}}{}_2\mathbf{P{=}NSiMe_3)}\text{-}6\text{-}\mathbf{CH(Pr}^{\boldsymbol{i}}{}_2\mathbf{P{=}NSiMe_3)}\}\mathbf{C_5H_3NGe}\{2\text{-}\{\mathbf{C(Pr}^{\boldsymbol{i}}{}_2\mathbf{P{=}NSiMe_3)Ge}\}\text{-}6\text{-}\mathbf{CH_2(Pr}^{\boldsymbol{i}}{}_2\mathbf{P{=}NSiMe_3)}\}\mathbf{C_5H_3N}]$ (6).** To a suspension of $\mathrm{GeCl_2}$(dioxane) (0.37 g, 1.60 mmol) in $\mathrm{Et_2O}$ (10 mL) was added a solution of **3** (0.89 g, 1.46 mmol) in $\mathrm{Et_2O}$ (20 mL) at 0 °C. The mixture was warmed to room temperature, stirred for 2 days, and then filtered. Volatiles were removed under vacuum, and the residue was extracted with THF. The resulting bright orange solution was concentrated to afford **6** as bright orange crystals (0.49 g, 57.4%), mp = 186.2−189.1 °C. Anal. Calcd (%) for $\mathrm{C_{50}H_{102}Ge_2N_6P_4Si_4}$: C 51.38, H 8.80, N 7.19. Found: C 50.34, H 8.87, N 7.17. $^1$H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta$ (ppm) 0.11

**Table 5. X-ray Crystallographic Data for Compounds 3−6**

| | **3** | **4** | **5** | **6** |
|---|---|---|---|---|
| formula | $C_{29}H_{59}MgN_3OP_2Si_2$ | $C_{50}H_{100}Cl_2N_6P_4Si_2Sn_4$ | $C_{62}H_{136}N_8P_4Pb_4Si_8$ | $C_{50}H_{102}Ge_2N_6P_4Si_2$ |
| fw | 608.22 | 1567.26 | 2171.15 | 1168.80 |
| color/ shape | bright yellow block | orange prism | orange block | orange block |
| cryst syst | monoclinic | monoclinic | triclinic | triclinic |
| space group | $C2/c$ | $C2/c$ | $P\bar{1}$ | $P\bar{1}$ |
| cryst size (mm$^3$) | 1.20 × 0.62 × 0.41 | 0.529 × 0.526 × 0.298 | 0.30 × 0.20 × 0.10 | 0.40 × 0.30 × 0.30 |
| $a$ (Å) | 38.2658(18) | 17.3273(9) | 11.702(2) | 13.638(3) |
| $b$ (Å) | 10.8370(5) | 32.3481(17) | 13.933(3) | 15.684(3) |
| $c$ (Å) | 18.0881(9) | 14.4214(8) | 17.285(4) | 16.274 (3) |
| $\alpha$ (deg) | 90 | 90 | 89.48(3) | 71.738(3) |
| $\beta$ (deg) | 104.0880(10) | 109.2650(10) | 72.35(3) | 80.697(3) |
| $\gamma$ (deg) | 90 | 90 | 67.73(3) | 84.728(3) |
| $V$ (Å$^3$), $Z$ | 7275.3(6), 8 | 7630.6(7), 4 | 2467.3(9), 1 | 3259.0(11), 2 |
| density (Mg/m$^3$) | 1.111 | 1.364 | 1.461 | 1.191 |
| abs coeff (mm$^{-1}$) | 0.227 | 1.543 | 6.999 | 1.129 |
| $F$(000) | 2656 | 3168 | 1064 | 1248 |
| $\theta$ range for data collection (deg) | 1.10 to 28.04 | 1.40 to 28.02 | 1.25 to 25.00 | 1.37 to 25.01 |
| no. of reflns collected | 24 044 | 25 663 | 6841 | 13 548 |
| no. of indep reflns ($R_{int}$) | 8785 (0.0395) | 9208 (0.0576) | 6841 (0.0000) | 11 276 (0.0379) |
| goodness-of-fit on $F^2$ | 1.021 | 0.982 | 1.059 | 1.048 |
| R1, wR2 [$I > 2\sigma(I)$] | 0.0548, 0.1509 | 0.0599, 0.1815 | 0.0780, 0.2056 | 0.0732, 0.1247 |
| R1, wR2 (all data) | 0.0853, 0.1775 | 0.1127, 0.2086 | 0.0849, 0.2151 | 0.1060, 0.1365 |
| largest diff peak and hole (e Å$^{-3}$) | 0.482 and −0.484 | 2.128 and −0.518 | 2.679 and −2.861 | 0.891 and −0.469 |

(s, 9H, Si$Me_3$), 0.23 (s, 9H, Si$Me_3$), 0.38 (s, 9H, Si$Me_3$), 0.58 (s, 9H, Si$Me_3$), 0.85−1.42 (m, 48H, C$Me_2$), 1.64−1.98 (m, 8H, C$H$Me$_2$), 2.95 (d, $J_{\mathrm{P-H}} = 6.0$ Hz, 2H, C$H_2$), 3.11 (d, $J_{\mathrm{P-H}} = 6.0$ Hz, 1H, C$H$), 4.62 (d, $J_{\mathrm{P-H}} = 18.0$ Hz, 1H, C=C$H$), 5.25 (d, $J = 6.0$ Hz, 1H, C$_5H_3$N), 6.46−6.51 (m, 1H, C$_5H_3$N), 7.97 (d, $J = 9.0$ Hz, 1H, C$_5H_3$N). $^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$, 25 °C): $\delta$ (ppm) 0.00 (Si$Me_3$), 0.40 (Si$Me_3$), 1.37 (Si$Me_3$), 1.58 (Si$Me_3$), 12.33−14.20 (m, CH$Me_2$), 22.61−26.84 (m, $C$HMe$_2$), 31.41 (d, $C$H$_2$), 40.33 (d, $C$H), 67.89 (d, $C$=C), 100.43, 112.37, 116.88, 120.51, 126.79, 131.59, 146.83, 150.80, 157.50, 159.35 ($C_5$H$_3$N). $^{31}$P{$^1$H} NMR (161.9 MHz, $C_6D_6$, 25 °C): $\delta$ (ppm) 31.11, 31.75, 65.01.

**X-ray Crystallography.** Selected single crystals were mounted and sealed in Lindemann glass capillaries under nitrogen.

X-ray intensities were measured on a MSC/Rigaku RAXIS IIc imaging-plate diffractometer for compound **5**. A self-consistent semiempirical absorption correction based on Fourier-coefficient fitting of symmetry-equivalent reflections was applied by using the ABSCOR program.[21]

Diffraction experiments of compounds **3**, **4**, and **6** were carried out on a Bruker SMART CCD diffractometer with a Mo K$\alpha$ sealed tube, $\omega$ scan mode with an increment of 0.3°. Preliminary unit cell parameters were obtained from 45 frames, while final unit cell parameters were obtained from global refinements of reflections by integrating all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants. SAINT-PLUS was used for integration of intensity of reflections and scaling. SADABS was used for absorption correction.[22]

All crystal structures were determined by a direct method that yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically (C−H bond distance was fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. They were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. All computations were performed on an IBM-compatible personal computer with the SHELXTL-PLUS, SHELXTL-93, or SHELXTL-97 program package.[23] Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[24] Crystallographic data collection and structure refinement of all compounds are summarized in Table 5.

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**Supporting Information Available:** Tables of crystallographic data, data collection details, bond distances and angles, atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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