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Synthesis and Structures of Novel Low-Valent Group 14 1,3-Dimetallacyclobutanes

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A series of group 14 1,3-dimetallacyclobutanes has been synthesized and structurally characterized. The reaction of the lithium compound $[\mathrm{Li}\{\mathrm{CH}(\mathrm{Pr}^i{}_2\mathrm{P{=}NSiMe_3})(2\text{-Py})\}]$ (**2**) with 1 equiv of $\mathrm{SnCl_2}$ afforded the tin(II) compound $[\mathrm{Sn}\{\mathrm{CH}(\mathrm{Pr}^i{}_2\mathrm{P{=}NSiMe_3})(2\text{-Py})\}\mathrm{Cl}]$ (**3**). However, the reaction of **2** and $\mathrm{MCl_2}$ (M = Ge, Sn, Pb) in a 2:1 ratio gave the corresponding metallacyclobutanes 1,3-$[\mathrm{M}\{\mathrm{C}(\mathrm{Pr}^i{}_2\mathrm{P{=}NSiMe_3})(2\text{-Py})\}]_2$ (**4**, M = Sn; **6**, M = Ge; **9**, M = Pb), respectively. Reaction of 2 equiv of **3** with $\mathrm{Pb[N(SiMe_3)_2]_2}$ gave the mixed-metal cyclobutane $[1\text{-Sn}\{\mathrm{C}(\mathrm{Pr}^i{}_2\mathrm{P{=}NSiMe_3})(2\text{-Py})\}\text{-}3\text{-Pb}\{\mathrm{C}(\mathrm{Pr}^i{}_2\mathrm{P{=}NSiMe_3})(2\text{-Py})\}]$ (**7**). It is noteworthy that the enantiomers of **4** and **7** containing "open-box" structures and their intermediates were isolated and their structures have been confirmed by X-ray crystallography. Compound **3** reacts with 1 equiv of $\mathrm{Pb[N(SiMe_3)_2]_2}$ to give $[\{(\mathrm{Pr}^i{}_2\mathrm{P{=}NSiMe_3})(2\text{-Py})\mathrm{CH}\}\mathrm{Pb}\{\mathrm{N(SiMe_3)_2}\}_2]$ (**8**), which can be converted to **9** after recrystallization in diethyl ether. It is suggested that compounds **4**, **6**, **7**, and **9** are formed from "head-to-tail" cycloaddition of the metallavinylidene intermediate $[{:}\mathrm{M{=}C}(\mathrm{Pr}^i{}_2\mathrm{P{=}NSiMe_3})(2\text{-Py})]$ (M = Ge, Sn, Pb).[1,12]

Introduction

The use of phosphoranimines ($\mathrm{R_3P{=}NSiMe_3}$) as supporting ligands in the synthesis of metal complexes has been studied over the past few decades. For example, neutral P−N type ligands such as $\mathrm{Me_3SiN{=}PPh_2CH_2PPh_2}$,[1,2] 5-F-2,4-$\mathrm{(NO_2)_2C_6H_2N{=}PPh_2CH_2PPh_2}$,[3] $\mathrm{(Me_3SiN{=}PPh_2)_2CH_2}$,[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] $[\mathrm{M}\{\mathrm{HC(Ph_2P{=}NSiMe_3)_2}\text{-}\kappa N,\kappa N'\}(\mathrm{THF})_2]$ (M = Na, K),[7] and $[\mathrm{K}\{\mathrm{P(Ph)C(Bu^t){=}C(H)(PPh_2){=}NSiMe_3}\}]_\infty$[8] have been reported. Transition-metal and lanthanide-metal methanide complexes based on phosphoranimine ligands have been investigated.[9−11] We have reported the synthesis of bis(germavinylidene) and group 14 1,3-dimetallacyclobutanes derived from different phosphoranimines.[12−14] Lewis acid chiral organotin complexes have been used in a variety of organic syntheses and have attracted much attention.[15−20] The isolation of distannoxane double ladders with eight chiral tin(IV) centers has been reported by Dakternieks et al. as an example of the fortuitous spontaneous crystallization of one enantiomer.[21] In this paper, we report the isolation of enantiomers of low-valent group 14 1,3-dimetallacyclobutane and mixed-metal 1,3-stannaplumbacyclobutane derived from the phosphoranimine $\mathrm{CH_2(Pr^i{}_2P{=}NSiMe_3)(2\text{-}Py)}$ (**1**).

Results and Discussion

Syntheses of of 1,3-Distannacyclobutanes. The reaction of the lithium compound $[\mathrm{Li}\{\mathrm{CH}(\mathrm{Pr}^i{}_2\mathrm{P{=}NSiMe_3})(2\text{-Py})\}]$ (**2**) with 1 equiv of $\mathrm{SnCl_2}$ afforded the chloro tin(II) compound $[\mathrm{Sn}\{\mathrm{CH}(\mathrm{Pr}^i{}_2\mathrm{P{=}NSiMe_3})(2\text{-Py})\}\mathrm{Cl}]$ (**3**) (Scheme 1). Further reaction of **3** with 1 equiv of **2** gave 1,3-$[\mathrm{Sn}\{\mathrm{C}(\mathrm{Pr}^i{}_2\mathrm{P{=}NSiMe_3})(2\text{-Py})\}]_2$ (**4**).[12] On the basis of the structure of **4**, it is proposed that **2** combined with 1 equiv of $\mathrm{SnCl_2}$ to form compound **3**. A further dehydrochlorination reaction of **3** with an additional 1 equiv of **2** accompanied by the elimination of LiCl and **1** gave the unstable intermediate stannavinylidene ($>\mathrm{C{=}Sn}{:}$), which then underwent a "head-to-tail" cyclodimerization to give the 1,3-distannacyclobutane ring. In these compounds, the pyridyl and imino nitrogen atoms are coordinated to the two tin(II) centers; this sequence leads to the formation of the enantiomers found in the X-ray studies of the products isolated. This was also

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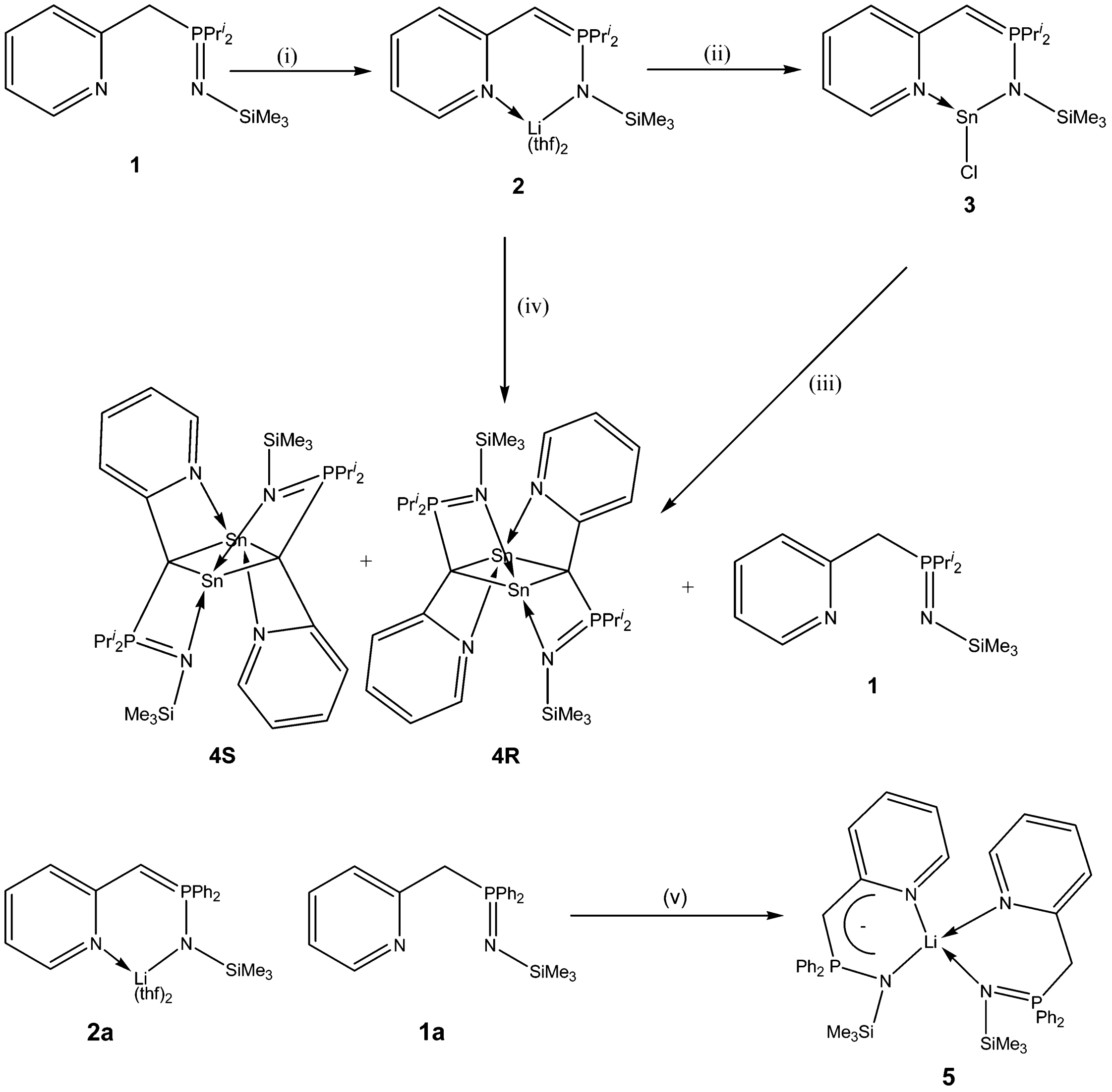
Scheme 1. Syntheses of Compounds 2−4[a]



[a] Reagents: (i) Bu^{n}Li, THF; (ii) $SnCl_2$, Et_2O; (iii) **2**, Et_2O; (iv) $^1/_2$ $SnCl_2$, Et_2O; (v) Et_2O.

supported by the isolation of a small amount of $[\{CH(R_2P{=}NSiMe_3)(2\text{-}Py)\}Li\{CH_2(Ph_2P{=}NSiMe_3)(2\text{-}Py)\}]$ (**5**)**.** Compound **5** is believed to be formed from the reaction of the phosphoranimine ligand and the slight excess of compound **2** (Scheme 1) used during the preparation of compound **4**. A similar mechanism has been reported in the reaction of $[Mg\{(Me_3SiN{=}PPr^{i}_2CH)_2C_5H_3N\text{-}2,6\}THF]$ with 1 equiv of $SnCl_2$ to yield the 1,3-distannacyclobutane $[\{2\text{-}\{Sn\{C(Pr^{i}_2P{=}NSiMe_3)\}\}\text{-}6\text{-}\{Sn\text{-}\{CH(Pr^{i}_2P{=}NSiMe_3)\}Cl\}\}C_5H_3N]_2$.[14]

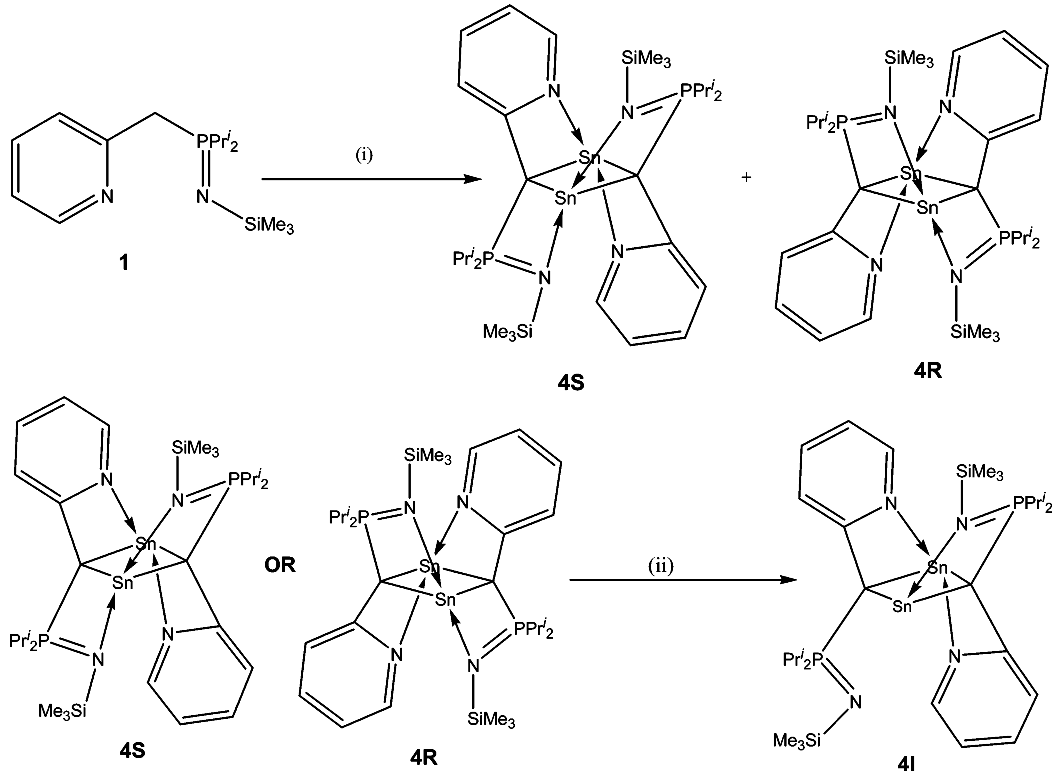
We have found that the direct reaction of $[CH_2(Pr^{i}_2P{=}NSiMe_3)(2\text{-}Py)]$ (**1**) with $Sn[N(SiMe_3)_2]_2$ afforded **4** as the major product (Scheme 2). It is suggested that the reaction proceeds through an initial deprotonation of the ligand by the strong base $Sn[N(SiMe_3)_2]_2$ to give an unstable stannavinylidene intermediate with the elimination of $HN(SiMe_3)_2$. The intermediate then undergoes a "head-to-tail" cycloaddition to yield compound **4**. The chelation of the pyridyl-*N* and imino-*N* atoms to the Sn(II) centers leads to the formation of enantiomers **4R** and **4S** in different solvents (toluene and diethyl ether). This has been confirmed by X-ray crystallography (Figure 1). Compound **4I** with one uncoordinated imine functionality was obtained if either **4R** or **4S** was recrystallized from THF (Scheme 2). The structure was confirmed by X-ray crystallography. The isolation of **4I** suggested that the opening and closing of the "open-box" structure is reversible in the solution state; this accounts for the lack of optical rotation of **4** in solution.

Syntheses of 1,3-Digermacyclobutane. The reaction of $GeCl_2$(dioxane) with 2 equiv of the lithium compound **2** in diethyl ether gave 1,3-$[Ge\{C(Pr^{i}_2P{=}NSiMe_3)(2\text{-}Py)\}]_2$ (**6**) (Scheme 3) as a yellow crystalline solid. It is believed that compound **6** is formed by a mechanism similar to that for compound **4.** The germanium analogue is a "steplike" structure, as compared with the "open-box" structure in **4**.

Isolation of Enantiomers of the 1,3-Stannaplumbacyclobutane 7. The reaction of **3** with $Pb[N(SiMe_3)_2]_2$ in a 2:1 ratio afforded $[1\text{-}Sn\{C(Pr^{i}_2P{=}NSiMe_3)(2\text{-}Py)\}\text{-}3\text{-}Pb\{C(Pr^{i}_2P{=}NSiMe_3)(2\text{-}Py)\}]$ (**7**) (Scheme 4) as an orange crystalline solid with a structure similar to that of **4** but with tin and lead in the metallacyclobutane ring. In addition, the enantiomers **7R** and **7S** can be isolated by recrystallization of **7** from toluene and diethyl ether, respectively. Compound **7** is believed to be a "head-to-tail" cycloaddition product from the stannavinylidene ":$Sn{=}C(Pr^{i}_2P{=}NSiMe_3)(2\text{-}Py)$" and plumbavinylidene ":$Pb{=}C(Pr^{i}_2P{=}NSiMe_3)(2\text{-}Py)$".

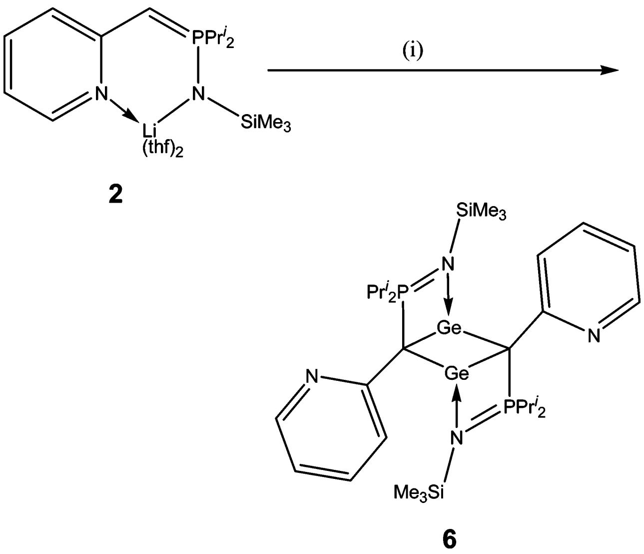
Syntheses of Azallyllead(II) Amide and 1,3-Diplumbacyclobutane. A similar reaction of **3** with $Pb[N(SiMe_3)_2]_2$ in a 1:1 ratio in toluene gave the heteroleptic lead(II) compound $[\{(Pr^{i}_2P{=}NSiMe_3)(2\text{-}Py)CH\}Pb\{N(SiMe_3)_2\}_2]$ (**8**) (Scheme 4).

Scheme 2. Syntheses of Compound 4[a]



[a] Reagents and conditions: (i) $\mathrm{Sn[N(SiMe_3)_2]_2}$, toluene; (ii) recrystallization from THF.

Scheme 3. Syntheses of Compound 6[a]



[a] Reagents: (i) $^1/_2$ $\mathrm{GeCl_2}$·(dioxane), $\mathrm{Et_2O}$.

Further reaction of **8** with **3** afforded 1,3-$\mathrm{[Pb\{C(Pr^i{}_2P{=}NSiMe_3)(2\text{-}Py)\}]_2}$ (**9**) as a yellow crystalline solid. Compound **9** can also be prepared from the reaction of $\mathrm{PbCl_2}$ with 2 equiv of **2** in diethyl ether. It is believed that enantiomers of **9** were also obtained, but only one of them has been isolated and confirmed by X-ray crystallography.

Molecular Structures. The molecular structures of compounds **4** and **6**−**9** are shown in Figures 1−5, respectively. Selected bond distances and angles are listed in Tables1−6, respectively.

Three different isomers, **4R**, **4S**, and **4I**, were isolated from **4**. Basically, each of the isomers consists of a 1,3-distannacyclobutane ring (Figure 1). For enantiomers **4R** and **4S**, each of the tin(II) centers adopts a distorted-trigonal-bipyramidal geometry. Compound **4** has a C_2 symmetry, with the two pyridyl nitrogen atoms bonded to the tin center at an average distance of 2.488 Å, while the two imino nitrogen atoms are bonded to the other tin center at an average distance of 2.543 Å. With the $\mathrm{C_2Sn_2}$ ring as the base, the nonplanar SnCC(Py)N(Py) and SnCPN(imino) rings form the flaps of an "open-box"-like structure framework. The average Sn−C distance of 2.324 Å is longer than the Sn−C distance of 2.025(4) Å in the stannene $\mathrm{[\{(Me_3Si)_2CH\}_2Sn{=}C\{(BBu^t)_2C(SiMe_3)_2\}]}$.[22] The Sn−Sn distances of 3.2806(13) Å for **4R** and 3.2811(4) Å for **4S** are too long to consider the existence of bonding interactions.

Compound **4I** also consists of a 1,3-distannacyclobutane ring (Figure 2), but it has a partial "open-box" structure. Only one imino nitrogen atom is bonded to the tin center at a distance of 2.589(5) Å, while the distance between the other imino nitrogen atom and the nearest tin center (2.607 Å) is too long to consider the existence of bonding interactions. The two pyridyl nitrogen atoms are bonded to the tin center at an average distance of 2.527 Å. There are two distinct tin(II) environments within the same compound; one is in a distorted-trigonal-bipyramidal form and the other in a distorted-tetrahedral geometry.

Compounds **4R** and **4S** were recrystallized from toluene and diethyl ether, respectively. Compound **4I** was isolated from THF. It is believed that different solvent properties contributed to the isolation of different enantiomers of **4**. Toluene provides pure ring-stacking properties with no coordinating properties; diethyl ether is a coordinating solvent with no ring-stacking character. However, THF has both ring-stacking and coordinating properties, making THF the most soluble solvent for **4** and also giving the intermediate structure **4I** during crystallization.

Compound **6** has C_i symmetry in the solid state. The germanium(II) centers are in a tetrahedral geometry. It is

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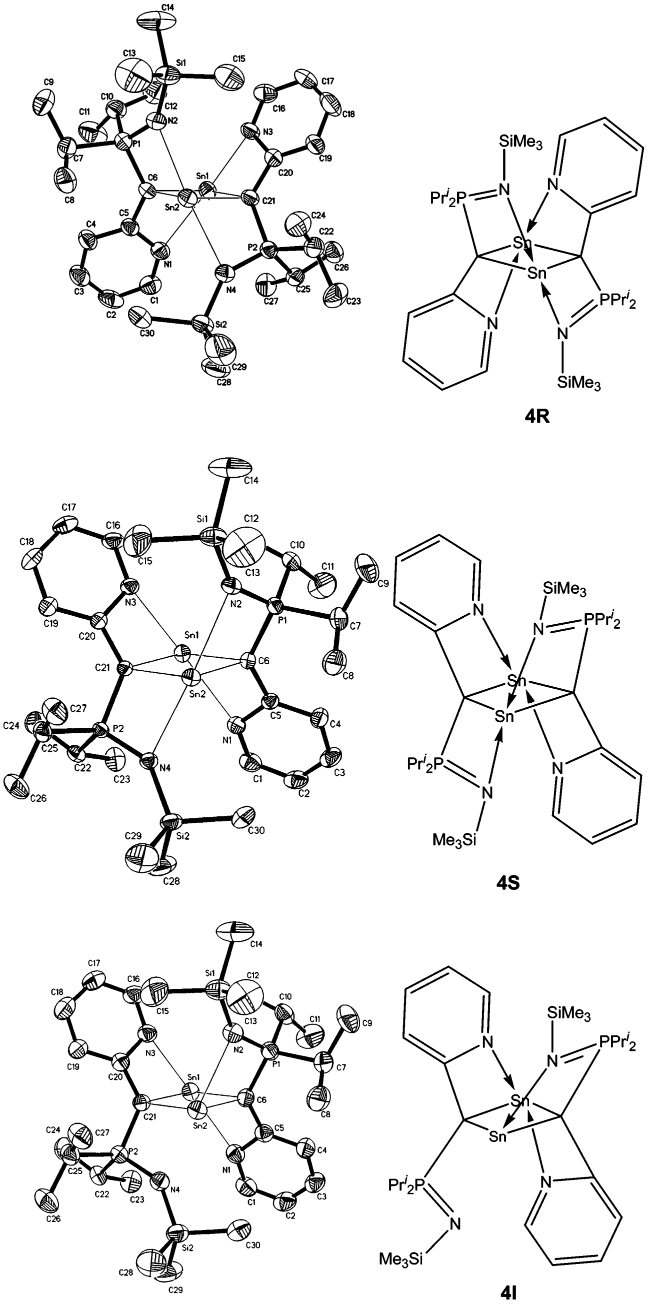

Figure 1. ORTEP and schematic drawings of **4R** (top), **4S** (middle), and **4I** (bottom). Hydrogen atoms are omitted for clarity. **4R** and **4S** are mirror images of each other.

noteworthy that the two imino nitrogens in **6** are bonded to different Ge(II) centers to give two GeCPN four-membered rings, which are fused via a cycloaddition reaction to form a Ge_2C_2 ring with a "steplike" structure (Figure 2). The two pyridyl rings are freely rotating.

Compound **7** contains a dimetallacyclobutane ring with tin and lead; it has an "open-box"-like structure. The enantiomers **7R** and **7S** were isolated from a solution of **7**. Each metal center is in a distorted-trigonal-bipyramidal geometry (Figure 3). Both pyridyl nitrogens are bonded to the tin(II) center, while the two imino nitrogens are bonded to the lead(II) center. The average Sn−C distance of 2.320 Å is similar to the average Sn−C distances of 2.324 Å in **4**. The average Pb−C distance of 2.442 Å is similar to the average Pb−C distance of 2.411 Å in **9**. **7R** and **7S** were separated by recrystallization from toluene and diethyl ether, respectively. It is believed that the formation of different forms of **7** is also due to the different solvent properties.

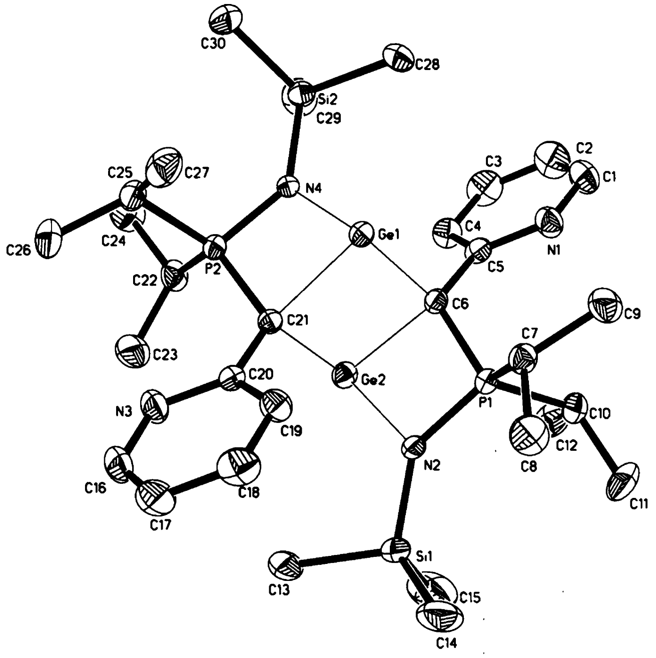

Figure 2. ORTEP drawing of **6**. Hydrogen atoms are omitted for clarity.

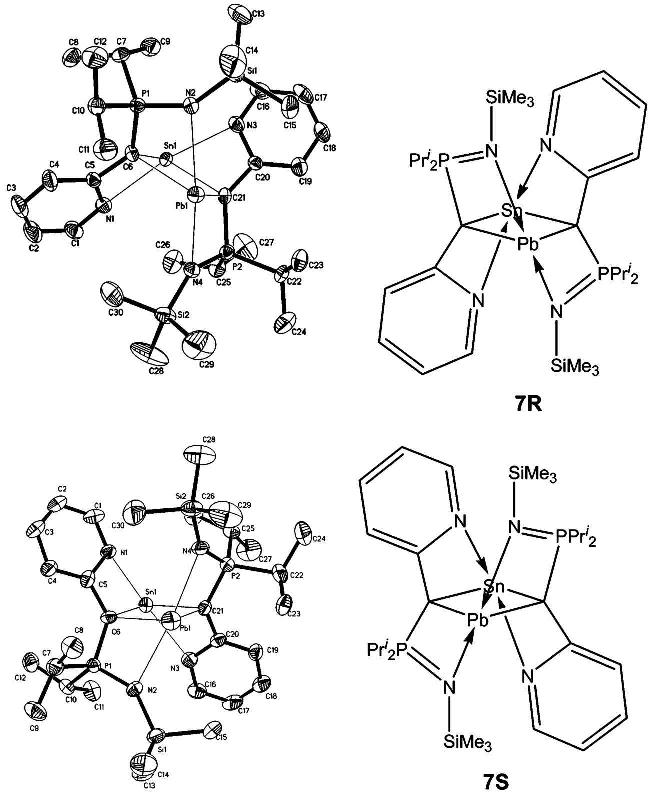

Figure 3. ORTEP and schematic drawings of **7R** (top) and **7S** (bottom). Hydrogen atoms are omitted for clarity.

The X-ray structure of compound **8** shows that it is a monomeric lead(II) compound (Figure 4). The lead(II) center adopts a tetrahedral geometry; it is bonded to one anionic imino nitrogen at a distance of 2.393(5) Å and one amido nitrogen atom at a distance of 2.224(5) Å. The Pb−C distance is 2.416(6) Å, which is longer than the Pb−C distance of 2.336(3) Å in $[Pb\{CH(SiMe_3)(C_9H_6N\text{-}8)\}_2]$.[23]

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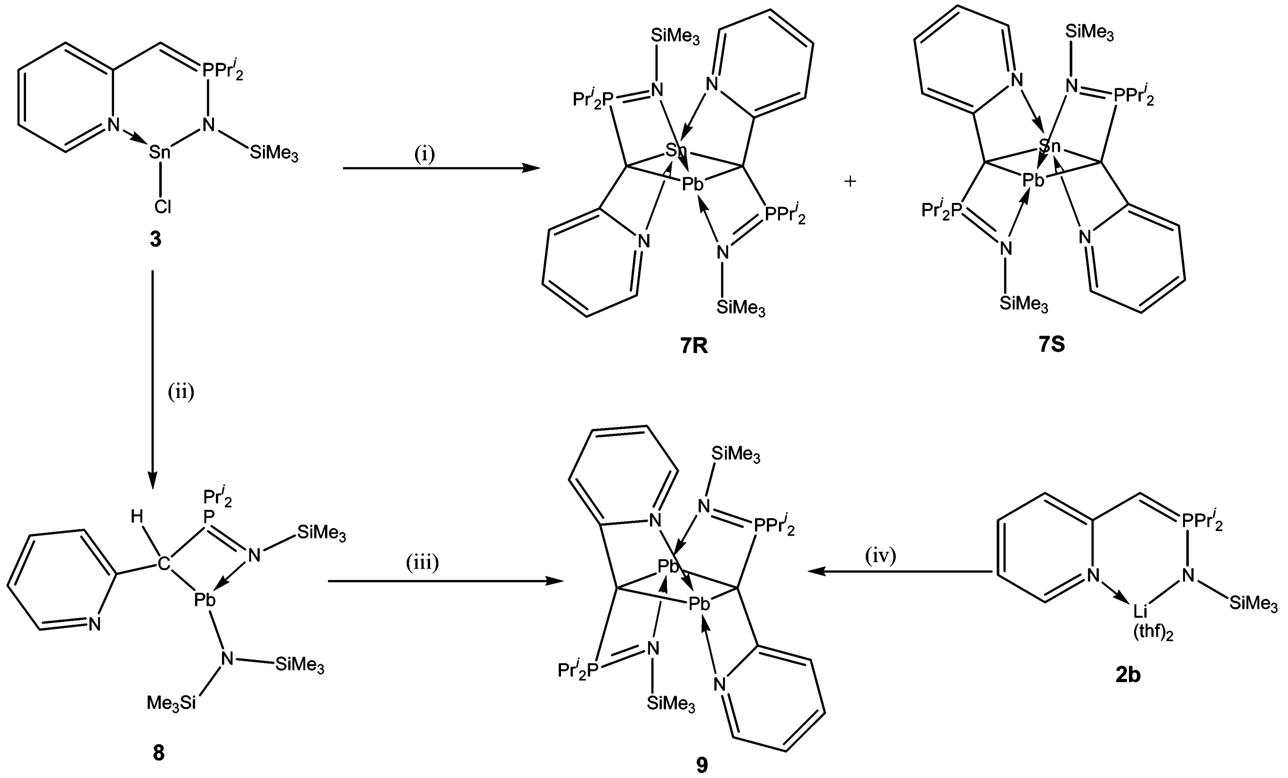
[23] Leung, W.-P.; Kwok, W.-H.; Weng, L.-H.; Law, L. T. C.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1997**, 4301.

Scheme 4. Syntheses of Compounds 7−9[a]



[a] Reagents: (i) $^1/_2$ Pb[N(SiMe$_3$)$_2$]$_2$, toluene; (ii) Pb[N(SiMe$_3$)$_2$]$_2$, toluene; (iii) **3**, Et$_2$O; (iv) $^1/_2$ PbCl$_2$, Et$_2$O.

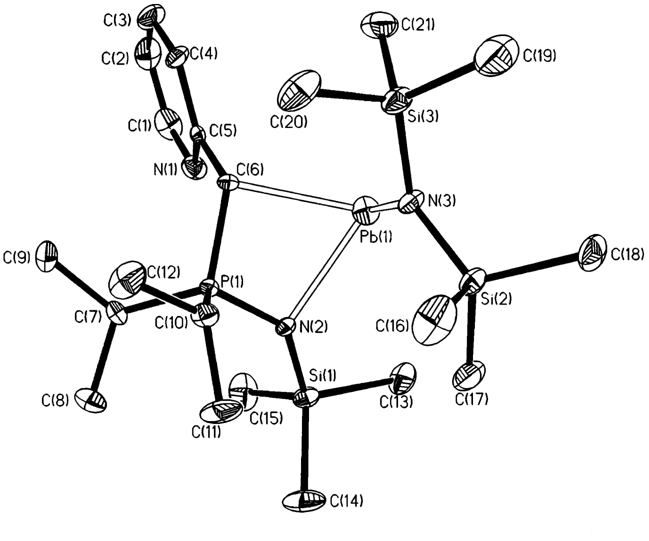


Figure 4. ORTEP drawing of **8**. Hydrogen atoms are omitted for clarity.

The structure of **9** is similar to the "open-box"-like structure of **4R** (Figure 5). The geometry of the lead(II) centers is also a distorted trigonal bipyramid. The average Pb−C distance of 2.411 Å in the dimetallacyclobutane rings is similar to that of 2.477 Å in [Pb{μ_2-C(Ph$_2$P=NSiMe$_3$)$_2$}]$_2$[12] but longer than the Pb−C distance of 2.336(3) Å in [Pb{CH(SiMe$_3$)(C$_9$H$_6$N-8)}$_2$].[23] The molecular structure of compound **5** has been reported in a previous publication.[24]

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of dinitrogen. Solvents were dried over and distilled from sodium/benzophenone (diethyl ether and tetrahydrofuran) or sodium/potassium alloy (toluene). 2-Picoline, Bu^{n}Li, TMEDA, Pr$^i_2$-PCl, Ph$_2$PCl, Me$_3$SiN$_3$, Bu^{n}Li, and SnCl$_2$ were purchased from Aldrich Chemical Co. 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. R$_2$P(2-CH$_2$Py) (R = Ph, Pr^i) was prepared according to the literature with some modifications.[1,2,25]

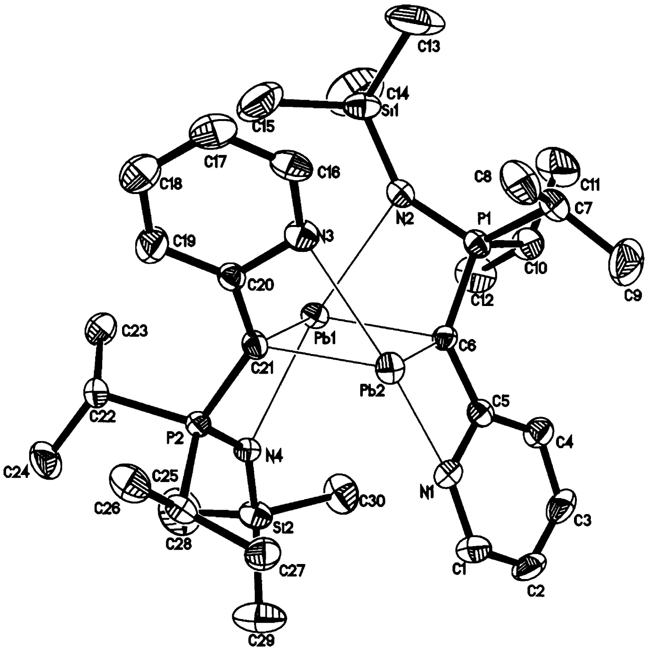


Figure 5. ORTEP drawing of **9**. Hydrogen atoms are omitted for clarity.

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Table 1. Selected Bond Distances (Å) and Angles (deg) of Compounds 4R, 4S, and 4I

	4R	**4S**	**4I**
Sn(1)−C(6)	2.281(6)	2.293(3)	2.338(5)
Sn(1)−C(21)	2.285(6)	2.296(3)	2.308(6)
Sn(2)−C(6)	2.361(7)	2.352(4)	2.380(6)
Sn(2)−C(21)	2.351(6)	2.346(3)	2.405(5)
Sn(1)−N(1)	2.491(6)	2.497(3)	2.535(6)
Sn(1)−N(3)	2.4485(5)	2.491(3)	2.518(6)
Sn(2)−N(2)	2.542(6)	2.5503)	2.589(5)
Sn(2)−N(4)	2.550(5)	2.556(3)	
C(6)−Sn(1)−C(21)	91.8(2)	91.43(12)	91.3(2)
C(6)−Sn(2)−C(21)	88.2(2)	88.76(12)	87.93(19)
Sn(1)−C(6)−Sn(2)	89.9(2)	89.86(12)	90.3(2)
Sn(2)−C(21)−Sn(1)	90.1(2)	89.95(12)	90.4(2)
N(1)−Sn(1)−N(3)	157.02(19)	156.89(10)	157.07(17)
N(2)−Sn(2)−N(4)	161.61(18)	161.94(10)	
P(1)−C(6)−C(5)	131.1(5)	131.1(3)	130.6(4)
P(2)−C(21)−C(20)	130.2(5)	130.4(3)	129.9(4)

Table 2. Selected Bond Distances (Å) and Angles (deg) of Compound 6

Ge(1)−C(6)	2.132(3)	Ge(2)−C(21)	2.154(3)
Ge(1)−C(21)	2.107(3)	Ge(1)−N(4)	2.055(2)
Ge(2)−C(6)	2.079(3)	Ge(2)−N(2)	2.064(2)
C(6)−Ge(1)−C(21)	88.58(10)	P(1)−C(6)−Ge(1)	110.87(13)
C(6)−Ge(2)−C(21)	88.69(10)	P(2)−C(21)−Ge(2)	107.47(13)
Ge(1)−C(6)−Ge(2)	91.68(10)	N(2)−Ge(2)−C(21)	96.91(9)
Ge(2)−C(21)−Ge(1)	90.29(10)	N(4)−Ge(1)−C(6)	98.35(9)

Table 3. Selected Bond Distances (Å) and Angles (deg) of Compounds 7R and 7S

	7R	**7S**
Pb(1)−C(6)	2.450(8)	2.447(12)
Pb(1)−C(21)	2.434(7)	2.446(13)
Sn(1)−C(6)	2.329(7)	2.358(12)
Sn(1)−C(21)	2.310(8)	2.348(12)
Pb(1)−N(2)	2.617(6)	2.634(11)
Pb(1)−N(4)	2.640(6)	2.629(11)
Sn(1)−N(1)	2.503(6)	2.547(11)
Sn(1)−N(3)	2.500(6)	2.534(11)
C(6)−Pb(1)−C(21)	87.7(2)	89.0(4)
C(6)−Sn(1)−C(21)	93.6(3)	93.5(4)
Pb(1)−C(6)−Sn(1)	88.9(2)	88.6(4)
Sn(1)−C(21)−Pb(1)	89.8(2)	88.9(4)
P(1)−C(6)−C(5)	132.6(6)	132.3(10)
P(2)−C(21)−C(20)	131.7(6)	133.1(10)
N(2)−Pb(1)−N(4)	160.31(19)	161.1(3)
N(1)−Sn(1)−N(3)	155.8(2)	156.9(4)

Table 4. Selected Bond Distances (Å) and Angles (deg) of Compound 8

Pb(1)−C(6)	2.416(6)	Pb(1)−N(3)	2.224(5)
Pb(1)−N(2)	2.393(5)		
P(1)−C(6)−Pb(1)	89.4(2)	Pb(1)−C(6)−C(5)	108.3(3)
N(3)−Pb(1)−C(6)	93.27(19)	N(2)−Pb(1)−N(3)	104.57(18)

Table 5. Selected Bond Distances (Å) and Angles (deg) of Compound 9

Pb(1)−C(6)	2.447(5)	Pb(1)−N(2)	2.625(4)
Pb(1)−C(21)	2.448(5)	Pb(1)−N(4)	2.631(4)
Pb(2)−C(6)	2.369(5)	Pb(2)−N(1)	2.598(5)
Pb(2)−C(21)	2.389(5)	Pb(2)−N(3)	2.589(5)
C(6)−Pb(1)−C(21)	88.96(17)	N(2)−Pb(1)−N(4)	160.42(13)
C(6)−Pb(2)−C(21)	92.96(18)	N(1)−Pb(2)−N(3)	154.53(15)
Pb(1)−C(6)−Pb(2)	89.64(17)	P(1)−C(6)−C(5)	130.8(4)
Pb(2)−C(21)−Pb(1)	89.14(18)	P(2)−C(21)−C(20)	130.5(4)

The ^{1}H chemical shifts were referenced to internal CDCl$_3$ (δ 7.24 ppm) or C$_6$D$_5$H (δ 7.15 ppm) and ^{13}C resonances to CDCl$_3$ (δ 77.0 ppm) or C$_6$D$_6$ (δ 128.0 ppm). ^{31}P and ^{119}Sn NMR spectra were recorded at 161.9 and 149.1 MHz, respectively, by using a Varian INOVA 400 spectrometer; the chemical shifts were quoted relative to external SnMe$_4$ and 85% H$_3$PO$_4$, respectively. Elemental analyses were carried out by MEDAC Ltd. (Brunel University, U.K.).

[(Pr$^i_2$P═NSiMe$_3$)(2-Py)CH$_2$] (1). A mixture of Pr$^i_2$P(2-CH$_2$Py) (8.5 g, 40.28 mmol) and Me$_3$SiN$_3$ (5.4 mL, 40.69 mmol) in toluene (50 mL) was heated gently with stirring at 110 °C (bath temperature) for 1 h, followed by reflux at 140 °C for 5 h. Solvent and excess Me$_3$SiN$_3$ were removed in vacuo, and the residue was distilled at reduced pressure to obtain a colorless oil of **1**. Yield: 11.2 g (92.6%). Bp: 88−90 °C/0.01 mmHg. ^{1}H NMR (CDCl$_3$; δ (ppm)): −0.08 (s, 9H, Si*Me*$_3$), 0.95 (dd, J = 9.0, 15.0 Hz, 6H, CH*Me*$_2$), 1.00 (dd, J = 9.0, 15.0 Hz, 6H, CH*Me*$_2$), 1.81−1.93 (m, 2H, C*H*Me$_2$), 3.12 (d, J = 12.0 Hz, C*H*$_2$), 7.03−7.07 (m, 1H, Py), 7.41 (d, J = 9.0 Hz, 1H, Py), 7.48−7.53 (m, 1H, Py), 8.40 (d, J = 6.0 Hz, 1H, Py). ^{13}C{^{1}H} NMR (CDCl$_3$; δ (ppm)): 4.92 (Si*Me*$_3$), 16.66 (d, CH*Me*$_2$), 27.49 (d, *C*H), 37.15 (d, *C*H$_2$), 121.94, 125.65, 136.09, 149.44, 155.97 (Py). ^{31}P{^{1}H} NMR (CDCl$_3$; δ (ppm)): 20.41. MS (m/z): 296 (M^+).

[{(Pr$^i_2$P═NSiMe$_3$)(2-Py)CH}Li] (2). To a cooled (−90 °C) solution of **1** (1.68 g, 5.68 mmol) in THF (30 mL) was added Bu^{n}Li (3.55 mL, 1.6 M in hexane, 5.68 mmol) slowly with stirring. The mixture was warmed to room temperature and stirred for 18 h. Solvent was removed from the reaction mixture at reduced pressure, and the residue was washed with pentane to give a yellow crystalline solid of **2**. Yield: 2.27 g (89.5%). Mp: 60−61 °C. Anal. Found: C, 60.91; H, 9.35; N, 6.54. Calcd for C$_{23}$H$_{44}$N$_2$LiO$_2$PSi: C, 61.86; H, 9.93; N, 6.27. ^{1}H NMR (C$_6$D$_6$; δ (ppm)): 0.30 (s, 9H, Si*Me*$_3$), 1.14−1.25 (m, 12 H, CH*Me*$_2$), 1.28−1.37 (m, 8H, THF), 1.83−1.95 (m, 2H, C*H*Me$_2$), 2.82 (d, J = 19.8 Hz, C*H*), 3.50−3.55 (m, 8H, THF), 5.79−5.83 (m, 1H, Py), 6.45 (d, J = 8.7 Hz, 1H, Py), 6.73−6.79 (m, 1H, Py), 7.27−7.30 (m, 1H, Py). ^{13}C NMR (C$_6$D$_6$; δ (ppm)): 5.17 (d, Si*Me*$_3$), 17.18 (d, CH*Me*$_2$), 25.42 (THF), 29.26 (d, *C*H), 51.11 (d, *C*HMe$_2$), 68.20 (THF), 103.56, 118.58 (d), 133.37 (d), 146.73, 168.99 (Py). ^{31}P{^{1}H} NMR (C$_6$D$_6$; δ (ppm)): 33.83.

[{(Pr$^i_2$P═NSiMe$_3$)(2-Py)CH}SnCl] (3). To a cooled solution (−90 °C) of **2** (0.78 g, 1.75 mmol) in Et$_2$O (20 mL) was added SnCl$_2$ (0.34 g, 1.78 mmol) with stirring. The mixture was warmed to room temperature and stirred for 18 h. The mixture was filtered, and the filtrate was concentrated to yield yellow crystals of **3**. Yield: 0.51 g (64.9%), Mp: 88−90 °C. Anal. Found: C, 39.93; H, 6.35; N, 6.38. Calcd for C$_{15}$H$_{28}$N$_2$ClPSiSn: C, 40.07; H, 6.28; N, 6.23. ^{1}H NMR (C$_6$D$_6$; δ (ppm)): 0.36 (s, 9H, Si*Me*$_3$), 0.81 (dd, J = 6.9, 16.5 Hz, 6H, CH*Me*$_2$), 0.87−0.96 (m, 6H, CH*Me*$_2$), 1.68−1.83 (m, 2H, C*H*Me$_2$), 2.93 (d, J = 7.5 Hz, 1H, C*H*), 6.06 (t, J = 6.3 Hz, 1H, Py), 6.43 (d, J = 8.4 Hz, 1H, Py), 6.68−6.74 (m, 1H, Py), 8.34 (d, J = 4.8 Hz, 1H, Py). ^{13}C{^{1}H} NMR (C$_6$D$_6$; δ (ppm)): 4.10 (Si*Me*$_3$), 16.95 (d, CH*Me*$_2$), 29.57 (d, *C*HMe$_2$), 40.54 (d, *C*H), 113.09, 121.89 (d), 136.07, 145.16, 164.76 (Py). ^{31}P{^{1}H} NMR (C$_6$D$_6$; δ (ppm)): 43.14. ^{119}Sn{^{1}H} NMR (C$_6$D$_6$; δ (ppm)): −339.45.

1,3-[Sn{C(Pr$^i_2$P═NSiMe$_3$)(2-Py)}]$_2$ (4). Method 1. To a cooled (−90 °C) solution of **2** (1.67 g, 3.74 mmol) in Et$_2$O (30 mL) was added SnCl$_2$ (0.36 g, 1.90 mmol) with stirring. The mixture was slowly warmed to room temperature and stirred for 18 h. Volatiles were removed in vacuo, and the residue was extracted with toluene. After filtration the filtrate was concentrated to give yellow-orange crystals of **4**. Yield: 0.490 g (62.1%), Mp: 268−270 °C. Anal. Found: C, 44.10; H, 6.31; N, 6.86. Calcd for C$_{30}$H$_{54}$N$_4$P$_2$Si$_2$Sn$_2$: C, 43.61; H, 6.59; N, 6.78. ^{1}H NMR (C$_6$D$_6$; δ (ppm)): 0.02 (s, 18H, Si*Me*$_3$), 1.03 (dd, J = 6.9, 15.9 Hz, 12H, CH*Me*$_2$), 1.29 (dd, J = 7.2, 14.7 Hz, 12H, CH*Me*$_2$), 1.94−2.08 (m, 4H, *CH*Me$_2$), 6.31 (t, J = 6.0 Hz, 2H, Py), 6.52 (d, J = 8.4 Hz, 2H, Py), 7.03−7.08 (m, 2H, Py), 8.21 (d, J = 4.5 Hz, 2H, Py). ^{13}C{^{1}H} NMR (C$_6$D$_6$; δ (ppm)): 4.04 (Si*Me*$_3$), 16.12 (CH*Me*$_2$), 17.28 (CH*Me*$_2$), 30.86 (d, *C*HMe$_2$), 113.64, 119.15, 135.75, 146.08 (d), 164.50 (d) (Py). ^{31}P{^{1}H} NMR (C$_6$D$_6$; δ (ppm)): 38.45.

Table 6. X-Ray Crystallographic Data for Compounds 4 and 6−9

	4R	**4S**	**4I**	**6**
formula	$C_{30}H_{54}N_4P_2Si_2Sn_2$	$C_{30}H_{54}N_4P_2Si_2Sn_2$	$C_{30}H_{54}N_4P_2Si_2Sn_2$	$C_{30}H_{54}N_4P_2Si_2Ge_2$
fw	826.27	826.27	826.27	734.07
color/shape	yellow block	yellow block	yellow block	orange block
cryst syst (mm^3)	orthorhombic	orthorhombic	orthorhombic	triclinic
a (Å)	13.4117(5)	13.420(5)	13.634(3)	12.2138(9)
b (Å)	18.2367(7)	18.214(12)	18.426(4)	12.7921(10)
c (Å)	31.5142(12)	31.50(2)	32.261(7)	13.2064(10)
α (deg)	90	90	90	80.997(2)
β (deg)	90	90	90	85.355(2)
γ (deg)	90	90	90	63.9230(10)
V ($Å^3$), *Z*	7707.9(5), 8	7699(7), 8	8105(3)	1830.3(2), 2
density (Mg/m^3)	1.424	1.426	1.354	1.332
abs coeff (mm^{-1})	1.465	1.467	1.394	1.820
F(000)	3360	3360	3360	768
θ range for data collecn (deg)	1.29−28.71	1.99−25.49	1.26−25.27	1.56−28.04
no. of rflns collected	52 411	18 536	19 993	12 945
no. of indep rflns (R_{int})	9946 (0.0545)	6276 (0.1038)	6582 (0.0737)	8678 (0.0259)
goodness of fit on F^2	1.012	1.071	1.204	0.898
R1, wR2 ($I > 2\sigma(I)$)	0.0375, 0.0844	0.0726, 0.1714	0.0552, 0.1395	0.0370, 0.0753
R1, wR2 (all data)	0.0711, 0.1028	0.0825, 0.1803	0.0626, 0.1451	0.0670, 0.0825
largest diff peak and hole (e $Å^{-3}$)	1.122 and −0.505	1.422 and − 1.983	0.704 and −1.143	0.531 and −0.355

	7R	**7S**	**8**	**9**
formula	$C_{30}H_{54}N_4P_2Si_2SnPb$	$C_{30}H_{54}N_4P_2Si_2SnPb$	$C_{21}H_{46}N_3PSi_3Pb$	$C_{30}H_{54}N_4P_2Si_2Pb_2$
fw	914.77	914.77	663.04	1003.27
color/shape	orange block	orange block	yellow block	orange block
cryst syst (mm^3)	orthorhombic	orthorhombic	monoclinic	orthorhombic
a (Å)	13.4402(7)	13.582(3)	14.9927(6)	13.448(3)
b (Å)	18.2669(10)	18.654(4)	17.5143(7)	18.352(4)
c (Å)	31.5543(18)	32.091(6)	12.1551(5)	31.591(7)
α (deg)	90	90	90	90
β (deg)	90	90	111.1560(10)	90
γ (deg)	90	90	90	90
V ($Å^3$), *Z*	7746.9(7), 8	8112(3), 8	2976.6(2), 4	7797(3), 8
density (Mg/m^3)	1.569	1.498	1.480	1.709
abs coeff (mm^{-1})	5.154	4.922	5.855	8.793
F(000)	3616	3616	1328	3872
θ range for data collecn (deg)	1.99−25.00	1.27−25.00	1.46−24.99	1.98−28.04
no. of rflns collected	41 215	19 736	16 050	52 167
no. of indep rflns (R_{int})	6796 (0.0636)	6597 (0.0751)	5218 (0.0265)	9386 (0.0787)
goodness of fit on F^2	0.963	1.146	0.903	0.876
R1, wR2 ($I > 2\sigma(I)$)	0.0404, 0.1022	0.0902, 0.2619	0.0418, 0.1299	0.0324, 0.0590
R1, wR2 (all data)	0.0672, 0.1116	0.1055, 0.2755	0.0507, 0.1363	0.0743, 0.0673
largest diff peak and hole (e $Å^{-3}$)	1.881 and −1.543	4.237 and −3.702	1.413 and −0.809	1.106 and −1.349

Method 2. To a solution of **1** (2.56 g, 8.66 mmol) in toluene (30 mL) at 0 °C was added a solution of $Sn[N(SiMe_3)_2]_2$ (3.93 g, 9.02 mmol) in toluene (30 mL) with stirring. The mixture was warmed to room temperature and stirred for 2 days. After filtration the filtrate was concentrated to give yellow-orange crystals of **4**. Yield: 5.58 g (78.3%).

1,3-[Ge{C(Pr^i_2P=NSiMe$_3$)(2-Py)}]$_2$ (6). To a cooled (−90 °C) solution of **2** (0.73 g, 1.64 mmol) in Et_2O (20 mL) was added $GeCl_2$·(dioxane) (0.19 g, 0.81 mmol) with stirring. The mixture was slowly warmed to room temperature and stirred for 18 h. After filteration, the yellow-orange filtrate was concentrated to give yellow crystals of **6**. Yield: 0.242 g (81.6%), Mp: 202−203 °C. Anal. Found: C, 48.93; H, 7.51; N, 7.53. Calcd for $C_{30}H_{54}N_4P_2Si_2Ge_2$: C, 49.09; H, 7.41; N, 7.63. ^{1}H NMR (C_6D_6; *δ* (ppm)): −0.01 (s, 18H, Si*Me*$_3$), 1.11−1.24 (m,, 12H, CH*Me*$_2$), 1.41 (b, 12H, CH*Me*$_2$), 2.58 (b, 4H, C*H*Me$_2$), 6.54−6.58 (m, 2H, Py), 7.25−7.30 (m, 2H, Py), 7.48 (d, *J* = 6.0 Hz, 2H, Py), 8.42 (d, *J* = 3.0 Hz, 2H, Py). ^{13}C{^{1}H} NMR (C_6D_6; *δ* (ppm)): 3.09 (Si*Me*$_3$), 16.53 (CH*Me*$_2$), 17.65 (CH*Me*$_2$), 27.56, 32.10 (*C*HMe$_2$), 116.62, 125.45, 135.21, 149.14, 163.36 (Py). ^{31}P{^{1}H} NMR (C_6D_6; *δ* (ppm)): 63.61.

[1-Sn{C(Pr^i_2P=NSiMe$_3$)(2-Py)}-3-Pb{C(Pr^i_2P=NSiMe$_3$)(2-Py)}] (7). A solution of **3** (0.92 g, 2.05 mmol) and $Pb[N(SiMe_3)_2]_2$ (0.73 g, 1.39 mmol) in toluene (20 mL) was stirred for 45 h at room temperature. The yellow filtrate was concentrated to give orange crystals of **7**. Yield: 0.35 g (37.3%), Mp: 231−233 °C. Anal. Found: C, 39.22; H, 6.05; N, 6.30. Calcd for $C_{30}H_{54}N_4P_2Si_2SnPb$: C, 39.39; H, 5.95; N, 6.12. ^{1}H NMR (C_6D_6; *δ* (ppm)): 0.01 (s, 9H, Si*Me*$_3$), 0.73 (dd, *J* = 6.9, 17.4 Hz, 3H, CH*Me*$_2$), 1.08 (dd, *J* = 6.2, 14.7 Hz, 3H, CH*Me*$_2$), 1.17 (dd, *J* = 6.9, 14.7 Hz, 3H, CH*Me*$_2$), 1.52 (dd, *J* = 6.9, 14.7 Hz, 3H, CH*Me*$_2$), 1.76−1.84 (m, 1H, *CH*Me$_2$), 2.07−2.14 (m, 1H, *CH*Me$_2$), 6.06−6.10 (m, 1H, Py), 6.35 (d, *J* = 8.4 Hz, 1H, Py), 7.07−7.16 (m, 1H, Py), 8.30−8.31 (m, 1H, Py). ^{13}C{^{1}H} NMR (C_6D_6; *δ* (ppm)): 4.16 (Si*Me*$_3$), 15.39, 15.82, 16.80, 17.19 (CH*Me*$_2$), 27.99 (d, *C*HMe$_2$), 38.99 (d, *C*HMe$_2$), 113.77, 119.58, 134.83, 145.43 (d), 162.42 (d) (Py). ^{31}P-{^{1}H} NMR (C_6D_6; *δ* (ppm)): 30.19. ^{119}Sn{^{1}H} NMR (C_6D_6; *δ* (ppm)): −130.19.

[{(Pr^i_2P=NSiMe$_3$)(2-Py)CH}Pb{N(SiMe$_3$)$_2$}$_2$] (8). A solution of complex **3** (0.27 g, 0.60 mmol) and $Pb[N(SiMe_3)_2]_2$ (0.33 g, 0.63 mmol) in toluene (20 mL) was stirred for 45 h at room temperature. After filtration, the solution was concentrated to give yellow crystals of **8**. Yield: 0.26 g (64.1%), Mp: 104−106 °C. ^{1}H NMR (C_6D_6; *δ* (ppm)): 0.33 (s, 18H, Si*Me*$_3$), 0.43 (s, 9H, Si*Me*$_3$), 0.85−1.00 (m, 6H, CH*Me*$_2$), 1.08 (dd, *J* = 7.5, 15.3 Hz, 6H, CH*Me*$_2$), 2.25 (d, *J* = 1.5 Hz, 1H, C*H*), 2.54−2.64 (m, 2H, *CH*Me$_2$), 6.24−6.28 (m, 1H, Py), 6.45−6.50 (m, 1H, Py), 6.98−7.04 (m, 1H, Py), 8.28−8.30 (m, 1H, Py). ^{13}C{^{1}H} NMR (C_6D_6; *δ* (ppm)): 5.74, 6.40 (SiMe$_3$), 16.19, 17.15 (CH*Me*$_2$), 33.49, (d, *C*HMe$_2$), 55.72 (d, *C*H), 116.88, 121.74 (d), 135.33, 148.46, 161.01 (Py). ^{31}P{^{1}H} NMR (C_6D_6; *δ* (ppm)): 37.93 with satellites (*J* = 2645.9 Hz).

1,3-[Pb{C(Pr^i_2P=NSiMe$_3$)(2-Py)}]$_2$ (9). To a cooled (−90 °C) solution of **2** (1.55 g, 3.47 mmol) in Et_2O (30 mL) was added $PbCl_2$

(0.48 g, 1.73 mmol) with stirring. The mixture was slowly warmed to room temperature and stirred for 18 h. The yellow-orange filtrate was concentrated and kept at −90 °C, to give yellow-orange crystals of **9**. Yield: 0.53 g (86.5%), Mp: 220 °C dec. ^{1}H NMR (C_6D_6 + [D_8]THF; δ (ppm)): −0.22 (s, 18H, Si*Me*$_3$), 0.92 (dd, *J* = 9.0, 15.1 Hz, 12H, CH*Me*$_2$), 1.25 (dd, *J* = 6.0, 12.1 Hz, 12H, CH*Me*$_2$), 1.95−2.07 (m, 4H, C*H*Me$_2$), 6.01−6.05 (m, 2H, Py), 6.18 (d, *J* = 6.0 Hz, 2H, Py), 7.17−7.26 (m, 2H, Py), 8.33 (d, *J* = 3.1 Hz, 2H, Py). ^{13}C{^{1}H} NMR (C_6D_6 + [D_8]THF; δ (ppm)): 3.94 (Si*Me*$_3$), 15.52 (CH*Me*$_2$), 16.92 (CH*Me*$_2$), 34.89 (d, *C*HMe$_2$), 113.38, 123.89, 134.12, 144.83 (d), 162.31 (d) (Py). ^{31}P{^{1}H} NMR (C_6D_6 + [D_8]-THF; δ (ppm)): 29.75.

X-ray Crystallography. Selected single crystals were mounted and sealed in Lindemann glass capillaries under nitrogen. Diffraction experiments for all compounds were carried out on a Bruker SMART CCD diffractometer with a Mo Kα sealed tube, in ω-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 determining lattice constants. SAINT-PLUS was used for the integration of reflection intensities and scaling. SADABS was used for absorption corrections.[26] 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 (the 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 calculations 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.[27] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[28] Details of the crystallographic data collection and structure refinement of all compounds are summarized in Table 6.

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Supporting Information Available: CIF files giving 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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