

Synthesis of Heteroleptic Tin(II) and Lead(II) Compounds from Pyrazyl-Linked Bisphosphoranoimine

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The synthesis and characterization of a series of tin(II) and lead(II) heteroleptic compounds derived from a novel pyrazyl-linked bisphosphoranoimine, 2,3-C₄H₂N₂[(CH₂)ⁱPr₂P=N(SiMe₃)₂]₂ (**1**), are reported. The reaction of **1** with 2 equiv of M[N(SiMe₃)₂]₂ (M = Sn, Pb) afforded the dinuclear heteroleptic compounds [(Me₃Si)N(Sn(L)SnN(SiMe₃))] (L = {2,3-C₄H₂N₂[(CH)ⁱPr₂P=N(SiMe₃)₂]²⁻) (**2**) and {Pb[N(SiMe₃)₂][N(SiMe₃)=PPrⁱCH]-2,3-C₄H₂N₂-[Pb(CHⁱPr₂P=N(SiMe₃))][N(SiMe₃)₂]} (**3**), respectively. Dilithium compound [Li(L)(THF)₂] (**4**) obtained from the reaction of **1** with 2 equiv of ⁿBuLi was used to prepare tin(II) metallacycle [Sn(CHⁱPr₂P=N(SiMe₃)₂-2,3C₄H₂N₂] (**5**) and heteroleptic compound [ClSn(L)SnCl] (**6**), respectively. Compounds **2–6** have been characterized by X-ray structural analysis.

Introduction

The continuing development of sterically hindered phosphoranoimines has been inspired by their extensive usage in forming stable mono- and dimetallic complexes with main group and transition metals, and even lanthanide metals.¹ Phosphoranoimines can be deprotonated by base to give mono- or dianionic ligand transfer reagents. A variety of metal complexes have been derived from the neutral or anionic phosphoranoimino ligands. Since the ligands can be used to stabilize low-coordinate metal centers by offering a sterically hindered environment, our group became interested in using this kind of ligand system to synthesize various metal complexes.

We have reported the synthesis of some group 14 metal complexes including the bisgermavinylidene **I** and 1,3-dimetalcyclobutanes **II–IV** (Figure 1) derived from phosphoranoimino ligands previously.² In this paper we report the

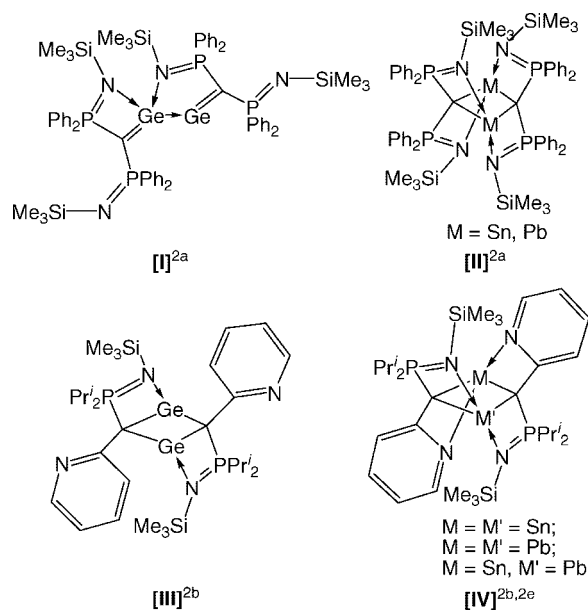


Figure 1

synthesis of a novel pyrazyl-linked bis(phosphoranoimine), 2,3-C₄H₂N₂[(CH₂)ⁱPr₂P=N(SiMe₃)₂]₂ (**1**), and several group 14 metal complexes derived from it. The bonding modes of the ligand and reactivity of the synthesized group 14 metal complexes have also been investigated.

Results and Discussion

Synthesis of Group 14 Heteroleptic Metal Complexes. The reaction of 2,3-C₄H₂N₂[(CH₂)ⁱPr₂P=N(SiMe₃)₂]₂ (**1**) with 2 equiv of Sn[N(SiMe₃)₂]₂ afforded the heteroleptic bis(trimethylsilyl)-amido metal complexes [(Me₃Si)N(Sn(L)SnN(SiMe₃))] (L = {2,3-C₄H₂N₂[(CH)ⁱPr₂P=N(SiMe₃)₂]²⁻) (**2**). However, a similar reaction of **1** with Pb[N(SiMe₃)₂]₂ gave {Pb[N(SiMe₃)₂][N(SiMe₃)=PPrⁱCH]-2,3-C₄H₂N₂-[Pb(CHⁱPr₂P=N(SiMe₃))][N(SiMe₃)₂]} (**3**) (Scheme 1). Compound **3** is a compound with the lead(II) centers bonded to the ligand in different modes. The results suggested that further deprotonation of the me-

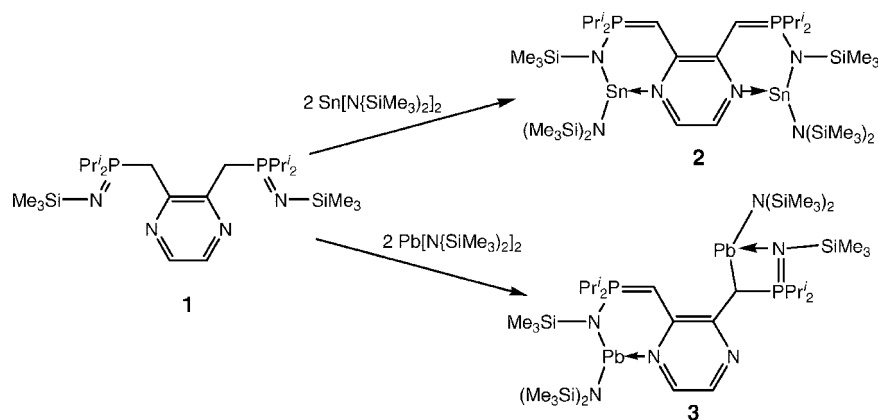
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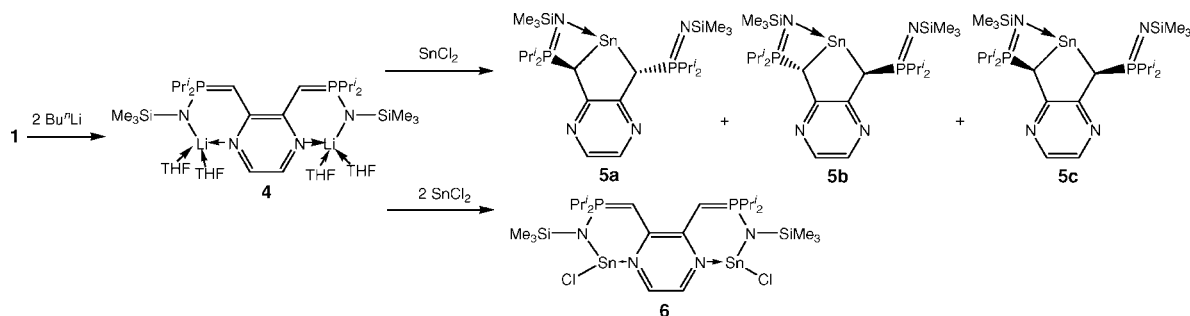
(2) Selected reviews and examples of (phosphoranoimido) group 14 metal complexes: (a) Leung, W.-P.; Wang, Z.-X.; Li, H.-W.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 2501. (b) Leung, W.-P.; Wang, Z.-X.; Li, H.-W.; Yang, Q.-C.; Mak, T. C. W. *J. Am. Chem. Soc.* **2001**, *123*, 8123. (c) Leung, W.-P.; Ip, Q. W.-Y.; Wong, S.-Y.; Mak, T. C. W. *Organometallics* **2003**, *22*, 4604. (d) Leung, W.-P.; So, C.-W.; Wang, Z.-X.; Wang, J.-Z.; Mak, T. C. W. *Organometallics* **2003**, *22*, 4305. (e) Leung, W.-P.; Wong, K.-W.; Wang, Z.-X.; Mak, T. C. W. *Organometallics* **2006**, *25*, 2037.

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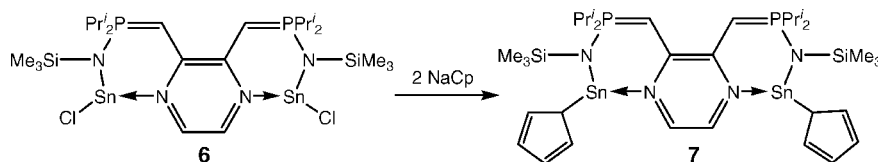
Scheme 1



Scheme 2



Scheme 3



thine protons of the ligand has not occurred. We have reported that similar reactions of imino(phosphoranopyridyl)methane with $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$ ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$) afforded 1,3-dimetallacyclobutanes via the reactive metallavinylidene intermediate.^{2b}

Treatment of **1** with 2 equiv of $^n\text{BuLi}$ in THF gave bis(phosphoranoimido) dilithium complex $[\text{Li}(\text{L})(\text{THF})_2]$ (**4**). Metathesis reaction of **4** with 1 equiv of SnCl_2 in diethyl ether afforded a stannacyclopentane, $[\text{Sn}(\text{CH}^i\text{Pr}_2\text{P}=\text{NSiMe}_3)_2\text{-}2,3\text{-C}_4\text{H}_2\text{N}_2]$ (**5**). The formation of **5** is a result of charge delocalization of the dianionic ligand from imino nitrogens to the methine carbons, and it becomes a chelating C-centered dialkyl ligand. It will therefore generate a racemic mixture of (2*S*,5*S*)- $[\text{Sn}(\text{CH}^i\text{Pr}_2\text{P}=\text{NSiMe}_3)_2\text{-}2,3\text{-C}_4\text{H}_2\text{N}_2]$ (**5a**), (2*R*,5*R*)- $[\text{Sn}(\text{CH}^i\text{Pr}_2\text{P}=\text{NSiMe}_3)_2\text{-}2,3\text{-C}_4\text{H}_2\text{N}_2]$ (**5b**), and *meso*-(2*S*,5*R*)- $[\text{Sn}(\text{CH}^i\text{Pr}_2\text{P}=\text{NSiMe}_3)_2\text{-}2,3\text{-C}_4\text{H}_2\text{N}_2]$ (**5c**) (Scheme 2). However, a similar metathesis reaction of **4** with 2 equiv of SnCl_2 gave the binuclear chlorostannylene $[\text{ClSn}(\text{L})\text{SnCl}]$ (**6**). The pyrazyl-linked bis(phosphoranoimino) dianionic ligand (**L**) behaves as a di-imido ligand and forms a bridge between two SnCl moieties. Attempts to further dehydrochlorinate using bases to generate the stannavinylidene intermediate have not been successful.

We have also explored the reactivity of **6** by the reaction with two equivalents of sodium cyclopentadienide in THF. The chloride group can be substituted to a σ -bonded cyclopentadienyl group to give $[(\eta^1\text{-C}_5\text{H}_5)\text{Sn}(\text{L})\text{Sn}(\eta^1\text{-C}_5\text{H}_5)]$ (**7**) (Scheme 3).

Spectroscopic Properties. Compounds **2**, **3**, **6**, and **7** are orange crystalline solids, while compounds **4** and **5** are yellow

crystalline solids. These compounds are soluble in THF, Et_2O , and toluene and sparingly soluble in hydrocarbon solvents. In the ^1H and ^{13}C NMR spectra of compounds **2** and **4–7**, one set of signals assignable to the pyrazine-linked bisphosphoranoimino ligand was observed, suggesting that the two side arms at the 2,3 position of the pyrazyl ring are symmetrical and in the same chemical environment.

However, in the ^1H and ^{13}C NMR spectra of compound **3**, two sets of signals due to the ligand and the metal amide group were observed, which suggests that the two side arms at the 2,3 position of the pyrazyl ring are in different chemical environments. This is consistent with the solid-state X-ray structure of **3**. The structure has shown that one lead(II) center is σ -bonded to the amido nitrogens, and the other lead(II) center is σ -bonded to the amido nitrogen and the methine carbon of the ligand. The ^{31}P NMR spectra of compounds **2** and **4–7** displayed one signal that corresponds to the two phosphorus atoms in the same environment. Compound **3** showed two signals at δ 54.63 and 58.72 ppm, which corresponds to two different phosphorus environments as a result of different bonding modes of the lead(II) centers.

The ^1H NMR spectrum of compound **5** displayed an AB quartet at δ 3.45 and 3.48 ppm, which corresponds to the two diastereotopic methine protons of the stereoisomers. The ^1H , ^{13}C , and ^{31}P NMR spectra of all the compounds are consistent with their solid-state structures except for compound **5**. This may be due to the fluxional coordination of the imino nitrogen atoms at the tin center in solution.

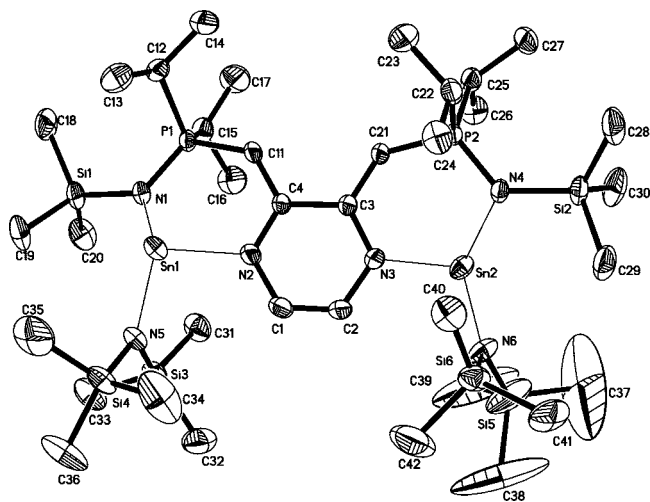


Figure 2. ORTEP drawing of **2**; 30% thermal ellipsoids are shown.

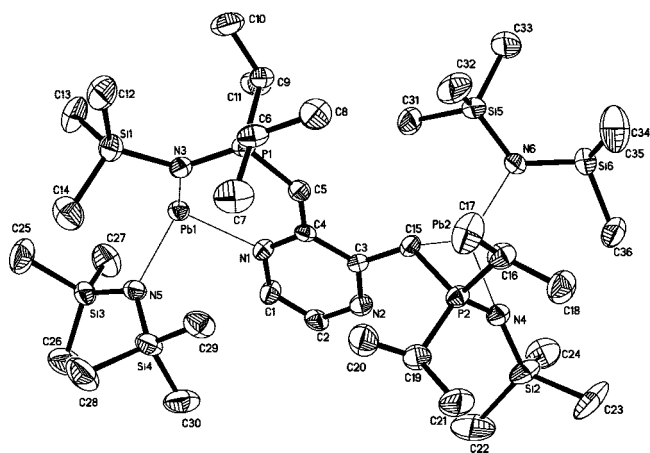


Figure 3. ORTEP drawing of **3**; 30% thermal ellipsoids are shown.

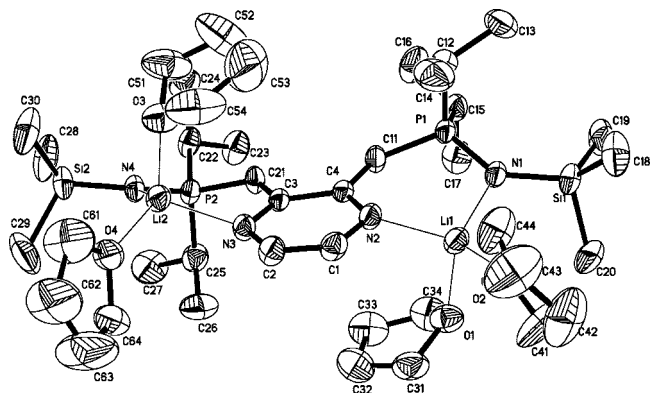


Figure 4. ORTEP drawing of **4**; 30% thermal ellipsoids are shown.

X-ray Structures. The molecular structures with the atom-numbering schemes of compounds **2–7** are shown in Figures 2–7, respectively. Selected bond lengths and angles of compounds **2–7** are listed in Tables 1–5.

The structure of **2** consists of two tin atoms bonded to the pyrazyl-linked bis(phosphoranoimido) ligand in an *N,N'*-chelate fashion, forming two six-membered metallacycles linked by a 2,3-pyrazyl ring. Each tin center is also bonded to a bis(trimethylsilyl)amide group. The geometry around the tin centers

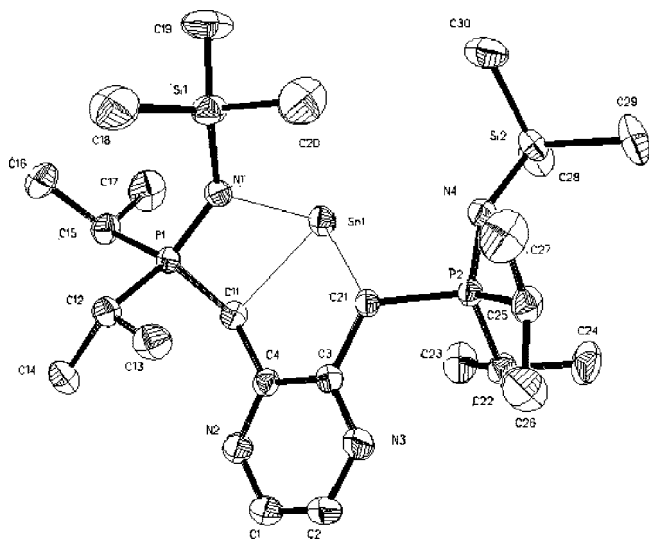


Figure 5. ORTEP drawing of **5a**; 30% thermal ellipsoids are shown.

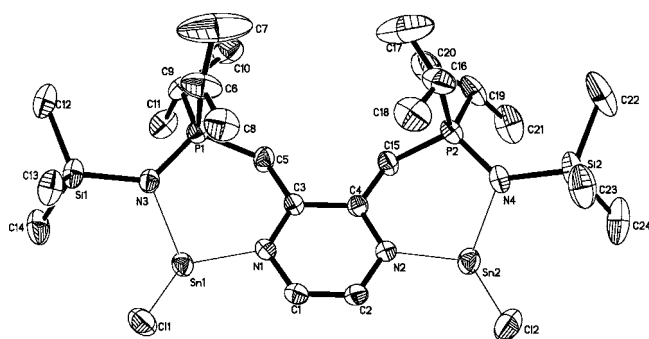


Figure 6. ORTEP drawing of **6**; 30% thermal ellipsoids are shown.

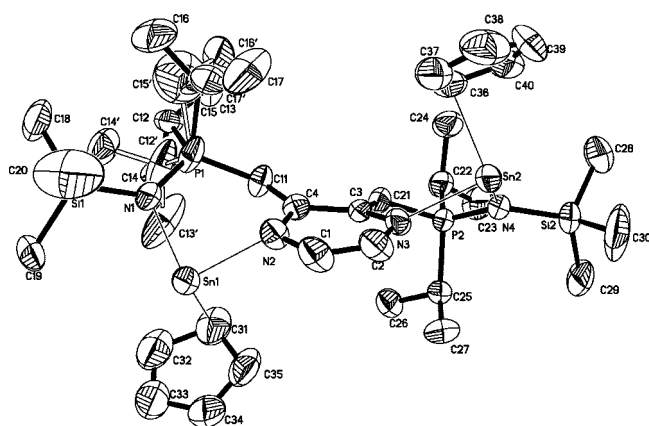


Figure 7. ORTEP drawing of **7**; 30% thermal ellipsoids are shown.

is a distorted trigonal pyramid with one vertex occupied by a lone pair of electrons. The average Sn–N bond distance of 2.233 Å is comparable to those of 2.225 Å in $[[\{N(\text{SiMe}_3)\text{C}(\text{Ph})_2\text{CH}\}\text{SnN}(\text{SiMe}_3)_2]^4$ and 2.201 Å in $\{\text{ClSn}[\text{CH}(\text{Pr}_2\text{P}=\text{NSiMe}_3)(2\text{-Py})]\}^{2b}$.

Compound **3** is an asymmetric compound. The structure of **3** consists of two lead atoms bonded to the ligand in two

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 2 and 3

[[{N(SiMe ₃) ₂ }Sn(Me ₃ SiN=P ^r Pr ₂ CH)] ₂ -2,3-C ₄ H ₂ N ₂] (2)			
Sn(1)–N(5)	2.147(3)	Sn(1)–N(2)	2.199(3)
Sn(1)–N(1)	2.257(3)	Sn(2)–N(6)	2.155(3)
Sn(2)–N(3)	2.184(3)	Sn(2)–N(4)	2.286(3)
P(1)–N(1)	1.622(3)	P(1)–C(11)	1.739(3)
P(2)–N(4)	1.621(3)	P(2)–C(21)	1.748(3)
C(4)–C(11)	1.378(4)	C(3)–C(21)	1.375(4)
N(5)–Sn(1)–N(2)	94.8(2)	N(5)–Sn(1)–N(1)	107.2(2)
N(2)–Sn(1)–N(1)	89.1(2)	N(6)–Sn(2)–N(3)	94.3(3)
N(6)–Sn(2)–N(4)	108.4(2)	N(3)–Sn(2)–N(4)	90.8(2)
C(4)–N(2)–Sn(1)	118.2(2)	P(1)–N(1)–Sn(1)	110.7(3)
C(3)–N(3)–C(2)	119.3(3)	C(4)–N(2)–C(1)	119.9(3)
P(2)–N(4)–Sn(2)	110.4(3)	C(3)–N(3)–Sn(2)	117.7(2)
[[{N(SiMe ₃) ₂ }Pb(Me ₃ SiN=P ^r Pr ₂ CH)] ₂ -2,3-C ₄ H ₂ N ₂ -{Pb(CH ^r Pr ₂ P=NSiMe ₃){N(SiMe ₃) ₂ }] (3)			
Pb(1)–N(5)	2.245(6)	Pb(1)–N(1)	2.330(7)
Pb(1)–N(3)	2.421(7)	Pb(2)–N(6)	2.296(6)
Pb(2)–N(4)	2.459(7)	Pb(2)–C(15)	2.471(8)
P(1)–C(5)	1.730(8)	P(1)–N(3)	1.6596(7)
P(2)–C(15)	1.753(8)	P(2)–N(4)	1.604(7)
C(3)–C(15)	1.460(2)	C(4)–C(5)	1.376(2)
N(5)–Pb(1)–N(1)	92.9(3)	N(5)–Pb(1)–N(3)	105.7(2)
N(1)–Pb(1)–N(3)	89.6(2)	N(6)–Pb(2)–N(4)	105.7(3)
N(6)–Pb(2)–C(15)	94.6(3)	N(4)–Pb(2)–C(15)	67.2(3)
P(1)–N(3)–Pb(1)	114.0(3)	C(4)–N(1)–Pb(1)	128.0(5)
P(2)–C(15)–Pb(2)	89.2(3)	P(2)–N(4)–Pb(2)	93.3(3)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds 4 and 5

[[{(THF) ₂ Li(Me ₃ SiN=P ^r Pr ₂ CH)] ₂ -2,3-C ₄ H ₂ N ₂] (4)			
N(1)–Li(1)	2.020(8)	N(2)–Li(1)	2.019(8)
N(3)–Li(2)	2.003(8)	N(4)–Li(2)	2.029(8)
O(1)–Li(1)	2.009(8)	O(2)–Li(1)	1.996(8)
O(3)–Li(2)	2.017(8)	O(4)–Li(2)	1.988(8)
P(1)–N(1)	1.583(3)	P(1)–C(11)	1.728(4)
P(2)–N(4)	1.592(3)	P(2)–C(21)	1.724(4)
C(3)–C(21)	1.398(5)	C(4)–C(11)	1.399(5)
P(1)–N(1)–Li(1)	106.9(3)	C(4)–N(2)–Li(1)	112.9(3)
C(3)–N(3)–Li(2)	114.7(3)	P(2)–N(4)–Li(2)	108.3(3)
O(2)–Li(1)–O(1)	99.7(3)	O(2)–Li(1)–N(2)	107.9(4)
O(1)–Li(1)–N(2)	104.0(4)	O(2)–Li(1)–N(1)	115.6(4)
O(1)–Li(1)–N(1)	118.7(4)	N(2)–Li(1)–N(1)	109.8(3)
O(4)–Li(2)–O(3)	103.2(4)	O(4)–Li(2)–N(3)	106.9(4)
O(4)–Li(2)–N(4)	119.1(4)	N(3)–Li(2)–O(3)	103.6(4)
O(3)–Li(2)–N(4)	113.8(4)	N(3)–Li(2)–N(4)	108.9(4)
(2 <i>S</i> ,5 <i>S</i>)-[Sn(CH ^r Pr ₂ P=NSiMe ₃) ₂ -2,3-C ₄ H ₂ N ₂] (5a)			
Sn(1)–C(21)	2.271(2)	Sn(1)–N(1)	2.3076(2)
Sn(1)–C(11)	2.375(2)	P(1)–C(11)	1.770(2)
P(1)–N(1)	1.599(2)	P(2)–C(21)	1.802(2)
P(2)–N(4)	1.545(2)	C(4)–C(11)	1.489(3)
C(3)–C(21)	1.487(3)		
C(21)–Sn(1)–N(1)	89.19(7)	C(21)–Sn(1)–C(11)	78.17(7)
N(1)–Sn(1)–C(11)	69.43(7)	P(1)–N(1)–Sn(1)	95.11(9)
N(1)–P(1)–C(11)	104.63(1)	C(4)–C(3)–C(21)	119.67(2)
P(1)–C(11)–Sn(1)	88.39(9)	C(3)–C(4)–C(11)	121.2(2)
C(3)–C(21)–Sn(1)	110.64(1)	C(4)–C(11)–Sn(1)	106.38(1)

different modes. Pb(1) is bonded to the ligand in *N,N'*-chelate fashion, forming a six-membered metallacyclic ring similar to that of compound **2**, while Pb(2) is bonded to the ligand in *C,N'*-chelate mode, forming a PbCPN(imino) four-membered ring. In the PbCPN(imino) four-membered ring, the bond distances of Pb–C [2.469(8) Å] and Pb–N [2.459(7) Å] are comparable to those of 2.416(6) and 2.393(5) Å in [[(P^rPr₂P=NSiMe₃)(2-Py)CH]Pb[N(SiMe₃)₂]₂]^{2c} and those of 2.427(2) and 2.524(3) Å in [[{2-{Pb[C(^rPr₂P=NSiMe₃)]₂}-6-{Pb[CH(^rPr₂P=NSiMe₃)]-N(SiMe₃)₂]}C₅H₃N₂]₂]^{2d} respectively. The structural difference between compounds **2** and **3** may be due to the difference in the atomic size of tin and lead. The methine carbon is more open and favors the approach of a larger atom.

Table 3. Selected Bond Lengths (Å) and angles (deg) for Compounds 6 and 7

[[ClSn(Me ₃ SiN=P ^r Pr ₂ CH)] ₂ -2,3-C ₄ H ₂ N ₂] (6)			
Sn(1)–N(3)	2.178(3)	Sn(1)–N(1)	2.208(3)
Sn(1)–Cl(1)	2.469(1)	Sn(2)–N(4)	2.190(3)
Sn(2)–N(2)	2.202(3)	Sn(2)–Cl(2)	2.474(2)
P(1)–N(3)	1.613(3)	P(1)–C(5)	1.734(4)
P(2)–N(4)	1.619(4)	P(2)–C(15)	1.736(4)
C(3)–C(5)	1.384(5)	C(4)–C(15)	1.403(5)
N(3)–Sn(1)–N(1)	91.53(1)	N(3)–Sn(1)–Cl(1)	96.27(9)
N(1)–Sn(1)–Cl(1)	90.16(9)	N(4)–Sn(2)–N(2)	90.17(1)
N(4)–Sn(2)–Cl(2)	96.18(1)	N(2)–Sn(2)–Cl(2)	89.51(9)
C(4)–N(2)–Sn(2)	111.1(3)	C(3)–N(1)–Sn(1)	112.5(2)
P(2)–N(4)–Sn(2)	108.06(2)	P(1)–N(3)–Sn(1)	111.96(2)
[[(η^1 -C ₅ H ₅)Sn(Me ₃ SiN=P ^r Pr ₂ CH)] ₂ -2,3-C ₄ H ₂ N ₂] (7)			
Sn(1)–N(2)	2.212(5)	Sn(1)–N(1)	2.251(6)
Sn(1)–C(31)	2.359(9)	P(1)–N(1)	1.605(6)
P(1)–C(11)	1.736(6)	C(34)–C(35)	1.344(6)
C(33)–C(34)	1.371(6)	C(4)–C(11)	1.367(8)
C(31)–C(35)	1.422(4)	C(31)–C(32)	1.473(5)
C(32)–C(33)	1.33(2)		
N(2)–Sn(1)–N(1)	87.5(9)	N(2)–Sn(1)–C(31)	90.8(3)
N(1)–Sn(1)–C(31)	100.0(3)	N(1)–P(1)–C(11)	114.2(3)
C(4)–N(2)–Sn(1)	122.7(4)	P(1)–N(1)–Sn(1)	119.3(3)
C(35)–C(31)–Sn(1)	85.8(6)	C(35)–C(31)–C(32)	104.1(2)
C(33)–C(32)–C(31)	107.8(2)	C(32)–C(31)–Sn(1)	87.8(7)
C(35)–C(34)–C(33)	110.3(3)	C(32)–C(33)–C(34)	109.7(3)
C(34)–C(35)–C(31)	108.1(2)		

Compound **4** is a dilithium complex consisting of two lithium atoms bonded to the ligand in an *N,N'*-chelation and coordinated to two THF molecules with a distorted tetrahedral geometry. Similar to compound **2**, the lithium atoms are bonded to both imino nitrogen and pyrazyl nitrogen atoms to form two six-membered metallacycles linked by a pyrazyl ring. The average Li–N(imino) bond distance of 2.024 Å and Li–N(pyrazyl) bond distance of 2.011 Å are comparable to those of 1.980(9) and 2.017(9) Å found in [HC(PPh₂=NSiMe₃)₂Li·THF]^{2d}.

Compound **5a** (a 2*S*,5*S* stereoisomer) is a stannacyclopentane. It consists of a tin(II) center bonded to two methine carbons of the chelating dialkyl ligand, forming a five-membered metallacycle. One of the imino nitrogens is coordinated to the tin(II) center, forming a C–P–N–Sn four-membered ring in a *C,N*-chelate fashion. The tin center adopts a trigonal-pyramidal geometry. The

Table 4. Crystallographic Data for Compounds 2–4

	2	3	4
empirical formula	C ₃₆ H ₈₆ N ₆ P ₂ Si ₆ Sn ₂	C ₃₆ H ₈₆ N ₆ P ₂ Pb ₂ Si ₆	C ₄₀ H ₈₂ Li ₂ N ₄ O ₄ P ₂ Si ₂
formular mass	1070.97	1247.97	815.10
color	orange	orange	yellow
cryst syst	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	12.192(2)	12.4223(15)	10.186(2)
<i>b</i> (Å)	15.576(3)	15.818(2)	15.616(3)
<i>c</i> (Å)	15.974(3)	16.737(2)	18.308(4)
α (deg)	83.363(4)	66.813(2)	105.08(3)
β (deg)	69.356(4)	75.262(2)	99.53(3)
γ (deg)	89.615(4)	69.288(2)	108.25(3)
<i>V</i> (Å ³)	2817.8(9)	2802.2(6)	2571.9(9)
<i>Z</i>	2	2	2
<i>D</i> _{calcd} (mg/m ³)	1.262	1.479	1.053
abs coeff (mm ⁻¹)	1.099	6.214	0.168
<i>F</i> (000)	1116	1244	892
cryst size (mm ³)	0.50 × 0.40 × 0.30	0.50 × 0.40 × 0.30	0.50 × 0.40 × 0.20
θ range for data collect (deg)	1.37 to 28.30	1.34 to 28.31	2.13 to 25.00
index ranges	−16 ≤ <i>h</i> ≤ 12 −20 ≤ <i>k</i> ≤ 20 −21 ≤ <i>l</i> ≤ 19	−16 ≤ <i>h</i> ≤ 15 −21 ≤ <i>k</i> ≤ 15 −22 ≤ <i>l</i> ≤ 17	−12 ≤ <i>h</i> ≤ 11 0 ≤ <i>k</i> ≤ 18 −21 ≤ <i>l</i> ≤ 21
no. of reflns collected	19 480	19 650	9418
no. of indept reflns (<i>R</i> _{int})	13 679 (0.0181)	13 615 (0.0366)	9052 (0.0373)
goodness of fit, <i>F</i> ²	1.019	0.988	0.994
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0384, 0.0970	0.0446, 0.1146	0.0699, 0.1780
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0607, 0.1105	0.0703, 0.1309	0.1806, 0.2272
no. of data/restraints/params	13 679/0/469	13 615/0/470	9052/0/487
largest diff peaks (e Å ⁻³)	1.017 and −0.868	1.968 and −2.290	0.255 and −0.324

Table 5. Crystallographic Data for Compounds 5–7

	5	6	7
empirical formula	C ₂₄ H ₅₀ N ₄ P ₂ Si ₂ Sn	C ₂₄ H ₅₀ Cl ₂ N ₄ P ₂ Si ₂ Sn ₂	C ₃₄ H ₆₀ N ₄ P ₂ Si ₂ Sn ₂
formular mass	631.49	821.08	880.36
color	yellow	orange	orange
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	12.667(2)	13.704(3)	17.645(7)
<i>b</i> (Å)	21.268(4)	16.533(3)	16.011(6)
<i>c</i> (Å)	13.067(2)	16.125(3)	15.407(6)
α (deg)	90	90	90
β (deg)	111.222(3)	92.341(4)	102.609(7)
γ (deg)	90	90	90
<i>V</i> (Å ³)	3281.5(9)	3650.3(12)	4248(3)
<i>Z</i>	4	4	4
<i>D</i> _{calcd} (mg/m ³)	1.278	1.494	1.377
abs coeff (mm ⁻¹)	0.967	1.688	1.334
<i>F</i> (000)	1320	1656	1800
cryst size (mm ³)	0.50 × 0.40 × 0.30	0.50 × 0.40 × 0.30	0.50 × 0.40 × 0.30
θ range for data collect (deg)	1.92 to 28.04	1.49 to 28.31	1.74 to 28.10
index ranges	−16 ≤ <i>h</i> ≤ 16 −28 ≤ <i>k</i> ≤ 26 −16 ≤ <i>l</i> ≤ 17	−18 ≤ <i>h</i> ≤ 18 −22 ≤ <i>k</i> ≤ 14 −20 ≤ <i>l</i> ≤ 21	−23 ≤ <i>h</i> ≤ 20 −21 ≤ <i>k</i> ≤ 14 −18 ≤ <i>l</i> ≤ 20
no. of reflns collected	22 047	24 783	28 660
no. of indept reflns (<i>R</i> _{int})	7893 (0.0260)	9039 (0.0363)	10 302 (0.0502)
goodness of fit, <i>F</i> ²	1.093	1.012	0.996
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0321, 0.0816	0.0364, 0.0784	0.0557, 0.1379
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0453, 0.0896	0.0846, 0.1007	0.1380, 0.1849
no. of data/restraints/params	7893/0/298	9039/0/325	10 302/18/451
largest diff peaks (e Å ⁻³)	0.304 and −0.961	0.645 and −0.580	0.993 and −1.170

average Sn–C bond distance of 2.323 Å is comparable to those of 2.284 Å in [Sn{2,4,6-(CF₃)C₆H₂}₂]⁵ and 2.367 Å in [Sn{ μ^2 -C(Ph₂P=NSiMe₃)₂}₂]^{2a}. Sn(1) is coordinated to the imino nitrogen atom at a distance of 2.307(2) Å, which is comparable to that of 2.256(6) Å found in [{2- $\{$ Sn[C(Pr₂P=NSiMe₃)]-6- $\{$ Sn[CH(Pr₂P=NSiMe₃)Cl]C₃H₃N]₂]^{2d}.

The structure of **6** consists of two equivalent tin(II) centers. The tin(II) centers are bonded to the chloride group and the ligand in a *N,N'*-chelate fashion. Similar to that of compound **2**, two six-membered metallacycles are linked by a 2,3-pyrazyl ring. The tin(II) center adopts a distorted trigonal pyramid

geometry. The average bond distances of Sn–N(imino) (2.184 Å) and Sn–N(pyrazyl) (2.205 Å) are comparable to those of 2.256(6) and 2.316(5) Å in [{2- $\{$ Sn{C(Pr₂P=NSiMe₃)}-6- $\{$ Sn[CH(Pr₂P=NSiMe₃)Cl]C₃H₃N]₂]^{2d} as well as 2.177(5) and 2.225(6) Å in [ClSn[CH(Pr₂P=NSiMe₃)(2-Py)]]^{2b}. The average Sn–Cl bond distance of 2.472 Å is also comparable to that of 2.466(2) Å in {ClSn[C(SiMe₃)₂(SiMe₂C₃H₄N-2)]⁶ and 2.501(7) Å in {ClSn[CH(Pr₂P=NSiMe₃)(2-Py)]]^{2b}.

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Compound **7** is a bis-stannylene bridged by the pyrazyl-linked bisphosphoranoimido ligand. The structure is similar to that of compound **6**, but with the chloride group replaced by a σ -bonded cyclopentadienyl group. The Sn(1)–C(31) bond distance of 2.359(9) Å is within the normal range of a Sn–C single bond,^{7–9} supporting the η^1 bonding of the cyclopentadienyl ring. The average Sn–N bond distance of 2.232 Å is comparable to that of 2.195 Å in compound **6**. The average bond distances of P–N (1.614 Å) and P–C (1.741 Å) are also comparable to those of 1.616 and 1.735 Å in compound **6**, respectively. Moreover, other bond distances within the ligand backbones are also comparable to those in compound **6**, indicating the structure of the ligand backbone was retained after the nucleophilic substitution reaction.

The structures of **2**, **6**, and **7** are very similar to each other, except that they have different substituents at the tin(II) centers. The Sn–N(imino) distances are 2.257(3) and 2.286(3) Å [for a substituent of N(SiMe₃)₂], 2.178(3) and 2.190(3) Å [for a substituent of Cl], and 2.251(6) Å [for a substituent of (η^1 -C₅H₅)], respectively. This parallels with the sizes of the substituents.

Conclusions

A series of tin(II) and lead(II) metal complexes based on the novel pyrazyl-linked bis(phosphoranoimino) ligand [(Me₃SiN=PⁱPr₂CH₂)₂-2,3-C₄H₂N₂] (**1**) has been synthesized and structurally characterized. The results have shown that the ligand can behave as a bis-imido ligand, a chelating dialkyl ligand, or a mixed imido-alkyl ligand. The chloride group of [ClSn(L)SnCl] (**6**) can be substituted by alkylating reagents such as sodium cyclopentadienide.

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled from CaH₂ (hexane) and/or Na (Et₂O, toluene, and THF). M{N(SiMe₃)₂}₂ (M = Sn, Pb) was prepared by literature procedures.³ 2,3-Dimethylpyrazine, SnCl₂, PbCl₂, and NaCp were purchased from Aldrich Chemicals and used without further purification. The ¹H, ¹³C, ³¹P, and ¹¹⁹Sn NMR spectra were recorded on Bruker WM-300 or Varian 400 instruments. The NMR spectra were recorded in THF-*d*₈ or benzene-*d*₆, and the chemical shifts δ are relative to SiMe₄, 85% H₃PO₄, and SnMe₄ for ¹H, ¹³C ³¹P, and ¹¹⁹Sn, respectively.

(Me₃SiN=PⁱPr₂CH₂)₂-2,3-C₄H₂N₂ (1**).** To a mixture of 2,3-dimethylpyrazine (7.0 mL, 66.15 mmol), TMEDA (20.7 mL, 136.8 mmol), and Et₂O (60 mL) was added dropwise ^tBuLi (85.5 mL, 1.6 M in hexane, 136.8 mmol) at 0 °C. The mixture was stirred at room temperature for 5 h and was then added slowly to a cooled (–78 °C) solution of ⁱPr₂PtCl (22.0 mL, 136.8 mmol) in Et₂O (60 mL). The mixture was stirred at –78 °C for 30 min and at room temperature for 15 h. After filtration, the yellow filtrate was concentrated and cooled at –30 °C, and the compound (PⁱPr₂CH₂)₂-C₄H₂N₂-2,3 was washed with hexane to give colorless crystals. Then the compound (PⁱPr₂CH₂)₂-2,3-C₄H₂N₂ (18.4 g, 54.13 mmol) was added with Me₃SiN₃ (14.5 mL, 110.26 mmol) in toluene (50 mL) followed by refluxing at 120 °C for 8 h. Solvent and excess Me₃SiN₃

were then removed *in vacuo*, and the residue was recrystallized from Et₂O to give colorless crystals. Yield: 19.3 g (57%). Mp: 78.3–80.5 °C. Anal. Calcd (%) for C₂₄H₅₂N₄P₂Si₂: C 55.99, H 10.18, N 10.88. Found: C 55.39, H 10.19, N 10.83. ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.28 (s, 18H, SiMe₃), 1.00–1.19 (m, 24H, CHMe₂), 1.74–1.86 (m, 4H, CHMe₂), 4.06 (d, *J*_{P–H} = 11.7 Hz, 4H, CH₂), 7.98 (s, 2H, C₄H₂N₂). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ (ppm) 4.61 (SiMe₃), 16.36 (d, *J* = 42.3 Hz, CHMe₂), 27.68 (d, *J* = 36.3 Hz, CHMe₂), 33.67 (d, *J* = 82.3 Hz, CH₂), 141.56 (C₄H₂N₂), 153.88 (d, *J* = 12.6 Hz, C₄H₂N₂). ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ (ppm) 41.24.

[(Me₃Si)₂NSn(Me₃SiN=PⁱPr₂CH)₂-2,3-C₄H₂N₂] (2**).** To a solution of Sn[N(SiMe₃)₂]₂ (0.76 g, 1.74 mmol) in toluene (10 mL) was added a solution of **1** (0.44 g, 0.85 mmol) in toluene (10 mL) at room temperature with stirring. The mixture was stirred for 3 days. Volatiles were removed *in vacuo*, and the residue was dissolved in Et₂O. After filtration and concentration of the filtrate, **2** was obtained as bright orange crystals. Yield: 0.46 g (51%). Mp: 169.2–172.4 °C. Anal. Calcd (%) for C₃₆H₈₆N₆P₂Si₆Sn₂: C 40.37, H 8.09, N 7.85. Found: C 40.07, H 8.13, N 7.80. ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.40 (s, 18H, SiMe₃), 0.49 (s, 36H, SiMe₃), 0.98–1.05 (m, 24H, CHMe₂), 1.69–1.72 (m, 4H, CHMe₂), 3.45 (d, *J*_{P–H} = 15.0 Hz, 2H, CH), 6.93 (s, 2H, C₄H₂N₂). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ (ppm) 5.24, 6.84 (SiMe₃), 17.56 (d, *J* = 41.7 Hz, CHMe₂), 27.96 (d, *J* = 67.8 Hz, CHMe₂), 51.64 (d, *J* = 117.5 Hz, CH), 116.75, 154.53 (C₄H₂N₂). ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ (ppm) 61.85. ¹¹⁹Sn{¹H} NMR (149.1 MHz, C₆D₆): δ (ppm) –124.94.

{[N(SiMe₃)₂]Pb(Me₃SiN=PⁱPr₂CH)-2,3-C₄H₂N₂-(Pb(CHⁱPr₂-P=NSiMe₃)[N(SiMe₃)₂])} (3**).** To a solution of Pb[N(SiMe₃)₂]₂ (0.68 g, 1.29 mmol) in toluene (10 mL) was added a solution of **1** (0.33 g, 0.65 mmol) in toluene (10 mL) at room temperature with stirring. The mixture was stirred for 3 days. Volatiles were removed *in vacuo*, and the residue was dissolved in Et₂O. After filtration and concentration of the filtrate, **3** was obtained as orange crystals. Yield: 0.32 g (40%). Mp: 125.7–128.9 °C. Anal. Calcd (%) for C₃₆H₈₆N₆P₂Pb₂Si₆: C 34.65, H 6.95, N 6.73. Found: C 34.57, H 6.85, N 6.63. ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.20 (s, 9H, SiMe₃), 0.26 (s, 18H, SiMe₃), 0.33 (s, 9H, SiMe₃), 0.39 (s, 18H, SiMe₃), 0.62–0.69 (m, 12H, CHMe₂), 0.93–0.98 (m, 12H, CHMe₂), 1.54–1.72 (m, 2H, CHMe₂), 1.76–1.94 (m, 2H, CHMe₂), 2.80 (d, *J*_{P–H} = 9.0 Hz, 1H, CH), 3.02 (d, *J*_{P–H} = 9.0 Hz, 1H, CH), 7.82 (s, 1H, C₄H₂N₂), 7.88 (s, 1H, C₄H₂N₂). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ (ppm) 4.38, 4.72, 5.55, 6.63 (SiMe₃), 14.66 (d, *J* = 21.9 Hz, CHMe₂), 16.03 (d, *J* = 25.3 Hz, CHMe₂), 27.14 (d, *J* = 61.4 Hz, CHMe₂), 29.60 (d, *J* = 57.5 Hz, CHMe₂), 52.74 (d, *J* = 108.4 Hz, CH), 61.28 (d, *J* = 91.2 Hz, CH), 123.00, 138.44, 141.04, 159.68 (C₄H₂N₂). ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ (ppm) 54.63, 58.72.

{[(THF)₂Li(Me₃SiN=PⁱPr₂CH)₂-2,3-C₄H₂N₂] (4**).** To a solution of **1** (0.46 g, 0.88 mmol) in THF (30 mL) was added dropwise BuⁿLi (1.10 mL, 1.6 M in hexane, 1.76 mmol) with stirring at –78 °C. The mixture was allowed to warm to room temperature and stirred for 18 h. Filtration followed by concentration of the filtrate and cooling at 0 °C yielded **4** as yellow crystals. Yield: 0.57 g (80%). Mp: 108.2–112.6 °C. Anal. Calcd (%) for C₃₆H₇₄Li₂N₄O₃P₂Si₂ (**4**-THF): C 58.43, H 9.67, N 7.57. Found: C 57.96, H 10.17, N 6.94. ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.45 (s, 18H, SiMe₃), 1.32–1.36 (m, 24H, CHMe₂), 1.42–1.46 (m, 8H, THF), 1.98–2.14 (m, 4H, CHMe₂), 3.08 (d, *J*_{P–H} = 18.6 Hz, 2H, CH), 3.52–3.57 (m, 8H, THF), 6.68 (s, 2H, C₄H₂N₂). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ (ppm) 5.05 (SiMe₃), 17.00 (d, *J* = 57.1 Hz, CHMe₂), 25.50 (THF), 28.45 (d, *J* = 64.1 Hz, CHMe₂), 46.46 (d, *J* = 126.2 Hz, CH), 68.13 (THF), 121.36 (C₄H₂N₂), 158.95 (d, *J* = 12.8 Hz, C₄H₂N₂). ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ (ppm) 51.36.

[Sn(CHⁱPr₂P=NSiMe₃)₂-2,3-C₄H₂N₂] (5**).** To a solution of **4** (0.82 g, 1.01 mmol) in Et₂O (20 mL) at 0 °C was added dropwise

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a solution of SnCl_2 (0.21 g, 1.10 mmol) in Et_2O (20 mL) with stirring. The reaction mixture was raised to ambient temperature and stirred for 18 h. The mixture was filtered, the filtrate was concentrated to about 3 mL, and then hexane (about 0.5 mL) was added to give yellow crystals of **5**. Yield: 0.31 g (49%). Mp: 136.5–138.8 °C. Anal. Calcd (%) for $\text{C}_{24}\text{H}_{50}\text{N}_4\text{P}_2\text{Si}_2\text{Sn}$: C 45.65, H 7.98, N 8.87. Found: C 45.22, H 8.27, N 8.85. ^1H NMR (300 MHz, C_6D_6): δ (ppm) 0.38 (s, 18H, SiMe_3), 0.56–0.64 (dd, $J = 7.2, 15.0$ Hz, 6H, CHMe_2), 0.72–0.80 (dd, $J = 7.2, 15.5$ Hz, 6H, CHMe_2), 1.11–1.19 (dd, $J = 7.2, 15.0$ Hz, 6H, CHMe_2), 1.36–1.44 (dd, $J = 7.2, 15.3$ Hz, 6H, CHMe_2), 1.61–1.68 (m, 2H, CHMe_2), 1.92–1.96 (m, 2H, CHMe_2), 3.45 (AB quartet, $J_{\text{P-H}} = 17.4$ Hz, 2H, CHP), 3.48 (AB quartet, $J_{\text{P-H}} = 17.4$ Hz, 2H, $\text{CH}'\text{P}$), 8.04 (s, 2H, $\text{C}_4\text{H}_2\text{N}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): δ (ppm) 4.76 (SiMe_3), 17.48 (d, $J = 20.9$ Hz, CHMe_2), 28.33 (m, CHMe_2), 40.79 (d, $J = 62.4$ Hz, CH), 139.56 ($\text{C}_4\text{H}_2\text{N}_2$), 159.43 (d, $J = 7.4$ Hz, $\text{C}_4\text{H}_2\text{N}_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): δ (ppm) 56.12. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.1 MHz, C_6D_6): δ (ppm) –17.45.

[[ClSn(Me₃SiN=PⁱPr₂CH)]₂-2,3-C₄H₂N₂] (6). To a solution of **4** (1.14 g, 1.40 mmol) in Et_2O (20 mL) at 0 °C was added dropwise a solution of SnCl_2 (0.54 g, 2.87 mmol) in Et_2O (20 mL) with stirring. The reaction mixture was raised to ambient temperature and stirred for 18 h. The mixture was filtered, and the filtrate was added with THF (ca. 2 mL). The resulting red solution was concentrated to afford **6** as orange crystals. Yield: 0.65 g (57%). Mp: 177.8–181.4 °C. Anal. Calcd (%) for $\text{C}_{24}\text{H}_{50}\text{Cl}_2\text{N}_4\text{P}_2\text{Si}_2\text{Sn}_2$: C 35.11, H 6.14, N 6.82. Found: C 34.59, H 6.13, N 6.69. ^1H NMR (300 MHz, $\text{THF}-d_8$): δ (ppm) 0.36 (s, 18H, SiMe_3), 1.04–1.18 (m, 24H, CHMe_2), 2.21–2.31 (m, 4H, CHMe_2), 3.63 (d, $J_{\text{P-H}} = 15.0$ Hz, 2H, CH), 6.93 (s, 2H, $\text{C}_4\text{H}_2\text{N}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, $\text{THF}-d_8$): δ (ppm) 2.34 (SiMe_3), 15.36 (d, $J = 15.8$ Hz, CHMe_2), 27.54 (d, $J = 61.4$ Hz, CHMe_2), 48.85 (d, $J = 102.8$ Hz, CH), 117.21 ($\text{C}_4\text{H}_2\text{N}_2$), 155.07 (d, $J = 10.6$ Hz, $\text{C}_4\text{H}_2\text{N}_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $\text{THF}-d_8$): δ (ppm) 60.94. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.1 MHz, $\text{THF}-d_8$): δ (ppm) –314.32.

[[(η^1 -C₅H₅)Sn(Me₃SiN=PⁱPr₂CH)]₂-2,3-C₄H₂N₂] (7). To a solution of **6** (0.82 g, 1.00 mmol) in THF (40 mL) at 0 °C was added dropwise a solution of NaCp (1.10 mL, 2.20 mmol, 2 M in THF) with stirring. The reaction mixture was raised to ambient temperature and stirred for 18 h. Volatiles were removed *in vacuo*,

and the residue was dissolved in Et_2O . The mixture was filtered and the filtrate was added with THF (ca. 2 mL). The resulting orange solution was concentrated to afford **7** as orange crystals. Yield: 0.39 g (44%). Mp: 134.7–136.3 °C. Anal. Calcd (%) for $\text{C}_{34}\text{H}_{60}\text{N}_4\text{P}_2\text{Si}_2\text{Sn}_2$: C 46.38, H 6.87, N 6.36. Found: C 45.91, H 7.01, N 6.50. ^1H NMR (300 MHz, $\text{THF}-d_8$): δ (ppm) 0.39 (s, 18H, SiMe_3), 0.80–1.18 (m, 24H, CHMe_2), 1.93–1.97 (m, 4H, CHMe_2), 3.46 (d, $J_{\text{P-H}} = 15.0$ Hz, 2H, CH), 6.32 (s, 5H, C_5H_5), 6.69 (s, 2H, $\text{C}_4\text{H}_2\text{N}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, $\text{THF}-d_8$): δ (ppm) 4.39 (SiMe_3), 16.96 (d, $J = 14.3$ Hz, CHMe_2), 28.33 (d, $J = 60.7$ Hz, CHMe_2), 40.79 (d, $J = 104.8$ Hz, CH), 111.54 (C_5H_5), 139.56 ($\text{C}_4\text{H}_2\text{N}_2$), 159.44 (d, $J = 12.2$ Hz, $\text{C}_4\text{H}_2\text{N}_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $\text{THF}-d_8$): δ (ppm) 61.12. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.1 MHz, $\text{THF}-d_8$): δ (ppm) –17.47.

X-ray Crystallographic Study. Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of **2–7** were collected at 293(2) K on a Rigaku R-Axis II imaging plate using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data for **2–7** are summarized in Tables 4 and 5. The structures were solved by direct phase determination using SHELXTL-PC¹⁰ on a PC 486 and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factor calculations.

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Supporting Information Available: Details about the X-ray crystal structures, including ORTEP diagrams and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **2–7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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