Metal 1,3-Benzobis(thiophosphinoyl)methanediide Complexes and a Base-Stabilized 2-Silaallene Derivative

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2013
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Abbreviations

Ad adamantyl
Ar aryl
Br broad
Bu butyl
calcd calculated
cod 1,5-cyclooctadiene
Cp cyclopentadienyl
Cp* pentamethylcyclopentadienyl
CPMAS cross polarization magic angle spinning
Cy cyclohexyl
d doublet
DCM dichloromethane
dd a doublet of doublets
dec. decomposed
deg degree(s)
DMP 2,6-dimesitylphenyl

et al. and others (Latin alii)

etc. and the rest (Latin et cetera)

Et ethyl
g gram(s)
h hour(s)
<table>
<thead>
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<tr>
<td>$i$</td>
<td>iso</td>
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<tr>
<td>IMes</td>
<td>N,N’-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene</td>
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<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>Mes</td>
<td>2,4,6-Me$_3$C$_6$H$_2$</td>
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<td>Mes*</td>
<td>2,4,6-tri-tert-butylphenyl</td>
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<tr>
<td>m.p.</td>
<td>melting point</td>
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<td>NMR</td>
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<tr>
<td>Pr</td>
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</tr>
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<td>quartet</td>
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<tr>
<td>Tbt</td>
<td>2,4,6-{$\text{CH(SiMe}_3\text{)}_2$)$_3$C$_6$H$_2$}</td>
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<td>TEMPO</td>
<td>(2,2,6,6-tetramethylpiperidin-1-yl)oxide</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMAO</td>
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</tr>
<tr>
<td>TIP</td>
<td>2,4,6-tri-isopropylphenyl</td>
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<tr>
<td>TMEDA</td>
<td>tetramethylethlenediamine</td>
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Å  angstrom(s)
## List of Synthesized Compounds

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Abstract

This thesis mainly describes the synthesis of metal bis(thiophosphinoyl) and 1,3-benzobis(thiophosphinoyl)methanediide complexes.

Chapter 1 describes the synthesis of the 1,3-benzobis(thiophosphinoyl)methane \([1,3-\text{C}_6\text{H}_4(\text{PhP=S})_2\text{CH}_2]\) (19) from the bis(thiophosphinoyl)methane reported. The corresponding lithium and potassium methanide complexes have also been presented.

Chapter 2 describes the synthesis of metal 1,3-benzobis(thiophosphinoyl)methanediide complexes. The magnesium (118), aluminum (119), tin(II) (120) and lead(II) (121) 1,3-benzobis(thiophosphinoyl)methanediide complexes, which have a 1,3-dimetallacyclobutane structure, were synthesized by the double deprotonation reaction of 19 with metal alkyl or metal amides, respectively.
The reactivity of compound 120, which has a 1,3-dimetallacyclobutane structure, is investigated. Compound 120 undergoes an insertion reaction with AlCl₃ to form 122 and 123, or with GaCl₃ to form 125 and 126 as cocrystal. Compound 120 also undergoes a transmetalation reaction with AlMe₃ to give compound 124.

The reaction of compound 120 with ZnEt₂ and the reaction of zinc complex 130
with Sn amide give two Zn/Sn sulfide heterobimetallic complexes 129 and 131, respectively.

Chapter 3 describes the synthesis of a base-stabilized 2-silaallene derivative 149 and its reactivity toward unsaturated substrates.
Chapter 1 Synthesis of 1,3-Benzobis(thiophosphinoyl)methane Ligand and Group 1 Metal Methanide Complexes

1.1 Introduction

Bis(phosphinoyl)methane \([\text{CH}_2(\text{Ph}_2\text{P}=\text{E})_2]\) \((\text{E} = \text{NR}, \text{S}; \text{R} = \text{supporting substituent})\) has been studied extensively in the past decades due to its ability to stabilize metal complexes with a variety of oxidation states and coordination geometries.\(^1\)

The bis(phosphinoyl)methane \([\text{CH}_2(\text{Ph}_2\text{P}=\text{E})_2]\) can be synthesized easily. The bis(iminophosphinoyl)methane \([\text{CH}_2(\text{Ph}_2\text{P}=\text{NR})_2]\) \((\text{E} = \text{NR}, \text{R} = \text{supporting substituent})\) can be obtained by the reaction of the bis(diphenylphosphino)methane \(1\) and corresponding azides.\(^2\) The bis(thiophosphinoyl)methane \([\text{CH}_2(\text{Ph}_2\text{P}=\text{S})_2]\) \((3)\) can be synthesized by the reaction of bis(diphenylphosphino)methane \(1\) and sulfur in refluxing toluene (Scheme 1.1).\(^3\)

\[
\begin{align*}
\text{Ph} & \quad \text{P} & \quad \text{P} \\
\text{Ph} & \quad \text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} \\
\text{Ph} & \quad \text{P} & \quad \text{P} & \quad \text{P} & \quad \text{P} \\
\text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} \\
\end{align*}
\]

\(1\)

\[
\begin{align*}
\text{Ph} & \quad \text{P} & \quad \text{P} & \quad \text{S} & \quad \text{S} \\
\text{Ph} & \quad \text{P} & \quad \text{P} & \quad \text{S} & \quad \text{S} \\
\text{Ph} & \quad \text{P} & \quad \text{P} & \quad \text{S} & \quad \text{S} \\
\text{Ph} & \quad \text{P} & \quad \text{P} & \quad \text{S} & \quad \text{S} \\
\end{align*}
\]

\(3\)

\text{Scheme 1.1}

In general, the monoanionic bis(phosphinoyl)methanides \([\text{CH}(\text{Ph}_2\text{P}=\text{E})_2]^-\) and the dianionic bis(phosphinoyl)methanediides \([\text{C}(\text{Ph}_2\text{P}=\text{E})_2]^2^-\) can be obtained by the reaction of the bis(phosphinoyl)methane \([\text{CH}_2(\text{Ph}_2\text{P}=\text{E})_2]\) with metal alkyls and amides.
Both the monoanionic and dianionic compounds tend to show different coordination modes. The crystal structures of metal bis(phosphinoyl)methanide complexes \([\text{CH}(\text{Ph}_2\text{P}={\text{E}})_2]\) show that the two sulfur or nitrogen atoms chelate the metal center to form a six-membered ring \((\text{E}-\text{P}-\text{C}-\text{P}-\text{E}-\text{M})\) which adopts a pseudo-boat conformation. The carbon center coordinates to the metal atom via a long interaction (Scheme 1.2).

![Scheme 1.2](image)

\(\text{E} = \text{NSiMe}_3\) or \(\text{S}\)

In contrast, the dianionic bis(phosphinoyl)methanediide complexes \([\text{C}(\text{Ph}_2\text{P}={\text{E}})_2]\)^2 have the “pincer” type A, C, D, E and the bridged type B bonding modes (Scheme 1.3).

![Scheme 1.3](image)

Stephan’s and Cavell’s groups reported the lithiation of bis(iminophosphinoyl)methane \([\text{CH}_2(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]\) (2a) (Scheme 1.4) in which the lithium methanide compound \([\text{Li(THF)}\{\text{CH}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2}\}\) (4) was obtained by the reaction of 2a with one equivalent of \(^{n}\text{BuLi}\) in THF.\(^5\) The lithium methanediide
complex \([\text{Li}_2\text{C(Ph}_2\text{P}=\text{NSiMe}_3)_2]\) (5) was synthesized by the treatment of 2a with two equivalents of MeLi or PhLi in benzene or toluene.\(^6\)

![Scheme 1.4](image)

The lithiation of bis(thiophosphinoyl)methane \([\text{CH}_2\text{(Ph}_2\text{P}=\text{S})_2]\) (3) were reported by the research groups of Leung and Le Floch (Scheme 1.5). The reaction of 3 with one equivalent of \(^n\text{BuLi}\) in THF, followed by crystallization in \(\text{Et}_2\text{O}\) gave the lithium methanide \([\text{Li}((\text{S}=\text{PPh}_2)\text{CH})(\text{THF})(\text{Et}_2\text{O})]\) (6).\(^7\) The reaction of 3 with two equivalents of MeLi in \(\text{Et}_2\text{O}\) gave the lithium methanediide \([\text{Li}_2\text{C(Ph}_2\text{P}=\text{S})_2]\) (7).\(^8\)

![Scheme 1.5](image)

Metal alkyls, amides or hydrides can also be used to prepare group 1 bis(iminophosphinoyl)methanide compounds. Moreover, the reaction of 2a with 2 equivalents of \(^n\text{BuNa}\) gave \([\text{Na}_2\{\text{C(Ph}_2\text{P}=\text{NSiMe}_3)_2}\}\] (8).\(^8-9\) Furthermore, 2a reacted with one equivalent of \([\text{M}\{\text{N(SiMe}_3)_2\}\] (\(\text{M} = \text{Li, Na}\)) in toluene gave bis(aminophosphinoyl)methanide complexes \([\text{M}\{\text{CH(Ph}_2\text{P}=\text{NSiMe}_3)_2}\}\] (\(\text{M} = \text{Li}\) (9),

---

**Scheme 1.4**

The lithiation of bis(thiophosphinoyl)methane \([\text{CH}_2\text{(Ph}_2\text{P}=\text{S})_2]\) (3) were reported by the research groups of Leung and Le Floch (Scheme 1.5). The reaction of 3 with one equivalent of \(^n\text{BuLi}\) in THF, followed by crystallization in \(\text{Et}_2\text{O}\) gave the lithium methanide \([\text{Li}((\text{S}=\text{PPh}_2)\text{CH})(\text{THF})(\text{Et}_2\text{O})]\) (6).\(^7\) The reaction of 3 with two equivalents of MeLi in \(\text{Et}_2\text{O}\) gave the lithium methanediide \([\text{Li}_2\text{C(Ph}_2\text{P}=\text{S})_2]\) (7).\(^8\)

**Scheme 1.5**

Metal alkyls, amides or hydrides can also be used to prepare group 1 bis(aminophosphinoyl)methanide compounds. Moreover, the reaction of 2a with 2 equivalents of \(^n\text{BuNa}\) gave \([\text{Na}_2\{\text{C(Ph}_2\text{P}=\text{NSiMe}_3)_2}\}\] (8).\(^8-9\) Furthermore, 2a reacted with one equivalent of \([\text{M}\{\text{N(SiMe}_3)_2\}\] (\(\text{M} = \text{Li, Na}\)) in toluene gave bis(aminophosphinoyl)methanide complexes \([\text{M}\{\text{CH(Ph}_2\text{P}=\text{NSiMe}_3)_2}\]\) (\(\text{M} = \text{Li}\) (9),
Na (10). 2a reacted with one equivalent of MH (M = Na, K) in THF afforded [M(THF)₂{CH(Ph₂P=NSiMe₃)_2}] (M = Na (11), K (12)) (Scheme 1.6).

The K (13) and Rb (14) complexes of bis(iminophosphinoyl)methanediide were also reported by Harder’s group. In case of Cs, a cyclic bis(phosphinoyl)methanediide 15 was obtained. The mechanism was proposed. The first step of the reaction mechanism is the displacement reaction of Li⁺ by Cs⁺ to give intermediate F. Orthometalation on one of the Ph₂P groups followed by nucleophilic attack at another phosphonium unit results in ring closure. Elimination of PhCs followed by the deprotonation of the methanide carbon gives 15 (Scheme 1.7).
These results prompted our interest to isolate a 1,3-benzobis(thiophosphinoyl)methane ligand as an iminophosphorane is isovalent with a thiophosphorane. We also want to discover whether the corresponding methanide and methanediide complexes can be isolated (Scheme 1.8).

1.2 Results and Discussion

1.2.1 Synthesis of a Lithium Bis(thiophosphinoyl)methanide Complex

Treatment of [CH\(_2\)(Ph\(_2\)P=S)\(_2\)] (3) with \(^n\)BuLi in THF at –78 °C afforded the lithium bis(thiophosphinoyl)methanide [Li\{(S=PPh\(_2\))\(_2\)CH\}(THF)\(_2\)] (16) (68%, Scheme 1.9). Similar compound [Li\{(S=PPh\(_2\))\(_2\)CH\}(THF)(Et\(_2\)O)] (6) has been reported recently,\(^7\) in which, the lithium atom is coordinated to two different solvent molecules.
Compound 16 was isolated in THF/hexane as an extremely air- and moisture-sensitive pale yellow crystalline solid in 68% yield, which is soluble in THF only. It has been analyzed by NMR spectroscopy and X-ray crystallography. The $^1$H NMR spectrum displays a triplet at $\delta$ 2.02 ppm ($^2$J$_{P\cdot H}$ = 2.74 Hz) for the methine proton. The $^{31}$P$^\text{1H}$ NMR spectrum displays a singlet at $\delta$ 38.73 ppm for the equivalent P nuclei. The $^{13}$C$^\text{1H}$ NMR spectrum shows a triplet for the methanide carbon at $\delta$ 20.14 ppm ($J_{P\cdot C}$ = 108.8 Hz). All data is comparable to that of [Li{(S=PPh$_2$)CH}(THF)(Et$_2$O)] (6).$^7$

Figure 1.1 Molecular structure of 16 with thermal ellipsoids at the 50% probability level. One of two independent molecules in the asymmetric unit is shown. Disordered 16 atoms and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Li(1)-S(1) 2.470(6), Li(1)-S(2) 2.458(6), Li(1)-O(1) 1.945(6), Li(1)-O(2) 1.941(6), P(1)-S(1) 2.0010(11), P(2)-S(2) 1.9945(12), C(1)-P(1) 1.715(3), C(1)-P(2) 1.706(3), C(1)-Li(1) 3.943(6), S(1)-Li(1)-S(2) 106.4(2), Li(1)-S(1)-P(1) 107.08(15), S(1)-P(1)-C(1) 117.39(11), P(2)-C(1)-P(1) 126.91(19), C(1)-P(2)-S(2) 118.34(11), P(2)-S(2)-Li(1) 102.52(15).

The molecular structure of 16 (Figure 1.1) is similar to that of [Li{(S=PPh$_2$)CH}(THF)(Et$_2$O)] (6).$^7$ The Li(1) is bound to two oxygen atoms of two
THF molecules and displays tetrahedral geometry. In contrast, the Li atom in compound 6 is bound to one THF molecule and Et₂O molecules. The Li(1)-S(1) bond lengths (2.470(6) and 2.458(6) Å) are comparable to those of [Li{(S=PPPh₂)₂N}(THF)] (2.478 and 2.473 Å). The C(1)-Li(1) distance (3.943(6) Å) is comparable with that of [Li{(S=PPPh₂)₂CH}(THF)(Et₂O)] (3.920(13) Å). The P-S bonds (2.0010(11), 1.9945(12) Å) are lengthened and the C-P bonds (1.715(3), 1.706(3) Å) are shortened compared with those in [CH₂(Ph₂P=S)₂] (3) (P-S, average 1.945 Å; P-C, average 1.829 Å).

1.2.2 Synthesis of a Potassium Bis(thiophosphinoyl)methanide Complex

The reaction of [CH₂(Ph₂P=S)₂] (3) with 1 equivalent of nBuLi in THF, followed by the reaction with 1 equivalent of tBuOK in THF gave [K{(S=PPPh₂)₂CH}] (17) (73%). Moreover, treatment of [CH₂(Ph₂P=S)₂] (3) with tBuOK in refluxing THF afforded compound 17, which has been confirmed by NMR spectroscopy (66%, Scheme 1.10).

Compound 17 has been synthesized in situ to further prepare vinylidene phosphine sulfide. However, its isolation and characterization were not reported. Compound 17 was isolated as a highly air- and moisture-sensitive pale yellow...
crystalline solid which is soluble in Et₂O and THF. The ¹H NMR spectrum of 17 shows a triplet at δ 1.48 ppm (²Jₚ-H = 2.32 Hz) for the proton on the C₅methanide atom. The ¹³C{¹H} NMR spectrum shows a triplet at δ 20.12 ppm (Jₚ-C = 107.3 Hz) for the C₅methanide atom. The ³¹P{¹H} NMR spectrum displays a singlet at δ 38.03 ppm for the equivalent P nuclei.

Figure 1.2 Molecular structure of 17: (a) perspective view of the molecule with thermal ellipsoids at the 50% probability level; (b) its polymeric form (15% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): K(1)-S(1) 3.187(3), K(1)-S(2) 3.234(3), K(1)-S(1C) 3.137(3), K(1)-S(2B) 3.117(2), C(1)-P(1) 1.696(7), C(1)-P(2) 1.718(7), P(1)-S(1) 1.997(2), P(2)-S(2) 1.982(2), K(1)-C(15) 3.453(8), K(1)-C(16) 3.336(8), K(1)-C(17) 3.432(8), C(1)···K(1) 4.807(8), S(1)-K(1)-S(2) 81.34(6), K(1)-S(1)-P(1) 103.65(9), S(1)-P(1)-C(1) 119.7(2), P(2)-C(1)-P(1) 124.8(4), C(1)-P(2)-S(2) 116.6(2).

The molecular structure of 17 is shown in Figure 1.2. Compound 17 has a polymeric structure by the electrostatic interaction of the K(1) atoms with the thiophosphinooyl substituents of the adjacent molecules. The coordination sphere on the K(1) atoms is further supplemented by an η³ interaction with the phenyl substituents (K(1)···C(15) = 3.453(8) Å, K(1)···C(16) = 3.336(8) Å, K(1)···C(17) = 3.432(8) Å). In the monomeric form, the K(1) atom is coordinated with the S(1) and S(2) atoms of the thiophosphinooyl substituents to form a twisted six-membered
metallacycle. The C(1)···K(1) distance (4.807(7) Å) is significantly longer than that in [K(THF)$_2$(CH$_2$P=NSiMe$_3$)$_2$] (12) (4.145(2) Å),$^{11a}$ which indicates that there is no contact between the C(1) and K(1) atoms. The K(1)-S(1) (3.187(3) Å) and K(1)-S(2) bonds (3.234(3) Å) are comparable with those in the potassium bis(thiophosphinoyl)amide [KN(PPh$_2$=S)$_2$] (3.203(1), 3.279(1) Å).$^{16}$ The P-S bonds (1.982(2), 1.997(2) Å) are lengthened and the C-P bonds (1.696(7), 1.718(7) Å) are shortened compared with those in [CH$_2$(Ph$_2$P=S)$_2$] (3) (P-S, average 1.945 Å; P-C, average 1.829 Å).$^{14}$

1.2.3 Synthesis of a Potassium 1,3-Benzobis(thiophosphinoyl)methanide Complex

The reaction of [CH$_2$(Ph$_2$P=S)$_2$] (3) with 1 equivalent of tBuOK and 1.2 equivalents of $^9$BuLi in refluxing THF afforded the potassium 1,3-benzobis(thiophosphinoyl)methanide [1,3-C$_6$H$_4$(PhP=S)$_2$CHK·3THF] (18) (47%). Furthermore, treatment of 17 with PhLi or $^9$BuLi in refluxing THF afforded compound 18, which has been confirmed by NMR spectroscopy (27%, Scheme 1.11). In contrast, there is no reaction between 17 and tBuOLi. According to these results, the reaction of 3 with tBuOK/$^9$BuLi in refluxing THF probably proceeds via the formation of 17. Consequently, the ortho position of the phenyl ring is lithiated by $^9$BuLi, followed by an intramolecular displacement of a PhLi molecule to form 18 (Scheme 1.12). The PhLi molecule then is involved in the lithiation of the ortho position of the phenyl ring. As a result, a slight excess of $^9$BuLi (1.2 equivalents) is enough to initiate the ortho metalation of the phenyl ring. Similar ortho metalation of
the PPh2 moiety of the bis(iminophosphinoyl)methanediide and (iminophosphinoyl)(trimethylsilyl)methanide ligands has been reported.12,17

![Scheme 1.11](image1.png)

**Scheme 1.11**

Compound 18 was isolated as a highly air- and moisture-sensitive orange crystalline solid which is soluble only in THF. It is stable in the solid state at room temperature under an inert atmosphere. The 1H NMR spectrum of 18 shows a triplet at δ 1.35 ppm (2J_P-H = 11.2 Hz) for the proton on the C_methanide atom. The 13C{1H} NMR spectrum shows a triplet at δ 26.0 ppm (J_P-C = 101.1 Hz) for the C_methanide atom. The 31P{1H} NMR spectrum displays a singlet at δ 44.12 ppm for the equivalent P nuclei.
The molecular structure of 18 is shown in Figure 1.3. It shows that the K(1) atom is coordinated with the C(1), S(1), and S(2) atoms of the ligand to form a couchlike conformation. The dihedral angle between the C(8)C(13)P(2)C(1)P(1) and P(1)S(1)S(2)P(2) least-squares planes is 80.41°. The K(1)S(1)P(1)C(1)P(2)S(2) metallacycle adopts a pseudo-boat conformation in which the C(1) and K(1) atoms are displaced from the P(1)S(1)S(2)P(2) least-squares plane by 0.897 and 0.637 Å, respectively. The coordination sphere on the K(1) atom is further supplemented by coordinating with three THF molecules. The K(1)-C(1) bond (3.196(6) Å) is comparable to that in [(PPh2=NSiMe3)(PPh2)CHK]n (3.166(7) Å),18 which suggests that there is a contact between the C(1) and K(1) atoms. The K(1)-S(1) (3.2667(18) Å) and K(1)-S(2) bonds (3.3622(19) Å) are comparable with those in 17.
1.2.4 Synthesis of the 1,3-Benzobis(thiophosphinoyl)methane

Compound 18 was then hydrolyzed by water in THF to form [1,3-C₆H₄(PhP=S)₂CH₂] (19) (84%, Scheme 1.13).

![Scheme 1.13](image)

Compound 19 was isolated as a pale yellow crystalline solid which is soluble in toluene and THF. Its molecular structure is shown in Figure 1.4. The P=S moieties are cis to each other. The result is in contrast to the X-ray crystal structure of [CH₂(Ph₂P=S)₂] (3), in which the P=S moieties are at opposite sides. The C–P bonds (1.8229(14), 1.8373(14) Å) are lengthened and the P−S bonds (1.9463(5), 1.9498(5) Å) are shortened compared with those in 18 (C−P = 1.698(5), 1.721(5) Å; PtS = 1.9846(19), 1.987(2) Å).

![Figure 1.4](image)

Figure 1.4 Molecular structure of 19 with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(1)-P(2) 1.8229(14), C(1)-P(1) 1.8373(14), P(1)-S(1) 1.9463(5), P(2)-S(2) 1.9498(5), P(1)-C(1)-P(2) 110.41(7).

The molecular structure of 19 is shown in Figure 1.4. Compound 19 also retains
its solid-state structure in solution. The $^1$H NMR spectrum displays a quartet at $\delta$ 3.26 ($^2J_{P-H} = 15.9$ Hz) and a multiplet at $\delta$ 3.61 ppm for two nonequivalent $-\text{PCH}_2\text{P}-$ protons. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows a triplet at $\delta$ 41.62 ppm ($J_{P-C} = 40.0$ Hz) for the $\text{C}_{\text{PCP}}$ atom. The $^{31}\text{P}\{^1\text{H}\}$ displays a singlet at $\delta$ 45.80 ppm for the P nuclei.

### 1.2.5 Synthesis of a Lithium 1,3-Benzobis(thiophosphinoyl)methanide Complex

The reaction of 19 with 1 equivalent of $n$BuLi in THF afforded $[1,3-\text{C}_6\text{H}_4(\text{PhP}=\text{S})_2\text{CHLi} \cdot 3\text{THF}]$ (20) (52%, Scheme 1.14).

![Scheme 1.14](image)

Compound 20 was isolated as a highly air- and moisture-sensitive yellow crystalline solid which is soluble only in THF. It is stable in the solid state at room temperature under an inert atmosphere. The $^1$H NMR spectrum of 20 shows a triplet at $\delta$ 3.46 ppm ($^2J_{P-H} = 11.9$ Hz) for the proton on the $\text{C}_{\text{methanide}}$ atom. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows a triplet at $\delta$ 41.62 ppm ($J_{P-C} = 70.9$ Hz) for the $\text{C}_{\text{methanide}}$ atom. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a singlet at $\delta$ 48.51 ppm.
The molecular structure of compound 20 shows that the Li(1) atom is only coordinated to the ligand via the S(1) atom. The P=S moieties of the ligand are trans to each other. The coordination sphere on the Li(1) atom is further supplemented by coordinating with three THF molecules. The Li(1)-S(1) bond (2.503(6) Å) is comparable with those in 16 (2.470(6) and 2.458(6) Å). Both the P-S bonds are lengthened and the P-C bonds are shortened compared with those in 19 (P-S = 1.9463(5), 1.9498(5) Å, P-C = 1.8229(14), 1.8373(14) Å).

1.3 Conclusion

In summary, the 1,3-benzobis(thiophosphinoyl)methane (19) have been synthesized from the bis(thiophosphinoyl)methane (3). The synthesis and characterization of the corresponding lithium and potassium methanide complexes have also been reported.
1.4 Experimental Section

All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. CH₂Cl₂ were dried over and distilled over CaH₂ prior to use. Other solvents were dried over and distilled over Na/K alloy prior to use. The ¹H, ¹³C and ³¹P NMR spectra were recorded on a JEOL ECA 400 spectrometer at 25 °C. The chemical shifts δ are relative to SiMe₄ for ¹H, ¹³C and 85% H₃PO₄ for ³¹P. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

[Li{(S=PPh₂)₂CH}](THF)₂] (16). nBuLi (0.52 mL, 1.05 mmol, 2 M solution in cyclohexane) was added slowly to the solution of 3 (0.45 g, 1.0 mmol) in THF (10 mL) at –78 °C. The yellow solution was warmed to ambient temperature and stirred overnight. After filtration, the filtrate was concentrated to give compound 16 as pale yellow crystal. Yield: 0.41 g (68%). MP: 178 °C (dec.). Anal. Found: C 65.32, H 6.71; Calcd for C₂₅H₂₁KP₂S₂: C, 66.21; H, 6.23. ¹H NMR (399.5 MHz, C₆D₆, 22 °C): δ 1.24 (m, 8H, THF), 2.02 (t, Jₚ−H = 2.74 Hz, 1H, PCH₃), 3.45 (m, 8H, THF), 7.00 – 7.10 (m, 12H, Ph), 8.27 – 8.32 ppm (m, 8H, Ph); ¹³C{¹H}NMR (100.5 MHz, C₆D₆, 22 °C): δ 20.14 (t, PCP, Jₚ,C = 108.8 Hz), 25.76 (s, THF), 68.63 (s, THF), 128.06 (d, ³Jₚ,C = 6.71 Hz, C_meta of Ph), 129.76 (s, C para of Ph), 132.28 (t, ²Jₚ,C = 5.27 Hz, Cortho of Ph), 142.30 (t, ¹Jₚ,C = 93.9 Hz, Cipso of Ph). ³¹P{¹H}NMR (161.7 MHz, C₆D₆, 22 °C): δ 38.73 ppm.

[K{(S=PPh₂)₂CH}] (17). Method A. nBuLi (1.8 mL, 3.6 mmol, 2 M solution in
cyclohexane) was added slowly to a solution of 3 (1.57 g, 3.5 mmol) in THF (20 mL) at −78 °C. The yellow solution was warmed to ambient temperature and stirred overnight. The resulting solution was then added dropwise to a solution of tBuOK (0.39 g, 3.5 mmol) in THF (5 mL) at −78 °C. The yellow solution was warmed to ambient temperature and stirred for 24 h. Volatiles were removed under reduced pressure. After washing with hexane, the residue was extracted by Et₂O/THF (1:1, 30 mL). The insoluble precipitate was filtered. The filtrate was concentrated to give compound 17 as pale yellow crystals. Yield: 1.24 g (73%).

**Method B.** THF (20 mL) was added to a mixture of 3 (1.57 g, 3.5 mmol) and tBuOK (0.39 g, 3.5 mmol) at ambient temperature. The yellow solution was refluxed at 70 °C overnight. After filtration, the filtrate was concentrated to give compound 17 as pale yellow crystal. Yield: 1.13 g (66%).

Mp: 305 °C. Anal. Calcd for C₂₅H₂₁KP₂S₂: C, 61.71; H, 4.35. Found: C, 61.51; H 4.35. ¹H NMR (399.5 MHz, THF-­d₈, 22 °C): δ 1.48 (t, 2J_P−H = 2.32 Hz, 1H, PCH₂P), 7.18−7.21 (m, 12H, Ph), 8.00−8.05 ppm (m, 8H, Ph). ¹³C{¹H} NMR (100.5 MHz, THF-d₈, 22 °C): δ 20.12 (t, PCP, J_P−C = 107.3 Hz), 126.73 (t, 3J_P−C = 5.75 Hz, C_mεta of Ph), 128.24 (s, C_parα of Ph), 131.47 (t, 2J_C−P = 5.76 Hz, C_orθho of Ph), 142.97 ppm (dd, J_P−C = 96.9 Hz, 3J_P−C = 2.87 Hz, C_ipso of Ph). ³¹P{¹H} NMR (161.7 MHz, THF-d₈, 22 °C): δ 38.03 ppm.

**[1,3-C₆H₄(PhP=S)₂CHK·3THF]** (18). **Method A.** nBuLi (1.8 mL, 3.6 mmol, 2 M solution in cyclohexane) was added slowly to a solution of 3 (1.34 g, 3.0 mmol) and tBuOK (0.34 g, 3.0 mmol) in THF (20 mL) at ambient temperature. The orange
solution was refluxed at 70 °C overnight to give a reddish brown solution. Volatiles were removed under vacuum, and Et₂O was added to the residue to afford a red solid after 16 h. The red solid was then recrystallized in THF to give compound 18 as orange crystals. Yield: 0.88 g (47%).

Method B. PhLi (0.5 mL, 1.0 mmol, 2 M solution in dibutyl ether) was added slowly to a solution of 17 (0.48 g, 1.0 mmol) in THF (10 mL) at ambient temperature. The orange solution was refluxed at 70 °C overnight to give a reddish brown solution. Volatiles were removed under vacuum, and the residue was extracted by Et₂O. After filtration, a red crystalline solid was obtained in the filtrate. The red solid was then recrystallized in THF to give compound 18 as orange crystals. Yield: 0.17 g (27%).

Mp: 274 °C (dec.). Anal. Calcd for C₃₁H₃₉KO₃P₂S₂: C, 59.59; H, 6.30. Found: C, 59.54; H, 6.31. ¹H NMR (399.5 MHz, THF-d₈, 22 °C): δ 1.35 (t, J_P−H = 11.2 Hz, 1H, PCHP), 7.22−7.33 (m, 8H, Ph and C₆H₄), 7.52−7.58 (m, 2H, Ph and C₆H₄), 8.00−8.06 ppm (m, 4H, Ph and C₆H₄). ¹³C{¹H} NMR (100.5 MHz, THF-d₈, 22 °C): δ 26.0 (t, J_P−C = 101.1 Hz, PCP), 127.76 (t, J_P−C = 6.71 Hz, C_meta of Ph), 128.90 (t, J_P−C = 11.5 Hz, C₆H₄), 129.68 (s, Cpara of Ph), 130.14 (t, J_P−C = 3.83 Hz, Cortho of Ph), 131.94 (t, J_P−C = 4.79 Hz, Cortho of Ph), 143.61 (t, J_P−C = 44.1 Hz, Cips of Ph/C₆H₄), 144.63 ppm (t, J_P−C = 52.7 Hz, Cips of Ph/C₆H₄). ³¹P{¹H} NMR (161.7 MHz, THF-d₈, 22 °C): δ 44.12 ppm.

[1,3-C₆H₄(PhP=S)₂CH₂] (19). Excess degassed H₂O was added to a solution of 18 (1.87 g, 3.0 mmol) in THF (20 mL) at room temperature. The resulting pale yellow suspension was stirred at room temperature for 1 h. Volatiles were removed under
reduced pressure. The residue was washed with 10 mL of toluene. The pale yellow residue was then extracted by CH$_2$Cl$_2$/hexane (1/1). After filtration and concentration of the filtrate, compound **19** was obtained as pale yellow crystals. Yield: 0.93 g (84%).

**Mp: 172 °C. Analy. Calcd for C$_{19}$H$_{16}$P$_2$S$_2$: C, 61.62; H, 4.36. Found: C, 61.29; H, 4.29.**

$^1$H NMR (395.9 MHz, CDCl$_3$, 22 °C): δ 3.26 (quartet, $^2$J$_{P-H} = 15.9$ Hz, 1H, PC$_2$H$_2$P), 3.61 (m, 1H, PC$_2$H$_2$P), 7.12–7.18 (m, 4H, Ph and C$_6$H$_4$), 7.27–7.32 (m, 6H, Ph and C$_6$H$_4$), 7.73–7.79 (m, 2H, Ph and C$_6$H$_4$), 7.91–7.99 ppm (m, 2H, Ph and C$_6$H$_4$).

$^{13}$C{$^1$H} NMR (100.5 MHz, THF-$_d_8$, 22 °C): δ 41.62 (t, $^3$J$_{P-C} = 40.0$ Hz, P$_2$C$_2$), 129.41 (d, $^3$J$_{P-C} = 6.71$ Hz, C$_{meta}$ of Ph), 131.49 (d, $^2$J$_{P-C} = 11.4$ Hz, C$_6$H$_4$), 131.70 (t, $^3$J$_{P-C} = 10.5$ Hz, C$_6$H$_4$), 132.43 (s, C$_{para}$ of Ph), 134.38 (d, $^2$J$_{P-C} = 11.4$ Hz, C$_{ortho}$ of Ph), 135.60 (d, $^3$J$_{P-C} = 52.7$ Hz, C$_6$H$_4$), 140.17 ppm (dd, $^3$J$_{P-C} = 86.8$ Hz, $^3$J$_{P-C} = 15.3$ Hz, C$_{ipso}$ of Ph).

$^{31}$P{$^1$H} NMR (160.2 MHz, CDCl$_3$, 22 °C): δ 45.80 ppm.

[1,3-C$_6$H$_4$(PhP=S)$_2$CHLi·3THF] (20). i$^n$BuLi (0.52 mL, 1.05 mmol, 2 M solution in cyclohexane) was added slowly to the solution of **19** (0.37 g, 1.0 mmol) in THF (10 mL) at −78 °C. The yellow solution was warmed to ambient temperature and stirred overnight. After filtration, the filtrate was concentrated to give compound **20** as pale yellow crystal. Yield: 0.31 g (52%). MP: 213 °C (dec.). Anal. Found: C 62.34, H 6.87; Calcd for C$_{31}$H$_{39}$LiO$_3$P$_2$S$_2$: C, 62.82; H, 6.63. $^1$H NMR (399.5 MHz, THF-$d_8$, 23 °C): δ 1.77 (m, THF), 3.46 (t, $^3$J$_{P-H} = 11.89$ Hz, 1H, PCHP), 3.62 (m, THF), 7.48 – 7.56 (m, 6H, Ph and C$_6$H$_4$), 7.65 – 7.68 ppm (m, 4H, Ph and C$_6$H$_4$), 7.97 – 8.03 ppm (m, 4H, Ph and C$_6$H$_4$); $^{13}$C{$^1$H}NMR (100.5 MHz, THF-$d_8$, 23 °C): 41.35 (t, $^3$J$_{P-C} = 70.9$ Hz, PCP), 129.26 (t, $^3$J$_{P-C} = 13.42$ Hz, C$_{meta}$ of Ph), 130.04 (t, $^3$J$_{P-C} = 11.5$ Hz, C$_6$H$_4$),
132.06 (d, $^2J_{P-C} = 11.5$ Hz, $C_{ortho}$ of Ph), 132.60 (s, $C_{para}$ of Ph), 143.61 (dd, $J_{P-C} = 12.0$ Hz, $^3J_{P-C} = 3.8$ Hz, $C_{ipso}$ of Ph). $^{31}$P{$^1$H} NMR (161.7 MHz, THF-$d_8$, 23 °C): $\delta$ 48.51 ppm.

**Crystal Structure Determinations of Compounds 16 to 20.** X-ray data collection and structural refinement: The crystal data were collected on a Bruker APEX II diffractometer. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full matrix least squares methods on $F^2$. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to reside in their respective parents atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations.
References for Chapter 1


(11) (a) Kamalesh Babu, R. P.; Aparna, K.; McDonald, R.; Cavell, R. G.


Chapter 2 Synthesis and Reactivity of Metal 1,3-Benzobis(thiophosphinoyl)methanediide Complexes

2.1 Introduction

2.1.1 Synthesis of Main Group Methanide and Methanediide Complexes

2.1.1.1 Group 2 Metal Methanide and Methanediide Complexes

Magnesium bis(iminophosphinoyl)methanide complex

\[
\left\{\text{CH} \left( \text{Ph}_2\text{P} = \text{NSiMe}_3 \right)_2\right\} \text{Mg}(\mu-\text{Cl})_2 \quad (21)
\]

was synthesized by the reaction of

\[
\text{CH}_2 \left( \text{Ph}_2\text{P} = \text{NSiMe}_3 \right)_2 \quad (2a)
\]

with MeMgCl. The reaction of 2a with Li[N(SiMe$_3$)$_2$]

followed by the reaction with MeMgI gave compound

\[
\left\{\text{CH} \left( \text{Ph}_2\text{P} = \text{NSiMe}_3 \right)_2\right\} \text{MgI}(\text{THF}) \quad (22)
\]

(Scheme 2.1).

![Scheme 2.1](image)

Scheme 2.1

The reaction between 3 and Mg[N(SiMe$_3$)$_2$]$_2$ gave magnesium bis(thiophosphinoyl)methanide complex 23 (Scheme 2.2).

![Scheme 2.2](image)

Scheme 2.2

The calcium, strontium and barium bis(iminophosphinoyl)methanide complexes
were synthesized by the salt elimination reaction of \([\text{K}[\text{CH}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]]\) (12) with the corresponding metal diiodides.\(^3\) Another approach is by the reaction between 2a and the corresponding metal amides \([\text{M}\{\text{N(SiMe}_3)\}_2]\) (\(\text{M} = \text{Ca} (27), \text{Ba} (28)\)) (Scheme 2.3).\(^4\)

The group 2 metal bis(iminophosphinoyl)methanediide complexes were usually synthesized by the reaction of \([\text{CH}_2(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]\) (2a) and the corresponding metal alkyls or amides. The reaction of 2a with Mg\(^{\text{\text{a}}Bu}_2\), [[(C\(_6\)H\(_4\)-4'-Bu)CH\(_2\)]\(_2\)Ca(THF)]\(_4\)] or [(PhCH\(_2\)]\(_2\)Ba] gave alkaline earth metal bis(iminophosphinoyl)methanediide complexes \([(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{CM}]_2\) (\(\text{M} = \text{Mg} (29), \text{Ca} (30), \text{Ba} (31)\))\(^5\), respectively. They were crystallized as a dimer (Scheme 2.4)
Leung et al. recently reported the synthesis of the magnesium bis(thiophosphinoyl)methanediide complex \[((\text{Ph}_2\text{P}=\text{S})_2\text{CMg(THF)})_2\] (32) which is obtained by the reaction of \[[\text{CH}_2(\text{Ph}_2\text{P}=\text{S})_2\]\] (3) with Mg\((^6\text{Bu})_2\) in refluxing THF (Scheme 2.5).\(^6\)

**Scheme 2.4**

2.1.1.2 **Group 13 Metal Methanide and Methanediide Complexes**

The aluminium bis(thiophosphinoyl)methanide complex 33 was synthesized by the reaction of 3 with 2 equivalents of AlMe\(_3\) (Scheme 2.6).\(^7\)
The reaction of $[\text{Li(THF)}\{\text{CH(Ph}_2\text{P=NSiMe}_3\}_2}\} (4)$ with stoichiometric amount of GaCl$_3$ gave the gallium bis(iminophosphinoyl)methanide complex 34 (Scheme 2.7).

The reaction of 2a with one equivalent of AlMe$_3$ gave the aluminium bis(iminophosphinoyl)methanide 35. The aluminum bis(iminophosphinoyl)methanediide complex $[\text{(AlMe}_2\}_2\{\mu\text{-C(Ph}_2\text{P=NSiMe}_3\}] (36)$ can be synthesized by the reaction of $[\text{CH}_2\text{(Ph}_2\text{P=NSiMe}_3\}_2]$ (2a) with two equivalents of AlMe$_3$ or by the reaction of 35 with one equivalent of AlMe$_3$ (Scheme 2.8).
The reaction of \([\text{Li}\{(S=\text{PPh}_2)_2\text{CH}\}(\text{THF})(\text{Et}_2\text{O})]\) (6) with \(\text{AlCl}_3\), \(\text{GaCl}_3\) or \(\text{InCl}_3\) in \(\text{Et}_2\text{O}\) at 0 °C gave the group 13 metal bis(thiophosphinoyl)methanediide chloride \([\text{MCl}_2\{\text{C}(\text{Ph}_2\text{P}=\text{S})_2\}]_2\) (M = Al (37), Ga (38), In (39)), respectively.\(^6\) It is proposed that the intermediate \([\text{MCl}_2\{\text{CH}(\text{Ph}_2\text{P}=\text{S})_2\}]\) (M = Al, Ga, In) underwent further dehydrochlorination with 6 to give the final compound (Scheme 2.9).

Cavell’s group reported the synthesis of thallium bis(phosphinoyl)methanediide complex \([\text{Tl}_2\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\}]_2\) (40) which is obtained by the reaction of \([\text{Li}_2\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]\) (5) with two equivalents of \(\text{TlCl}\) (Scheme 2.10).\(^10\)

2.1.1.3 Group 14 Element Methanide and Methanediide Complexes

Group 14 element bis(phosphinoyl)methanide complexes 41-43 were synthesized by the reaction of lithium bis(phosphinoyl)methanide with corresponding metal halide (Scheme 2.11).\(^11\)
Low-valent group 14 element bis(phosphinoyl)methanediide complexes of composition \([:MC(\text{Ph}_2P=E)\text{H}]_2\) (\(M = \text{Ge, Sn, Pb, } E = \text{NSiMe}_3, S\)) have been studied in the past decade.\(^\text{11b,12}\) They have either a 1,3-dimetallacyclobutane structure or a metallavinylidene structure.

The reaction of 2a or 3 with metal amides \([\text{M}\{\text{N(SiMe}_3\}_2]\] (\(M = \text{Sn, Pb}\)) gave the corresponding low valent tin and lead bis(iminophosphinoyl)methanediide complexes \([M\{\mu-C(\text{Ph}_2P=E)\text{H}\}]_2\) (\(E = \text{NSiMe}_3, M = \text{Sn (44), Pb (45)}\) or \(E = S, M = \text{Sn (46), Pb (47)}\)), which have a 1,3-dimetallacyclobutane structure (Scheme 2.12).\(^\text{12a, 11b}\)
[(Me₃SiN=PPh₂)₂C=Ge→Ge=C(Ph₂P=NSiMe₃)₂] (48) reported by Leung’s group is the first example of bisgermavinyldene.¹²a The reaction of GeCl₂-dioxane with two equivalents of [Li(THF){CH(Ph₂P=NSiMe₃)₂}] (4) gave compound 48 (Scheme 2.13).

Scheme 2.13

The reactivity of 48 has been well studied. It can behave as a Lewis base or undergoes an 1,2-addition or cycloaddition toward various transition-metal complexes and organic and inorganic substrates. For example, the reaction of 48 with Ni(PPh₃)₄ and 2,2,6,6-tetramethylpiperidine N-oxide (TEMPO) gave compounds 49¹³ and 50,¹⁴ respectively. Cycloaddition reaction of 48 with AdNCO (Ad = Admantyl) and benzil afforded the corresponding products 51¹⁵ and 52,¹⁴ respectively. Compound 48 also can undergo an oxidative reaction with elemental chalcogens to give 53-55 (Scheme 2.14).¹¹a
2.1.4 Group 15 Element Methanide and Methanediide Complexes

The group 15 element methanediide complexes were reported recently. The reaction of [Li₂C(Ph₂P=S)](7) with one equivalent of SbCl₃ or BiCl₃ in toluene gave compounds 56 and 57, respectively (Scheme 2.15).16

2.1.2 Synthesis of Transition Metal Methanide and Methanediide Complexes

2.1.2.1 Group 3 Metal Methanide and Methanediide Complexes

The yttrium bis(iminophosphinoyl)methanide complexes can be synthesized from...
the solvent-free potassium compound 58 which is obtained by the recrystallization of 12 in toluene.\textsuperscript{17} For example, complexes 59 and 60 can be synthesized by the reaction of 58 with YCl\textsubscript{3} or Y(BH\textsubscript{4})\textsubscript{3}(THF)\textsubscript{3}, respectively. Moreover, compound 59 can further react with two equivalents of NaBH\textsubscript{4} to give compound 60 (Scheme 2.16).\textsuperscript{18} Similar reaction of 58 with Sc(BH\textsubscript{4})\textsubscript{3}(THF)\textsubscript{3} gave compound 61.\textsuperscript{19}

The yttrium bis(iminophosphinoyl)methanediide complexes 62 and 63 were synthesized by the reaction of [CH\textsubscript{2}(Ph\textsubscript{2}P=NSiMe\textsubscript{3})\textsubscript{2}] (2a) with [Y(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{3}(THF)\textsubscript{3}] or [Y(CH\textsubscript{2}C\textsubscript{6}H\textsubscript{5})\textsubscript{3}(THF)\textsubscript{3}] (Scheme 2.17).\textsuperscript{20}

The reaction between [Li\textsubscript{2}C(Ph\textsubscript{2}P=S)\textsubscript{2}] (7) and ScCl\textsubscript{3}(THF)\textsubscript{3} gave the scandium bis(thiophosphinoyl)methanediide complex 64 (Scheme 2.18).\textsuperscript{21}
2.1.2.2 Group 4 Metal Methanide and Methanediide Complexes

Group 4 methanediide complexes \([\{\text{C(PPh}_2\text{=NSiMe}_3\}\text{MCl}\}_2\] (M = Ti (65), Zr (66), Hf (67)) were synthesized by the reaction of 5 with corresponding metal halide or by the reaction of 2 with HfCl\(_2[\text{N(SiMe}_3\text{)}_2]_2\) (Scheme 2.19).\(^{22}\)

Zirconium bis(iminophosphinoyl)methanediide complexes 68 and 69 can also be obtained by the reaction of 2a with Zr(CH\(_2\text{Ph}_4\)) and by the reaction of 58 with ZrCp\(_2\text{Cl}_2\), respectively (Scheme 2.20).\(^{23}\)

Le Floch’s group reported the synthesis of zirconium bis(thiophosphinoyl)methanediide complexes. The reaction of 7 with ZrCp\(_2\text{Cl}_2\) or ZrCl\(_4\) gave complexes 70 and 71 (Scheme 2.21).\(^{24}\)
2.1.2.3 Group 5 Metal Methanide and Methanediide Complexes

The vanadium bis(iminophosphinoyl)methanide complex 72 can be synthesized by the reaction of neutral ligand 2a or the lithium salt 4 with VCl$_3$(THF)$_3$ (Scheme 2.22).$^{25}$

![Scheme 2.21](image)

The reaction of 58 with Nd(BH$_4$)$_3$(THF)$_3$ gave niobium bis(iminophosphinoyl)methanide complex 73 (Scheme 2.23).$^{19}$

![Scheme 2.22](image)

2.1.2.4 Group 6 Metal Methanide and Methanediide Complexes

The reaction of 4 with CrCl$_3$(THF)$_2$ in THF produced complex 74 (Scheme 2.24).$^{26}$
Cavell and co-workers reported the synthesis of chromium bis(iminophosphinoyl)methanediide complexes 75 and 76. The treatment of 5 with two equivalents of CrCl₂(THF)₂ afforded compound 75. Compound 76 can be synthesized by the reaction of 5 with one equivalent of CrCl₂(THF)₂ or by the reaction of 5 with compound 75 (Scheme 2.25).

2.1.2.5 Group 8-10 Metal Methanide and Methanediide Complexes

The cobalt and rhodium bis(phosphinoyl)methanide complexes 77-79 can be synthesized by the reaction of 4 or 6 with the corresponding metal halide, respectively (Scheme 2.26).
The reaction of $[\text{Li}_2\text{C(Ph}_2\text{P}≡\text{NSiMe}_3)_2]$ (5) with one equivalent of $[\text{ClRh(COD)}]_2$ gave compound 80. The rhodium bis(iminophosphinoyl)methanediide complex 81 can be synthesized by the reaction of 5 with two equivalents of $[\text{ClRh(COD)}]_2$ or by the reaction of 80 with one equivalent of $[\text{ClRh(COD)}]_2$.\textsuperscript{28a,29} The reaction of 5 with PtCl$_2$(COD) gave compound 82 (Scheme 2.27).\textsuperscript{30}

Similarly, the reaction of $[\text{Li}_2\text{C(Ph}_2\text{P}≡\text{S})_2]$ (7) with RuCl$_2$(PPh$_3$)$_4$, PdCl$_2$(PPh$_3$)$_2$ and CoCl$_2$ gave compounds 83,\textsuperscript{31} 84\textsuperscript{32} and 85,\textsuperscript{28b} respectively. Moreover, the transmetalation reaction of 71 or 64 with the corresponding metal halides gave complexes 83-86 (Scheme 2.28).\textsuperscript{33}
2.1.2.6 Group 11 Metal Methanide and Methanediide Complexes

Roesky’s research group explored the synthesis of group 11 metal bis(iminophosphinoyl)methanide complexes. The transmetalation reaction of 58 with [(Ph₃P)₂CuI] or [Ph₃PAuCl] gave the copper complex [(CH(PPh₂=NSiMe₃)₂]CuPPh₃ (87) and dinuclear gold complex [(Ph₃PAu)₂{C(PPh₂NSiMe₃)₂}] (88), respectively (Scheme 2.29).³⁴

Cavell et al. reported the synthesis of copper bis(iminophosphinoyl)methanediide complexes. The reaction of [Li₂C(Ph₂P=NSiMe₃)₂] (5) with copper halides gave copper clusters 89-92, respectively (Scheme 2.30).³⁵
2.1.2.7 Group 12 Metal Methanide and Methanediide Complexes

The reaction of [CH₂(Ph₂P=NSiMe₃)₂] (2a) with zinc alkyl, aryl or amide gave the corresponding zinc bis(iminophosphinoyl)methanide complexes 93, 94, and 95, respectively. Furthermore, the reaction of [CH₂(Ph₂P=NSiMe₃)₂] (2a) with Cp*₂Zn gave compound 96 (Scheme 2.31).

The zinc bis(thiophosphinoyl)methanide 97 synthesized by the reaction of [CH₂(Ph₂P=S)₂] (3) with ZnMe₂ was reported recently by Chivers et al. The zinc center bound to two methanide ligands via four sulfur atoms (Scheme 2.32).
2.1.3 Formation of Trichalcogeno PCP Bridged Anions from Bis(chalcogenophosphinoyl)methane

The formation of the triseleno dianion \([(\text{Se})\text{C(PP}_2\text{=Se})_2]^{-2}\) was reported recently by Chivers’s research group. The reaction of \([\text{Li(TMEDA)}\{\text{HC(PP}_2\text{=Se})_2\}]\) (98) with metal chlorides and TlOEt gave complexes 99, 100a, 101a, 102-104 respectively (Scheme 2.33).

\[
\begin{align*}
\text{Ti}^+ & \quad \begin{array}{c}
\text{Ph}_2\text{P=Se} & \text{Se} & \text{Ph}_2\text{P=Se} \\
\text{Se} & \text{Ph}_2\text{P=Se} & \text{Se} & \text{Ph}_2\text{P=Se} \\
\end{array}
\quad 4 \text{ TiOEt} \\
\text{or} & \quad \frac{1}{2} \quad \quad \begin{array}{c}
\text{Ph}_2\text{P=Se} & \text{Se} & \text{Ph}_2\text{P=Se} \\
\text{Se} & \text{Ph}_2\text{P=Se} & \text{Se} & \text{Ph}_2\text{P=Se} \\
\end{array}
\quad 4 \text{ Se} \\
\begin{array}{c}
\text{Ph}_2\text{P=Se} & \text{Se} & \text{Ph}_2\text{P=Se} \\
\text{Se} & \text{Ph}_2\text{P=Se} & \text{Se} & \text{Ph}_2\text{P=Se} \\
\end{array} \
\begin{array}{c}
\text{Ph}_2\text{P=Se} & \text{Se} & \text{Ph}_2\text{P=Se} \\
\text{Se} & \text{Ph}_2\text{P=Se} & \text{Se} & \text{Ph}_2\text{P=Se} \\
\end{array}
\end{align*}
\]

Scheme 2.33

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture shown two mutually coupled doublets indicating the formation of the neutral monoseleno compound $[(\text{H}_2\text{C(PP}_2\text{)}\text{(PP}_2\text{=Se})]$. A selenium/hydrogen exchange at the carbon center in 98 is proposed for the formation of 102-104. There is a redox process at the Sn metal center $[\text{Sn(II)→Sn(IV)+Sn(0)}]$.

Other approaches reported by Leung and Chivers’s group are by the reaction of
elemental sulfur or selenium with bis(thiophosphinoyl)methanediide complexes (Scheme 2.34).\textsuperscript{11b,43}

\begin{align*}
\text{Li}_2\text{P} & \text{Li}\text{P} \quad \text{Ph}_2\text{P} \quad \text{Ph}_2\text{P} \\
\text{S} & \quad \text{E} \quad \text{S} \\
\text{Pb} & \quad \text{Pb} \quad \text{Pb}
\end{align*}

\text{(Scheme 2.34)}

The reaction of compound 105 with I\textsubscript{2} gave compounds 107-109, respectively (Scheme 2.35).\textsuperscript{43}

\begin{align*}
\text{Li}_2\text{P} & \text{Li}\text{P} \quad \text{Ph}_2\text{P} \quad \text{Ph}_2\text{P} \\
\text{S} & \quad \text{E} \quad \text{S} \\
\text{Pb} & \quad \text{Pb} \quad \text{Pb}
\end{align*}

\text{(Scheme 2.35)}

A series of compounds 100b-c,\textsuperscript{40} 101b-c,\textsuperscript{41,44} 110, 111\textsuperscript{44} and 112\textsuperscript{40} can be further synthesized from compounds 105 and 109, respectively (Scheme 2.36).
According to previous results, most of the metal methanediide complexes have either a metallavinylidene structure or a 1,3-dimetallacyclobutane structure. Both types can undergo 1,2-addition or cycloaddition toward various organic and inorganic substrates. Moreover, compound 30, 66 and 67 can form Lewis acid-base adduct complexes with benzophenone, adamantly cyanide and THF solvent molecules etc. Compound 48 can act as a Lewis-base toward various transition-metal complexes. However, the reactivity of low-valent group 14 1,3-dimetallacyclobutane has been less studied.

According to the theoretical studies of [Li2C(Ph2P=S)]2 (7), it is suggested that the C_methanediide atom contains two lone pairs of electrons (LP). One of the LPs is
stabilized by the negative hyperconjugation with the P-C_Ph of four Ph substituents and P-S σ* orbitals.\textsuperscript{46} Since the 1,3-benzobis(thiophosphinoyl)methanediide anion [1,3-C\textsubscript{6}H\textsubscript{4}(PhP=S)\textsubscript{2}C]\textsuperscript{2-} has only two terminal phenyl substituents and one bridging phenyl substituent on the P atoms, the stabilization of the metal 1,3-benzobis(thiophosphinoyl)methanediide complexes should be different from that of bis(thiosphosphinoyl)methanediide ligand. Moreover, the 1,3-benzobis(thiophosphinoyl)methane ligand [1,3-C\textsubscript{6}H\textsubscript{4}(PhP=S)\textsubscript{2}CH\textsubscript{2}] (19) only has cis- structure, which is different from [CH\textsubscript{2}(Ph\textsubscript{2}P=S)\textsubscript{2}] (3) have a trans conformation. It’s expected that the coordination chemistry of 19 will be different from that of 3.

Therefore, we are highly interested in exploring the syntheses and reactivities of 1,3-benzobis(thiophosphinoyl)methanediide complexes.

In chapter 1, we describe the synthesis of 1,3-benzobis(thiophosphinoyl)methane ligand [1,3-C\textsubscript{6}H\textsubscript{4}(PhP=S)\textsubscript{2}CH\textsubscript{2}] (19). In this chapter we describe its coordination chemistry toward metal alkyls and metal amides. Moreover, the reactivity of a tin(II) 1,3-benzobis(thiophosphinoyl)methanediide compound toward Lewis acids, which has a 1,3-dimetallacyclobutane structure, is described.

2.2 Results and Discussion

2.2.1 Synthesis of a Magnesium 1,3-Benzobis(thiophosphinoyl)methanediide Complex

The reaction of 19 with Mg\textsuperscript{(n)Bu}\textsubscript{2} in refluxing toluene afforded the magnesium 1,3-benzobis(thiophosphinoyl)methanediide complex \[[\mu-1,3-C\textsubscript{6}H\textsubscript{4}(PhP=S)\textsubscript{2}C]Mg(THF)]\textsubscript{2} (118) (39%, Scheme 2.38).
Compound 118 was isolated as a highly air- and moisture-sensitive colorless crystalline solid which is soluble only in THF. It is stable in the solid state at room temperature under an inert atmosphere. The $^1$H NMR spectrum displays resonances for the phenyl protons. The signal for the C$_{\text{methanediide}}$ atom is not observed in the $^{13}$C($^1$H) NMR spectrum. Similarly, there is no $^{13}$C($^1$H) NMR resonance for the C$_{\text{methanediide}}$ atom in [(Ph$_2$P=S)$_2$CMg(THF)]$_2$ (32). The $^{31}$P($^1$H) NMR spectrum displays a singlet at $\delta$ 55.48 ppm for the equivalent P nuclei, which is downfield shifted compared with that of [1,3-C$_6$H$_4$(PhP=S)$_2$CH$_2$] (19) ($\delta$ 45.80 ppm). Similarly, the $^{31}$P($^1$H) NMR spectrum of [(Ph$_2$P=NSiMe$_3$)$_2$CMg]$_2$ (29) shows a downfield signal at $\delta$ 18.6 ppm compared with that of [CH$_2$(Ph$_2$P=NSiMe$_3$)$_2$] (2a) ($\delta$ –4.67 ppm).  

**Figure 2.1** Molecular structure of 118 with thermal ellipsoids at the 50% probability level. Hydrogen atoms and disordered THF molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-Mg(1) 2.483(4), C(1)-Mg(1A) 2.152(4), Mg(1)-S(1) 2.5716(15), Mg(1)-S(2) 2.5801(15), Mg(1)-O(1) 2.088(9), C(1)-P(1) 1.705(4), C(1)-P(2) 1.709(4), P(1)-S(2) 2.0216(13), P(2)-S(1) 2.0231(13), C(1)-Mg(1)-C(1A) 95.51(12), Mg(1)-C(1)-Mg(1A) 84.49(12), P(1)-C(1)-P(2) 107.11(19), P(1)-C(1)-Mg(1) 88.41(14), P(1)-C(1)-Mg(1A) 124.85(19), P(2)-C(1)-Mg(1) 88.36(15), P(2)-C(1)-Mg(1A) 127.18(19), C(1)-P(1)-S(2) 113.25(13), P(1)-S(2)-Mg(1) 79.48(5), S(2)-Mg(1)-C(1) 75.98(9), C(1)-P(2)-S(1) 113.43(13), P(2)-S(1)-Mg(1) 79.67(5), S(1)-Mg(1)-C(1) 76.34(9), S(1)-Mg(1)-S(2) 122.19(6).
The molecular structure of 118 (Figure 2.1) shows that the Mg atoms are coordinated with the thiophosphinoyl substituents and the C_methanediide atom. The \( \text{Mg}(1) \text{S}(1) \text{P}(2) \text{C}(1) \text{P}(1) \text{S}(2) \) metallacycle adopts a pseudo-boat conformation in which the C(1) and Mg(1) atoms are displaced from the P(1)S(2)S(1)P(2) least-squares plane by 1.010 and 1.104 Å, respectively. Two magnesium metal centers are bridged by two methanediide carbon atoms to form a planar \( \text{Mg}_2 \text{C}_2 \) four-membered ring. The coordination sphere on the Mg(1) atom is further supplemented by coordinating with one THF molecule to adopt a distorted trigonal bipyramidal geometry at the metal center. The Mg(1)-C(1) bond length (2.483(4) Å) is significantly longer than that of reported magnesium methanediide complexes \([\{ \text{PPh}_2=\text{NSiMe}_3 \}(\text{PPh}_2=\text{E})\text{CMg}\}_2 \text{(E = S: average 2.241 Å; NSiMe}_3 \text{: average 2.235 Å})\) which have a 1,3-dimettallacyclobutane structure,\(^5\) while it is comparable to that of the magnesium methanide complex \([\{ \text{CH(Ph}_2\text{P=NSiMe}_3 \}_2 \text{Mg(µ-Cl)}\}_2 \text{(21) (2.460(8 Å))}\)\(^1\). In contrast, the Mg(1A)-C(1) bond length (2.152(4) Å) is much shorter than the Mg(1)-C(1) bond, and it is comparable to that of \([\{ \text{PH}_2\text{P=S} \}_2 \text{CMg(THF)}\}_2 \text{(32) (2.156(5) Å) which has a vinylidene structure}\)\(^6\). The difference between the Mg-C bond lengths in 118 (0.331 Å) is significantly bigger than that in \([\{ \text{PPh}_2=\text{NSiMe}_3 \}(\text{PPh}_2=\text{E})\text{CMg}\}_2 \text{(E = S (Δ = 0.020 Å); NSiMe}_3 \text{ (Δ = 0.010 Å))}\)\(^1\).

### 2.2.2 Synthesis of an Aluminum 1,3-Benzobis(thiophosphinoyl)methanediide Complex

The reaction of 19 with AlMe\(_3\) in refluxing toluene afforded the aluminum 1,3-benzobis(thiophosphinoyl)methanediide complex.
Compound 119 was isolated as a highly moisture-sensitive colorless crystalline solid which are soluble in CH₂Cl₂. It has been characterized by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectrum of 119 displays resonances for the AlMe and phenyl protons. The ¹³C{¹H} NMR spectrum of 119 shows no signal for the C₆methanediide atom. Similarly, there is no ¹³C{¹H} NMR resonance for the C₆methanediide atom in [(PPh₂=NSiMe₃)(PPh₂=S)]CAlMe]² and [(AlMe₂)₂{µ-C(PPh₂=NSiMe₃)}₂] (36).⁹ The ³¹P{¹H} NMR spectrum of 119 displays a singlet at 51.30 ppm. The ²⁷Al NMR spectrum shows one broad signal at 58.51 ppm.

The molecular structure of 119 is shown in Figure 2.2. It has a...
1,3-dimetallacyclobutane structure in which the Al(1) and Al(1A) atoms are coordinated with two C\textsubscript{methanediide} atoms (C(1), C(1A)). The Al(1) and Al(1A) atoms are also coordinated with one of the thiophosphinoyl substituents of the ligand and one methyl group to display a distorted tetrahedral geometry. The Al-C(1) bond lengths (2.0638(16) and 2.0206(16) Å) are intermediate between that of [(AlMe\textsubscript{2})\textsubscript{2}\{μ\textsuperscript{2}-C(PPh\textsubscript{2}=NSiMe\textsubscript{3})\textsubscript{2}\}] \textsuperscript{36} (2.117(3) and 2.121(3) Å)\textsuperscript{9} and [(PPh\textsubscript{2}=NSiMe\textsubscript{3})(PPh\textsubscript{2}=S)]CALMe\textsubscript{2} (1.976(1) Å).\textsuperscript{5} According to the theoretical studies of [(PPh\textsubscript{2}=NSiMe\textsubscript{3})(PPh\textsubscript{2}=S)]CALMe\textsubscript{2},\textsuperscript{5} the C\textsubscript{methanediide}-Al bond is ionic. Similar observation can be found in \textsuperscript{119}, in which the Al-C(1) bonds (2.0638(16) and 2.0206(16)) are longer than the terminal Al-C\textsubscript{methyl} bond (1.9434(17) Å).

\subsection*{2.2.3 Synthesis of a Tin(II) 1,3-Benzobis(thiophosphinoyl)methanediide Complex}

The reaction of \textsuperscript{19} with [Sn{N(SiMe\textsubscript{3})\textsubscript{2}}\textsubscript{2}] in refluxing toluene gave the tin(II) 1,3-benzobis(thiophosphinoyl)methanediide complex \textsuperscript{[μ-1,3-C\textsubscript{6}H\textsubscript{4}(PhP=S)\textsubscript{2}C]Sn\textsubscript{2}} \textsuperscript{(120)} (83\%, Scheme 2.40).

![Scheme 2.40](image)

Compound \textsuperscript{120} was isolated as an air- and moisture-sensitive yellow crystalline solid which is soluble in CH\textsubscript{2}Cl\textsubscript{2}. The \textsuperscript{1}H NMR spectrum displays resonances for the phenyl protons. It is noteworthy that the \textsuperscript{13}C{\textsuperscript{1}H} NMR signal for the C\textsubscript{methanediide} atom in \textsuperscript{120} is not observed. Similarly, there is no \textsuperscript{13}C{\textsuperscript{1}H} NMR resonance for the
C\text{methanediide} atom in [Sn\{\mu-C(PPh_2=E)\}_2]_2 (E = NSiMe_3 (44), S (46)).\textsuperscript{11b,12a} The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a singlet with satellites due to coupling to $^{117/119}\text{Sn}$ at $\delta$ 54.91 ppm ($^2J_{\text{Sn-P}} = 47.7, 160.4$ Hz). The results are not consistent with the solid-state structure. It is suggested that the thiophosphinoyl substituents are fluxional in solution. Similar observations can be found in [Sn\{\mu-C(PPh_2=S)\}_2].\textsuperscript{11b} The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum shows a triplet at $\delta$ 26.28 ppm ($^2J_{\text{Sn-P}} = 50.2$ Hz). On comparison of the $^{119}\text{Sn}$ NMR signal of 120 with those of [(PPh_2=NSiMe_3)(PPh_2=S)CSn:],\textsuperscript{120} (\(\delta\) 132.1 ppm)\textsuperscript{47} and the 6-stannapentafulvene [(Tbt)(Mes)Sn=CR_2] (Tbt = 2,4,6-{CH(SiMe_3)_2}_3C_6H_2, Mes = 2,4,6-Me_3C_6H_2, CR_2 = fluorenylidene) (\(\delta\) 270 ppm),\textsuperscript{48} it is suggested that compound 120 does not have a vinylidene structure in solution.

**Figure 2.3** Molecular structure of 120 with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (\AA) and angles (deg): C(1)–Sn(1) 2.334(2), C(1)–Sn(1A) 2.301(2), Sn(1)–S(1) 2.7174(6), C(1)–P(1) 1.750(2), C(1)–P(2) 1.766(2), P(1)–S(1) 2.0111(8), C(1)–Sn(1)–C(1A) 84.13(8), Sn(1)–C(1)–Sn(1A) 95.88(8), P(1)–C(1)–P(2) 110.28(12), P(1)–C(1)–Sn(1) 96.71(10), P(1)–C(1)–Sn(1A) 113.55(11), P(2)–C(1)–Sn(1) 106.36(11), P(2)–C(1)–Sn(1A) 127.50(11), C(1)–P(1)–S(1) 106.13(8), P(1)–S(1)–Sn(1) 79.63(2), S(1)–Sn(1)–C(1) 72.71(6), C(1)–P(2)–S(2) 114.43(8).

The molecular structure of 120 (Figure 2.3) is comparable to that of [Sn\{\mu-C(PPh_2=S)\}_2] (46).\textsuperscript{11b} It has a 1,3-dimetallacyclobutane structure in which the Sn(1) and Sn(1A) atoms are coordinated with two C\text{methanediide} atoms (C(1), C(1A)).
The Sn(1) and Sn(1A) atoms are also coordinated with one of the thiophosphinoyl substituents of the ligand and display a distorted-trigonal pyramidal geometry (sum of bond angles 254.02°). The results illustrate that the Sn atoms possess a high-s-character lone pair. The C(1)–Sn(1) (2.334(2) Å) and C(1A)–Sn(1) bonds (2.301(2) Å) in 120 are longer than the C methanediide–Sn bond in [(PPh₂=NSiMe₃)(PPh₂=S)CSn]₂ (2.2094(9) Å). The difference between the C–Sn bond lengths in 120 (0.033 Å) is significantly smaller than that in [Sn{µ-C(PPh₂=S)₂}]₂ (46) (2.327(3), 2.514(3) Å; Δ = 0.187 Å). It is noteworthy that the P=S moieties are cis to each other. The result is in contrast to the X-ray crystal structure of [Sn{µ-C(PPh₂=S)₂}]₂ (46), in which the P=S moieties are on opposite sides.

2.2.4 Synthesis of a Lead(II) 1,3-Benzobis(thiophosphinoyl)methanediide Complex

The reaction of 19 with [Pb{N(SiMe₃)₂}]₂ in refluxing toluene gave the lead(II) 1,3-benzobis(thiophosphinoyl)methanediide complex [({µ-1,3-C₆H₄(PhP=S)₂C}Pb]₂ (121) (53%, Scheme 2.41).

Compound 121 was isolated as a highly air, moisture and light-sensitive yellow crystalline solid which are soluble in CH₂Cl₂ only. It has been characterized by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectrum of 121 displays
resonances for the phenyl protons. The $^{13}\text{C}\{^1\text{H}\}$ NMR signal for the C\textsubscript{methanediide} atom in \textbf{121} is not observed. Similarly, there is no $^{13}\text{C}\{^1\text{H}\}$ NMR resonance for the C\textsubscript{methanediide} atom in $[\text{Pb}(\mu-\text{C(PPh}_2\text{E})_2)]_2$ (E = NSiMe\textsubscript{3} (\textbf{45}), S (\textbf{47})).\textsuperscript{11b,12a} The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of \textbf{121} displays a singlet with satellites at $\delta$ 54.81 ppm ($^{2}J_{P\text{--}Pb}$ = 147.39 Hz), which is downfield shifted compared with that of compound \textbf{45} ($\delta$ 5.46 ppm) and \textbf{47} ($\delta$ 33.83 and 35.72 ppm). The $^{31}\text{P}$ NMR at -95 °C still shows a singlet without satellites at $\delta$ 55.56 ppm. The singlet shown in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of \textbf{121} are not consistent with the solid-state structure. It is suggested that the thiophosphinoyl substituents are fluxional in solution. The $^{207}\text{Pb}$ NMR spectrum shows one weak singlet at $\delta$ -16.1 ppm. In contrast, $^{207}\text{Pb}$ NMR signal in compound \textbf{45} and \textbf{47} has not been observed.\textsuperscript{11b,13}

**Figure 2.4** Molecular structure of \textbf{121} with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–Pb(1) 2.444(5), C(1)–Pb(2) 2.405(4), C(2)–Pb(1) 2.404(4), C(2)–Pb(2) 2.448(4), Pb(1)–S(1) 2.8100(11), Pb(2)–S(3) 2.8833(12), C(1)–P(1) 1.744(4), C(1)–P(2) 1.744(4), P(1)–S(1) 2.0101(15), P(2)–S(2) 1.9789(16), C(2)–P(3) 1.736(4), C(2)–P(4) 1.739(4), P(3)–S(3) 1.9960(16), P(4)–S(4) 1.9738(15), C(1)–Pb(1)–C(2) 84.11(14), C(1)–Pb(2)–C(2) 84.01(15), Pb(1)–C(1)–Pb(2) 94.36(15), Pb(1)–C(2)–Pb(2) 94.28(14), P(1)–C(1)–P(2) 110.7(2), P(3)–C(2)–P(4) 110.7(2), P(1)–C(1)–Pb(1) 96.80(19), P(1)–C(1)–Pb(2) 123.7(2), P(2)–C(1)–Pb(1) 104.2(2), P(2)–C(1)–Pb(2) 119.4(2), P(3)–C(2)–Pb(1) 130.1(2), P(3)–C(2)–Pb(2) 96.29(19), P(4)–C(2)–Pb(1) 114.6(2), P(4)–C(2)–Pb(2) 101.4(2), C(1)–P(1)–S(1) 109.88(16), P(1)–S(1)–Pb(1) 80.25(5), S(1)–Pb(1)–C(1) 71.31(10), C(1)–P(2)–S(2) 112.80(17), C(2)–P(3)–S(3) 109.84(16), P(3)–S(3)–Pb(2) 78.17(5), S(3)–Pb(2)–C(2) 69.46(10), C(2)–P(4)–S(4) 111.44(15), C(2)–Pb(1)–S(1) 99.33(11), C(1)–Pb(2)–S(3) 97.94(11).
The molecular structure of 121 is shown in Figure 2.4. It has a 1,3-dimetallacyclobutane structure in which the Pb(1) and Pb(2) atoms are coordinated with two C\textsubscript{methanediide} atoms (C(1), C(2)). The structure is different from that of \([\text{Pb}\{\mu-\text{C(PPh}_2\text{=E)}\}_2]\) (E = NSiMe\textsubscript{3} (45), S (47)).\textsuperscript{11b,12a} Different from the coplanar Pb\textsubscript{2}C\textsubscript{2} rings in 45 and 47, the Pb\textsubscript{2}C\textsubscript{2} four-membered ring is not coplanar in 121. The dihedral angle between C(1)Pb(1)Pb(2) and C(2)Pb(1)Pb(2) planes is 159.9\textdegree. The Pb(1) and Pb(2) atoms are only coordinated with one of the thiophosphinoyl substituents of the ligand and display a distorted trigonal pyramidal geometry (sum of the bond angles: 254.35\textdegree and 251.41\textdegree, respectively). This indicates that there is a stereoactive lone pair of electrons at the Pb(1) atom. The C-Pb bonds (2.404(5) to 2.448(5) \text{\AA}) in 121 are comparable to the C\textsubscript{methanediide}-Pb bond in \([\text{Pb}\{\mu-\text{C(Ph}_2\text{P=NSiMe}_3\}_2}\] (45) (2.452(7), 2.493(6) \text{\AA})\textsuperscript{12a} and slightly shorter than that in \([\text{Pb}\{\mu-\text{C(Ph}_2\text{P=S)}\}_2]\) (47) (2.419(6), 2.593(7) \text{\AA}).\textsuperscript{11b}

2.2.5 Reactivity of the Tin(II) 1,3-Benzobis(thiophosphinoyl)methanediide Complex

2.2.5.1 Reactivity of the Tin(II) 1,3-Benzobis(thiophosphinoyl)methanediide Complex toward Aluminum Compounds
The reaction of 120 with 1 equivalent of AlCl₃ in CH₂Cl₂ gave [1,3-C₆H₄(PhP=S)₂C(Sn){Sn(S=PPh)₂C(AlCl₃)-1,3-C₆H₄}] (122) (56%, Scheme 2.42). The results show that the low valent Sn atoms in 120 do not form any adduct with AlCl₃. Instead, the reaction appears to proceed via an insertion of AlCl₃ into one of the Sn–C bonds in 120 to give the intermediate G. The C–Sn bond is then cleaved to release the steric congestion between two 1,3-benzobis-(thiophosphinoyl)methanediide ligands. These results illustrate that the C₇methanediide–Sn bonds in 120 are polar and the C₇methanediide atom is nucleophilic. Hence, the lone pair electrons on the tin atoms are less favorable for bond formation.

Similarly, the reaction of 120 with 2 equivalents of AlCl₃ in CH₂Cl₂ afforded [1,3-C₆H₄(PhP=S)₂C(Sn)(AlCl₃)] (123) (63%). The reaction appears to proceed via the formation of compound 122, which then undergoes an insertion with another AlCl₃ molecule to form compound 123.

The transmetalation reaction of 120 with 2 equivalents of AlMe₃ in CH₂Cl₂ afforded [1,3-C₆H₄(PhP=S)₂CAlMe]₂ (124) (51%). The by-products are SnMe₄ and Me₃Sn–SnMe₃, which were confirmed by ¹¹⁹Sn{¹H} NMR spectroscopy. The reaction
appears to proceed through the formation of \([1,3-\text{C}_6\text{H}_4(\text{PhP}=\text{S})_2\text{C}(\text{Sn})\text{AlMe}_3]\) (Scheme 2.43). The methyl groups are then transferred from the Al atom to the Sn atom, which leads to the formation of 124 and SnMe₂. Subsequently, the reactive SnMe₂ intermediate may decompose to form SnMe₄ and Me₃Sn–SnMe₃. The mechanism is similar to that proposed for the transmetalation reactions of transition-metal bis(thiophosphinoyl)methanediide complexes.³³

Compound 122 was isolated as a highly air- and moisture sensitive yellow crystalline solid which is soluble only in CH₂Cl₂. The \(^1\text{H}\) NMR spectrum displays resonances for the phenyl protons. The \(^{13}\text{C}\{^1\text{H}\}\) NMR signal for the C_methanediide atom in 122 cannot be observed. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum displays two singlets with satellites due to coupling to the Sn nuclei at \(\delta 55.05\) \((^{2}J_{\text{Sn-P}} = 47.7 \text{ Hz}, \quad ^{2}J_{\text{Sn'-P}} = 160.4 \text{ Hz})\) for the PCP nuclei and \(\delta 58.45 \text{ ppm} \((^{2}J_{\text{Sn-P}} = 164.7 \text{ Hz})\) for the PC(AlCl₃)P nuclei. The \(^{119}\text{Sn}\{^1\text{H}\}\) NMR spectrum displays two triplets at \(\delta 22.15\) \((^{2}J_{\text{Sn-P}} = 48.1 \text{ Hz})\) for the Sn(2) atom (Figure 2.5) and \(\delta -160.40 \text{ ppm} \((^{2}J_{\text{Sn-P}} = 164.3 \text{ Hz})\) for the Sn(1) atom, which show an upfield shift compared with those of 120. These indicate that the Sn atoms have a positive charge.
Figure 2.5 Molecular structure of 122 with thermal ellipsoids at the 50% probability level. Hydrogen atoms, disordered phenyl substituents, P(1A), P(2A), and S(1A) atoms, and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)−Al(1) 1.923(4), Sn(1)−S(1) 2.685(8), Sn(1)−S(2) 2.7094(11), C(1)−P(1) 1.724(8), C(1)−P(2) 1.670(15), P(1)−S(1) 2.059(8), P(2)−S(2) 2.036(16), C(20)−Sn(1) 2.310(4), C(20)−Sn(2) 2.297(4), Sn(2)−S(3) 2.8152(11), Sn(2)−S(4) 2.8055(11), C(20)−P(3) 1.763(4), C(20)−P(4) 1.753(4), P(3)−S(3) 2.0091(15), P(4)−S(4) 2.0087(14), C(1)···Sn(1) 3.065(4), P(1)−C(1)−Al(1) 123.1(3), P(2)−C(1)−Al(1) 128.9(3), P(1)−C(1)−P(2) 107.4(4), C(20)−Sn(1)−Sn(2) 81.7(3), C(20)−Sn(1)−S(2) 81.34(10), Sn(1)−Sn(1)−S(2) 101.8(2), Sn(1)−S(1)−P(1) 89.4(3), S(1)−P(1)−C(1) 117.8(4), P(2)−S(2)−Sn(1) 89.2(3), C(1)−P(2)−S(2) 118.3(6), C(20)−Sn(2)−S(4) 73.18(10), C(20)−Sn(2)−S(3) 73.18(9), Sn(2)−S(3)−P(3) 78.44(4), S(3)−Sn(2)−S(4) 100.08(3), P(3)−C(20)−Sn(2) 99.33(17), S(3)−P(3)−C(20) 109.05(14), P(3)−C(20)−P(4) 107.0(2), P(3)−C(20)−Sn(1) 121.96(19), Sn(2)−C(20)−P(4) 99.21(16), Sn(2)−C(20)−Sn(1) 100.38(14), P(4)−S(4)−Sn(2) 78.38(4), C(20)−P(4)−S(4) 109.14(13).

The molecular structure of 122 is shown in Figure 2.5. The Sn(1)S(1)P(1)C(1)P(2)S(2) and Sn(2)S(3)P(3)C(20)P(4)S(4) metallacycles adopt a pseudo-boat conformation. The C(20) atom is coordinated with the Sn(1) and Sn(2) atoms. The C(20)−Sn(1) (2.310(4) Å) and C(20)−Sn(2) bond lengths (2.297(4) Å) are comparable with those in 120. Each tin atom is also coordinated with two thiophosphinoyl substituents and adopts a distorted-trigonal-pyramidal geometry (Sn(1), 264.84°; Sn(2), 246.44°). These indicate that the tin atoms possess a high-s-character lone pair. The C(1)···Sn(1) distance (3.065(4) Å) is significantly longer than the C−Sn bond in base-stabilized stannylenes such as [[C5H4N-2-C(SiMe3)2]Sn{N(SiMe3)2}] (2.356(8) Å) and
but it is shorter than the sum of van der Waals radii (ca. 3.87 Å). The results suggest that there is a weak interaction between the C(1) and Sn(1) atoms. The C(1)−Al(1) bond (1.923(4) Å) is slightly shorter than the Al−Cmethanediide bonds in the aluminum (iminophosphinoyl)(thiophosphinoyl)methanediide complex [(PPh2=S)(PPh2=NSiMe3)CAlMe2] (1.976(1) Å). Moreover, the C(1)−P bonds (1.670(15), 1.724(8) Å) are significantly shorter than the C(20)−P bonds (1.753(4), 1.763(4) Å), while the P(1)−S(1) (2.059(8) Å) and P(2)−S(2) (2.036(16) Å) bonds are longer than the P(3)−S(3) (2.0091(15) Å) and P(4)−S(4) bonds (2.0087(14) Å). On the basis of the theoretical studies of the dilithium bis(thiophosphinoyl)methanediide complex, it is suggested that the C(1) atom contains two lone pairs of electrons (LP), as illustrated in Scheme 2.44. One of the LPs donates to the vacant p orbital of the Al(1) atom. Another LP is stabilized by the negative hyperconjugation with the P−CPh and P−S σ* orbitals, which results in shortening the C(1)−P bonds and lengthening the P(1)−S(1) and P(2)−S(2) bonds.

Scheme 2.44 Resonance Structure of the 1,3-Benzobis(thiophosphinoyl)methanediide Ligand

Compound 123 was isolated as a highly air- and moisture sensitive colorless crystalline solid, which is soluble only in CH2Cl2. The 1H NMR spectrum displays resonances for the phenyl protons. The 13C{1H} NMR signal for the Cmethanediide atom
in 123 cannot be observed. The $^{31}\text{P}\{^1\text{H}\}$ spectrum shows a singlet with satellites due to coupling to the Sn nuclei at $\delta$ 58.54 ppm ($^2J_{\text{Sn-P}}$ = 164.7 Hz). The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum displays a triplet at $\delta$ −140.25 ppm ($^2J_{\text{Sn-P}}$ = 170.8 Hz), which is comparable with that in the tin(II) $\beta$-diketiminate cation [HC(CMeNAr)$_2$Sn(OEt)$_2$][MeB(C$_6$F$_5$)$_3$] (Ar = 2,6-$^t$Pr$_2$C$_6$H$_3$, $\delta$ −139.50 ppm).

Figure 2.6 Molecular structure of 123 with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)−Al(1) 1.963(3), C(1)−Sn(1) 2.392(3), Sn(1)−S(1) 2.6435(9), Sn(1)−S(2) 2.6364(9), C(1)−P(1) 1.758(3), C(1)−P(2) 1.756(3), P(1)−Sn(1) 2.0191(11), P(2)−Sn(2) 2.0164(11), S(1)−Sn(1)−C(1) 74.22(8), S(2)−Sn(1)−C(1) 74.57(8), S(1)−Sn(1)−S(2) 100.29(3), Sn(1)−C(1)−Al(1) 102.33(13), Al(1)−C(1)−P(1) 123.27(18), Al(1)−C(1)−P(2) 124.45(18), Sn(1)−S(1)−P(1) 82.59(4), S(1)−P(1)−S(2) 107.22(11), P(1)−C(1)−P(2) 106.27(17), C(1)−P(2)−S(2) 107.81(11), P(2)−S(2)−Sn(1) 82.26(4).

The molecular structure of 123 (Figure 2.6) shows that the Sn(1) atom is coordinated with the thiophosphinoyl substituents and the C$_{\text{methanediide}}$ atom. The Sn(1)S(1)P(1)C(1)P(2)S(2) metallacycle adopts a pseudo-boat conformation in which the C(1) and Sn(1) atoms are displaced from the P(1)S(1)S(2)P(2) least-squares plane by 1.049 and 1.667 Å, respectively. Moreover, the geometry around the Sn(1) atom is distorted trigonal pyramidal (sum of bond angles 249.08°). This geometry indicates that the Sn(1) atom possesses a high-s-character lone pair. The C(1)−Sn(1) bond (2.392(3) Å) is comparable with those in 120 and 122. The C(1)−Al(1) bond (1.963(3)
Å) is longer than that in 122.

Compound 124 was isolated as a highly air- and moisture sensitive colorless crystalline solid, which is soluble only in CH₂Cl₂. The ¹H NMR spectrum shows signals for the Me substituents and phenyl protons. It is noteworthy that the ¹³C{¹H} NMR signal for the C₇methanediide atom cannot be observed. The ³¹P{¹H} spectrum displays a singlet at δ 52.43 ppm in CDCl₃ and 58.67 ppm in CD₂Cl₂, which shows a downfield shift compared with that of [(PPh₂=S)₂CAICl]₂ (37) (δ 32.24 ppm)⁶ and slightly downfield shift compared with that of 119 (δ 51.30 ppm in CD₂Cl₂). Compound 124 can not convert to compound 119 by recrystallization in toluene and vice versa in DCM.

**Figure 2.7** Molecular structure of 124 with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)−Al(1) 1.9469(17), C(2)−Al(1) 1.9547(18), Al(1A)-S(1) 2.3331(7), Al(1A)-S(2) 2.3312(6), C(1)−P(1) 1.7111(16), C(1)−P(2) 1.7102(16), P(1)−S(1) 2.0616(6), P(2)−S(2) 2.0596(6), C(1)−Al(1)−S(1A) 108.07(5), C(1)−Al(1)−S(2A) 109.94(5), S(1A)−Al(1)−S(2A) 113.44(2), C(2)−Al(1)−C(1) 116.56(8), Al(1)−C(1)−P(1) 125.68(9), Al(1)−C(1)−P(2) 127.19(9), Al(1A)−S(1)−P(1) 98.41(2), S(1)−P(1)−C(1) 115.75(6), P(1)−C(1)−P(2) 104.37(9), C(1)−P(2)−S(2) 117.59(6), P(2)−S(2)−Al(1A) 97.12(2).

The molecular structure of 124 (Figure 2.7) is comparable to that of
[(PPh$_2$=S)$_2$CAIC] (37). The Al(1) atom is bonded to the C$_{\text{metha}}$nediide atom, the methyl substituent, and the thiophosphinoyl substituent of the adjacent ligand, which adopts a tetrahedral geometry. The C(1)−Al(1) bond (1.9469(17) Å) is slightly shorter than that in [(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)CAIMe]$_2$ (1.976(1) Å)$^5$ and [(PPh$_2$=S)$_2$CAIC]$_2$ (1.975(2) Å)$^6$ and significantly shorter than that in 119 (2.0206(16) and 2.0638(16) Å). In addition, the C$_{\text{metha}}$nediide−Al bond in 124 is slightly shorter than the C$_{\text{Me}}$−Al bond (1.9547(18) Å). According to the theoretical studies of [(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)CAIMe]$_2$,$^5$ it is suggested that the C$_{\text{metha}}$nediide−Al bond in 113 is highly ionic and has weak covalent binding.

2.2.5.2 Reactivity of the Tin(II) 1,3-Benzobis(thiophosphinoyl)methanediide Complex toward Gallium Trichloride

The reaction of 120 with 2 equivalents of GaCl$_3$ in DCM afforded a mixture of [1,3-C$_6$H$_4$(PhP=S)$_2$C(Sn)(GaCl$_3$)] (125) and [[1,3-C$_6$H$_4$(PhP=S)$_2$C(Sn)(GaCl$_3$)]$_2$] (126) (71%). In contrast, for the reaction of 120 with 1 equivalent of GaCl$_3$ in DCM, [1,3-C$_6$H$_4$(PhP=S)$_2$CGaCl]$_2$ (127) was isolated in low yield (7%, Scheme 2.45).
A mixture of compounds 125 and 126 was isolated as a cocrystal in a ratio of 2:1. Similar to compound 123, the reaction appears to proceed via an insertion of two GaCl$_3$ into two Sn-C bonds in 120 to form compound 125. Compound 126 is the dimeric form of compound 125. The tin atoms in compound 126 are bridged between two sulfur atoms of the ligands.

A mixture of compounds 125 and 126 is isolated as a highly air- and moisture sensitive colorless crystalline solid, which is soluble in CH$_2$Cl$_2$ only. The $^1$H NMR spectrum displays resonances for the phenyl protons. The $^{13}$C{$^1$H} NMR signal for the C$_{methanediide}$ atom cannot be observed. The $^{31}$P{$^1$H} spectrum shows a singlet with satellites due to coupling to the Sn nuclei at $\delta$ 58.27 ppm ($^2J_{Sn-P} = 164.7$ Hz). The $^{31}$P NMR at -95 °C still shows a singlet with satellites at $\delta$ 57.53 ppm ($^2J_{Sn-P} = 147.4$ Hz). The results indicate that compound 126 dissociates to form compound 125 in solution. The $^{31}$P CPMAS solid state NMR shows two singlets at $\delta$ 55.97 and 59.82 ppm and
one singlet at 57.25 ppm for 126 and 125, respectively. The $^{119}$Sn$^{1}$H NMR spectrum displays a triplet at $\delta$ −157.83 ppm ($^{2}J_{\text{Sn-P}} = 176.5$ Hz), which is comparable to that in 123 (−140.25 ppm, $^{2}J_{\text{Sn-P}} = 170.8$ Hz).

Figure 2.8 Molecular structure of 125 with thermal ellipsoids at the 50% probability level. Hydrogen atoms, solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)−Ga(1) 1.973(3), C(1)−Sn(1) 2.419(3), Sn(1)−S(1) 2.6970(8), Sn(1)−S(2) 2.6662(7), C(1)−P(1) 1.761(3), C(1)−P(2) 1.760(3), P(1)−S(1) 2.0134(10), P(2)−S(2) 2.0219(10), S(1)−Sn(1)−C(1) 74.01(6), S(2)−Sn(1)−C(1) 73.60(6), S(1)−Sn(1)−S(2) 107.73(2), Sn(1)−C(1)−Ga(1) 98.80(11), Ga(1)−C(1)−P(1) 123.72(14), Ga(1)−C(1)−P(2) 124.17(14), Sn(1)−S(1)−P(1) 81.35(3), S(1)−P(1)−C(1) 109.58(10), P(1)−C(1)−P(2) 108.04(15), C(1)−P(2)−S(2) 107.46(10), P(2)−S(2)−Sn(1) 82.72(3).

The molecule structure of compound 125 is shown in Figure 2.8. It is isostructural with compound 123. The Sn(1) atom is coordinated with the thiophosphinoyl substituents and the C$_{\text{methanediide}}$ atom. The Sn(1)S(1)P(1)C(1)P(2)S(2) metallacycle adopts a pseudo-boat conformation in which the C(1) and Sn(1) atoms are displaced from the P(1)S(1)S(2)P(2) least-squares plane by 1.033 and 1.512 Å, respectively. The geometry around the Sn(1) atom is distorted trigonal pyramidal (sum of bond angles 255.34°). This indicates that there is a stereoactive lone pair of electrons at the Sn(1) atom. The C(1)−Sn(1) bond length (2.419(3) Å) is comparable to that in 123 (2.392(3) Å). The C(1)−Ga(1) bond length (1.973(3) Å) is comparable to that of [GaCl$_{3}$](IMes)] (IMes = N,N’-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) (1.954(4) Å).
Figure 2.9 Molecular structure of 126 with thermal ellipsoids at the 50% probability level. Hydrogen atoms, solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(20)-Ga(2) 1.996(3), C(20)-Sn(2) 2.397(3), Sn(2)-S(3) 2.6434(7), Sn(2)-S(4) 2.6667(7), C(20)-P(3) 1.764(3), C(20)-P(4A) 1.773(3), P(3)-S(3) 2.0099(10), P(4)-S(4) 2.0282(9), S(3)-Sn(2)-C(20) 74.62(6), S(4)-Sn(2)-C(20) 96.37(6), S(3)-Sn(2)-S(4) 86.54(2), Sn(2)-C(20)-Ga(2) 100.48(11), Ga(2)-C(20)-P(3) 119.91(13), Ga(2)-C(20)-P(4A) 117.27(14), Sn(2)-S(3)-P(3) 80.66(3), S(3)-P(3)-C(20) 108.23(9), P(3)-C(20)-P(4A) 109.17(14), C(20A)-P(4)-S(4) 110.74(9), P(4)-S(4)-Sn(2) 104.66(3).

The molecule structure of compound 126 is shown in Figure 2.9. Compound 126 can be considered as the dimeric form of compound 125. The S(4) atom coordinates to the Sn(2) atom instead of the Sn(2A) atom. The geometry around the Sn atoms is distorted trigonal pyramidal (sum of bond angles 257.53°). This indicates that there is a stereoactive lone pair of electrons at the Sn(2) atom. The S-Sn(2) (2.6434(7) and 2.6667(7) Å), C(20)–Sn(2) (2.397(3) Å) and C(20)–Ga(2) bond lengths (1.996(3) Å) are comparable to those in 125 (S-Sn: 2.6970(8) and 2.6662(7), C-Sn: 2.419(3), C-Ga: 1.973(3) Å).

Compound 127 was isolated as a highly air- and moisture sensitive colorless crystalline solid, which is soluble only in CH₂Cl₂. The ¹H NMR spectrum displays resonances for the phenyl protons. The ¹³C{¹H} NMR signal for the C₄methanediide atom in 127 cannot be observed. Similarly, there is no ¹³C{¹H} NMR resonance for the [GaCl{C(Ph₂P=S)₂}]₂ (38). The ³¹P{¹H} NMR spectrum shows a singlet with
satellites due to coupling to $^{69/71}\text{Ga}$ at $\delta$ 55.03 ppm ($^2J_{\text{P-Ga}} = 17.3, 82.4$ Hz), which is comparable with that of $[1,3-\text{C}_6\text{H}_4(\text{PhP=S})_2\text{CAIMe}]_2$ (124) ($\delta$ 52.43 ppm in CDCl$_3$). The $^{31}\text{P}$ NMR of the mother liquid shows another two singlets at 46.13 and 56.44 ppm, respectively. However, the compound is not isolated as yet. Compounds 125 and 126 can be obtained by the reaction of compound 127 with another one equivalent of GaCl$_3$. Thus compound 127 is an intermediate in the formation of 125 and 126. However, the reaction mechanism is still unknown.

![Molecular structure of 127](image.png)

Figure 2.10 Molecular structure of 127 with thermal ellipsoids at the 50% probability level. Hydrogen atoms, solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–Ga(1) 1.936(3), Cl(1)–Ga(1) 2.2156(9), Ga(1A)–S(1) 2.3173(9), Ga(1A)–S(2) 2.3237(9), C(1)–P(1) 1.711(3), C(1)–P(2) 1.714(3), P(1)–S(1) 2.0704(12), P(2)–S(2) 2.0600(12), C(1)–Ga(1)–S(1A) 112.36(10), C(1)–Ga(1)–S(2A) 109.68(10), S(1A)–Ga(1)–S(2A) 117.00(3), Cl(1)–Ga(1)–C(1) 114.49(10), Ga(1)–C(1)–P(1) 124.11(18), Ga(1)–C(1)–P(2) 125.11(18), Ga(1A)–S(1)–P(1) 96.13(4), S(1)–P(1)–C(1) 116.42(12), P(1)–C(1)–P(2) 105.61(17), C(1)–P(2)–S(2) 115.59(12), P(2)–S(2)–Ga(1A) 95.98(4).

The molecular structure of 127 (Figure 2.10) is comparable to that of 124 and $[\text{GaCl}(\text{C(Ph}_2\text{P=S})_2)]_2$ (38). The Ga(1) atom is bonded to the C$_{\text{methanediide}}$ atom, the chlorine atom, and the thiophosphinoyl substituent of the adjacent ligand, which adopts a tetrahedral geometry. The C(1)-Ga(1) bond length (1.936(3) Å) is slightly
shorter than that of $[\text{GaCl}\{\text{C(Ph}_2\text{P}=\text{S})_2\}]_2$ (38) (1.972(4) Å)\(^6\) and 125 (1.973(3) Å).

The Ga(1)-S bond lengths (2.3173(9) and 2.3237(9) Å) and Ga(1)-Cl(1) bond lengths (2.2156(9) Å) are comparable with those in $[\text{GaCl}\{\text{C(Ph}_2\text{P}=\text{S})_2\}]_2$ (38) (Ga-S: 2.294(2) and 2.302(2) Å; Ga-Cl: 2.219(2) Å).\(^6\)

### 2.2.5.3 Reactivity of the Tin(II) 1,3-Benzobis(thiophosphinoyl)methanediide Complex toward Germanium Tetrachloride

The reaction of 120 with 2 equivalents of GeCl\(_4\) in DCM afforded [(1,3-C\(_6\)H\(_4\)(PhP=S)_2C)(SnCl)(GeCl\(_3\))]\(_2\) (128) (69%, Scheme 2.46). The reaction appears to proceed via an insertion of two GeCl\(_4\) molecules into the C-Sn bonds to form intermediate H. Subsequently the C-Sn bond in the intermediate is cleaved and the Sn atom coordinates with the thiophosphinoyl substituent of another molecule to form 128.

![Scheme 2.46](image)

Compound 128 was isolated as a highly air- and moisture sensitive colorless crystalline solid, which is soluble only in CH\(_2\)Cl\(_2\). The \(^1\)H NMR spectrum displays resonances for the phenyl protons. The \(^{13}\)C\({}_1\)H\) NMR signal for the C\(_{\text{methanediide}}\) atom
in 128 cannot be observed. The $^{31}$P$^{1}$H NMR spectrum shows a singlet at $\delta$ 46.44 ppm. The $^{119}$Sn NMR spectrum shows a singlet at $\delta$ 75.30 ppm which is comparable with that of $[^n\text{BuC(NiPr)}_2\text{SnCl}]$ ($\delta$ 69.1 ppm)$^{51}$ and $[(\text{SiMe}_3)(\text{Ar}^*)\text{NSn}^+][\text{Al(OC(CF}_3)_3]_4^-$ ($\text{Ar}^* = \text{C}_6\text{H}_2[\text{C(H)}\text{Ph}_2]_2\text{Me}-2,6,4$, $\delta$ 46.3 ppm)$^{52}$.

Figure 2.11 Molecular structure of 128 with thermal ellipsoids at the 50% probability level. One of two independent molecules in the asymmetric unit is shown. Hydrogen atoms, solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-Ge(1) 1.866(8), C(1)-P(2) 1.731(8), P(2)-S(2) 2.011(2), Sn(1)-S(2A) 2.7274(19), C(1)-P(1) 1.727(8), P(1)-S(1) 2.036(3), S(1)-Sn(1) 2.6289(17), Sn(1)-Cl(4) 2.5192(19), C(1)···Sn(1) 3.527(9), Ge(1)-C(1)-P(1) 123.5(4), Ge(1)-C(1)-P(2) 124.7(4), P(1)-C(1)-P(2) 111.8(4), C(1)-P(1)-S(1) 118.1(3), C(1)-P(2)-S(2) 114.5(3), P(1)-S(1)-Sn(1) 99.34(8), P(2)-S(2)-Sn(1A) 103.76(9), S(1)-Sn(1)-Cl(4) 83.55(6), S(2A)-Sn(1)-S(2A) 86.38(6), S(1)-Sn(1)-S(2A) 87.12(6).

The molecular structure of 128 is shown in Figure 2.11. The Sn(1) atom is coordinated with the thiophosphinoyl substituents and Cl(4) atom. The geometry around the Sn(1) atom is distorted trigonal pyramidal (sum of bond angles: 257.05°). This geometry indicates that the Sn(1) atom possesses a stereoactive lone pair. The C(1)···Sn(1) distance (3.527(9) Å) is significantly longer than the C(1)···Sn(1) distance (3.065(4) Å) in compound 122, but it is still shorter than the sum of van der Waals radii (ca. 3.87 Å). The results suggest that there is a very weak interaction.
between the C(1) and Sn(1) atoms. The Sn(1)-S(1) bond length (2.6289(17) Å) is longer than the Sn-S single bonds in [(Tbt)(Mes)Sn(µ-S)]2 (Tbt = 2,4,6-{CH(SiMe3)2}3C6H2, 2.434(3), 2.432(3) Å) but is comparable with that of the aryl tin(II) dithiocarboxylate [:Sn(Ar){S2CAr}] (average 2.659 Å). The Sn(1)-S(2A) bond length (2.7274(19) Å) is longer and comparable with that in compound 120 (2.7174(6) Å). The Sn(1)-Cl(4) bond length (2.5192(19) Å) is within the range of Sn(II)-Clterminal bond lengths in [SnCl2·SC(NH2)2] (2.492-2.606 Å). The Sn(1)-Cl(4) bond length (2.5192(19) Å) is within the range of Sn(II)-Clterminal bond lengths in [SnCl2·SC(NH2)2] (2.492-2.606 Å). The C(1)-Ge(1) bond (1.866(8) Å) is comparable with the reported C-Ge single bond (range 1.90-2.05 Å).

2.2.5.4 Reactivity of the Tin(II) 1,3-Benzobis(thiophosphinoyl)methanediide Complex toward Diethylzinc

The reaction of 120 with 2 equivalents of ZnEt2 in refluxing toluene afforded [1,3-C6H4(PhP=S)2C{(SnEt2)(µ-SZn)}]2 (129) (16%) and unidentified compounds (Scheme 2.47). Compound 129 appears that a ZnS moiety coordinates with [1,3-C6H4(PhP=S)2C=SnEt2]. The ethyl substituents were transferred from ZnEt2 to Sn atom in 120. The reaction mixture was filtered and compound 129 was obtained as a highly air- and moisture sensitive yellow crystalline solid after concentration of the filtrate. There are many signals in the 31P and 119Sn NMR spectra of the mother liquid and the mixture cannot be identified. No triplet or doublet of doublets for PCHnP can be found in the 1H NMR spectrum of the mother liquid. The byproducts may be a methanediide complexes observed from the chemical shift of P signals (δ 4.71-78.64 ppm). One set of doublet of doublets at δ 70.59 and 4.71 ppm (2Jp-p = 32.25 Hz) can
be found in the messy $^{31}$P NMR spectrum of the mother liquid, but there is no doublet of doublets in $^{119}$Sn NMR spectrum. The results show that the sulfur source cannot come from 120 or tin methanediide intermediates. The reaction appears to proceed through the formation of intermediate J and [Zn]. The [Zn] takes one sulfur atom from the ligand backbone to give [ZnS] followed by the reaction with intermediate I to give compound 129.

Scheme 2.47

Compound 129 is hardly soluble in CH$_2$Cl$_2$. The $^1$H NMR spectrum displays resonances for the ethyl and the phenyl protons. The $^{13}$C{$^1$H} NMR signal for the C$_{\text{methanediide}}$ atom in 129 cannot be observed. The $^{31}$P{$^1$H} spectrum shows a singlet with satellites due to coupling to the Sn nuclei at $\delta$ 51.65 ppm ($^2J_{\text{Sn-P}}$ = 46.3 Hz). The $^{119}$Sn{$^1$H} NMR spectrum displays a triplet at $\delta$ 53.11 ppm ($^2J_{\text{Sn-P}}$ = 41.1 Hz).
The molecular structure of 129 is shown in Figure 2.12. It has a Zn₂S₂ four-membered ring. The Zn(1) atom is coordinated with the thiophosphinoyl substituents and S(1/1A) atoms to adopt a tetrahedral geometry. The Sn(1) atom is coordinated with two ethyl substituents, the S(1) and C₂methanediide atoms to adopt a tetrahedral geometry. The C₂methanediide-Sn bond length (2.1070(17) Å) is intermediate between that in 120 (2.334(2) and 2.301(2) Å) and the stannaethene [(Me₃Si)₂CH]₂Sn=C[(B'Bu)₂C(SiMe₃)₃] (2.025(4) Å). The results indicate that the C-Sn bond has some double bond character. The C₂methanediide-Sn bond should be intermediate between C=Sn and C—Sn⁺. It is noteworthy that the C₂methanediide-Sn bond is shorter than the C₂ethyl-Sn bond lengths (2.162(7) and 2.165(2) Å). The
Sn(1)-S(1) bond (2.4277(4) Å) is comparable with the Sn-S single bonds in [(Tbt)(Mes)Sn(µ-S)]2 (Tbt = 2,4,6-{CH(SiMe3)2}3C6H2, 2.434(3), 2.432(3) Å)53 and [Sn{N(SiMe3)2}2(µ-S)]2 (2.416(5), 2.413(6) Å)58 It is anticipated that the positive charge on the Sn atom shorten the Sn-S bond. The Zn-S bond lengths (2.3394(5), 2.3445(5), 2.3785(5) and 2.3741(5) Å) are within the range of Zn-S terminal (ca. 2.25 to 2.35 Å) and Zn-S bridging (2.281-2.425 Å) bond lengths for four coordinated Zn compounds, respectively.59

2.2.6 Synthesis of a Zinc Complex of the Dianionic Trithio Ligand

[µ-1,3-C6H4(PhP=S)2C(S)]2-

The reaction of 19 with ZnMe2 in refluxing toluene gave the zinc complex [(µ-1,3-C6H4(PhP=S)2C(S))Zn]2 (130) as a highly moisture-sensitive yellow crystalline solid (25%, Scheme 2.48). It is noteworthy that an extra sulfur atom inserts between the ligand and zinc metal center. The 31P{1H} NMR spectrum of the mother liquid shows a set of doublet of doublets at δ 64.62 and -6.86 ppm (2JPC = 26.46 Hz), which shows that one sulfur atom on the ligand is removed during the reaction and become the sulfur source for the formation of 130. The 1H NMR spectrum of the mother liquid shows a set of doublet of doublets at δ 3.05 ppm (2JPH = 13.42, 19.54 Hz). The LC-MS investigation of the mother liquid shows a single species, which has a mass fragments of m/z 339 [1,3-C6H4(PhP)(PhP=S)CH3]+. The results indicate that [1,3-C6H4(PhP)(PhP=S)CH2] or [1,3-C6H4(PhP)(PhP=S)CH] is formed during the reaction.
Compound 130 was isolated as a highly moisture-sensitive yellow crystalline solid which is slightly soluble in CH$_2$Cl$_2$. Solution NMR spectra can not be obtained due to low solubility in deuterated solvents. The $^{31}$P CPMAS solid state NMR shows two singlets at $\delta$ 64.01 and 66.41 ppm for two P nuclei. The $^{13}$C CPMAS solid state NMR shows a singlet at $\delta$ 29.87 ppm for the C$_{\text{methanide}}$ atom.

![Scheme 2.48](image-url)

**Figure 2.13** Molecular structure of 130 with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn(1)-S(1A) 2.3117(8), Zn(1)-S(2) 2.4035(7), Zn(1)-S(3) 2.3222(8), Zn(1)-S(2A) 2.4075(8), C(10)-S(2) 1.781(3), C(10)-P(1) 1.728(3), P(1)-S(1) 2.0264(10), C(10)-P(2) 1.727(3), P(2)-S(3) 2.0337(10), Zn(1)--Zn(1A) 2.8812(6), S(1A)-Zn(1)-S(3) 120.42(3), S(3)-Zn(1)-S(2) 101.69(3), S(2)-Zn(1)-S(2A) 112.51(3), S(1A)-Zn(1)-S(2A) 100.96(3), Zn(1)-S(2)-Zn(1A) 73.58(2), C(10)-S(2)-Zn(1A) 95.18(10), C(10)-S(2)-Zn(1) 95.10(9), S(2)-C(10)-P(1) 120.90(15), C(10)-P(1)-S(1) 115.49(10), P(1)-S(1)-Zn(1A) 96.40(4), S(2)-C(10)-P(2) 119.45(15), C(10)-P(2)-S(3) 115.54(10), P(2)-S(3)-Zn(1) 95.33(3).

Compound 130 comprises of two trithio dianion ligands coordinating to two zinc centers (Figure 2.13). The zinc centers display a distorted tetrahedral geometry, being bound to four sulfur atoms. The thiolate S(2) atom is bridged by two zinc atoms,
showing a trigonal pyramidal geometry. With the planar Zn(1)-S(2)-Zn(1A)-S(2A) ring as the seat, compound 130 shows an armchair-like structure framework. The structure of compound 130 is similar to that of [Hg{(Se)C(PPh₂=Se)₂}]₂ (104). The Zn(1)-S(1A) bond (2.3117(8) Å) and Zn(1)-S(3) bond (2.3222(8) Å) are slightly shorter than those in [(PPh₂=S)₂CH]₂Zn] (97) (2.3490(6) and 2.3500(6) Å). The Zn-S(2) bond lengths (2.4035 (7) and 2.4075(8) Å) are within the range of bridging Zn-S bond lengths (2.281-2.425 Å). The C-P bond lengths (1.727(3), 1.728(3) Å) are almost identical and they are slightly longer than those in [(PPh₂=S)₂CH]₂Zn] (97) (1.715(2) and 1.722(2) Å). The P-S bonds (2.0264(10) and 2.0337(10) Å) in 130 are slightly shorter than those in [(PPh₂=S)₂CH]₂Zn] (97) (2.0340(8) and 2.0428(8) Å). The results indicate the negative charge on the C₆H₄PhP=S(10) atom may delocalize along the S(1)-P(1)-C(10)-P(2)-S(3) skeleton. The Zn(1)···Zn(1A) distance (2.8812(6) Å) in 130 is longer than the sum of van der Waals’ radii (2.78 Å).

2.2.7 Reaction of the Zinc Complex 130 with [Sn{N(SiMe₃)₂}]₂

The reaction of 130 with [Sn{N(SiMe₃)₂}]₂ in refluxing toluene gave a mixture of [{1,3-C₆H₄(PhP=S)₂C}SnN(SiMe₃)₂]₂(μ³-S)₂Zn]₂ (131) (15%, Scheme 2.49) and unidentified products. The reaction mixture was filtered and concentrated to give 131 as a highly air- and moisture sensitive yellow crystalline solid. The mother liquid was filtered and volatiles were removed from vacuo. The ³¹P and ¹¹⁹Sn NMR spectra of the crude product indicate a number of unidentified products. Thus, the mechanism for the formation of 131 is still unknown as yet.
Compound 131 is slightly soluble in CH₂Cl₂ only. The ¹H NMR spectrum displays resonances for the methyl and phenyl protons. The ¹³C{¹H} NMR signal for the C-methanide atom in 131 is not located. The ³¹P{¹H} spectrum shows a AB quartet at δ 49.93, 50.37 ppm (J_AB = 34.68 Hz). The ¹¹¹Sn{¹H} NMR spectrum displays a AB quartet at δ 24.86, 25.97 ppm (J_AB = 27.24 Hz).

**Figure 2.14** Molecular structure of 131 with thermal ellipsoids at the 50% probability level. Hydrogen atoms, disordered phenyl substituents and solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-Sn(1) 2.082(9), Sn(1)-N(1) 2.053(7), Sn(1)-S(3) 2.437(2), Sn(1)-S(4) 2.413(2), Sn(2)-N(2) 2.103(7), Sn(2)-S(3) 2.701(2), Sn(2)-S(1) 2.678(2), Zn(1)-S(3) 2.355(2), Zn(1)-S(4) 2.467(2), Zn(1)-S(4A) 2.344(2), Zn(1)-S(2A) 2.284(2), C(1)-P(1) 1.746(8), C(1)-P(2) 1.737(9), P(1)-S(1) 2.022(3), P(2)-S(2) 2.023(3), C(1)-Sn(1)-N(1) 114.4(3), C(1)-Sn(1)-S(4) 112.9(2), C(1)-Sn(1)-S(3) 109.7(2), N(1)-Sn(1)-S(4) 111.2(2), N(1)-Sn(1)-S(3) 112.5(19), S(3)-Sn(1)-S(4) 94.52(7), S(1)-Sn(2)-N(2) 98.49(19), S(1)-Sn(2)-S(3) 83.89(7), S(3)-Sn(2)-N(2) 97.4(2), S(3)-Zn(1)-S(2A) 114.51(8), S(3)-Zn(1)-S(4) 95.19(7), S(3)-Zn(1)-S(4A) 106.91(8), S(4)-Zn(1)-S(4A) 104.42(7), Sn(1)-S(3)-Sn(2) 96.00(7), Sn(1)-S(3)-Zn(1) 85.77(7), Sn(2)-S(3)-Zn(1) 98.73(7), Sn(1)-S(4)-Zn(1A) 100.80(8), Sn(1)-S(4)-Zn(1) 83.87(7), Zn(1)-S(4)-Zn(1A) 75.58(7), P(1)-C(1)-P(2) 109.9(5), P(1)-C(1)-Sn(1) 119.8(5), P(2)-C(1)-Sn(1) 129.3(4), C(1)-P(1)-S(1) 118.4(3), C(1)-P(2)-S(2) 121.4(3), P(1)-S(1)-Sn(2) 93.48(10), P(2)-S(2)-Zn(1A) 111.16(12).
The molecular structure of 131 is shown in Figure 2.14. The Zn(1) atom is coordinated with four sulfur atoms (S(2A), S(3), S(4) and S(4A)) to adopt a tetrahedral geometry. The Sn(1) atom is coordinated with the S(3), S(4), C\text{methanediide} atoms and one N(SiMe\textsubscript{3})\textsubscript{2} substituent to adopt a distorted tetrahedral geometry. The Sn(2) atom is coordinated with the S(3) atom, one thiophosphinoyl substituent and one N(SiMe\textsubscript{3})\textsubscript{2} substituent. The geometry around the Sn(2) atom is distorted trigonal pyramidal (sum of bond angles 279.78°). This indicates that there is a stereoactive lone pair of electrons at the Sn(2) atom. The C\text{methanediide}-Sn(1) bond (2.082(9) Å) is comparable to that of 129 (2.1070(17) Å). The results indicate that the C-Sn bond has some double bond character. The C\text{methanediide}-Sn bond should be intermediate between C=Sn and C—Sn\textsuperscript{+}. The Sn-S bond lengths (2.413(2)-2.701(2) Å) are within the range of reported Sn-S single bonds (2.413(6)-2.7076(4) Å).\textsuperscript{58,60-61} The Sn-N (2.103(7) and 2.053(7) Å) are comparable with that in [Sn\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}(\mu-S)\textsubscript{2}] (2.034(13), 2.08(2) Å).\textsuperscript{58} The Zn(1)-S(2A) (2.284(2) Å), Zn(1)-S(3) (2.355(2) Å) and Zn(1)-S(4A) (2.344(2) Å) bond lengths are within the range of bridging Zn-S bond lengths (2.281-2.425 Å).\textsuperscript{59} The Zn(1)-S(4) bond length (2.467(2) Å) is slightly longer than the upper limit of bridging Zn-S bond length. The Zn(1)···Sn(1) distance (3.262(4) Å) is slightly shorter than the sum of van der Waals’ radii (3.56 Å). The results suggest that there is a very weak interaction between the Zn(1) and Sn(1) atoms.

2.3 Conclusion

In summary, magnesium (113), aluminum (119), tin(II) (120) and lead(II) (121) 1,3-benzobis(thiophosphinoynyl)methanediide complexes, which have a
1,3-dimetallacyclobutane structure, were synthesized. Furthermore, the reactivity of compound 120 is also studied. Compound 120 undergoes an insertion reaction with AlCl$_3$ to form compound 122 and 123, or with GaCl$_3$ to form compound 125 and 126 as cocrystals. Compound 120 also undergoes a transmetalation reaction with AlMe$_3$ to give compound 124. The reaction of compound 120 with ZnEt$_2$ and the reaction of zinc complex 130 with Sn amide give two Zn/Sn sulfide hetrobimetallic complexes 129 and 131, respectively.

### 2.4 Experimental Section

All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. CH$_2$Cl$_2$ was dried over and distilled over CaH$_2$ prior to use. Other solvents were dried over and distilled over Na/K alloy prior to use. The $^1$H, $^{13}$C, $^{31}$P, $^{27}$Al, $^{119}$Sn, $^{207}$Pb NMR, $^{31}$P CPMAS and $^{13}$C CPMAS spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts $\delta$ are relative to SiMe$_4$ for $^1$H and $^{13}$C, 0.5 M AlCl$_3$ in MeOH for $^{27}$Al, 85% H$_3$PO$_4$ for $^{31}$P, 90% Me$_4$Sn for $^{119}$Sn, saturated Pb(NO$_3$)$_2$ in D$_2$O for $^{207}$Pb, hexa-methylbenzene for $^{13}$C CPMAS and ammonium dihydrogen phosphorus for $^{31}$P CPMAS. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

19 was prepared as described in Chapter 1. $[[\mu-1,3-C_6H_4(PhP=S)_{2}C]Mg(THF)]_2$ (118). Mg($^{\text{t-Bu}}$)$_2$ (1.0 mL, 1.0 mmol, 1 M solution in heptane) was added to a solution of 19 (0.37 g, 1.0 mmol) in THF (15 mL)
at ambient temperature. The yellow solution was refluxed at 70 °C overnight. After filtration and concentration of the filtrate, 118 was isolated as yellow crystal. Yield: 0.18 g (39%). M.p. 215°C (dec.). Elemental analysis (%) calcd for C₆H₄₃Mg₂O₂P₄S₄: C, 59.43; H, 4.77. Found: C, 59.07; 4.63. ¹H NMR: (399.5 MHz, C₆D₆, 21 °C): δ 6.87 – 6.90 (m, 4H, Ph), 7.05 – 7.09 (m, 4H, Ph), 7.16 – 7.20 (m, 8H, Ph), 7.48 – 7.53 (m, 4H, Ph), 8.46 – 8.51 ppm (m, 8H, Ph); ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 23 °C): δ 127.31 (t, ³J_C−P = 6.68 Hz, C meta of Ph and C₆H₄), 129.23 (m, C para of Ph and C₆H₄), 107.73 (s, C ortho of Ph), 131.53 (t, ³J_C−P = 6.68 Hz, C ipso of Ph and C₆H₄); ³¹P{¹H} NMR (161.7 MHz, C₆D₆, 21 °C): δ 55.48 ppm (s).

[(µ-1,3-C₆H₄(PhP=S)₂C)AlMe]₂ (119) AlMe₃ (0.5 mL, 1.0 mmol, 2 M solution in toluene) was added to a solution of 19 (0.37 g, 1.0 mmol) in toluene (15 mL) at ambient temperature. The yellow suspension was then refluxed at 140°C overnight. After filtration and concentration of the filtrate, 119 was isolated as colorless crystal. Yield: 0.18 g (37%). M.p. 210°C (dec.). Elemental analysis (%) calcd for C₄₀H₃₄Al₂P₄S₄: C, 58.53; H, 4.18. Found: C, 57.91; 3.95. ¹H NMR (399.5 MHz, CD₂Cl₂, 23 °C): δ –1.10 (s, 6H, AlMe), 7.45 – 7.61 (m, 20H, Ph & C₆H₄), 7.93 – 7.99 ppm (m, 8H, Ph & C₆H₄); ¹³C{¹H} NMR (100.5 MHz, CD₂Cl₂, 23 °C): δ –3.59 (s, AlMe), 21.54 (s, toluene), 125.63 (s, toluene), 127.77 (t, ³J_P−C = 12.0 Hz, C meta of Ph), 128.55 (s, toluene), 128.71 – 129.02 (m, C₆H₄), 129.36 (s, toluene), 131.82 – 132.63 (m, C ortho of Ph & C₆H₄), 133.54 (dd, ³J_P−C = 88.2 Hz, ³J_P−C = 5.75 Hz, C₆H₄), 133.87 (s, toluene), 144.14 (dd, ³J_P−C = 84.4 Hz, ³J_P−C = 21.1 Hz, C ipso of Ph); ³¹P{¹H} NMR (161.7 MHz, CD₂Cl₂, 23 °C): δ 51.30 ppm (s); ²⁷Al{¹H} NMR (MHz, CDCl₃, 23 °C):
\[ \delta 58.51 \text{ ppm (br).} \]

\[[\mu-1,3-C_6H_4(PhP=S)C]Sn]_2 (120).\] Toluene (30 mL) was added to a mixture of 19 (1.11 g, 3.0 mmol) and Sn[N(SiMe_3)_2]_2 (1.40 g, 3.2 mmol) at ambient temperature. The orange suspension was then refluxed at 140 °C overnight. After filtration, the residue was then extracted by CH_2Cl_2. After filtration and concentration of the filtrate, 120 was isolated as yellow crystals. Yield: 1.42 g (83%). M.p: 230 °C (dec.). Anal. Calcd for C_{38}H_{28}P_4S_4Sn_2: C, 46.85; H, 2.90. Found: C, 46.79; H, 2.87. \(^1\)H NMR (395.9 MHz, CDCl_3, 23 °C): \(\delta 7.37-7.43\) (m, 8H, Ph and C_6H_4), \(7.47-7.51\) (m, 4H, Ph and C_6H_4), \(7.61-7.73\) ppm (m, 16H, Ph and C_6H_4). \(^{13}\)C\{{^1\text{H}}\} NMR (99.5 MHz, CD_2Cl_2, 21 °C): \(\delta 129.17\) (m, C_{meta} of Ph and C_6H_4), \(130.84\) (d, \(^2J_{C-P}\) = 12.4 Hz, C_6H_4), \(132.26\) (s, C_{para} of Ph), \(137.11\) (d, \(J_{C-P}\) = 80.1 Hz, C_6H_4), \(143.18\) ppm (dd, \(J_{P-C}\) = 75.3 Hz, \(^3J_{P-C}\) = 23.8 Hz, C_{ipso} of Ph). \(^{31}\)P\{{^1\text{H}}\} NMR (161.7 MHz, CDCl_3, 23 °C): \(\delta 54.91\) ppm (\(^2J_{Sn-P}\) = 47.7, 160.4 Hz). \(^{119}\)Sn\{{^1\text{H}}\} NMR (147.6 MHz, CDCl_3, 23 °C): \(\delta 26.28\) ppm (t, \(^2J_{Sn-P}\) = 50.2 Hz).

\[[\mu-1,3-C_6H_4(PhP=S)C]Pb]_2 (121).\] Toluene (30 mL) was added to a mixture of 19 (1.11 g, 3.0 mmol) and Pb[N(SiMe_3)_2]_2 (1.69 g, 3.2 mmol) at ambient temperature. The orange suspension was then refluxed at 140 °C overnight in dark. After filtration, the residue was then extracted by CH_2Cl_2. After filtration and concentration of the filtrate, 121 was isolated as yellow crystals. Yield: 1.05 g (53%). M.p. 197°C (dec.). Elemental analysis (%) calcd for C_{38}H_{28}Pb_2S_4: C, 39.65, H, 2.45. Found: C: 39.47, H: 2.51. \(^1\)H NMR (399.5 MHz, CD_2Cl_2, 23 °C): \(\delta 7.41-7.45\) (m, 8H, Ph & C_6H_4), 7.49 – 7.52 (m, 4H, Ph & C_6H_4), 7.59 – 7.69 (m, 8H, Ph & C_6H_4), 7.74 – 7.79 (m, 8H,
Ph & C₆H₄); ¹³C{¹H} NMR (100.5 MHz, CDCl₃, 23 °C): δ 128.37-128.90 (m, C meta of Ph & C₆H₄), 129.72 (d, J C-P = 12.40 Hz, C₆H₄), 130.09 (m, C ortho of Ph), 131.45 (s, C para of Ph), 132.01 (d, J C-P = 8.59 Hz, C₆H₄), 140.82-145.32 ppm (C ipso of Ph & C₆H₄); ³¹P{¹H} NMR (161.7 MHz, CDCl₂, 23 °C): δ 54.81 ppm (2J Pb-P = 147.4 Hz); ²⁰⁷Pb{¹H} NMR (MHz, CDCl₃, 24 °C): δ -16.13 ppm (s).

[1,3-C₆H₄(PhP=S)₂C(Sn)(Sn=SPh)₂C(AlCl₃)-1,3-C₆H₄] (122). A solution of 120 (0.57 g, 0.6 mmol) in CH₂Cl₂ (30 mL) was added to a suspension of AlCl₃ (0.06 g, 0.5 mmol) in CH₂Cl₂ (10 mL) at ambient temperature. The resulting yellow suspension was stirred overnight to give a clear yellow solution. After filtration, the filtrate was concentrated to give compound 122 as yellow crystals. Yield: 0.31 g (56%). Mp 225 °C (dec.). Anal. Calcd for C₃₈H₂₈AlCl₃P₄S₄Sn₂: C, 41.20; H, 2.55. Found: C, 41.13; H, 2.46. ¹H NMR (395.9 MHz, CDCl₃, 22 °C): δ 7.34–7.94 ppm (m, 28H, Ph and C₆H₄). ¹³C{¹H} NMR (99.5 MHz, CDCl₃, 22 °C): δ 128.6–129.0 (m, Ph and C₆H₄), 130.3–130.4 (m, C ortho of Ph and C₆H₄), 131.68 (s, C para of Ph), 132.24–132.37 (m, C₆H₄), 133.81–134.09 ppm (m, C ipso of Ph). ³¹P{¹H} NMR (160.3 MHz, CDCl₃, 22 °C): δ 55.05 (2J Sn-P = 47.7 Hz, 2J Sn-P = 160.4 Hz, PCP) and 58.45 ppm (2J Sn-P = 164.7 Hz, PC(AlCl₃)P). ¹¹⁹Sn{¹H} NMR (147.6 MHz, CD₂Cl₂, 23 °C): δ 22.15 (t, 2J Sn-P = 48.1 Hz), -160.40 ppm (t, 2J Sn-P = 164.3 Hz).

[1,3-C₆H₄(PhP=S)₂C(Sn)(AlCl₃)] (123). A solution of 120 (0.57 g, 0.6 mmol) in CH₂Cl₂ (30 mL) was added to a suspension of AlCl₃ (0.13 g, 1.0 mmol) in CH₂Cl₂ (10 mL) at ambient temperature. The resulting yellow suspension was stirred overnight to give a clear yellow solution. After filtration, the filtrate was concentrated to give
compound **123** as colorless crystals. Yield: 0.39 g (63%). Mp 257 °C (dec.). Anal. Calcd for C_{19}H_{14}AlCl_{3}P_{2}S_{2}Sn: C, 36.77; H, 2.28. Found: C, 36.64; H, 2.17. \(^1\)H NMR (395.9 MHz, CDCl\(_3\), 23 °C): \(\delta\) 7.51−7.63 (m, 6H, Ph and C\(_6\)H\(_4\)), 7.69−7.76 (m, 4H, Ph and C\(_6\)H\(_4\)), 7.88−7.94 ppm (m, 4H, Ph and C\(_6\)H\(_4\)); \(^{13}\)C\{\(^1\)H\} NMR (99.5 MHz, CDCl\(_3\), 22 °C): \(\delta\) 128.64−129.06 (m, C\(_{\text{meta}}\) of Ph and C\(_6\)H\(_4\)), 132.19−132.41 (m, C\(_{\text{ortho}}\) of Ph and C\(_6\)H\(_4\)), 133.85−133.93 (m, C\(_6\)H\(_4\)), 134.01 (s, C\(_{\text{para}}\) of Ph), 142.46 ppm (dd, \(J_{P-C} = 80.11\) Hz, \(J_{P-C}', = 21.93\) Hz, C\(_{\text{ipso}}\) of Ph); \(^{31}\)P\{\(^1\)H\} NMR (160.3 MHz, CDCl\(_3\), 15 °C): \(\delta\) 58.54 ppm (\(\beta J_{Sn-P} = 164.7\) Hz); \(^{119}\)Sn\{\(^1\)H\} NMR (147.6 MHz, CDCl\(_3\), 23 °C): \(\delta\) −140.25 ppm (\(\beta J_{Sn-P} = 170.8\) Hz).

\[^{1,3-C_6H_4(PhP=S)2CAlMe}_2\] (124). AlMe\(_3\) (0.5 mL, 1.0 mmol, 2 M solution in toluene) was added to a solution of **120** (0.57 g, 0.5 mmol) in CH\(_2\)Cl\(_2\) (30 mL) at 0 °C. The resulting orange solution was stirred overnight. After filtration, the orange filtrate was concentrated to give compound **124** as yellow crystals. Yield: 0.21 g (51%). Mp: 266 °C (dec.). Anal. Calcd for C\(_{40}\)H\(_{34}\)Al\(_2\)P\(_4\)S\(_4\): C, 58.54; H, 4.18. Found: C, 58.21; H, 3.95. \(^1\)H NMR (399.5 MHz, CDCl\(_3\)): \(\delta\) −1.03 (s, 6H, AlMe), 7.45−7.61 (m, 20H, Ph and C\(_6\)H\(_4\)), 7.92−7.97 ppm (m, 8H, Ph and C\(_6\)H\(_4\)); \(^{13}\)C\{\(^1\)H\} NMR (100.5 MHz, CDCl\(_3\), 23 °C): \(\delta\) 1.18 (s, AlMe), 127.90 (t, \(^3J_{P-C} = 11.5\) Hz, C\(_{\text{meta}}\) of Ph), 128.43−128.57 (m, C\(_6\)H\(_4\)), 131.67−133.00 (m, C\(_{\text{ortho}}\) of Ph and C\(_6\)H\(_4\)), 132.21 (s, C\(_{\text{para}}\) of Ph), 133.74 (dd, \(J_{P-C} = 84.8\) Hz, \(^3J_{P-C} = 4.79\) Hz, C\(_6\)H\(_4\)), 143.41 ppm (dd, \(J_{P-C} = 83.87\) Hz, \(^3J_{P-C} = 23.0\) Hz, C\(_{\text{ipso}}\) of Ph); \(^{31}\)P\{\(^1\)H\} NMR (161.7 MHz, CDCl\(_3\)): \(\delta\) 52.43 ppm (s).

\[^{1,3-C_6H_4(PhP=S)2C(Sn)(GaCl_3)}_2\] (125) \[^{1,3-C_6H_4(PhP=S)2C(Sn)(GaCl_3)}\] (126). A solution of **120** (0.57 g, 0.6 mmol) in CH\(_2\)Cl\(_2\) (30 mL) was added to a solution of
GaCl$_3$ (0.18 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 mL) at ambient temperature. The resulting yellow suspension was stirred overnight to give a white suspension. After filtration, the filtrate was concentrated to give compound 125 and 126 as colorless co-crystals. Yield: 0.53 g (71%). Mp 256 °C (dec.). Anal. Calcd for C$_{76}$H$_{56}$Cl$_2$Ga$_4$P$_8$S$_8$Sn$_4$: C, 34.41; H, 2.13. Found: C, 34.24; H, 2.10. $^1$H NMR (399.5 MHz, CDCl$_3$, 23 °C): $\delta$ 7.42–7.54 (m, 6H, Ph and C$_6$H$_4$), 7.60–7.69 (m, 4H, Ph and C$_6$H$_4$), 7.78–7.84 ppm (m, 4H, Ph and C$_6$H$_4$); $^{13}$C{$^1$H} NMR (99.5 MHz, CDCl$_3$, 23 °C): $\delta$ 128.90-129.42 (m, C$_{\text{meta}}$ of Ph and C$_6$H$_4$), 132.35-132.57 (m, C$_{\text{ortho}}$ of Ph), 134.40 (s, C$_{\text{para}}$ of Ph), 142.31 ppm (dd, $J_{P-C}$ = 96.80 Hz, $J_{P-C'}$ = 16.21 Hz, C$_{\text{ipso}}$ of Ph); $^{31}$P{$^1$H} NMR (160.3 MHz, CDCl$_3$, 24 °C): $\delta$ 58.27 ppm ($^2J_{\text{Sn-P}}$ = 164.7 Hz); $^{31}$P CPMAS (161.73 MHz, spinning speed = 10 kHz): $\delta$ 55.97 (s, 126), 57.25 (s, 125), 59.82 (s, 126); $^{119}$Sn{$^1$H} NMR (147.6 MHz, CDCl$_3$, 24 °C): $\delta$ $-157.83$ ppm (t, $^2J_{\text{Sn-P}}$ = 176.5 Hz).

$[1,3$-C$_6$H$_4$(PhP=S)$_2$CGaCl$_2$ (127). A solution of 120 (0.57 g, 0.6 mmol) in CH$_2$Cl$_2$ (30 mL) was added to a solution of GaCl$_3$ (0.18 g, 0.5 mmol) in CH$_2$Cl$_2$ (10 mL) at ambient temperature. The resulting yellow suspension was stirred overnight to give yellow solution. After filtration, the filtrate was concentrated to give compound 127. Yield: 0.02 g (7%). Mp 261 °C (dec.). Anal. Calcd for C$_{38}$H$_{28}$Cl$_2$Ga$_2$P$_4$S$_4$: C, 48.19; H, 2.98. Found: C, 47.83; H, 2.94. $^1$H NMR (399.5 MHz, CDCl$_3$, 23 °C): $\delta$ 7.39–7.47 (m, 4H, Ph and C$_6$H$_4$), 7.54–7.74 (m, 16H, Ph and C$_6$H$_4$), 7.82–7.88 ppm (m, 8H, Ph and C$_6$H$_4$); $^{13}$C{$^1$H} NMR (99.5 MHz, CDCl$_3$, 23 °C): $\delta$ 128.90–129.41 (m, C$_{\text{meta}}$ of Ph and C$_6$H$_4$), 132.35–132.53 (m, C$_{\text{ortho}}$ of Ph and C$_6$H$_4$), 134.13–134.21 (m, C$_6$H$_4$),
134.40 (s, C<sub>para</sub> of Ph), 140.23 ppm (dd, <em>J</em><sub>P−C</sub> = 37.38 Hz, <em>J</em><sub>P−C</sub>′ = 11.50 Hz, C<sub>ipso</sub> of Ph); <sup>31</sup>P{<sup>1</sup>H} NMR (160.3 MHz, CDCl<sub>3</sub>, 24 °C): δ 55.03 ppm (2<sup>1</sup>J<sub>Sn−P</sub> = 17.3, 82.4 Hz).

[(1,3-C<sub>6</sub>H<sub>4</sub>(PhP=S))<sub>2</sub>C(SnCl)(GeCl<sub>3</sub>)]<sub>2</sub> (128). GeCl<sub>4</sub> (1.0 mL, 1.0 mmol, 1.0 M in toluene) was added to a solution of 120 (0.57 g, 0.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at ambient temperature. The resulting white suspension was stirred overnight. After filtration, the filtrate was concentrated to give compound 128 as colorless crystals. The white solid was pure compound 128 confirmed by NMR spectroscopy. Yield: 0.54 g (69%). Mp 190 °C (dec.). Anal. Calcd for C<sub>38</sub>H<sub>28</sub>Cl<sub>8</sub>Ge<sub>2</sub>P<sub>4</sub>S<sub>4</sub>Sn<sub>2</sub>: C, 32.53; H, 2.01. Found: C, 32.17; H, 2.09. <sup>1</sup>H NMR (395.9 MHz, THF-d<sub>8</sub>, 23 °C): δ 7.41−7.47 (m, 4H, Ph and C<sub>6</sub>H<sub>4</sub>), 7.51−7.62 (m, 16H, Ph and C<sub>6</sub>H<sub>4</sub>), 8.01−8.07 ppm (m, 8H, Ph and C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (99.5 MHz, THF-d<sub>8</sub>, 22 °C): δ 128.91 (t, <em>J</em><sub>P−C</sub> = 11.5 Hz, C<sub>meta</sub> of Ph), 129.19-129.33 (m, C<sub>6</sub>H<sub>4</sub>), 132.39-132.87 (m, C<sub>ortho</sub> of Ph and C<sub>6</sub>H<sub>4</sub>), 133.17 (s, C<sub>para</sub> of Ph), 142.13 ppm (t, <em>J</em><sub>P−C</sub> = 54.6 Hz, C<sub>ipso</sub> of Ph); <sup>31</sup>P{<sup>1</sup>H} NMR (160.3 MHz, THF-d<sub>8</sub>, 25 °C): δ 46.44 ppm (s); <sup>119</sup>Sn{<sup>1</sup>H} NMR (147.6 MHz, THF-d<sub>8</sub>, 24 °C): δ 75.30 ppm (s).

[1,3-C<sub>6</sub>H<sub>4</sub>(PhP=S)<sub>2</sub>C{((SnEt<sub>2</sub>)(µ-SZn))}<sub>2</sub>] (129). ZnEt<sub>2</sub> (1.0 mL, 1.0 mmol, 1.0 M in hexane) was added to a suspension of 120 (0.57 g, 0.6 mmol) in toluene (20 mL). The resulting mixture was refluxed at 140 °C overnight to give orange solution. After filtration, the filtrate was concentrated to give compound 129 as colorless crystals. Yield: 0.10 g (16%). Mp 284 °C (dec.). Anal. Calcd for C<sub>46</sub>H<sub>48</sub>P<sub>4</sub>S<sub>6</sub>Sn<sub>2</sub>Zn<sub>2</sub>: C, 42.98; H, 3.76. Found: C, 43.49; H, 4.03. <sup>1</sup>H NMR (399.5 MHz, CDCl<sub>3</sub>, 23 °C): δ 1.05 (t, 12H, <em>J</em><sub>H−H</sub> = 7.78 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.17-1.32 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 7.30-7.40 (m, 12H, Ph
and C₆H₄), 7.48-7.52 (m, 4H, Ph and C₆H₄), 7.77-7.84 ppm (m, 12H, Ph and C₆H₄).

¹³C{¹H} NMR (99.5 MHz, CDCl₃, 24 °C): δ 9.31 (t, ³J_P-C = 3.7 Hz, SnCH₂CH₃),
10.60 (s, SnCH₂CH₃), 128.16 (t, ³J_P-C = 6.9 Hz, Ph), 128.63-128.97 (m, C₆H₄), 130.28 (t, ²J_P-C = 5.1 Hz, Ph), 130.69 (s, C₆H₄), 131.34-131.89 (m, C₆H₄), 140.68 (dd, ²J_P-C = 134.2 Hz, ³J_P-C = 4.8 Hz, C₆H₄), 141.95 ppm (dd, ²J_P-C = 75.4 Hz, ³J_P-C = 7.7 Hz, C ipso of Ph);

³¹P{¹H} NMR (160.3 MHz, CDCl₃, 25 °C): δ 51.65 ppm (²J_Sn-P = 46.3 Hz);

¹¹⁹Sn{¹H} NMR (147.6 MHz, CDCl₃, 25 °C): δ 53.11 ppm (²J_Sn-P = 41.1 Hz).

[{{µ-1,3-C₆H₄(PhP=S)₂CS}Zn}₂ (130). ZnMe₂ (1.0 mL, 1.0 mmol, 1.0 M in hexane)
was added to a solution of 19 (0.37 g, 1.0 mmol) in toluene (15 mL) at ambient
temperature. The yellow solution was then heated at 110 °C overnight without stirring.

130 was obtained as yellow crystals during the reaction. Yield: 0.14 g (25%). M.p.
332°C (dec.). Elemental analysis (%) calcd for C₃₈H₂₈P₄S₆Zn₂: C, 48.96, H, 3.03.
Found: C, 49.47, H: 3.19. ³¹P CPMAS (161.73 MHz, spinning speed = 10 kHz): δ
64.01 (s), 66.41 ppm (s); ¹³C CPMAS (100.46 MHz, spinning speed = 10 kHz): δ 29.87
(s, PCP), 124.13-146.69 ppm (m, Ph).

[{{µ-1,3-C₆H₄(PhP=S)₂CS}Zn}₂ (131). Toluene (20 mL) was
added to a mixture of 130 (0.56 g, 0.5 mmol) and Sn[N(SiMe₃)₂]₂ (0.48 g, 1.1 mmol).
The resulting orange suspension was refluxed at 140 °C overnight to give orange red
suspension. After filtration, the filtrate was concentrated to give compound 131 as
colorless crystal. Yield: 0.17 g (15%). Mp 277 °C (dec.). Anal. Calcd for
C₆₂H₁₀₀N₄P₄S₈Si₈Sn₄Zn₂: C, 35.25; H, 4.77. Found: C, 35.61; H, 4.67. ¹H NMR
(399.5 MHz, CDCl₃, 24 °C): δ −0.20 (s, SiMe₃), −0.19 (s, SiMe₃), 0.05 (s, SiMe₃),

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0.16, (s, SiMe₃), 7.27–7.40 (m, 12H, Ph and C₆H₄), 7.50–7.57 (m, 4H, Ph and C₆H₄), 7.64–7.70 (m, 6H, Ph and C₆H₄), 7.80–7.93 ppm (m, 6H, Ph and C₆H₄). $^{13}$C{¹H} NMR (100.5 MHz, CDCl₃, 23 °C): δ 0.15 (s, SiMe₃), 5.66 (s, SiMe₃), 6.43 (s, SiMe₃), 9.98 (s, SiMe₃), 127.54–128.48 (m, Cmeta of Ph and C₆H₄), 129.15–129.67 (m, Cortho of Ph and C₆H₄), 130.49–131.20 (m, Cpara of Ph and C₆H₄). $^{31}$P{¹H} NMR (161.7 MHz, CDCl₃, 24 °C): δ 49.93, 50.37 ppm (ABq, $J_{AB} = 34.68$ Hz); $^{119}$Sn{¹H} NMR (147.6 MHz, CDCl₃, 24 °C): δ 24.86, 25.97 ppm (ABq, $J_{AB} = 27.24$ Hz).

**Crystal Structure Determinations of Compounds 118 to 131.** X-ray data collection and structural refinement: The crystal data were collected on a Bruker APEX II diffractometer. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full matrix least squares methods on $F^2$. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to reside in their respective parents atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations.
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Chapter 3 Synthesis and Reactivity of A Base-Stabilized 2-Silaallene

3.1 Introduction

In the past two decades, the concepts of thermodynamic and/or kinetic stabilization have been applied successfully in the isolation of stable multiple bonded group 14 compounds. It was found that the M=C (M = Si, Ge, Sn) bond is unstable, and it can undergo oligomerization easily. However, stable silenes (>Si=C<) (Scheme 3.1),1 germines (>Ge=C<)2 (Scheme 3.2) and stannenes (>Sn=C<)3 (Scheme 3.3) were isolated by incorporating sterically hindered substituents at both carbon and heavier group 14 elements. They have been the focus of several reviews in the past 20 years.4

Scheme 3.1

\[
\begin{align*}
\text{(Mes}_{3}\text{Si})_{3}\text{Si} & \text{C} & \text{R} & \xrightarrow{hv} & \text{Mes}_{3}\text{Si} & \text{Si} & \text{C} & \text{SiMe}_{3} & \text{R} \\
\text{Mes}_{3}\text{Si} & \text{Ge} & \text{C} & \text{SiMe}_{2} & \xrightarrow{\text{NEt}_{2} \text{Li}} & \text{Mes}_{3}\text{Si} & \text{Si} & \text{C} & \text{SiMe}_{2} & \text{Br} & \text{Li} & \xrightarrow{-\text{LiBr}} & \text{Mes}_{3}\text{Si} & \text{Si} & \text{C} & \text{SiMe}_{2} & \text{Ph} \\
\end{align*}
\]

Scheme 3.2

\[
\begin{align*}
\text{Mes}_{2}\text{Ge} & \text{C} & \text{F} & \xrightarrow{\text{BuLi} \text{Et}_{2} \text{O}} & \text{Mes}_{2}\text{Ge} & \text{C} & \text{R} & \xrightarrow{110^\circ \text{C} \text{/19h}} & \text{Mes}_{2}\text{Ge} & \text{C} & \text{R} \\
\text{Mes} & = & \text{2,4,6-tri-methylphenyl} & \text{CR}_{2} = & \text{structure} \\
\end{align*}
\]
Moreover, 1-silaalenes and 1-germaalenes of composition $R_2E=C=CR’_2$ (R, R’ = supporting ligand, E = Si, Ge), which comprise an E=C double bond, have also been investigated. The first stable 1-silaallene 140 is reported by West’s group.\textsuperscript{5} Compound 140 was formed by an intramolecular addition of a Li-C bond to a C=C triple bond of compound 139 followed by an elimination of lithium halide (Scheme 3.4).

\textbf{Scheme 3.3}

\textbf{Scheme 3.4}

Similar reactions were carried out to give compound 141 (Scheme 3.5).\textsuperscript{6}
The first stable 1-germaallene 143 was synthesized by the detelluration reaction of 142 or by the dechlorination of 144 (Scheme 3.6).\textsuperscript{7}

Other stable 1-metallaallene compounds have been synthesized by a slightly different route. Compound 145 underwent an intermolecular addition with lithium reagents followed by an elimination of lithium halide to give compound 146 (Scheme 3.7).\textsuperscript{8}

In contrast, heavier allene analogues with a >C=M=C< (M = Si, Ge, Sn) skeleton are rare due to the presence of two reactive E=C double bonds.\textsuperscript{9} Recently, the novel germanium and tin bis(methanediide) complexes [(Ph$_2$P=S)$_2$C=M=C(Ph$_2$P=S)$_2$] (M =
Ge, Sn) which are considered as base-stabilized 2-metalaallenes have been reported.

Compound 3 reacted with two equivalents of MeLi in toluene, followed by the addition of 0.5 equivalents of GeCl₄ gave compound 147. In contrast, the tin bis(methanediide) complex 148 was synthesized by the reaction of 32 with one equivalent of SnCl₄ (Scheme 3.8).

In this chapter, we describes: (1) the synthesis of a base-stabilized 2-silaallene derivative; (2) its reactivity toward unsaturated substrates.

3.2 Results and Discussion

3.2.1 Synthesis of the Base Stabilized 2-Silaallene Derivative

The reaction of 3 with two equivalents of MeLi in toluene followed by addition of 0.5 equivalent of SiCl₄ afforded [(PPh₂S)₂CSiC(PPh₂S)₂] (149) (71%, Scheme 3.9).

Compound 149 was isolated as a colorless crystalline solid which is soluble in CH₂Cl₂, THF and DME only. It has been characterized by NMR spectroscopy...
The $^1$H and $^{13}$C NMR spectra display resonances for the phenyl protons. The $^{13}$C spectrum shows a triplet at $\delta$ 42.3 ppm ($J_{P-C} = 67.1$ Hz) for the C$_{\text{methanediide}}$ atoms. The result is contrast to the heavier analogue [(PPh$_2$S)$_2$C=M=C(PPh$_2$S)$_2$] ($M = \text{Ge, Sn}$) in which there is no $^{13}$C NMR signal for the C$_{\text{methanediide}}$ atom.$^{10-11}$ The $^{31}$P NMR spectrum at room temperature shows one signal at $\delta$ 27.8 ppm, which is inconsistent with the solid-state structure. Hence, the $^{31}$P NMR spectroscopy was performed at $-100^\circ\text{C}$, which shows two singlets at $\delta$ 20.6 and 29.4 ppm for two non-equivalent P nuclei. The $^{31}$P NMR signal of 149 is comparable with that of [(PPh$_2$S)$_2$C=Sn=C(PPh$_2$S)$_2$] ($\delta$ 28.1 ppm) and [(PPh$_2$S)$_2$C=Ge=C(PPh$_2$S)$_2$] ($\delta$ 33.7 ppm). The $^{29}$Si NMR spectrum shows a quintet at $\delta$ –28.87 ppm ($J_{\text{Si-P}} = 7.6$ Hz), which shows an upfield shift compared with that of 1-silaallenenes ($\delta$ 13.1 – 58.6 ppm ).$^{5-8}$ The results indicate that the Si-C bonds in compound 149 do not have multiple bond character.

![ORTEP drawing of compound 149](image)

**Figure 3.1** ORTEP drawing of compound 149 (50% thermal ellipsoids). One of two independent molecules in the asymmetric unit is shown. Disordered 149 atoms, hydrogen
atoms and DME molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)-C(1) 1.810(8), Si(1)-C(2) 1.810(9), Si(1)-S(1) 2.204(8), Si(1)-S(3) 2.178(8), C(1)-P(1) 1.726(11), C(1)-P(2) 1.750(8), P(1)-S(1) 2.076(10), P(2)-S(2) 1.972(5), C(2)-P(3) 1.723(9), C(2)-P(4) 1.754(9), P(3)-S(3) 2.085(8), P(4)-S(4) 1.967(5), C(1)-Si(1)-C(2) 134.9(8), C(1)-Si(1)-S(1) 89.0(5), C(1)-Si(1)-S(3) 117.4(7), C(2)-Si(1)-S(1) 115.3(7), C(2)-Si(1)-S(3) 89.6(4), P(1)-C(1)-P(2) 123.6(6), P(1)-C(1)-Si(1) 98.1(5), P(2)-C(1)-Si(1) 127.8(7), P(3)-C(2)-P(4) 121.8(6), P(3)-C(2)-Si(1) 101.7(5), P(4)-C(2)-Si(1) 137.6(6).

Compound 149 has been characterized by X-ray crystallography (Figure 3.1). In the asymmetric unit, there are two independent molecules with slightly different bond lengths and angles. Only one of them is discussed here for clarity. It consists of two bidentate bis(thiophosphinoyl)methanediide ligands bound to the silicon center in a spirocyclic fashion. One of the thiophosphinoyl groups of the ligand remains uncoordinated. The C_{methanediide} atoms and Si(1) atom adopt a trigonal planar geometry (sum of bond angles: 357.1, 359.5°) and Si(1) atom adopt a trigonal planar and tetrahedral geometry, respectively. The C(1)-Si(1) and C(2)-Si(1) bond lengths (1.810 Å) are comparable with reported C-Si single bond lengths (1.87-1.91 Å). The results indicate that compound 149 has a ylidic C—Si^{2+}—C skeleton, which is also confirmed by theoretical studies. The P-C bonds (1.726(11)-1.754(9) Å) are shortened and P-S bonds (1.967(5)-2.085(8) Å) are lengthened comparable compared with those in [CH_2(PPh_2=S)_2] (C-P: 1.827(3), 1.831(3) Å; P-S: 1.941(1), 1.948(1) Å).

3.2.2 Reactivity of the Base Stabilized 2-Silaallene Derivative toward N,N'-diisopropylcarbodiimide

To further investigate the electronic structure of compound 149, several reactions were taken (Table 3.1). However, most of the reaction only gave the free ligand [CH_2(Ph_2P=S)_2] (3). Till now, only one reaction with ^{i}PrN=C=N^{i}Pr gave desirable
result.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Reaction Condition</th>
<th>Reaction Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>DCM</td>
<td>149 and 3 as major product.</td>
</tr>
<tr>
<td></td>
<td>THF, reflux</td>
<td>149 and 3 as major product. Failing to isolate.</td>
</tr>
<tr>
<td>Se</td>
<td>DCM</td>
<td>149 and 3 only.</td>
</tr>
<tr>
<td>B(C₆F₅)₃</td>
<td>Toluene, reflux</td>
<td>149 and 3 only.</td>
</tr>
<tr>
<td>TMAO</td>
<td>DCM</td>
<td>3 only.</td>
</tr>
<tr>
<td>S, N^\cdot\cdot\cdot\cdot^\cdot\cdot\cdotN</td>
<td>THF</td>
<td>149 and 3 only</td>
</tr>
<tr>
<td>Pd(PPh₃)₄</td>
<td>THF</td>
<td>149 and 3 as major product.</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>DCM</td>
<td>149 and 3 as major product.</td>
</tr>
<tr>
<td>GaCl₃</td>
<td>DCM</td>
<td>Have reaction, fail to isolate.</td>
</tr>
<tr>
<td>SnCl₂</td>
<td>THF</td>
<td>149 and 3</td>
</tr>
<tr>
<td>GeCl₄</td>
<td>DCM</td>
<td>149 and 3, have other product. Failing to isolate.</td>
</tr>
<tr>
<td>SnCl₄</td>
<td>DCM</td>
<td>3, have other product. Failing to isolate.</td>
</tr>
<tr>
<td>AlMe₃</td>
<td>DCM</td>
<td>149 and 3, have other product. Failing to isolate.</td>
</tr>
<tr>
<td>ZnEt₂</td>
<td>DCM</td>
<td>149 and 3 only.</td>
</tr>
<tr>
<td></td>
<td>Toluene, reflux</td>
<td>149 and more 3 only.</td>
</tr>
<tr>
<td>Ad−N^\cdot\cdot\cdot\cdot^\cdot\cdot\cdotC^-</td>
<td>DCM</td>
<td>149 and 3 only.</td>
</tr>
<tr>
<td></td>
<td>toluene, reflux</td>
<td>149 and 3 only.</td>
</tr>
<tr>
<td>N^\cdot\cdot\cdot\cdot^\cdot\cdot\cdotO</td>
<td>DCM</td>
<td>149 and 3 only.</td>
</tr>
<tr>
<td></td>
<td>toluene, reflux</td>
<td>149 and 3 only.</td>
</tr>
<tr>
<td>N^\cdot\cdot\cdot\cdot^\cdot\cdot\cdotS</td>
<td>DCM</td>
<td>149 and 3 only.</td>
</tr>
<tr>
<td></td>
<td>toluene, reflux</td>
<td>149 and 3 only.</td>
</tr>
<tr>
<td>iPrN=C=NiPr</td>
<td>DCM</td>
<td>150 and 149.</td>
</tr>
<tr>
<td></td>
<td>toluene, reflux</td>
<td>150.</td>
</tr>
</tbody>
</table>

The reaction of 149 with excess iPrN=C=NiPr (two equivalents) in refluxing toluene to give the base-stabilized silene 150 (23%, Scheme 3.10). The reaction appears to proceed through an insertion reaction of the C—Si²⁺ bond with the N=C
bond of $^1\text{PrN}=\text{C}^=\text{N}^\text{Pr}$ to form intermediate $\text{J}$. The $\text{C}_{\text{methanide}}$-$\text{Si}$ bond is then cleaved and the $\text{C}^=\text{N}$ bond attacks on the silicon center to form $\text{150}$ (Scheme 3.11).

Scheme 3.10

Scheme 3.11

Compound $\text{150}$ was isolated as a colorless crystalline solid in 23% yield, which is soluble in CH$_2$Cl$_2$ and THF. It has been characterized by NMR spectroscopy. The $^1\text{H}$ and $^{13}\text{C}$ NMR spectra display resonances for the iso-propyl and phenyl protons. The $^{13}\text{C}$ NMR spectrum also shows a triplet at $\delta$ 173.6 ppm for the NCN atom, but no signals were observed for the PCP atoms. The $^{31}\text{P}$ NMR spectrum at room temperature shows one singlet at $\delta$ 40.5 and 27.0 ppm for the $PC(C)P$ and $PC(Si)P$ atoms, respectively. In addition, the $^{31}\text{P}$ NMR spectrum at $-100^\circ\text{C}$ displays a sharp singlet at $\delta$ 39.8 ppm [$PC(C)P$] and a broad signal at $\delta$ 26.6 ppm [$PC(Si)P$]. The results indicate that the thiophosphinoyl substituents at the $\text{C}_{\text{methanide}}$ atom are fluxional in solution. The $^{29}\text{Si}$ NMR shows a triplet at $\delta$ $-30.65$ ppm ($J_{\text{Si-P}} = 7.5$ Hz).
Figure 3.2 ORTEP drawing of compound 150 (50% thermal ellipsoids). Disordered ‘Pr and Ph substituents, CH$_2$Cl$_2$ molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (Å): Si(1)-S(1) 2.1961(13), Si(1)-C(1) 1.788(4), Si(1)-N(1) 1.735(3), Si(1)-N(2) 1.752(3), C(1)-P(1) 1.725(4), C(1)-P(2) 1.751(4), P(1)-S(1) 2.0722(13), P(2)-S(2) 1.9612(15), C(32)-N(2) 1.392(4), C(32)-N(1) 1.400(4), C(32)-C(33) 1.388(5), C(33)-P(3) 1.799(4), C(33)-P(4) 1.818(4), P(3)-S(3) 1.9674(13), P(4)-S(4) 1.9643(17), C(1)-Si(1)-S(1) 89.91(13), C(1)-Si(1)-N(1) 130.64(16), C(1)-Si(1)-N(2) 134.44(16), N(1)-Si(1)-N(2) 76.23(14), P(1)-C(1)-P(2) 137.2(2), P(1)-C(1)-Si(1) 97.60(18), P(2)-C(1)-Si(1) 125.0(2), P(3)-C(33)-C(32) 123.2(3), P(4)-C(33)-C(32) 119.4(3), P(3)-C(33)-P(4) 117.14(19).

The results of the X-ray crystallographic data confirm that compound 150 is a thiophosphinoyl-stabilized silene (Figure 3.2). The C(1)-Si(1) bond (1.788(4) Å) is comparable with the base-stabilized silenes such as [(2,6-(CH$_2$NMe$_2$)$_2$C$_6$H$_3$)PhSi=C(SiMe$_3$)$_2$] (1.744(2) Å)$^{14}$ and (Me$_2$EtN)Me$_2$Si=C(SiMe$_2$Ph)$_2$ (1.761(4) Å)$^{15}$. It is intermediate between the Si-C single (1.87 Å) and double (1.70 Å) bond lengths.$^{16}$ The results indicate that the C(1)-Si(1) bond has some double bond character. Thus, compound 150 could be in between the resonance forms [(PPh$_2$S)$_2$C=Si(N'$^t$Bu)$_2$C=C(PPh$_2$S)$_2$]$_2$ and [(PPh$_2$S)$_2$C—Si$(^t$N'$^t$Bu)$_2$C=C(PPh$_2$S)$_2$]$_2$. The Si(1)-N bonds are similar to the Si-N$_{amide}$ bonds in [SiCl$_2$[N('Bu)C(Ph)C(Ph)N('Bu)]] (average 1.701 Å)$^{17}$ The C(32)-C(33) bond (1.388(5) Å) is a typical C=C double bond. The C(33)-P bonds are
lengthened and the P(4)-S(4) and P(3)-S(3) are shortened compared with the C(1)-P, P(1)-S(1) and P(2)-S(2) bonds.

3.3 Conclusion

In summary, a base-stabilized 2-silaallene ylide (PPh₂S)₂CSiC(PPh₂S)₂ (149) was synthesized by a simple procedure. X-ray structural, spectroscopic and theoretical studies show conclusively that compound 149 has a C⁻—Si²⁺—C⁻ ylidic skeleton. The reaction of 149 with N,N’-diisopropylcarbodiimide gave compound 150 further verify the electronic structure of 138.

3.4 Experimental Section

All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. CH₂Cl₂ was dried over and distilled over CaH₂ prior to use. Other solvents were dried over and distilled over Na/K alloy prior to use. The ¹H, ¹³C, ³¹P and ²⁹Si NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to SiMe₄ for ¹H, ¹³C and ²⁹Si, and 85% H₃PO₄ for ³¹P. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

[(PPh₂S)₂CSiC(PPh₂S)₂] (149). Methyllithium (1.3 mL, 1.6 M in Et₂O, 2.1 mmol) was added to a solution of 3 (0.45 g, 1.0 mmol) in Et₂O (10 mL) at -78 °C. The resulting mixture was warmed to room temperature and stirred for 3 h. SiCl₄ (0.5 mL, 1.0 M in toluene, 0.5 mmol) was added dropwise to the reaction mixture at -78 °C. The resulting yellow solution was warmed to room temperature and stirred overnight
to form white suspension. Volatiles in the reaction mixture were removed under reduced pressure and the residue was extracted with DME. After filtration and concentration of the filtrate, 149 was afforded as colorless crystals. Yield: 0.35 g (71 %). Mp: 245 °C. Elemental analysis calcd for C_{52}H_{45}OP_4S_4Si: C, 64.64; H, 4.69. Found: C, 64.03; H, 4.91. ¹H NMR (399.5 MHz, C₆D₆): δ 6.85 – 6.90 (m, 16H, Ph), 6.95 – 6.98 (m, 8H, Ph), 7.94-7.99 ppm (m, 16H, Ph). ¹³C NMR (100.5 MHz, C₆D₆): δ 42.33 (t, J_P-C = 67.1 Hz, PCP); 128.16 (s, C_m of Ph), 131.08 (s, C_p of Ph), 132.98 (d, J_P-C = 11.5 Hz, C_o of Ph), 135.2 (d, J_P-C = 85.3 Hz, C_ipso of Ph). ³¹P NMR (161.7 MHz, C₆D₆): δ 27.83 ppm.

[(PPh₂S)₂C≡Si(NiPr₂)₂C≡(PPh₂S)₂]₂ (150). Toluene (15 mL) was added to a mixture of iPrN=C=NiPr (0.13 g, 1.0 mmol) and 149 (0.48 g, 0.5 mmol) at room temperature. The resulting mixture was refluxed at 140 °C overnight to form yellow solution. Volatiles in the reaction mixture were removed under reduced pressure and the residue was extracted with DCM/Et₂O (1/1). After filtration and concentration of the filtrate, 150 was obtained as colorless crystals. Yield: 0.14 g (23 %). Mp: 229 °C (dec.). Elemental analysis (%) calcd for C_{59}H_{58}Cl₄N₂P₂S₄Si: C, 58.22; H, 4.80; N, 2.30; S, 10.54; Found: C, 59.08; H, 5.05; N, 2.55; S, 11.67. ¹H NMR (399.5 MHz, CDCl₃): δ 1.06 (d, 12H, ³J_H-H = 6.0 Hz, CH(CH₃)₂), 5.14 (sept, 2H, ³J_H-H = 6.4 Hz, CH(CH₃)₂), 7.29 – 7.39 (m, 20H, Ph), 7.48 – 7.51 (m, 4H, Ph), 7.61 – 7.66 (m, 8H, Ph), 8.03 – 8.08 ppm(m, 8H, Ph). ¹³C{¹H} NMR (100.5 MHz, CDCl₃): δ 23.44 (s, CH(CH₃)₂), 47.52 (s, CH(CH₃)₂), 127.61 (d, ³J_P-C = 6.7 Hz, C_m of Ph), 128.47 (d,
\[ ^3J_{P-C} = 13.3 \text{ Hz, } C_{\text{meta}} \text{ of Ph}, \]

130.51 (s, C_{\text{para}} \text{ of Ph}), 131.91 (s, C_{\text{para}} \text{ of Ph}), 132.36-133.29 (m, C_{\text{ortho}} \text{ and } C_{\text{ipso}} \text{ of Ph}), 173.56 (t, ^2J_{P-C} = 4.29 \text{ Hz, } C=\text{CP}_2). \]

\[ ^{31}P\{^1H\} \]

NMR (161.7 MHz, CDCl\textsubscript{3}): \( \delta \) 26.96 (s, PC(Si)P), 40.45 ppm (s, PC(C)P); \[ ^{29}Si\{^1H\} \]

NMR (79.4 MHz, CDCl\textsubscript{3}): \( \delta \) –30.65 ppm (t, \( J_{Si-P} = 7.5 \text{ Hz} \)).

**Crystal Structure Determinations of Compounds 149 and 150.** X-ray data collection and structural refinement: The crystal data were collected on a Bruker APEX II diffractometer. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full matrix least squares methods on \( F^2 \).\textsuperscript{18}

All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to reside in their respective parents; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations.
References for Chapter 3


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Summary

The syntheses of metal bis(thiophosphinoyl) and 1,3-benzobis(thiophosphinoyl)methanediide complexes are reported.

The reaction of bis(thiophosphinoyl)methane \([\text{CH}_2(\text{Ph}_2\text{P}=\text{S})_2]\) (3) with 1 equivalent of KO'Bu and 1.2 equivalents of \(n\text{BuLi}\), followed by the hydrolysis to form the 1,3-benzobis(thiophosphinoyl)methane \([1,3-\text{C}_6\text{H}_4(\text{PhP}=\text{S})_2\text{CH}_2]\) (19). Metal 1,3-benzobis-(thiophosphinoyl)methanediide complexes \([\{\mu-1,3-\text{C}_6\text{H}_4(\text{PhP}=\text{S})_2\text{C}\}M\}_2\) \([M = \text{Mg} (113), \text{AlMe} (114), \text{Sn} (115), \text{Pb} (116)]\), which have a 1,3-dimetallacyclobutane structure, were then synthesized by the reaction of \([1,3-\text{C}_6\text{H}_4(\text{PhP}=\text{S})_2\text{CH}_2]\) (19) with Mg(\(n\text{Bu})_2\), AlMe\(_3\), Sn[N(SiMe\(_3\))]\(_2\) or Pb[N(SiMe\(_3\))]\(_2\), respectively. Moreover, the reactivity of the tin(II) 1,3-benzobis(thiophosphinoyl)methanediide complex \([\{\mu-1,3-\text{C}_6\text{H}_4(\text{PhP}=\text{S})_2\text{C}\}\text{Sn}\}_2\) (115) toward Lewis acids is reported. The reactivity of 115 toward Lewis acids shows that the \(\text{C}_{\text{methanediide}}-\text{Sn}\) bonds in 115 are polar and the \(\text{C}_{\text{methanediide}}\) atom is nucleophilic. Hence, the lone pair of electrons on the tin atoms is less favorable for bond formation. These results indicate that compound 115 can activate small molecules via coordination or insertion reaction with small molecules. The physical and chemical properties (e.g., geometry, electron density, bond length, etc.) of the bound molecules will be different from those of free one.

The synthesis of a base-stabilized 2-silaallene derivative \([(\text{PPh}_2\text{S})_2\text{CSiC}(\text{PPh}_2\text{S})_2]\) (149) and its reactivity toward unsaturated substrates are also reported. The results show that \([(\text{PPh}_2\text{S})_2\text{CSiC}(\text{PPh}_2\text{S})_2]\) has a \(\text{C}^-—\text{Si}^{2+}—\text{C}^-\) ylidic
skeleton. The reactivity of 149 with \textit{PrN=C=NPr} also shows that compound 149 has potential application to activate unsaturated compounds.
Appendix

Table 1. Crystallographic Data for Compounds 16-20

Table 2. Crystallographic Data for Compounds 113-117

Table 3. Crystallographic Data for Compounds 118-123

Table 4. Crystallographic Data for Compounds 124-126, 144-145
Table 1. Crystallographic Data for Compounds 16-20

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<th>19</th>
<th>20</th>
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<tbody>
<tr>
<td>formula</td>
<td>C₃₁H₃₁LiO₂P₂S₂</td>
<td>C₃₁H₃₁KP₂S₂</td>
<td>C₃₁H₃₁KO₂P₂S₂</td>
<td>C₃₁H₃₁P₂S₂</td>
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<td>0.40 x 0.30 x 0.20</td>
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<td>$\text{C}<em>{39}\text{H}</em>{38}\text{Al}_2\text{P}_4\text{S}_4$</td>
<td>$\text{C}<em>{60}\text{H}</em>{50}\text{Cl}_4\text{P}_4\text{S}_4\text{Sn}_2$</td>
<td>$\text{C}<em>{60}\text{H}</em>{50}\text{Cl}_4\text{P}_4\text{S}_4\text{Sn}_2$</td>
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<td>Triclinic</td>
<td>Monoclinic</td>
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<td>$Pbca$</td>
<td>$P$-1</td>
<td>$P2(1)/c$</td>
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### Table 3. Crystallographic Data for Compounds 118-123

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<td>P2(1)/c</td>
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<td>21.070(2)</td>
<td>38.866(3)</td>
<td>22.8318(8)</td>
</tr>
<tr>
<td><strong>α / deg</strong></td>
<td>78.5380(10)</td>
<td>67.4850(10)</td>
<td>90</td>
<td>90.112(4)</td>
<td>90</td>
</tr>
<tr>
<td><strong>β / deg</strong></td>
<td>69.7290(10)</td>
<td>89.613(2)</td>
<td>101.021(4)</td>
<td>90.192(4)</td>
<td>111.954(2)</td>
</tr>
<tr>
<td><strong>γ / deg</strong></td>
<td>65.4820(10)</td>
<td>77.786(2)</td>
<td>90</td>
<td>105.038(3)</td>
<td>90</td>
</tr>
<tr>
<td><strong>V / Å³</strong></td>
<td>1244.91(4)</td>
<td>1231.99(6)</td>
<td>4987.5(10)</td>
<td>4787.6(5)</td>
<td>5907.2(4)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>d_{calc} / mg cm⁻³</strong></td>
<td>1.714</td>
<td>1.504</td>
<td>1.529</td>
<td>1.340</td>
<td>1.369</td>
</tr>
<tr>
<td><strong>µ / mm⁻¹</strong></td>
<td>2.356</td>
<td>1.394</td>
<td>1.827</td>
<td>0.396</td>
<td>0.511</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>640</td>
<td>572</td>
<td>2320</td>
<td>2012</td>
<td>2528</td>
</tr>
<tr>
<td><strong>crystal size / mm³</strong></td>
<td>0.36 x 0.20 x 0.18</td>
<td>0.16 x 0.14 x 0.10</td>
<td>0.20 x 0.20 x 0.10</td>
<td>0.40 x 0.20 x 0.10</td>
<td>0.30 x 0.30 x 0.24</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>-11&lt;=h&lt;=14</td>
<td>-15&lt;=h&lt;=14</td>
<td>-19&lt;=h&lt;=19</td>
<td>-13&lt;=h&lt;=13</td>
<td>-26&lt;=h&lt;=27</td>
</tr>
<tr>
<td></td>
<td>-13&lt;=k&lt;=15</td>
<td>-16&lt;=k&lt;=16</td>
<td>0&lt;=k&lt;=21</td>
<td>-18&lt;=k&lt;=19</td>
<td>-18&lt;=k&lt;=18</td>
</tr>
<tr>
<td></td>
<td>-14&lt;=l&lt;=18</td>
<td>-16&lt;=l&lt;=16</td>
<td>0&lt;=l&lt;=28</td>
<td>-53&lt;=l&lt;=56</td>
<td>-31&lt;=l&lt;=30</td>
</tr>
<tr>
<td><strong>F_{calc} / mg cm⁻³</strong></td>
<td>7319 / 3 / 294</td>
<td>7874 / 496 / 421</td>
<td>23061 / 591 / 628</td>
<td>29109 / 5313 / 2197</td>
<td>15774 / 1036 / 871</td>
</tr>
<tr>
<td><strong>largest diff peak, hole/eÅ⁻³</strong></td>
<td>0.815, -0.644</td>
<td>0.684, -0.880</td>
<td>1.574, -1.926</td>
<td>0.644, -0.733</td>
<td>1.376, -1.320</td>
</tr>
</tbody>
</table>