Synthesis of metal (Iminophosphinoyl)(thiophosphinoyl) methanide and methanediide complexes

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**NANYANG
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**SYNTHESIS OF METAL
(IMINOPHOSPHINOYL)(THIOPHOSPHINOYL)
METHANIDE AND METHANEDIIDE
COMPLEXES**

**GUO JIAYI
SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES 2012**

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METHANIDE AND METHANEDIIDE
COMPLEXES**

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the requirement for the degree of Doctor of Philosophy

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Abbreviations

Ad	adamantyl
Ar	aryl
Bu	butyl
calcd	calculated
cod	1,5-cyclooctadiene
conc.	concentrated
Cp	cyclopentadienyl
CPMAS	cross polarization magic angle spinning
Cy	cyclohexyl
d	doublet, day(s)
DCM	dichloromethane
dd	a doublet of doublets
DEAD	diethylazodicarboxylate
dec.	decomposed
deg	degree(s)
Dipp	2,6-diisopropylphenyl
DPPM	1,2-bis(diphenylphosphino)methane
<i>et al.</i>	and others (Latin <i>alii</i>)
Et	ethyl
g	gram(s)
h	hour(s)

<i>i.e.</i>	that is (Latin <i>id est</i>)
<i>i</i>	iso
m	multiplet
Me	methyl
Mes	2,4,6-Me ₃ C ₆ H ₂
m.p.	melting point
NMR	Nuclear Magnetic Resonance
o	ortho
p	para
Pr	propyl
Ph	phenyl
ppm	parts per million
py	pyridine
q	quartet
qn	quintet
s	singlet
t	triplet
Tbt	2,4,6- {CH(SiMe ₃) ₂ } ₃ C ₆ H ₂
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl)oxyl
THF	tetrahydrofuran
TTP	<i>meso</i> -tetra- <i>p</i> -tolylporphyrinato dianion
Å	angstrom(s)

List of Compounds Synthesized

Formula	Numbering Scheme	Page	Structure
$C_{28}H_{31}NP_2SSi$	26	22	
$C_{28}H_{30}NLiP_2SSi_3$	27	24	
$C_{56}H_{58}Li_4N_2P_4S_2Si_2$	28	24	
$C_{25}H_{25}BOP_2$	30	28	
$C_{54}H_{56}B_2MgO_3P_4$	31	29	
$C_{56}H_{58}N_2Mg_2P_4S_2Si_2$	61	45	
$C_{58}H_{64}N_2Al_2P_4S_2Si_2$	62	48	
$C_{28}H_{30}ClNP_2SSiSn$	63	50	
$C_{34}H_{48}N_2P_2SSi_3Sn$	64	52	

Formula	Numbering	Page	Structure
	Scheme		
$C_{56}H_{58}N_2P_4S_2Si_2Sn_2$	65	52
$C_{39}H_{44}N_2OP_2SSiSn$	66	57	Ad = adamantyl
$C_{41}H_{46}N_2OP_2SSiSn$	67	57	Ar = 2,6-diisopropylphenyl
$C_{36}H_{41}ClNP_2RhSSiSn$	68	60
$C_{84}H_{87}N_3P_6S_7Si_3Sn_4$	69	63
$C_{34}H_{48}Cl_2N_2P_2SSi_3Zr$	110	89
$C_{32}H_{41}N_3P_2SSiZr$	111	90
$C_{60}H_{70}N_4OP_4S_2Si_2Zr_2$	112	90

Formula	Numbering Scheme	Page	Structure
$C_{91}H_{110}N_4O_3P_4S_2Si_2Zr_2$	113	94	<p>Ad = Adamantyl</p>
$C_{56}H_{58}N_2P_4S_2Si_2Zr$	114	96
$C_{34}H_{48}Cl_2HfN_2P_2SSi_3$	115	98
$C_{32}H_{41}HfN_3P_2SSi$	116	99
$C_{60}H_{70}Hf_2N_4O_2P_4S_2Si_2$	117	99
$C_{86}H_{92}Cu_6N_3O_{0.50}P_6S_3Si_3$	118	103
$C_{64}H_{59}Au_2NP_4SSi$	119	107

Formula	Numbering Scheme	Page	Structure
$C_{84}H_{87}N_3P_6S_3Si_3$	120	108	
$C_{84}H_{87}N_3P_6S_3Si_3$	121	108	
$C_{56}H_{60}ClN_2P_4S_2Si_2Yb$	122	113	

Abstract

This thesis describes the synthesis of metal bis(phosphinoyl)methanide (L') and methanediide (L'') complexes.

Chapter 1 describes the synthesis of bis(phosphinoyl)methane with two different coordination sites, the (iminophosphinoyl)(thiophosphinoyl)methane $[CH_2(PPh_2=NSiMe_3)(PPh_2=S)]$ (L_1) (**26**) and the (phosphine-borane)(oxophosphinoyl)methane $[CH_2(PPh_2=O)(PPh_2\rightarrow BH_3)]$ (L_2) (**30**). The extremely air- and moisture-sensitive lithium methanide complex $[Li(L_1')]$ (**27**) and germinal dianion $[Li_2(L_1'')]$ (**28**) have been synthesized by the deprotonation of **26**. The coordination chemistry of L_1 and L_2 is demonstrated in the following chapters.

Chapter 2 describes the synthesis of main-group metals (iminophosphinoyl)(thiophosphinoyl)methanide $[CH(PPh_2=NSiMe_3)(PPh_2=S)]^-$ (L_1') and methanediide $[C(PPh_2=NSiMe_3)(PPh_2=S)]^{2-}$ (L_2'') complexes. The magnesium, aluminium and tin(II) (iminophosphinoyl)(thiophosphinoyl)methanediide complexes $(\mu-L_1''Mg)_2$ (**61**), $(L_1''AlMe)_2$ (**62**) and $(L_1''Sn)_2$ (**65**) have been synthesized by double deprotonation of **26** with metal alkyls or metal amides respectively.

The reactivity of **65** toward isocyanates, $[\text{RhCl}(\text{cod})]_2$ and sulfur afforded $[\text{L}_1''\{\text{C}(\text{O})\text{N}(\text{Ad})\}\text{Sn}:]$ (**66**), $[(\text{L}_1'')^-\{\text{C}(\text{O})\text{N}(\text{Ar})\}\text{Sn}^+:]$ (**67**), $[\text{L}_1''\{\text{Rh}(\text{cod})\}(\text{SnCl})]$ (**68**) and $[\{(\mu\text{-S})\text{Sn}^{\text{IV}}\text{L}_1''\}_3\text{Sn}^{\text{II}}(\mu_3\text{-S})]$ (**69**). The X-ray crystallography shows **69** comprises a $\text{Sn}^{\text{II}}\text{S}$ moiety coordinated with the Sn^{IV} and S atoms of a trimeric 2-stannathiomethanediide $[\text{L}_1''\text{Sn}(\mu\text{-S})]_3$. The results indicate that the $\text{CSn}:$ bond in $(\text{L}_1''\text{Sn}:)_2$ (**65**) has some multiple bond character.

Chapter 3 describes the synthesis of transition and lanthanide metals (iminophosphinoyl)(thiophosphinoyl)methanide and methanediide complexes. The zirconium and the hafnium (iminophosphinoyl)(thiophosphinoyl)methanediide complexes $[L_1''\{Zr(NMe_2)_2\}]$ (**111**) and $[L_1''\{Hf(NMe_2)_2\}]$ (**116**) have been obtained. The reactivity of **111** and **116** toward water afforded the μ -oxo bridged zirconium and the μ -oxo bridged hafnium (iminophosphinoyl)(thiophosphinoyl)methanediide complexes $[\{\mu-L_1''Zr(NMe_2)\}_2O]$ (**112**) and $[\{\mu-L_1''Hf(NMe_2)\}_2O]$ (**117**) containing ionic C-Zr and C-Hf bonds.

Group 11 metal (iminophosphinoyl)(thiophosphinoyl)methanediide complexes ($(L_1''Cu)_3$ (**118**), $[L_1''Au_2(PPh_3)_2]$ (**119**) and $(L_1''Ag)_3$ (**120**) have been presented. The X-ray crystallography shows that **118** and **120** contain the Cu^I_6 and Ag^I_6 cluster structures coordinated with three methanediide ligands (L_1''). One ytterbium (iminophosphinoyl)(thiophosphinoyl)methanide complex $[(L_1')_2YbCl]$ (**122**) was also reported.

Chapter 1

Synthesis of Bis(phosphinoyl)methane and Its Geminal Dianion

1.1 Introduction

1.1.1 Bis(phosphinoyl)methane

The coordination chemistry of bis(phosphinoyl)methane $[\text{CH}_2(\text{Ph}_2\text{P}=\text{E})_2]$ ($\text{E} = \text{NR}$, S ; R = supporting substituent) has attracted much attention in the past decades. They can stabilize metal complexes with a variety of oxidation states and coordination geometries.¹

The bis(iminophosphinoyl)methanes $[\text{CH}_2(\text{Ph}_2\text{P}=\text{NR})_2]$ ($\text{R} = \text{SiMe}_3$ (**2**), Cy (**2a**), Mes (**2b**), 2,6-Dipp (**2c**)) can be synthesized by the reaction of bis(diphenylphosphino)methane (**1**) and corresponding azides (N_3R , $\text{R} = \text{SiMe}_3$ or aryl).^{2,3}

Le Floch *et al.* synthesized the bis(thiophosphinoyl)methane $[\text{CH}_2(\text{Ph}_2\text{P}=\text{S})_2]$ (**3**) by the reaction of bis(diphenylphosphino)methane (**1**) with elemental sulfur in refluxing toluene (Scheme 1.1).⁴ They also have reported the synthesis of phosphine-iminophosphorane containing two donor sites of different hardness.⁵

Scheme 1.1

There are three general methods for the synthesis of phosphine-iminophosphoranes. The first one is the Staudinger reaction^{6,7} which is achieved by the addition of an azide to a bis-phosphine with the N_2 elimination (Scheme 1.2).

Scheme 1.2

The second method is the reaction of bis-phosphines with DEAD (DEAD= diethylazodicarboxylate) followed by activated RNH_2 trapping (Scheme 1.3).⁸

Scheme 1.3

The third method was developed by Kirsanov in 1950.^{7,9} The bis-phosphine is reacted with amine upon bromination. Then the desired iminophosphorane can be obtained by subsequent treatment with base (Scheme 1.4).

Scheme 1.4

The fact is that an iminophosphorane is isoelectronic with a thiophosphorane. Thus the synthesis of the (iminophosphinoyl)(thiophosphinoyl)methane ligands (**5a-h**) containing two different donor sites have been reported (Scheme 1.5).¹⁰

Scheme 1.5

It is anticipated that the (iminophosphinoyl)(thiophosphinoyl)methane ligands **5a-h** with one hard nitrogen and one soft sulfur can enhance the hemilabile character via different hardness of two donor sites compared with the bis(phosphinoyl)methane ligands $[\text{CH}_2(\text{Ph}_2\text{P}=\text{E})_2]$ ($\text{E} = \text{NSiMe}_3, \text{S}$).

1.1.2 The Anionic Ligands of Bis(phosphinoyl)methane

The bis(phosphinoyl)methane $[\text{CH}_2(\text{Ph}_2\text{P}=\text{E})_2]$ ($\text{E} = \text{NSiMe}_3, \text{S}$) can be deprotonated to give the monoanionic bis(phosphinoyl)methanides $[\text{CH}(\text{Ph}_2\text{P}=\text{E})_2]^-$ ($\text{E} = \text{NSiMe}_3, \text{S}$) and the dianionic bis(iminophosphinoyl)methanediides $[\text{C}(\text{Ph}_2\text{P}=\text{E})_2]^{2-}$. Theoretical study shows that the successive deprotonation of bis(phosphinoyl)methanes $[\text{CH}_2(\text{Ph}_2\text{P}=\text{E})_2]$ ($\text{E} = \text{NSiMe}_3, \text{S}$) resulted mainly in an increase of negative charge on the carbon center of the ligand backbone and the charges on the terminal nitrogen or sulfur atoms are much less affected.^{1b} Thus

$[\text{C}(\text{Ph}_2\text{P}=\text{E})_2]^{2-}$ ($\text{E} = \text{NSiMe}_3, \text{S}$) is considered a geminal dianion (Scheme 1.6).

Scheme 1.6

Both of the monoanion and dianion show unusual coordination modes. The molecular structures of metal bis(phosphinoyl)methanide species $[\text{CH}(\text{Ph}_2\text{P}=\text{E})_2]^-$ ($\text{E} = \text{NSiMe}_3, \text{S}$) shows that the carbon center coordinates via a long interaction onto the metal atom. The six-membered metallacycle ($\text{E}-\text{P}-\text{C}-\text{P}-\text{E}-\text{M}$) ($\text{E} = \text{NSiMe}_3, \text{S}$) formed by the chelation of the two imine or sulfur groups to the metal center adopts a pseudo boat conformation (Scheme 1.7).¹¹

Scheme 1.7

The dianionic bis(phosphinoyl)methanediides $[\text{C}(\text{Ph}_2\text{P}=\text{E})_2]^{2-}$ ($\text{E} = \text{NSiMe}_3, \text{S}$) have the “pincer” type **A**, **C**, **D**, **E** and the bridged type **B** bonding modes (Scheme 1.8).¹² The metal methanediide complexes can be obtained by the double deprotonation of the methylene protons of bis(phosphinoyl)methane $[\text{CH}_2(\text{Ph}_2\text{P}=\text{E})_2]$ ($\text{E} = \text{NSiMe}_3, \text{S}$) with suitable metal precursors or by the salt elimination of the dianions $[\text{Li}_2\text{C}(\text{Ph}_2\text{P}=\text{E})_2]$ ($\text{E} = \text{NSiMe}_3, \text{S}$) with metal halides.

Scheme 1.8

Lithiation of bis(iminophosphinoyl)methane [$\text{CH}_2(\text{PPh}_2=\text{NSiMe}_3)_2$] (**2**) was carried out by the research groups of Stephan and Cavell.^{13,14} The lithium methanide [$\text{Li}(\text{THF})\{\text{CH}(\text{PPh}_2=\text{NSiMe}_3)_2\}$] (**6**) was obtained by treating **2** with one equivalent of $^n\text{BuLi}$ in THF. The germinal dianion [$\text{Li}_2\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2$] (**7**) was obtained by the reaction of **2** with two equivalents of MeLi or PhLi in benzene or toluene. Recently Henderson *et al.* reported the dimeric geminal heavier group 1 bis(iminophosphinoyl)methanide complex [$\text{Na}_2\{\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2\}_2$] (**8**) by the reaction of **2** with the strong base $^n\text{BuNa}$ (Scheme 1.9).¹⁵

Scheme 1.9

Another approach to synthesize group 1 bis(iminophosphinoyl)methanide

complexes was the use of metal amides or metal hydrides. The reaction of **2** with one equivalent of $[M\{N(SiMe_3)_2\}]$ ($M = Li, Na$) in toluene afforded bis(iminophosphinoyl)methanide complexes $[M\{CH(PPh_2=NSiMe_3)_2\}]$ ($M = Li$ (**9**), Na (**10**)).¹⁶ The reaction of **2** with one equivalent of MH ($M = Na, K$) in THF gave $[M(THF)_2\{CH(PPh_2=NSiMe_3)_2\}]$ ($M = Na$ (**11**), K (**12**)) (Scheme 1.10).^{17,18}

Scheme 1.10

Harder *et al.* reported the first bis(phosphinoyl)methandiide complexes $[\{PhN(Ph)_2P\}_2CM_2]$ of the heavier alkali metals K (**13**) and Rb (**14**). For Cs , a cyclic bis(phosphinoyl)methandiide (**15**) with a dicesiated carbon atom was obtained (Scheme 1.11).¹⁹

Scheme 1.11

Dilithium bis(thiophosphinoyl)methanediide $[Li_2C(PPh_2=S)_2]$ (**16**) was synthesized by the reaction of **3** and $MeLi$ (Scheme 1.12).²⁰

Scheme 1.12

For group 2 metal methanide complexes, the reaction of $[\text{CH}_2(\text{PPh}_2=\text{NSiMe}_3)_2]$ (**2**) with MeMgCl afforded $[\{\text{CH}(\text{PPh}_2=\text{NSiMe}_3)_2\}\text{Mg}(\mu\text{-Cl})]_2$ (**17**). $[\{\text{CH}(\text{PPh}_2=\text{NSiMe}_3)_2\}\text{MgI}(\text{THF})]$ (**18**) was synthesized by the reaction of **2** with $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$ followed by MeMgI in THF.²¹

Scheme 1.13

The calcium (**19**), strontium (**20**), and barium (**21**) bis(phosphinonyl)methanide complexes have been prepared from the corresponding metal diiodides with $[\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}]$ (**12**) (Scheme 1.14).²² Compound **22** was prepared from the reaction of two equivalents of **12** with SrI_2 . Bis(methanide) complexes **23** and **24** have been prepared by the reactions between **2** and the corresponding metal amides $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}]$ ($\text{M} = \text{Ca}, \text{Ba}$).^{23,24}

Scheme 1.14

The group 1 and group 2 monoanionic and dianionic complexes can serve as the synthon for the preparation of various methanide and mathanediide complexes.

1.1.3 Aim of the Project

As aforementioned, the coordination chemistry of (iminophosphinoyl)(thiophosphinoyl)methane ligand containing two donor sites of different hardness is rare. In this thesis, we aim at the synthesis of (iminophosphinoyl)(thiophosphinoyl)methanide and methanediide complexes of main-group, transition and lanthanide metals and compare its coordination chemistry with those of bis(iminophosphinoyl)methane and bis(thiophosphinoyl)methane.

1.2 Results and Discussion

1.2.1 Synthesis of (Iminophosphinoyl)(thiophosphinoyl)methane

The reaction of the phosphine-phosphinimine $[\text{Ph}_2\text{PCH}_2(\text{PPh}_2=\text{NSiMe}_3)]$ (**25**)²⁵ with elemental sulfur in toluene at 0 °C afforded the

(iminophosphinoyl)(thiophosphinoyl)methane (L_1) (**26**) (Scheme 1.18).

Scheme 1.18

Compound **26** was isolated in toluene as a colorless crystalline solid in 80.1 % yield. It has been analyzed by NMR spectroscopy and X-ray crystallography. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **26** shows two doublets at δ -5.23 and 36.7 ppm with $^2J_{\text{P-P}} = 17.3$ Hz due to $\text{PPh}_2=\text{NSiMe}_3$ and $\text{PPh}_2=\text{S}$, respectively. One signal [δ -5.23 ppm ($\text{PPh}_2=\text{NSiMe}_3$)] shows upfield shift compared with that of **25** [δ -2.1 ppm ($\text{PPh}_2=\text{NSiMe}_3$)].²⁰ The $^{31}\text{P}\{^1\text{H}\}$ NMR resonances of **26** are comparable to those of $[\text{CH}_2(\text{PPh}_2=\text{S})\{\text{PPh}_2=\text{N}(4\text{-C}_6\text{H}_4\text{OMe})\}]$ [δ -4.8 (d), 36.2 ppm (d); $^2J_{\text{P-P}} = 16$ Hz].²⁵ The ^1H NMR spectrum of **26** shows one doublet of doublets for the methylene protons at δ 3.56 ppm ($^2J_{\text{P-H}} = 14.64, 12.36$ Hz).

Figure 1.1 Molecular structure of **26** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(13)-P(1) 1.820(3), C(13)-P(2) 1.831(3), P(1)-N(1) 1.547(2), P(2)-S(1) 1.960(1); N(1)-P(1)-C(13) 113.0(1), P(1)-C(13)-P(2) 122.5(1), C(13)-P(2)-S(1) 111.1(9), P(1)-N(1)-Si(1) 138.5(2).

The molecular structure of **26** is shown in Figure 1.1. The P(1)-N(1) bond length

(1.547(2) Å) and P(2)-S(1) bond length (1.960(1) Å) in **26** are comparable to those of [CH₂(PPh₂=S){PPh₂=N(4-C₆H₄Me)}] (P-N = 1.556(4) Å; P-S = 1.952(2) Å).²⁶

1.2.2 Synthesis of Lithium (Iminophosphinoyl)(thiophosphinoyl)methanide and Methanediide Complexes

Treatment of **26** with ⁿBuLi in THF at -78 °C afforded the lithium (iminophosphinoyl)(thiophosphinoyl)methanide [Li(L₁')] (**27**). The geminal dianion [Li₂(L₁'')] (**28**) was synthesized by double deprotonation of **26** with two equivalents of ^tBuLi in Et₂O at -78 °C (Scheme 1.19).

Scheme 1.19

Compound **27** was isolated in THF/hexane as an extremely air- and moisture-sensitive colorless crystalline solid in 78 % yield, which is soluble in hydrocarbon solvents. It has been analyzed by NMR spectroscopy and X-ray crystallography. The ³¹P{¹H} NMR spectrum displays two doublets at δ 16.1 and 35.4 ppm (²J_{P-P'} = 21.7 Hz) due to PPh₂=NSiMe₃ and PPh₂=S, respectively. The ¹³C{¹H} NMR spectrum shows one doublet of doublets for the methanide carbon at δ 21.81 ppm (J_{P-C} = 91.5, J_{P'-C} = 126.4 Hz). In contrast, the ¹H NMR spectrum shows a

doublet for the methine proton at δ 2.17 ppm ($^2J_{\text{P-H}} = 3.68$ Hz). The lack of coupling of the methanide proton to two nonequivalent phosphorus nuclei is unusual.

Compound **28** was isolated in THF/hexane as a highly air- and moisture-sensitive colorless crystalline solid in 88 % yield, which is soluble in hydrocarbon solvents. It has been characterized by NMR spectroscopy and X-ray crystallography. The $^{31}\text{P}\{^1\text{H}\}$ NMR signals of **28** (δ 11.8, 17.7 ppm, $^2J_{\text{P-P}'} = 23.9$ Hz) show an upfield shift compared with those of **27**. The ^1H NMR spectrum of **28** displays resonances for the SiMe_3 and phenyl protons. It is noteworthy that there is no $^{13}\text{C}\{^1\text{H}\}$ NMR signal for the methanediide carbon. Similarly, there is no $^{13}\text{C}\{^1\text{H}\}$ NMR signal for the carbenic carbon in $[(\text{PPh}_2\text{=S})_2\text{C=Pd(PPh}_3)]$.²⁷

Figure 1.2 Molecular structure of **27** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Li(1)-S(1) 2.484(6), Li(1)-N(1) 2.065(6), P(1)-S(1) 1.989(1), P(2)-N(1) 1.588(3), C(13)-P(1) 1.708(4), C(13)-P(2) 1.715(3), Li(1)-O(1) 1.972(12), Li(1)-O(2) 1.964(7); S(1)-Li(1)-N(1) 106.2(2), Li(1)-N(1)-P(2) 112.2(2), N(1)-P(2)-C(13) 118.1(2), P(2)-C(13)-P(1) 122.7(2), C(13)-P(1)-S(1) 116.0(1), P(1)-S(1)-Li(1) 101.6(1).

The molecular structure of **27** is shown in Figure 1.2. Compound **27** is a monomeric lithium complex that contains the six-membered metallacycle Li(1)-S(1)-P(1)-C(13)-P(2)-N(1), formed by the ligand and the lithium atom. The Li(1)

is also bound to the oxygen atoms of two THF molecules and displays tetrahedral geometry. The metallacycle adopts a twist-boat conformation in which S(1) and N(1) are displaced from the P(1)-C(13)-P(2)-Li(1) least-squares plane by 1.015 and 0.750 Å, respectively. The C(13)-Li(1) distance (3.707 Å) is significantly longer than that of [Li(THF){CH(PPh₂=NSiMe₃)₂}] (2.560(8) Å).^{28a} The C(13)-P bonds (1.708(4), 1.715(3) Å) are significantly shorter than those in **26** (1.820(3), 1.831(3) Å). On the other hand, the P-S (1.989(1) Å) and P-N bonds (1.588(3) Å) are slightly longer than those in **26**. The Li(1)-N(1) bond (2.065(6) Å) in **27** is shorter than the Li(1)-S(1) bond (2.484(6) Å). Similar bis-phosphorus methanide complexes [Li{CH(PPh₂=E)₂}] (E = S, NSiMe₃) have been synthesized and structurally characterized.²⁸ The elongated P-N bonds (1.588(3) Å) in **27** are comparable to that of [Li{(C₅H₄N-2)CHPPh₂(=NSiMe₃)}] (P-N: (1.5904(2) Å) due to the polar P⁺-N⁻ bond studied by means of experimental charge density investigations.²⁹

Figure 1.3 Molecular structure of **28** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Li(1)-C(13) 2.213(10), Li(1)-C(41) 2.210 (10), Li(1)-N(2) 2.141(10), Li(1)-S(1) 2.445(9), Li(2)-S(1) 2.498(9), Li(2)-S(2) 2.450(10), Li(3)-C(13) 2.211(10), Li(3)-C(41) 2.206(10), Li(3)-N(1) 2.179(9), Li(3)-S(2) 2.446(8), Li(4)-N(1) 2.043(11), Li(4)-N(2) 2.011(11), C(13)-P(1) 1.677(5), C(13)-P(2) 1.685(5), P(1)-S(1) 2.042(2), P(2)-N(1) 1.617(4),

C(41)-P(3) 1.680(5), C(41)-P(4) 1.687(5), P(3)-S(2) 2.046(2), P(4)-N(2) 1.611(4); C(13)-Li(1)-C(41) 103.4(4), N(2)-Li(1)-S(1) 153.5(5), S(1)-Li(2)-S(2) 139.1(4), C(13)-Li(3)-C(41) 103.6(4), N(1)-Li(3)-S(2) 153.8(4), N(1)-Li(4)-N(2) 171.8(6), Li(1)-C(13)-Li(3) 76.0(4), Li(1)-C(41)-Li(3) 76.2(4), P(1)-C(13)-P(2) 131.7(3), C(13)-P(1)-S(1) 109.1(2), C(13)-P(2)-N(1) 104.1(2), P(1)-S(1)-Li(1) 76.5(2), P(1)-S(1)-Li(2) 89.3(3), P(2)-N(1)-Li(3) 87.5(3), P(2)-N(1)-Li(4) 94.2(4), P(3)-C(41)-P(4) 130.6(3), C(41)-P(3)-S(2) 108.6(2), C(41)-P(4)-N(2) 103.6(2), P(3)-S(2)-Li(2) 91.3(3), P(3)-S(2)-Li(3) 76.1(2), P(4)-N(2)-Li(1) 88.4(3), P(4)-N(2)-Li(4) 94.4(4).

The molecular structure of **28** is shown in Figure 1.3. Compound **28** crystallized as a dimer in which the lithium atoms Li(1) and Li(3) are bridged by the two carbon atoms C(13) and C(41) and coordinated with one nitrogen and one sulfur atom of each ligand. The other lithium atoms, Li(2) and Li(4), are bridged by two sulfur and two nitrogen atoms, respectively. The molecular structure of **28** is different from that of $[\text{Li}_2\{\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2\}]$, which has an octahedral Li_4C_2 cluster.¹⁴ On the other hand, it is similar to that of $[\text{Li}_2\{\text{C}(\text{PPh}_2=\text{S})_2\}]$, except that Li(2) is coordinated with one THF solvent molecule and has a short Li(4)···C(41) distance (2.560 Å).²⁸ The ligand chains N-P-C-P-S are almost planar, and the ligand planes are orthogonal to each other (85.7°). The Li(1)-C(13) and Li(1)-C(41) bonds (2.213(10), 2.210(10) Å) are similar to those of $[\text{Li}_2\{\text{C}(\text{PPh}_2=\text{S})_2\}]$ (2.159(5), 2.196(5) Å)²⁰ but are significantly shorter than those of $[\text{Li}_2\{\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2\}]$ (2.441(7), 2.451(7) Å).¹³ Since there are only weak interactions between the Li(2), Li(4) and the C(13), C(41) atoms (Li(2)-C(13) = 3.525 Å, Li(2)-C(41) = 3.503 Å; Li(4)-C(13) = 2.577 Å, Li(4)-C(41) = 2.560 Å), this allows stronger interaction between the C(13), C(41) and Li(1), Li(3) atoms. Similar to the case for $[\text{Li}_2\{\text{C}(\text{PPh}_2=\text{E})_2\}]$ (E = S, NSiMe₃),^{13, 14, 20} the structure of compound **28** also features short P-C(13) bonds (1.677(5), 1.685(5) Å), a long P(1)-S(1) bond (2.042(2) Å), and a long P(2)-N(1) bond (1.617(4) Å). It is noteworthy that the average P-C bond lengths shorten from 1.826 Å in **26** and 1.712 Å in **27** to

1.681 Å in **28**, while the P-N bond lengths increase from 1.547(2) Å in **26** and 1.588(3) Å in **27** to 1.611(4) Å in **28**. In addition, the P-S bond lengths increase from 1.960(1) Å in **26** and 1.989(1) Å in **27** to 2.042(2) Å in **28**. These are due to the negative hyperconjugation from carbon to phosphorus σ^* orbitals in **27** and **28**.

1.2.3 Synthesis of (Phosphine-borane)(oxophosphinoyl)methane

The reaction of the phosphine-phosphorane $[\text{Ph}_2\text{PCH}_2(\text{PPh}_2=\text{O})]$ (**29**)³⁰ with $\text{Me}_2\text{S}\cdot\text{BH}_3$ in THF afforded the (phosphine-borane)(oxophosphinoyl)methane (L_2) (**30**) (Scheme 1.20).

Scheme 1.20

Compound **30** was isolated in CH_2Cl_2 as a colorless crystalline solid in 60.5 % yield. It has been analyzed by NMR spectroscopy and X-ray crystallography. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **30** shows one broad signal at δ -15.4 ppm and one doublet at δ 22.6 ppm ($^2J_{\text{P-P}'} = 21.7$ Hz) due to $\text{PPh}_2\rightarrow\text{BH}_3$ and $\text{PPh}_2=\text{O}$, respectively. These are downfield shift compared with those of **29** [δ -26.0 ppm (PPh_2), δ 25.9 ppm ($\text{PPh}_2=\text{O}$)].³⁰ The ^1H NMR spectrum shows one doublet of doublets for the methylene protons at δ 3.10 ppm ($^2J_{\text{P-H}} = 17.9, 20.6$ Hz). The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum shows one broad signal at δ -20.37 ppm which shows a downfield shift compared with δ -56.07 ppm of $[\text{CH}_2(\text{PPh}_2\rightarrow\text{BH}_3)_2]$.³¹

Figure 1.4 Molecular structure of **30** with thermal ellipsoids at the 20% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-P(1) 1.823(7), C(1)-P(2) 1.809(7), P(1)-B(1) 1.916(9), P(2)-O(1) 1.497(4), B(1)-P(1)-C(1) 115.1(4), P(1)-C(1)-P(2) 115.4(4), C(1)-P(2)-O(1) 113.6(3).

The molecular structure of **30** is shown in Figure 1.4. The P(1)-B(1) bond length (1.916(9) Å) in **30** is similar to that of $[\text{CH}_2(\text{PPh}_2 \rightarrow \text{BH}_3)_2]$ (P-B = 1.917(2) Å).³¹ The P(2)-O(1) bond length (1.497(4) Å) is also comparable to the P-O bonds of $[\text{CH}_2(\text{PPh}_2=\text{O})_2]$ (average: 1.491(5) Å).³²

1.2.4 Synthesis of Magnesium (Phosphine-borane)(oxophosphinoyl)methanide

Complex

The magnesium (phosphine-borane)(oxophosphinoyl)methanide complex $[(\text{L}_2')_2\text{Mg}(\text{THF})]$ (**31**) was obtained by the reaction of **30** with $\text{Mg}^n(\text{Bu})_2$ in refluxing toluene (Scheme 1.21).

Scheme 1.21

Compound **31** was isolated in Et_2O /hexane as an air- and moisture-sensitive

colorless crystalline solid in 56.8 % yield. It is soluble in toluene and THF and has been characterized by NMR spectroscopy and X-ray crystallography. The ^1H NMR spectrum of **31** displays one AB quartet at δ 3.50 ppm ($^2J_{\text{P-H}} = 10.88$ Hz, *PCHP*) for the methine proton and one broad signal at δ 0.88-1.28 ppm for the protons of BH_3 substituent. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows one doublet at δ 36.8 ppm (d, $^2J_{\text{P-P}'} = 51.9$ Hz) and one broad signal at δ 22.1 ppm due to two nonequivalent phosphorus nuclei. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows one AB quartet for the methanide carbon at δ 24.71 ppm (ABq, *PCP*, $J_{\text{P-C}} = 20.02$ Hz).

Figure 1.5 Molecular structure of **31** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Mg(1)-O(3) 2.084(12), Mg(1)-B(1) 2.5875(14), Mg(1)-O(1) 1.9500(9), Mg(1)-B(2) 2.5258(16), Mg(1)-O(2) 1.9512(10), C(13)-P(1) 1.7082(12), C(13)-P(2) 1.7218(12), O(1)-P(1) 1.5140(9), B(1)-P(2) 1.9303(14), C(38)-P(3) 1.6954(13), C(38)-P(4) 1.7088(13), O(2)-P(3) 1.5157(9), B(2)-P(4) 1.9232(15); O(1)-Mg(1)-B(1) 86.09(4), O(2)-Mg(1)-B(2) 86.67(4), O(1)-Mg(1)-O(2) 177.23(5), B(1)-Mg(1)-B(2) 126.91(5), O(2)-Mg(1)-B(1) 93.26(4), O(1)-Mg(1)-B(2) 91.56(4).

The molecular structure of **31** is shown in Figure 1.5. Compound **31** displays as a homoleptic monomer. The Mg atom is coordinated by iminiophosphinoyl and borane substituents of the two ligands and one more THF molecule, which forms the

six-membered metallacycle (O-P-C-P-B-Mg). The distances between the carbon and magnesium atoms (3.999, 4.026 Å) are significantly longer than those C-Mg single bonds of other methanide analogues [HC(Ph₂P=NSiMe₃)₂Mg(μ -Cl)]₂ (**17**) (2.460(8) Å) and [CH(Ph₂P=NSiMe₃)₂MgI(THF)] (**18**) (2.573(6) Å).²¹ The Mg-O bond length (2.084(12) Å) is similar to that Mg-O bond of **18** (2.090 (5) Å).²¹ The P-C bonds are shortened and the P-B, P-O bonds are lengthened in **31** compared with those of **30**. It shows the delocalization of negative charge on carbon center over the “O-P-C-B-Mg” fragment.

1.3 Conclusion

In summary, the (iminophosphinoyl)(thiophosphinoyl)methane (L₁) (**26**) and (phosphine-borane)(oxophosphinoyl)methane (L₂) (**30**) have been synthesized. The lithium and magnesium bis(phosphinoyl)methanide and methanediide complexes [Li(L₁’)] (**27**), [Li₂(L₁’)] (**28**) and [(L₂’)₂Mg(THF)] (**31**) have also been presented. The enhanced hemilabile character of **26** compared with [{CH₂(PPh₂=E)₂}] (E = S, NSiMe₃) may lead to interesting coordination chemistry. More bis(phosphinoyl)methane containing two different donor sites are under investigation in our research project to serve as the metal-stabilizing precursors.

1.4 Experimental Section

All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled over Na/K alloy prior to use. The ¹H, ¹¹B, 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,

85% H_3PO_4 for ^{31}P and BF_3 for ^{11}B . 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.

29 was prepared as described in the literature.³⁰

[CH₂(PPh₂=NSiMe₃)(PPh₂)] (25). A solution of N_3SiMe_3 (6.7 mL, 50 mmol) and bis(diphenylphosphino)methane (19.5 g, 50 mmol) in toluene was refluxed at 140 °C for 15h. Volatiles were removed under reduced pressure. Pentane (100 mL) was added to the resulting white solid. After filtration and concentration white solids of **25** (11.9 g, 50.0 %) with 98% purity were obtained. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, 25 °C, C_6D_6): δ -26.7 ppm (d, PPh_2 , $^2J_{\text{P-P}'} = 17.3$ Hz), -2.1 ppm (d, $\text{PPh}_2=\text{NSiMe}_3$, $^2J_{\text{P-P}'} = 17.3$ Hz).

[CH₂(PPh₂=S)(PPh₂=NSiMe₃)] (26). A solution of sulfur (41 mg, 1.29 mmol) in toluene (5 mL) was added dropwise to a solution of **25** (0.61 g, 1.29 mmol) in toluene (1.5 mL) at 0 °C over a period of 2 h. The reaction mixture was stirred for 1 h at 0 °C. After concentration, **26** (0.52 g, 80.1 %) was obtained as colorless crystals. M.p.: 62 °C. Elemental analysis (%) Calcd for $\text{C}_{28}\text{H}_{31}\text{NP}_2\text{SSi}$: C 66.78, H 6.21, N 2.78; Found: C 66.42, H 6.17, N 2.46. ^1H NMR (399.5 MHz, 25 °C, C_6D_6): δ 0.23 (s, 9H, SiMe_3), 3.56 (dd, 2H, $^2J_{\text{P-H}} = 12.36, 14.64$ Hz, PCH_2P), 6.91-7.04 (m, 12H, Ph), 7.36-7.42 (m, 4H, Ph), 8.06-8.12 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, 25 °C, C_6D_6): δ 4.51 (SiMe_3), 39.86 (dd, $J_{\text{P-C}} = 45.1, 68.04$ Hz, PCH_2P), 131.08, 131.11, 131.39, 131.42, 131.70, 131.80, 132.88, 132.98, 134.01, 134.84, 135.68, 135.70, 136.66, 136.68 ppm (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, 25 °C, C_6D_6): δ -5.23 ppm (d, $\text{PPh}_2=\text{NSiMe}_3$, $^2J_{\text{P-P}'} =$

17.3 Hz), 36.7 ppm (d, $\text{PPh}_2=\text{S}$, $^2J_{\text{P-P}'} = 17.3$ Hz). ESI-MS: m/z : 504 $[\text{M} + \text{H}^+]$.

[Li{CH(PPh₂=S)(PPh₂=NSiMe₃)}] (27). ⁿBuLi (0.58 mL, 2 M in cyclohexane, 1.2 mmol) was added dropwise to **26** (0.5 g, 1.0 mmol) in THF (10 mL) at -78 °C. The resulting yellow solution was raised to ambient temperature and stirred for 17 h. Volatiles were removed under reduced pressure, and the residue was extracted with THF/hexane. After filtration and concentration of the filtrate, **27** (0.40 g, 78 %) was obtained as colorless crystals. M.p.: 96 °C. Elemental analysis (%) Calcd for $\text{C}_{28}\text{H}_{30}\text{NLiP}_2\text{SSi}_3 \cdot 2\text{THF}$: C 66.13, H 7.10, N 2.14; Found: C 65.91, H 7.07, N, 1.96. ¹H NMR (399.5 MHz, 25 °C, C_6D_6): δ 0.21 (s, 9H, SiMe₃), 2.17 (d, 1H, $^2J_{\text{P-H}} = 3.68$ Hz, PCHP), 6.95-7.05 (m, 12H, Ph), 7.87-7.92 (m, 4H, Ph), 8.07-8.12 (m, 4H, Ph). ¹³C{¹H} NMR (99.5 MHz, 25 °C, C_6D_6): δ 4.47 (SiMe₃), 21.81 (dd, $J_{\text{P-C}} = 91.5, 126.4$ Hz, PCHP), 129.83, 129.85, 129.94, 129.97, 131.52, 131.64, 131.85, 131.96, 140.16, 140.21, 141.03, 141.08, 141.10, 141.16, 141.86, 141.91 ppm (Ph). ³¹P{¹H} NMR (161.7 MHz, 25 °C, C_6D_6): δ 16.1 ppm (d, $\text{PPh}_2=\text{NSiMe}_3$, $^2J_{\text{P-P}'} = 21.7$ Hz), 35.4 ppm (d, $\text{PPh}_2=\text{S}$, $^2J_{\text{P-P}'} = 21.7$ Hz).

[Li₂{C(PPh₂=S)(PPh₂=NSiMe₃)}] (28). ^tBuLi (1.17 mL, 1.7 M in pentane, 2.0 mmol) was added dropwise to **26** (0.5 g, 1.0 mmol) in Et₂O (6.3 mL) at -78 °C. The resulting yellow solution was raised to ambient temperature and stirred for 1 h. Volatiles were removed under reduced pressure, and the residue was extracted with THF/hexane. After filtration and concentration of the filtrate, **28** (0.45 g, 88 %) was obtained as colorless crystals. M.p.: 141 °C. Elemental analysis (%) Calcd for $\text{C}_{56}\text{H}_{58}\text{Li}_4\text{N}_2\text{P}_4\text{S}_2\text{Si}_2$: C 65.22, H 5.67, N 2.72; Found: C 64.97, H 5.42, N 2.45. ¹H NMR (395.9 MHz, 25

$^{\circ}\text{C}$, C_6D_6): δ 0.12 (s, 9H, SiMe_3), 6.77-7.06 (m, 12H, Ph), 7.53-7.58 (m, 2H, Ph), 7.68-7.76 (m, 4H, Ph), 7.94-8.00 (m, 2H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.55 MHz, 25°C , C_6D_6): δ 4.66 (SiMe_3), 128.92, 129.39, 129.51, 129.68, 129.77, 130.86, 130.97, 131.31, 131.41, 131.67, 131.78, 132.04, 132.15, 132.41, 132.58, 138.22, 140.98, 141.75, 141.80, 142.32, 142.51, 142.54, 143.07, 143.19 ppm (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, 25°C , C_6D_6): δ 11.8 ppm, 17.7 ppm (d, $^2J_{\text{P-P}'} = 23.9$ Hz).

[CH₂(PPh₂=O)(PPh₂→BH₃)] (30). $\text{Me}_2\text{S}\cdot\text{BH}_3$ (0.1 mL, 1 mmol) was added dropwise to a solution of **29** (0.39 g, 0.98 mmol) in THF (20 mL). The reaction mixture was stirred for 12 h at room temperature. Volatiles were removed under reduced pressure and the residue was extracted by CH_2Cl_2 . Colorless crystals of **30** (0.25 g, 60.5 %) were obtained after filtration and concentration. M.p.: 218.1°C . Elemental analysis (%) Calcd for $\text{C}_{25}\text{H}_{25}\text{BOP}_2\cdot 0.5(\text{CH}_2\text{Cl}_2)$: C 67.06, H 5.74; Found: C 66.24, H 7.97. ^1H NMR (399.5 MHz, 25°C , C_6D_6): δ 1.86-2.14 (br, 3H, BH_3), 3.10 (dd, 2H, $^2J_{\text{P-H}} = 2.28$, 4.11 Hz, PCH_2P), 6.83-6.96 (m, 12H, Ph), 7.37-7.43 (m, 4H, Ph), 8.16-8.22 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, 25°C , C_6D_6): δ 29.68 (dd, $J_{\text{P-C}} = 35.48$, $J_{\text{P}'-C} = 87.25$ Hz, PCH_2P), 131.26 (d, $^2J_{\text{P-C}} = 9.59$ Hz), 131.79, 133.60 (d, $^2J_{\text{P-C}} = 9.59$ Hz), 134.56, 134.94 (d, $^3J_{\text{P-C}} = 9.59$ Hz) 135.57 ppm (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, 25°C , C_6D_6): δ -15.4 ppm (br, $\text{PPh}_2\rightarrow\text{BH}_3$), 22.6 ppm (d, $\text{PPh}_2=\text{O}$, $^2J_{\text{P-P}'} = 21.7$ Hz). ^{11}B NMR (128.2 MHz, 25°C , C_6D_6): δ -20.37 ppm (br).

[Mg(THF){CH(PPh₂=O)(PPh₂→BH₃)}₂] (31). $\text{Mg}(\text{nBu})_2$ (0.8 mL, 1.0 M in heptane, 1.20 mmol) was added to a solution of **30** (0.41 g, 0.8 mmol) in toluene (20 mL) at room temperature. The reaction mixture was refluxed at 140°C for 12 h. Volatiles

were removed under reduced pressure. The resulting yellow residue was stirred in THF and volatils were removed after 0.5 h. Colorless crystals (0.26 g, 56.8 %) of **31** were recrystallized in Et₂O/hexane. M.p.: 350.0 °C. Elemental analysis (%) calcd for C₅₈H₆₆B₂MgO₂P₄: C 64.93, H 6.20; Found: 65.26, H 8.58. ¹H NMR (399.5 MHz, 25 °C, THF-*d*₈): δ 0.88-1.28 (br, 3H, BH₃), 1.70-1.78 (m, 1H, THF), 3.50 (ABq, 1H, ²J_{P-H} = 10.88 Hz, PCHP), 3.55-3.62 (m, 2H, THF), 7.11-7.38 (m, 12H, Ph), 7.64-7.91 (m, 8H, Ph). ¹³C{¹H} NMR (99.5 MHz, 25 °C, THF-*d*₈): δ 24.71 (ABq, PCP, J_{P-C} = 20.02 Hz), 127.28 (d, C_{ortho} of Ph, ²J_{P-C} = 11.43 Hz), 128.00 (dd, C_{ipso} of Ph, J_{P-C} = 18.59 Hz, ³J_{P-C} = 10.48 Hz), 128.57 (d, C_{meta} of Ph, ³J_{P-C} = 1.91 Hz), 129.16 (d, C_{meta} of Ph, ³J_{P-C} = 6.67 Hz), 130.76 (dd, C_{ipso} of Ph, J_{P-C} = 20.02 Hz, ³J_{P-C} = 10.49 Hz), 130.96, 131.19 (d, C_{ortho} of Ph, ²J_{P-C} = 8.58 Hz), 131.79 (d, C_{ortho} of Ph, ²J_{P-C} = 9.53 Hz), 133.63 ppm (d, C_{ortho} of Ph, ²J_{P-C} = 9.53 Hz). ³¹P{¹H} NMR (160.3 MHz, 25 °C, THF-*d*₈): δ 36.8 ppm (d, ²J_{P-P'} = 51.9 Hz), 22.1 ppm (br).

Crystal Structure Determinations of Compounds 26, 27, 28, 30 and 31. 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 .³³ 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 2

Synthesis and Reactivity of Main-Group Metal (Iminophosphinoyl)(thiophosphinoyl)methanide and Methanediide Complexes

2.1 Introduction

The chemistry of main-group metal bis(phosphinoyl)methanediide complexes has been investigated extensively over the past ten years.¹ They were obtained either by the salt elimination of $[\text{Li}_2\text{C}(\text{PPh}_2=\text{E})_2]$ ($\text{E}=\text{NSiMe}_3$, S) with metal halides or by the double deprotonation of $[\text{CH}_2(\text{PPh}_2=\text{E})_2]$ ($\text{E}=\text{NSiMe}_3$, S) with metal alkyls or amides. Group 2 metal bis(iminophosphinoyl)methanediide complexes $[(\text{PPh}_2=\text{NSiMe}_3)_2\text{CM}]_2$ ($\text{M} = \text{Mg}$ (**32**),² Ca (**33**), Ba (**34**)^{1f,g}) have been synthesized by the reaction of $[\text{CH}_2(\text{PPh}_2=\text{NSiMe}_3)_2]$ (**2**) with $\text{Mg}(\text{nBu})_2$, $[\{(\text{C}_6\text{H}_4\text{-4-}^t\text{Bu})\text{CH}_2\}_2\text{Ca}(\text{THF})_4]$ and $[(\text{PhCH}_2)_2\text{Ba}]$, respectively. The reaction of **32** with water (0.042M in toluene) in toluene for 3 hours gave the magnesium hydroxide complex $[\text{HC}(\text{PPh}_2=\text{NSiMe}_3)_2\text{Mg}(\mu\text{-OH})]_2$ (**35**) (Scheme 2.1).²

The magnesium, calcium and barium complexes **32**, **33** and **34** were crystallized as a dimer. Unlike **32** and **33**, the barium atom in **34** is coordinated by an additional THF molecule at the terminal position.

Scheme 2.1

Recently the magnesium bis(thiophosphinoyl)methanediide complex $[(\text{PPh}_2=\text{S})_2\text{CMg}(\text{THF})]_2$ (**36**) has also been reported by Leung *et al.* It was obtained by the reaction of $[\text{CH}_2(\text{PPh}_2=\text{S})_2]$ (**3**) with $\text{Mg}(\text{nBu})_2$ in refluxing THF (Scheme 2.2).³

Scheme 2.2

The reactivity of compound **33** was investigated (Scheme 2.3). Addition of benzophenone to **33** gave the adduct **37**. Treatment of **33** with benzophenone in THF followed by water afforded **38**. Reaction of **33** with adamantyl cyanide gave the adduct **39**. Compound **33** underwent a [2+2] cycloaddition reaction with the C=O of cyclohexyl isocyanate to form **40**.^{1f, g}

Scheme 2.3

Aluminium bis(iminophosphinoyl)methanediide complex $[(\text{AlMe}_2)_2\{\mu_2\text{-C}(\text{PPh}_2\text{NSiMe}_3)_2\}]$ (**41**) was synthesized by the reaction of $[\text{CH}_2(\text{PPh}_2=\text{NSiMe}_3)_2]$ (**2**) with two equivalents of AlMe_3 under reflux condition (Scheme 2.4).^{1h} Compound **41** has a bimetallic structure in which two aluminium atoms bind to the $\text{C}_{\text{methanediide}}$ atom.

Scheme 2.4

The reactivity of compound **41** was investigated (Scheme 2.5).⁴ Treatment of **41** with dicyclohexylcarbodiimide in toluene yielded **42**. The reaction of **41** with

adamantyl isocyanate resulted in the formation of **43**. A C=C double bond is formed in the synthesis of **42** and **43**.

Scheme 2.5

Aluminium bis(thiophosphinoyl)methanediide chloride **46** was synthesized from the reaction of AlCl₃ with two equivalents of **44** in Et₂O at 0 °C. From the structure it is proposed that the intermediate [AlCl₂{CH(PPh₂=S)₂}] (**45**) underwent further dehydrochlorination with **44** (Scheme 2.6).³

Scheme 2.6

Low valent group 14 bis(iminophosphinoyl)methanediide complexes have attracted much attention in the past few years.⁵ They were considered as heavier vinylidene analogues (:M=C<; M = group 14 elements), which are scarcely known. Because of lacking bulky substituents at the low-coordinate metal(II) center, they are unstable and

expected to oligomerize more readily. The first example of the bisgermavinylidene $[(\text{Me}_3\text{SiN}=\text{PPh}_2)_2\text{C}=\text{Ge}\rightarrow\text{Ge}=\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2]$ (**48**) containing a weak Ge-Ge interaction was synthesized by Leung *et al.*^{1a}

Compound **48** was obtained by the reaction of $\text{GeCl}_2\cdot\text{dioxane}$ with two equivalents of $[\text{Li}(\text{THF})\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}]$ (**6**) stirring in Et_2O for two days. When the reaction was stirred for one day, the chlorogermylene $[\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\text{GeCl}]$ (**47**) was isolated, which is considered as an intermediate for the formation of the **48**. Low valent tin and lead bis(iminophosphinoyl)methanediide complexes $[\text{M}\{\mu_2\text{-C}(\text{Ph}_2\text{PNSiMe}_3)_2\}]_2$ ($\text{M} = \text{Sn}$ (**49**), Pb (**50**)) were synthesized by the reaction of $[\text{CH}_2(\text{PPh}_2=\text{NSiMe}_3)_2]$ (**2**) with the corresponding metal amides $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$ ($\text{M} = \text{Sn}$, Pb). The analogous 1,3-plumbacyclobutane $[\text{Pb}\{\mu_2\text{-C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\}]_2$ (**50**) also can be obtained by the reaction of **6** with PbCl_2 (Scheme 2.7).^{1a}

Scheme 2.7

Compound **48** comprises two germavinylidenes $[:\text{Ge}=\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]$ bonded together in a head-to-head manner, whilst compounds **49** and **50** is formed by the head

to tail dimerization of the metallavinylidene intermediates $[:M=C(Ph_2P=NSiMe_3)_2]$ ($M = Sn, Pb$) during the reaction.

The reactivity of compound **48** was investigated in order to demonstrate the existence of the germavinylidene intermediate $[:Ge=C(Ph_2P=NSiMe_3)_2]$ in solution (Scheme 2.8). Compound **48** can behave as a Lewis base due to the lone pair electrons on the Ge atom. For example, the products **51**⁶ and **52**⁷ were afforded by the reaction of $[CpMn(CO)_2(THF)]$ and 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) with **48**, respectively. Compound **48** can undergo cycloaddition reaction due to the presence of C=Ge double bond character. For example, treatment of **48** with AdNCO (Ad = Adamantyl) and azobenene afforded the corresponding products **53**⁸ and **54**⁷ respectively. Oxidative addition reactions of **48** with elemental chalcogens were performed to obtain the 2-germaketone analogues **55-57**.⁹

Scheme 2.8

The reaction of $[CH_2(PPh_2=S)_2]$ (**3**) with nBuLi in THF generated the monolithium

salt $[\text{Li}\{\text{CH}(\text{S}=\text{PPh}_2)_2\}(\text{THF})(\text{Et}_2\text{O})]$ as the ligand transfer reagent. Metathesis reaction of the monolithium salt with SnCl_2 in Et_2O afforded $[\text{SnCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$ (**58**).¹⁰ Recently the novel germanium and tin bis(methanediide) complexes have been reported. The reaction of **3** with two equivalents of MeLi in toluene followed by addition of 0.5 equivalents of GeCl_4 afforded compound **59**.¹¹ The reaction of **36** with one equivalent of SnCl_4 afforded tin bis(methanediide) complex **60** (Scheme 2.9).¹²

Scheme 2.9

Since **26**¹³ contains two different donors, we anticipate that its coordination chemistry is different from those of $[\text{CH}_2(\text{PPh}_2=\text{E})_2]$ ($\text{E} = \text{NSiMe}_3, \text{S}$). In Chapter 2, the synthesis of magnesium, aluminum and tin(II) (iminophosphinoyl)(thiophosphinoyl)methanide and methanediide complexes stabilized by **26** is described. The reactivity of the tin(II) (iminophosphinoyl)(thiophosphinoyl)methanediide complex is also reported.

2.2 Results and Discussion

2.2.1 Synthesis of Magnesium (Iminophosphinoyl)(thiophosphinoyl)methanediide Complex

The reaction of **26**¹³ with Mg(ⁿBu)₂ in refluxing toluene afforded the magnesium bis(phosphinoyl)methanediide complex (μ -L₁'Mg)₂ (**61**) (Scheme 2.10) .

Scheme 2.10

Compound **61** was isolated in toluene as highly moisture-sensitive colorless crystalline solids in 65.4 % yield. It has been characterized by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectrum of **61** displays resonances for the SiMe₃ and phenyl protons. The ¹³C{¹H} NMR spectrum of **61** shows one doublet of doublets for the methanediide carbon at δ 34.35 ppm (J_{P-C} = 32.6, $J_{P'-C}$ = 33.5 Hz), which is shifted upfield compared with that of [(PPh₂=NSiMe₃)₂CM]₂ (M = Ca 44.9 ppm; M = Ba 53.9 ppm).^{1f} The ³¹P{¹H} NMR displays two doublets at δ 19.9 and 29.9 ppm ($^2J_{P-P'}$ = 26.0 Hz) due to two nonequivalent phosphorus nuclei.

Figure 2.1 Molecular structure of **61** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond lengths (Å) and angles

(deg): Mg(1)-C(1) 2.277(3), Mg(1)-C(2) 2.257(3), C(1)-P(1) 1.724(3), C(1)-P(2) 1.706(3), P(1)-N(1) 1.611(3), P(2)-S(1) 2.045(1), Mg(1)-N(1) 2.036(3), Mg(1)-N(2) 2.033(3), Mg(2)-C(1) 2.219(3), Mg(2)-C(2) 2.212(3), C(2)-P(3) 1.720(3), C(2)-P(4) 1.702(3), P(3)-N(2) 1.619(3), P(4)-S(2) 2.038(1), Mg(2)-S(1) 2.433(1), Mg(2)-S(2) 2.429(1); C(1)-Mg(1)-C(2) 100.4(1), C(1)-Mg(1)-N(1) 75.2(1), C(2)-Mg(1)-N(2) 75.7(1), C(1)-Mg(2)-C(2) 103.6(1), C(1)-Mg(2)-S(1) 81.7(8), C(2)-Mg(2)-S(2) 81.4(8), Mg(1)-C(1)-Mg(2) 77.7(1), Mg(1)-C(2)-Mg(2) 78.3(9), P(1)-C(1)-P(2) 129.0(2), P(3)-C(2)-P(4) 130.4(2).

The molecular structure of **61** is shown in Figure 2.1. The magnesium centers in compound **61** adopt a distorted-tetrahedral geometry, being bound to the methanediide carbon atoms and coordinated to two nitrogen atoms or two sulfur atoms of the ligand. With the Mg(1)-C(1)-Mg(2)-C(2) ring as the base, compound **61** show an “open-box”-like structure framework. The structures of **61** is similar to that of $[(PPh_2=NSiMe_3)_2CCa]_2$.^{1f} The Mg-C bond length of **61** (average 2.241 Å) is significantly shorter than those of the magnesium methanide complexes $[HC(PPh_2=NSiMe_3)_2Mg(\mu-Cl)]_2$ (2.460(8) Å) and $[HC(PPh_2=NSiMe_3)_2MgI(THF)]$ (2.573(6) Å).¹⁴ The Mg-N bond length of **61** (average 2.035 Å) is shorter than those of $[HC(PPh_2=NSiMe_3)_2Mg(\mu-Cl)]_2$ (average 2.134 Å) and $[HC(PPh_2=NSiMe_3)_2MgI(THF)]$ (average 2.110 Å),¹⁴ but it is slightly longer than the Mg-N amide σ bonds in the magnesium amide complexes $[(Et_2O)Mg(Cl)\{N(SiMe_3)_2\}]_2$ (1.970(3) Å) and $[Mg\{N(SiMePh_2)_2\}]_2$ (1.963(6), 1.969(6) Å).¹⁵ The Mg-S bond lengths in **61** (2.433(1), 2.429(1) Å) are within the range of terminal Mg-S σ bond lengths (2.33-2.66 Å), while they are slightly shorter than bridging Mg-S bond lengths (2.46-2.61 Å).¹⁶ The P-C bonds (1.713 Å) are shortened and the P-N bonds (1.615 Å), P-S bonds (2.042 Å) are shortened compared with those of **26** (P-C: 1.826 Å, P-N: 1.547(2) Å, P-S: 1.960(1) Å)¹³. They are comparable to those of the germinal dianoin **28** (P-C: 1.681 Å, P-N: 1.611(4) Å, P-S:

2.042(2) Å)¹³ due to the negative hyperconjugation from the carbon to phosphorous σ* orbitals.

2.2.2 Synthesis of Aluminum (Iminophosphinoyl)(thiophosphinoyl)methanediide Complex

The reaction of **26**¹³ with AlMe₃ in refluxing toluene afforded the aluminum bis(phosphinoyl)methanediide complex (L₁'AlMe)₂ (**62**) (Scheme 2.11). Similar bimetallic methanediide complexes of aluminum, [(AlMe₂)₂{μ₂-C(PPh₂NSiMe₃)₂}] (**41**),^{1h} [(AlMe₂)₂{C(PPh₂=N^tBu)(8-C₉H₆N)}]¹⁷ and [{AlMe}{C(PPh₂=O)₂}₂{AlMe₂}₂]¹⁸ have been reported.

Scheme 2.11

Compound **62** was isolated in Et₂O as a highly air- and moisture-sensitive colorless crystalline solid in 21.0 % yield. It has been characterized by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectrum of **62** displays resonances for the SiMe₃ and phenyl protons. It is noteworthy that the ¹³C{¹H} NMR signal for the methanediide carbon in **62** is not observed. Similarly, there is no ¹³C{¹H} NMR resonance for the methanediide carbon in **41**.^{1h} The ³¹P{¹H} NMR spectrum of **62** displays two doublets at δ 22.8 and 25.9 ppm (²J_{P-P} = 13.0 Hz) due to two nonequivalent phosphorus nuclei. The ²⁷Al NMR spectrum of **62** shows one broad signal at δ 54.6 ppm.

Figure 2.2 Molecular structure of **62** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)-C(2) 1.976(1), Al(1)-C(1) 1.949(1), Al(1)-N(1) 1.915(1) Al(1)-S(1) 2.316(5), P(1)-C(2) 1.710(1), P(2A)-C(2) 1.686(1), P(1)-N(1) 1.634(1), P(2)-S(1) 2.044(5); C(2)-Al(1)-N(1) 81.5(5), C(2)-Al(1)-C(1) 125.2(6), C(2)-Al(1)-S(1) 111.3(4), N(1)-Al(1)-S(1) 99.6(4), P(1)-C(2)-P(2A) 129.7(8), Al(1)-C(2)-P(1) 87.7(6), C(2)-P(1)-N(1) 98.8(6), P(1)-N(1)-Al(1) 92.0(5).

The molecular structure of **62** is shown in Figure 2.2. It is symmetric and is comprised of two “{(PPh₂=NSiMe₃)(PPh₂=S)}CAI Me” moieties bonded together in a head-to head manner. The aluminum atom Al(1) is bonded to the methanediide carbon atom C(2), one nitrogen, and one sulfur atom of each ligand. Therefore, the geometry around the aluminum atom is tetrahedral. The Al(1)-C(2) bond length (1.976(1) Å) is shorter than that of **41** (2.121(3), 2.117(3) Å).^{1h} Similar to the case for **41**, the Al(1)-C(2) bond length in **62** is longer than the terminal Al-C_{methyl} bond (1.949(1) Å). The Al(1)-N(1) bond (1.915(1) Å) is shorter than those of **62** (1.926(3), 1.933(3) Å),^{1h} but it is longer than the Al-N amide σ bond in the aluminum amide complexes [(2,6-*i*Pr₂C₆H₃)N-(SiMe₃)AlMe₂]₂ (average 1.821 Å)¹⁹ and [(Me₃Si)N{CH₂CH₂(Me₃Si)N}₂AlCl] (average 1.807 Å).²⁰ The Al(1)-S(1) bond length (2.316(5) Å) in **62** is longer than the Al-S σ bond in [(^tBu)₂Al(SCH₂CH₂NEt₂)] (2.272(4) Å).²¹ Similar to **61**, the P-C bonds (1.698 Å) are shortened and the P-N

bonds (1.634(1) Å) and P-S bonds (2.044(5) Å) are lengthened compared with those of **26** (P-C: 1.826 Å, P-N: 1.547(2) Å, P-S: 1.960(1) Å)¹³. They are comparable to those of the germinal dianoin **28** (P-C: 1.681 Å, P-N: 1.611(4) Å, P-S: 2.042(2) Å)¹³ due to the negative hyperconjugation from the carbon to phosphorous σ^* orbitals.

2.2.3 Synthesis of Tin(II) (Iminophosphinoyl)(thiophosphinoyl)methanide Complex

The tin(II) (iminophosphinoyl)(thiophosphinoyl)methanide complex ($L_1'SnCl$) (**63**) was obtained from the reaction of **26**¹³ with $nBuLi$ in THF followed by the addition of $SnCl_2$ in Et_2O (Scheme 2.12).

Scheme 2.12

Compound **63** was isolated in toluene as an air- and moisture-sensitive colorless crystalline solid in 65.1% yield. It has been characterized by NMR spectroscopy and X-ray crystallography. The 1H NMR spectrum of **63** displays one doublet of doublets at δ 3.86 ppm (dd, $^2J_{P-H} = 5.86$ Hz) for the methine proton (PCHP) and resonances for the $SiMe_3$ and phenyl protons. The $^{31}P\{^1H\}$ NMR spectrum of **63** shows two triplets at δ 32.0 ppm (t, $^2J_{P-Sn} = 43.59$ Hz) and δ 35.0 ppm (t, $^2J_{P'-Sn} = 72.05$ Hz) due to two nonequivalent phosphorus nuclei. The $^{13}C\{^1H\}$ NMR spectrum of **63** shows one doublet of doublets at δ 30.26 ppm ($J_{P-C} = 56.24$, $J_{P'-C} = 73.40$ Hz) for the methanide carbon of PCHP. The $^{119}Sn\{^1H\}$ NMR spectrum of **63** shows one AB quartet at δ 67.63 ppm ($^2J_{Sn-P} = 161.0$ Hz).

Figure 2.3 Molecular structure of **63** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sn(1)-C(1) 2.3712(14), Sn(1)-Cl(1) 2.4966(4), Sn(1)-N(1) 2.2532(12), P(1)-C(1) 1.7899(14), P(1)-N(1) 1.6031(13), P(2)-C(1) 1.7801(14), P(2)-S(1) 1.9619(5); C(1)-Sn(1)-Cl(1) 90.89(4), C(1)-Sn(1)-N(1) 70.11(5), Cl(1)-Sn(1)-N(1) 92.10(3), C(1)-P(1)-N(1) 102.99(7), C(1)-P(2)-S(1) 111.38(5), P(1)-N(1)-Sn(1) 97.91(6), P(1)-C(1)-P(2) 120.59(8), P(1)-C(1)-Sn(1) 88.75(6), P(2)-C(1)-Sn(1) 105.08(6).

The molecular structure of **63** is shown in Figure 2.3. In compound **63**, the metal center is bonded to the ligand in a *C,N* chelate fashion and displays a trigonal pyramidal geometry. The angle sum at the tin is 253.1°, consistent with a stereochemically active electron pair at the metal centers. The MCPN four-membered ring is nearly planar, as indicated by the sum of bond angle (359.76°). The Sn-C bond length of 2.3712(14) Å in **63** is very close to the Sn-C single bond length of 2.374(2) Å in [SnCl{CH(PPh₂=S)₂}] (**58**),¹⁰ 2.35(2) Å in [Sn{C(SiMe₃)₂C₅H₄N-2}₂]²²⁻²³ and 2.329(4) Å in [Sn{CPh(SiMe₃)C₅H₄N-2}₂].²⁴ The Sn-Cl bond length of 2.4966(4) Å agrees well with the corresponding length of 2.521(1) Å in **58**¹⁰ and 2.473(9) Å in [HC(CMeNAr)₂SnCl].²⁵ The Sn-N length of 2.2532(12) Å is comparable with (Sn-N_{amide}: 2.144(5) Å, Sn-N_{pyridine}: 2.299(5) Å) in [C₅H₄N-2-C(SiMe₃)₂Sn{N(SiMe₃)₂}].²² The P-C bonds (1.785 Å) are shortened

and the P-N bond (1.6031(13) Å) and P-S bond (1.9619(5) Å) are lengthened compared with those of **26** (P-C: 1.826 Å, P-N: 1.547(2) Å, P-S: 1.960(1) Å).¹³ They are comparable to those of the mono anoin complex **27** (P-C: 1.712 Å, P-N: 1.588(3) Å, P-S: 1.989(1) Å)¹³ due to the negative hyperconjugation from the carbon to phosphorous σ^* orbitals.

2.2.4 Synthesis of Tin(II) (Iminophosphinoyl)(thiophosphinoyl)methanediide Complex-A Stannavinylidene Derivative

The reaction of **26**¹³ with two equivalents of $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$ in refluxing toluene afforded a novel tin(II) (iminophosphinoyl)(thiophosphinoyl)methanediide complex, which is regarded as a stannavinylidene ($:\text{Sn}=\text{C}<$) derivative **65** (Scheme 2.13).²⁶ Similar reaction of **26** with two equivalents of $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$ in toluene at room temperature gave $[\text{L}_1'\{\text{SnN}(\text{SiMe}_3)_2\}]$ (**64**) together with a small amount of **65**. It is suggested that **64** was dehydroaminated by $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$ in refluxing toluene to form **65**. In contrast, the reaction of $[\text{CH}_2(\text{PPh}_2=\text{NSiMe}_3)_2]$ (**2**) with $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$ afforded the 1,3-distannacyclobutane $[\text{Sn}\{\mu_2\text{-C}(\text{PPh}_2=\text{NSiMe}_3)_2\}]_2$ (**49**).^{1a}

Scheme 2.13

Compounds **64** and **65** are highly air- and moisture-sensitive colorless and yellow crystalline solids. **64** was isolated in Et₂O in 46.9 % yield and **65** was isolated in CH₂Cl₂ in 30.1 % yield. They have been characterized by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectra of **64** and **65** display resonances for the SiMe₃ and phenyl protons. It is noteworthy that the ¹³C{¹H} NMR signal for the methanediide carbon in **65** is not observed. Similarly, there is no ¹³C{¹H} NMR resonance for the carbenic carbon in the bisgermavinylidene.^{1a} The ³¹P{¹H} NMR signals of **65** [δ 20.5, 27.4 ppm (d, ²J_{P-P'} = 17.5 Hz)] show upfield shift compared with those of **64** [δ 30.2 ppm (t, ²J_{Sn-P} = 73.7 Hz), 34.7 ppm (t, ²J_{Sn-P'} = 39.0 Hz)]. Comparing the ¹¹⁹Sn{¹H} NMR signal of **65** [δ 132.1 ppm (dd, ²J_{Sn-P} = 177.1 Hz)] with that of **64** (δ -19.3 ppm), the 1,3-distannacyclobutane in [2-{Sn{C(ⁱPr₂P=NSiMe₃)}}]-6-{Sn{CH(ⁱPr₂P=NSiMe₃)}Cl}C₅H₃N]₂ (δ -10.96 ppm)²⁷ and the 6-stannapentafulvene [(Tbt)(Mes)Sn=CR₂] (Tbt = 2,4,6-{CH(SiMe₃)₂}₃C₆H₂, Mes = 2,4,6-Me₃C₆H₂, CR₂ = fluorenylidene) (δ 270 ppm),^{28b} it is suggested that compound **65** exists as a tin(II) bis(phosphinoyl)methanediide complex and does not undergo oligomerization in the solution.

Figure 2.4 Molecular structure of **64** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(2)-C(47) 2.384(4), Sn(2)-N(3) 2.152(4), Sn(2)-N(4) 2.275(3), P(3)-C(47) 1.776(4), P(4)-C(47) 1.780(4), P(3)-N(4) 1.612(3), P(4)-S(2) 1.960(2); C(47)-Sn(2)-N(3) 98.8(1), N(3)-Sn(2)-N(4) 106.6(1), C(47)-Sn(2)-N(4) 67.8(1), Sn(2)-N(4)-P(3) 96.0(2), N(4)-P(3)-C(47) 100.2(2), P(3)-C(47)-P(4) 123.4(2).

The molecular structure of **64** is shown in Figure 2.4. In the asymmetric unit, there are two independent molecules with slightly different bond distances and angles. Only one of them is discussed here for clarity. The methanide ligand is bonded in a *C,N'*-chelate fashion to the tin center and displays a trigonal pyramidal geometry. The thiophosphinoyl group of the ligand remains uncoordinated. The sum of the bond angles at the tin center is 273.3°, which is significantly smaller than that of 337.7° in the tetra-coordinate stannylene [Sn{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}₂].²⁹ This geometry is consistent with a stereoactive lone pair at the tin center. The Sn(2)-C(47) (2.384(4) Å), Sn(2)-N(3) (2.152(4) Å) and Sn(2)-N(4) (2.275(3) Å) bond lengths in **64** are comparable with those of [{C₅H₄N-2-C(SiMe₃)₂}Sn{N(SiMe₃)₂}] (Sn-C: 2.356(8) Å, Sn-N_{amide}: 2.144(5) Å, Sn-N_{pyridine}: 2.299(5) Å), respectively.²²

Figure 2.5 Molecular structure of **65** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Sn(1)-C(1A) 2.199(4), C(1)-P(1) 1.685(4), C(1)-P(2A) 1.711(4), P(1)-S(1) 2.032(1), P(2)-N(1) 1.615(3), Sn(1)-N(1) 2.244(3), Sn(1)-S(1) 2.692(9); C(1A)-Sn(1)-S(1) 96.5(1), N(1)-Sn(1)-S(1) 89.3(8), C(1A)-Sn(1)-N(1) 70.6(1), Sn(1)-N(1)-P(2) 94.7(1), N(1)-P(2)-C(1A) 101.1(2), P(1)-C(1)-P(2A) 135.2(2).

The molecular structure of **65** is shown in Figure 2.5. It is symmetric and comprised of two “(PPh₂=NSiMe₃)(PPh₂=S)CSn:” moieties bonded together in a head-to-head manner. The tin atom Sn(1) is bonded to the methanediide carbon atom C(1A), one nitrogen and one sulfur atom of each ligand. Therefore, the geometry around the tin atom is trigonal pyramidal geometry. The sum of the bond angles at the tin atom is 256.3°, which is comparable with that of **64** (273.3°). This geometry is consistent with a stereoactive lone pair at the tin center. The C(1A)-Sn(1) bond length (2.199(4) Å) in **65** is significantly shorter than that of **64** (2.384(4) Å) and the 1,3-distannacyclobutane [Sn{μ²-C(PPh₂=NSiMe₃)₂}]₂ (**50**) (average 2.322 Å).^{1a} This demonstrates some double character in the C(1A)-Sn(1) bond. The C(1A)-Sn(1) bond length is longer than that of the stannaethene [{(Me₃Si)₂CH}₂Sn=C{(tBu)₂C(SiMe₃)₂}] (2.025(4) Å)^{28a} and the 6-stannapentafulvene [(Tbt)(Mes)Sn=CR₂] (2.016(5) Å)^{28b} due to the lower oxidation state of tin atom in **65**. The Sn(1)-N(1) bond length (2.244(3) Å) in **65** is

comparable with that of **64** (2.275(3) Å), while it is longer than the terminal Sn-N σ bond in $[\text{:Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (2.096(1) Å).²² The Sn(1)-S(1) bond length (2.692(9) Å) is longer than the terminal Sn-S σ bond in $[\text{:Sn}(\text{SAr})_2]$ (Ar = C₆H₂-2,4,6-^tBu₃) (2.435(1) Å),³⁰ but it is comparable with that of the aryltin(II) dithiocarboxylate $[\text{:Sn}(\text{Ar})\{\text{S}_2\text{CAr}\}]$ (average 2.659 Å).³¹

2.2.5 Reactivity of Tin(II) (Iminophosphinoyl)(thiophosphinoyl)methanediide Complex

The tin(II) (iminophosphinoyl)(thiophosphinoyl)methanediide **65** which is stabilized by the coordination via nitrogen and sulfur donors can behave as (i) a Lewis base (ii) undergoing oxidative addition reaction (iii) undergoing addition reaction (Scheme 2.14).

Scheme 2.14

2.2.5.1 Reactivity of Tin(II)

(Iminophosphinoyl)(thiophosphinoyl)methanediide Complex toward Isocyanates

Treatment of **65** with two equivalents of AdNCO (Ad = Adamantyl) in THF afforded the [2+2] cycloaddition adduct $[\text{L}_1]''\{(\text{C}(\text{O})\text{N}(\text{Ad})\}\text{Sn:}]$ (**66**) (Scheme 2.15). It is probable that the reaction proceeds via a [2+2] cycloaddition of $>\text{C}=\text{Sn:}$ or an insertion reaction of the C^--Sn^+ bond with the $\text{N}=\text{C}$ bond of AdNCO.

Moreover, the reaction of **65** with two equivalents of ArNCO in THF afforded

$[(L_1'')^- \{ (C(O)N(Ar)) \} Sn^+ :]$ (**67**), in which the C-Sn bond is cleaved. It is proposed that the reaction proceeds via a cycloaddition intermediate which contains a four-membered CSnNC ring. Due to the steric hindrance of the Ar group, the C-Sn bond is cleaved in order to release the ring strain. The thiophosphinoyl substituent is then coordinated with the tin atom to form **67**.

Scheme 2.15

Compounds **66** and **67** were both isolated in toluene as colorless crystalline solids in 38.8 % yield and in 36.5 % yield respectively. They have been characterized by NMR spectroscopy and X-ray crystallography. The 1H NMR spectra of **66** and **67** show a set of signals due to the ligand backbone. The $^{13}C\{^1H\}$ NMR spectrum of **66** shows one doublet of doublets for the methanediide carbon at δ 56.70 ppm ($J_{P-C} = 56.6$ Hz, $J_{P'-C} = 70.0$ Hz), which is downfield shift compared with that of **67** [δ 40.64 ppm ($J_{P-C} = 56.6$ Hz, $J_{P'-C} = 74.3$ Hz)]. The $^{31}P\{^1H\}$ NMR spectrum of **66** shows two doublets with satellites due to coupling to $^{117/119}Sn$ at δ 22.29 ($J_{P-P'} = 15.2$ Hz, $^2J_{Sn-P} = 86.7, 121.4$ Hz) and 41.23 ppm ($J_{P-P'} = 15.2$ Hz, $^2J_{Sn-P} = 47.7, 73.7$ Hz). The $^{119}Sn\{^1H\}$ NMR

spectrum consists of a broad signal at δ -255.15 ppm, which shows an upfield shift compared with that of **65** (δ 132.1 ppm). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **67** shows two doublets with satellites due to coupling to $^{117/119}\text{Sn}$ at δ 27.79 ($J_{\text{P-P}'} = 8.7$ Hz, $^2J_{\text{Sn-P}} = 69.4, 86.7$ Hz) and 37.44 ppm ($J_{\text{P-P}'} = 8.7$ Hz, $^2J_{\text{Sn-P}} = 73.7, 134.4$ Hz). The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **67** consists of a broad signal at δ -129.25 ppm, which shows a downfield shift compared with that of **66**. The $^{13}\text{C}\{^1\text{H}\}$ NMR signal for the methanediide carbon and the $^{119}\text{Sn}\{^1\text{H}\}$ NMR signal indicate the zwitterionic $\text{C}^{\cdots}\text{Sn}^+$ character in **67**.

Figure 2.6 Molecular structure of **66** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)–C(2) 2.373(4), Sn(1)–N(2) 2.235(8), Sn(1)–N(1) 2.146(8), N(1)–C(1) 1.372(13), C(1)–O(1) 1.233(4), C(1)–C(2) 1.550(5), C(2)–P(2) 1.785(4), C(2)–P(1) 1.783(4), P(2)–N(2) 1.628(11), P(1)–S(1) 1.9599(15); C(1)–N(1)–Sn(1) 99.0(5), N(1)–Sn(1)–C(2) 64.1(3), Sn(1)–C(2)–C(1) 91.6(2), C(2)–C(1)–N(1) 110.8(4), N(2)–Sn(1)–N(1) 88.8(4), N(2)–Sn(1)–C(2) 71.5(3).

The molecular structure of **66** is shown in Figure 2.6. Compound **66** has an open book structure with the C(2)–Sn(1) bond lying on the spine. The dihedral angle between the C(2)P(2)N(2)Sn(1) and C(2)C(1)N(1)Sn(1) planes is 76.2°. The iminophosphinoyl substituent is coordinated with the Sn(1) atom, which adopts a

distorted trigonal pyramidal geometry (the sum of bond angles: 224.4°). This indicates that the Sn(1) atom possess a high s character lone pair. The C(2)-Sn(1) bond (2.373(4) Å) is significantly longer than the CSn: bond (2.199(4) Å) in **65**.²⁶ It is similar to that in [HC(PPh₂=NSiMe₃)(PPh₂=S)SnN(SiMe₃)₂] (2.384(4) Å).²⁶ The results suggest that the C-Sn bond in **66** has no multiple bond character. Moreover, the C(1)-N(1) (1.372(13) Å) and C(1)-O(1) bonds (1.233(4) Å) in **66** are single and double bonds respectively.

Figure 2.7 Molecular structure of **67** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)–N(1) 2.1477(12), Sn(1)–N(2) 2.1913(12), Sn(1)–S(1) 2.6418(4), C(26)–N(1) 1.3649(18), C(25)–C(26) 1.524(2), C(26)–O(1) 1.2279(17), C(25)–P(1) 1.7244(15), C(25)–P(2) 1.7367(15), P(2)–N(2) 1.6329(12), P(1)–S(1) 2.0545(5); N(1)–Sn(1)–N(2) 91.69(5), N(2)–Sn(1)–S(1) 94.02(4), N(1)–Sn(1)–S(1) 96.50(4).

The molecular structure of **67** is shown in Figure 2.7. Compound **67** has a propeller structure, in which the N and S donors adopt a tripodal rearrangement. Both the iminophosphinoyl and thiophosphinoyl substituent are coordinated with the Sn(1) atom, which adopts a distorted trigonal pyramidal geometry (the sum of bond angles: 282.2°). This indicates that there is a stereoactive lone pair of electrons at the Sn(1)

atom. The C(25)···Sn(1) distance (3.211(1) Å) is significantly longer than the C-Sn bond in base-stabilized stannylenes such as [$\{C_5H_4N-2-C(SiMe_3)_2\}Sn\{N(SiMe_3)_2\}$] (Sn-C: 2.356(8) Å)²² and [$\{2,6-(CH_2NMe_2)_2C_6H_3\}SnCl$] (2.158(8) Å),³² but it is shorter than the sum of van der Waal's radii (*ca.* 3.87 Å). The results suggest that there is a weak interaction between the C_{methanide} and Sn(1) atoms. The Sn(1)-S(1) bond (2.6418(4) Å) is longer than the terminal Sn-S σ bond in [$:Sn(SAr)_2$] (Ar = C₆H₂-2,4,6-^tBu₃) (2.435(1) Å),³¹ but it is comparable with that of the aryl tin(II) dithiocarboxylate [$:Sn(Ar)\{S_2C(Ar)\}$] (average 2.659 Å).³³ The Sn(1)-N(1) (2.1477(12) Å) and Sn(1)-N(2) (2.1913(12) Å) bonds in **67** are comparable to those in **66**. Moreover, the C(26)-N(1) (1.3649(18) Å) and C(26)-O(1) bonds (1.2279(17) Å) are single and double bonds respectively.

2.2.5.2 Reactivity of Tin(II)

(Iminophosphinoyl)(thiophosphinoyl)methanediide Complex toward [RhCl(cod)]₂

Treatment of **65** with two equivalents of [RhCl(cod)]₂ (cod = 1,5-cyclooctadiene) in THF afforded [$L, \eta^5\{(cod)Rh\}SnCl$] (**68**) (Scheme 2.16), in which [RhCl(cod)] underwent an 1,2-addition with the >C=Sn: bond in **65**. The addition also illustrates the nucleophilic character of the C_{methanediide} atom in **65**. Compound **68** is a heterobimetallic methanediide complex. Other examples of heterobimetallic methanediide complexes such as [$(PPh_2=NSiMe_3)_2C(M)\{Rh(cod)\}$] (M = Li or Pd(allyl)) and [$\{(C_6H_4N-2)(P^iPr_2=NSiMe_3)C\}_2(Sn)(Pb)$] have been reported.^{1b, 1c, 34}

Scheme 2.16

Compound **68** was isolated in CH_2Cl_2 as a red crystalline solid in 55.4 % yield, which is stable at room temperature in solution and the solid state in an inert atmosphere. It has been characterized by NMR spectroscopy and X-ray crystallography. The ^1H NMR spectrum of **68** shows a set of signals due to the SiMe_3 , cod and phenyl protons. Similar to **65**, the $^{13}\text{C}\{^1\text{H}\}$ NMR signal for the methanediide carbon is not observed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a doublet at δ 28.38 ppm ($^2J_{\text{P-P}'} = 26.0$ Hz) and a doublet of doublet at δ 37.86 ppm ($^2J_{\text{P-P}'} = 26.0$ Hz, $^2J_{\text{P-Rh}} = 13.0$ Hz) due to two non-equivalent phosphorus nuclei. The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum shows a multiplet at δ 110.74 ppm. The results indicate that **68** retains its solid-state structure in solution.

Figure 2.8 Molecular structure of **68** with thermal ellipsoids at the 30% probability level.

Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-Sn(1) 2.3617(16), Sn(1)-Cl(1) 2.5311(4), Sn(1)-N(1) 2.2535(13), P(2)-N(1) 1.6060(14), P(2)-C(1) 1.7370(15), C(1)-Rh(1) 2.1715(16), Rh(1)-S(1) 2.4005(4), P(1)-S(1) 2.0256(6), P(1)-C(1) 1.7233(15), Rh(1)-C(29) 2.1508(15), Rh(1)-C(30) 2.1608(17), Rh(1)-C(33) 2.1743(15), Rh(1)-C(34) 2.1800(17); C(1)-Sn(1)-Cl(1) 96.79(4), N(1)-Sn(1)-Cl(1) 100.17(4), Sn(1)-N(1)-P(2) 98.34(6), N(1)-P(2)-C(1) 101.84(7), P(2)-C(1)-P(1) 134.23(10), Sn(1)-C(1)-Rh(1) 76.66(5), Sn(1)-C(1)-P(2) 90.79(6), Rh(1)-C(1)-P(1) 50.63(5), C(1)-P(1)-S(1) 99.71(6), P(1)-S(1)-Rh(1) 78.247(17).

The molecular structure of **68** is shown in Figure 2.8. The methanediide C(1) atom is bonded with the Rh(1) and Sn(1) atoms. Moreover, it is spirocyclic with the thiophosphinoyl substituent coordinated to the Rh(1) atom and the iminophosphinoyl substituent coordinated to the Sn(1) atom. These indicate that the C(1) atom is chiral. However, **68** is racemic and the *R*- and *S*-enantiomer are present in the unit cell. It is because **68** was prepared from optically inactive reactants. The C(1)-Sn(1) bond (2.3617(16) Å) is comparable with that in **66**. The results indicate that the C-Sn bond in **68** does not have any multiple bond character. The Sn(1) atom adopts a distorted trigonal pyramidal geometry (the sum of bond angles: 265.38°), which indicates that the Sn(1) atom possess a high *s* character lone pair. The Sn(1)···Rh(1) distance (2.8155(2) Å) is significantly longer than the Sn-Rh bond in the rhodium-stannylene complex *cis*-[Rh{Sn(N^tBu)₂SiMe₂}₂(PPh₃)₂Cl] (2.571(2), 2.577(2) Å) and [Rh(η -C₆H₅Me)(η -C₈H₁₄){SnCl(NR₂)₂}] (R = SiMe₃, 2.554(1) Å).^{35a,b} However, it is shorter than the sum of van der Waal's radii (*ca* 4.0 Å). The results show that there is a weak interaction between the Sn(1) and Rh(1) atoms. The Rh(1)-C(1) bond (2.1715(16) Å) is comparable with the Rh-C_{methanediide} bond in [(PPh₂=NSiMe₃)₂C{Rh(cod)}(GeCl)] (2.204(3) Å)⁶ and [(PPh₂=NSiMe₃)₂C{Rh(cod)}₂] (2.148(2), 2.168(2) Å).^{34b}

2.2.5.3 Reactivity of Tin(II)

(Iminophosphinoyl)(thiophosphinoyl)methanediide Complex toward Sulfur

The reaction of **65** with two equivalents of elemental sulfur in toluene for 4 hours afforded a mixture of $[\{(\mu\text{-S})\overline{\text{Sn}}^{\text{IV}}\text{L}_1''\}_3\text{Sn}^{\text{II}}(\mu_3\text{-S})]$ (**69**) and **26**¹³ (Scheme 2.17). Compound **69** comprises a $\text{Sn}^{\text{II}}\text{S}$ moiety coordinated with the Sn^{IV} and S atoms of a trimeric 2-stannathiomethendiide $[\text{L}_1''\text{Sn}(\mu\text{-S})]_3$. For clarity, the tin(IV) atoms in **69** are labeled as Sn^1 , Sn^2 and Sn^3 , while the tin(II) and sulfur atoms of the SnS moiety in **69** are labeled as Sn^4 and S^4 .

Scheme 2.17

Pure compound **69** can be isolated in C_6D_6 as orange crystals in 29.2% yield.

The reaction appears to proceed through an oxidative addition of **65** with elemental sulfur to form an unstable 2-stannathiomethendiide intermediate “(PPh₂=NSiMe₃)(PPh₂=S)CSn=S”, which then decomposes to form intermediates “(PPh₂=NSiMe₃)(PPh₂=S)C:” and “SnS”. A monomeric SnS molecule is trapped by the Sn^{IV} and S atoms of a trimeric 2-stannathiomethendiide [L₁”Sn(μ-S)]₃ to form **69**. Subsequently, **26** could be formed by the hydrogen abstraction of “(PPh₂=NSiMe₃)(PPh₂=S)C:” with the solvents. Chivers *et al.* reported that the intermediate [:C(PPh₂=S)₂] dimerizes to form [(SPh₂P)₂C₂(PPh₂)₂S₂] which contains a six-membered C₂P₂S₂ ring.³⁶ However, the dimerization of “(PPh₂=NSiMe₃)(PPh₂=S)C:” cannot be observed in the reaction of **65** with elemental sulfur in toluene, instead **26** was formed. Moreover, when the reaction of **65** with elemental sulfur was performed in THF for 20 minutes, a mixture of **65** and **26** can be isolated in a ratio of 1:1, which was confirmed by NMR spectroscopy. The results illustrate that the decomposition of “(PPh₂=NSiMe₃)(PPh₂=S)CSn=S” and the hydrogen abstraction of “(PPh₂=NSiMe₃)(PPh₂=S)C:” are enhanced in a polar solvent.

Compound **69** is stable in the solid state at room temperature under an inert atmosphere. Orange crystals of **69** are soluble in CH₂Cl₂ only and it decomposes slowly in solution to give **26**. Compound **69** can be considered as an intermediate during the decomposition of the unstable 2-stannathiomethendiide intermediate “(PPh₂=NSiMe₃)(PPh₂=S)CSn=S”. Thus, when the reaction of **65** with elemental sulfur in toluene was performed overnight, only compound **26** formed.

Freshly prepared solution of **69** in CD₂Cl₂ was characterized by NMR spectroscopy. The ¹H NMR spectrum shows one singlet (δ -0.29 ppm) and multiples (δ 6.88-7.38 ppm) for the SiMe₃ and phenyl protons, respectively. In the molecular structure of **69** (Figure 2.8), the S(1-3) atoms have similar orientation toward the Sn(4) atom, but the Sn(4)-S(2-3) bond lengths are shorter than the Sn(4)⋯S(1) distance. These lead to non-equivalent P(2,4,6) atoms. The ³¹P{¹H} NMR at room temperature or -60 °C shows two doublets at δ 27.42 and 30.07 ppm, which correspond to two non-equivalent phosphorus nuclei. The results are not consistent with the solid-state structure. These indicate that the thiophosphinoyl substituents are fluxional in solution or the S(1-3) atoms may be equivalent in solution with equal Sn(4)⋯S(1-3) distances. The ¹¹⁹Sn NMR spectrum of **69** at room temperature or -60 °C shows a multiple at δ -242.1 ppm. The ¹¹⁹Sn solid-state NMR spectroscopy was performed. The ¹¹⁹Sn CPMAS NMR signals (δ_{iso} = -260.3 (Sn⁴), -232.3 ppm (Sn¹⁻³)) show two nonequivalent tin environments in **69**. The isotropic chemical shift for the Sn¹⁻³ atoms (δ_{iso} = -232.3 ppm) shows an upfield shift compared with ¹¹⁹Sn{¹H} NMR signal of [Sn{N(SiMe₃)₂(μ -S)}₂ (δ -106.6 ppm).³⁷ The isotropic chemical shift for the Sn⁴ atom (δ_{iso} = -260.3 ppm) shows an upfield shift compared with the ¹¹⁹Sn{¹H} NMR signal of :SnO trapped by the lutidine-bridged bisstannylene (δ -85.1 ppm).³⁸

Temperature-dependent ¹¹⁹Sn Mössbauer (ME) studies. The ME spectra of **69** were examined over the range 5.5 < T < 181 K and give evidence of three distinct tin sites. As usual, these resonances consist of well resolved doublets, and a typical spectrum at 91.7 K is shown in Figure 2.9.

Figure 2.9 ^{119}Sn Mössbauer spectrum of compound **69** at 91.7 K

As will be noted the spectrum consists of a "major" resonance at an isomer shift (IS) of about 1.17 mm sec^{-1} , a second absorbance at an IS of about 3.56 mm sec^{-1} and a third site at an IS of about 2.2 mm sec^{-1} , all with respect to the room temperature BaSnO_3 reference point. The "major" site is clearly due to Sn(IV) while the second resonance arises from a Sn(II) site. The third site cannot be identified, which may be due to the decomposition of **69**.

Table 3.1 ^{119}Sn Mössbauer spectroscopic data of **69** at 91.7 K

Atom	IS	QS	Γ	normal oxidation state	I_R
Sn(4)	3.57(3)	0.87(2)	0.84(7)	+II	0.203
Sn(1-3)	1.170(4)	1.550(4)	0.87(1)	+IV	1.00

IS: isomer shift (mm s^{-1}), QS: electric quadrupole splitting (mm s^{-1}), Γ : experimental line width (mm s^{-1}), I_R : relative intensity

Figure 3.1 Molecular structure of **69** with thermal ellipsoids at the 20% probability level. Phenyl substituents, disordered solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(4)-S(7) 2.6119(19), Sn(4)-S(2) 2.686(3), Sn(4)-S(3) 2.813(3), Sn(1)-S(7) 2.6771(19), Sn(2)-S(7) 2.678(2), Sn(3)-S(7) 2.659(2), Sn(1)-S(4) 2.407(2), Sn(1)-S(5) 2.410(2), Sn(2)-S(4) 2.412(2), Sn(2)-S(6) 2.404(2), Sn(3)-S(5) 2.415(2), Sn(3)-S(6) 2.412(2), C(1)-Sn(1) 2.104(8), C(1)-P(1) 1.717(8), C(1)-P(2) 1.698(8), P(1)-N(1) 1.612(7), P(2)-S(1) 2.015(3), C(29)-Sn(2) 2.119(7), Sn(1)-N(1) 2.223(6), C(29)-P(3) 1.722(8), C(29)-P(4) 1.701(8), P(3)-N(2) 1.620(7), P(4)-S(2) 2.031(3), C(57)-Sn(3) 2.119(8), Sn(2)-N(2) 2.217(7), C(57)-P(5) 1.722(8), C(57)-P(6) 2.119(8), P(5)-N(3) 1.606(7), P(6)-S(3) 2.011(3), N(3)-Sn(3) 2.250(7), Sn(4)...S(1) 2.920(2); S(2)-Sn(4)-S(3) 106.75(8), Sn(4)-S(7)-Sn(1) 127.97(8), S(2)-Sn(4)-S(7) 88.53(7), Sn(4)-S(7)-Sn(2) 129.63(8), S(3)-Sn(4)-S(7) 88.51(7), Sn(4)-S(7)-Sn(3) 129.95(8), Sn(1)-S(5)-Sn(3) 96.34(7), S(4)-Sn(1)-S(5) 114.63(8), S(5)-Sn(3)-S(4) 113.49(7), S(6)-Sn(2)-S(4) 111.41(7), Sn(3)-S(6)-Sn(2) 95.66(7), Sn(2)-S(4)-Sn(1) 96.49(7), P(1)-C(1)-P(2) 136.6(5), P(1)-C(1)-Sn(1) 94.3(3), P(2)-C(1)-Sn(1) 128.8(4), P(3)-C(29)-P(4) 133.3(5), P(3)-C(29)-Sn(2) 93.8(3), P(4)-C(29)-Sn(2) 130.1(4), P(5)-C(57)-P(6) 134.7(5), P(5)-C(57)-Sn(3) 93.8(4), P(6)-C(57)-Sn(3) 130.3(5).

The molecular structure of **69** is shown in Figure 3.1. Single crystals suitable for X-ray crystallography were obtained by the recrystallization of **69** in C₆D₆. Phenyl substituents and disordered solvent molecules are omitted for clarity in the figure. The numbering scheme of tin atoms in the molecular structure is same as in Scheme 2.17. The methanediide ligands are coordinated in a *C,N*-chelate fashion to the Sn(1), Sn(2) and Sn(3) atoms, which adopt a distorted trigonal bipyramidal geometry. The C(1)-Sn(1) (2.104(8) Å), C(29)-Sn(2) (2.119(7) Å) and C(57)-Sn(3) (2.119(8) Å)

bonds are shorter than that in **65** (2.199(4) Å) and the 1,3-distannacyclobutane $[\text{Sn}\{\mu^2\text{-C}(\text{PPh}_2\text{=NSiMe}_3)_2\}]_2$ (average 2.322 Å).^{1a} The Sn(1)-N(1) (2.223(6) Å), Sn(2)-N(2) (2.217(7) Å) and Sn(3)-N(3) (2.250(7) Å) bonds in **69** are comparable with that in **65** (2.2554(8) Å). Moreover, they are longer than the terminal Sn-N σ bond in $[\text{:Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (2.088(6), 2.096(1) Å).³⁰ The S(4), S(5) and S(6) atoms are bridged between the Sn(1), Sn(2) and Sn(3) atoms. The Sn-S(4), Sn-S(5) and Sn-S(6) bonds (2.404(2) – 2.415(2) Å) are comparable with the Sn-S single bonds in $[(\text{Tbt})(\text{Mes})\text{Sn}(\mu\text{-S})]_2$ (Tbt = 2,4,6- $\{\text{CH}(\text{SiMe}_3)_2\}_3\text{C}_6\text{H}_2$, 2.434(3), 2.432(3) Å)⁴¹ and $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2(\mu\text{-S})]_2$ (2.416(5), 2.413(6) Å).³⁷ In addition, the S(1-3) atoms of the thiophosphinoyl substituents have a similar orientation toward the Sn(4) atom. It is noteworthy that the S(1)⋯Sn(4) distance (2.920(2) Å) is significantly longer than the S(2)-Sn(4) (2.686(3) Å) and S(3)-Sn(4) bond lengths (2.813(3) Å), but the S(1)⋯Sn(4) distance is shorter than the sum of Van der Waals' radii (ca. 4 Å). This suggests that there is a weak interaction between the S(1) and Sn(4) atoms. The S(7)-Sn(4)-S(2) and S(7)-Sn(4)-S(3) angles are almost 90°, which imply that the Sn(4) atom possess high-s-character lone pairs. The Sn(4)-S(7) bond (2.6119(19) Å) is significantly longer than the Sn-S single bonds in $[(\text{Tbt})(\text{Mes})\text{Sn}(\mu\text{-S})]_2$ (2.434(3), 2.432(3) Å)⁴¹ and $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2(\mu\text{-S})]_2$ (2.416(5), 2.413(6) Å),³⁷ which indicates that there is no multiple bond character between the Sn(4) and S(7) atoms. Furthermore, the geometry around the S(7) atom is tetrahedral. These imply that there are three lone pairs of electrons on the S(7) atom for the formation of the S(7)-Sn(1-3) bonds (2.659(2) - 2.678(2) Å).

2.3 Conclusion

In summary, the magnesium, aluminium and tin(II) (iminophosphinoyl)(thiophosphinoyl)methanide and methanediide complexes **61**, **62**, **63**, **65** were synthesized.

The magnesium (iminophosphinoyl)(thiophosphinoyl)methanediide complex $(\mu\text{-L}_1''\text{Mg})_2$ (**61**) contain a strong $\text{Mg-C}_{\text{methanediide}}$ electrostatic bonding. The aluminium (iminophosphinoyl)(thiophosphinoyl)methanediide $(\text{L}_1''\text{AlMe})_2$ (**62**) contains highly polar with weak covalent $\text{Al-C}_{\text{methanediide}}$ bonding. The X-ray crystallography shows that the Sn-C bond in compound **65** has some double character which is stabilized by the lone pair of electrons on the nitrogen and sulfur donors. Thus **65** can be regarded as a stannavinylidene derivative. The reactivity of **65** towards isocyanates, $[(\text{cod})\text{RhCl}]_2$ and sulfur has been investigated. Two [2+2] cycloaddition products **66**, **67** and the 1,2-addition product **68** were afforded. A monomeric tin(II) sulfide molecule $:\text{SnS}$ trapped by a trimeric 2-stannathiomethanediide moiety $[\text{L}_1''\text{Sn}(\mu\text{-S})]_3$ was obtained. This results indicates that the methanediide is able to stabilize a Sn(II) center, which could be approached extensively.

2.4 Experimental Section

All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled over Na/K alloy prior to use. The ^1H , ^{13}C , ^{31}P , ^{27}Al , ^{119}Sn NMR and ^{119}Sn CPMAS spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to SiMe_4 for ^1H and ^{13}C , 0.5 M AlCl_3 in MeOH for ^{27}Al , 85% H_3PO_4 for ^{31}P , 90%

Me₄Sn for ¹¹⁹Sn, adamantane for ¹H CPMAS, hexa-methylbenzene for ¹³C CPMAS, ammonium dihydrogen phosphorus for ³¹P CPMAS and SnO₂ for ¹¹⁹Sn 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.

26 was prepared as described in Chapter 1.

[(PPh₂=NSiMe₃)(PPh₂=S)CMg]₂ (61). Mg(ⁿBu)₂ (1.20 mL, 1.0 M in heptane, 1.20 mmol) was added to a solution of **26** (0.50 g, 0.99 mmol) in toluene (20 mL) at room temperature. The reaction mixture was refluxed at 140 °C for 15 h. The resulting yellow solution was filtered and concentrated under reduced pressure to yield colorless crystals of **61** (0.34 g, 65.4 %). M.p.: 234.3 °C. Elemental analysis (%) Calcd for C₅₆H₅₈N₂Mg₂P₄S₂Si₂: C 63.99, H 5.57, N 2.67; Found: C 63.47, H 5.34, N 2.28. ¹H NMR (399.5 MHz, 25 °C, C₆D₆): δ -0.15 (s, 18 H, SiMe₃), 6.68-6.95 (m, 8H, Ph), 6.97-7.14 (m, 13H, Ph), 7.18-7.43 (m, 5H, Ph), 7.57-7.74 (m, 8H, Ph), 7.92-7.98 (m, 2H, Ph), 8.13-8.19 ppm (m, 4H, Ph). ¹³C{¹H} NMR (100.4 MHz, 25 °C, C₆D₆): δ 3.52 (SiMe₃), 34.35 (dd, PCP, *J*_{P-C} = 32.6 Hz, *J*_{P'-C} = 33.5 Hz), 129.68-130.70 (m), 131.92-133.12 (m), 137.12, 138.24, 138.68, 138.80, 139.41-140.13 (m), 140.60, 141.37 ppm (Ph). ³¹P{¹H} NMR (161.7 MHz, 25 °C, C₆D₆): δ 19.9, 29.9 ppm (d, ²*J*_{P-P'} = 26.0 Hz).

[(PPh₂=NSiMe₃)(PPh₂=S)CAI Me]₂ (62). AlMe₃ (0.72 mL, 2.0 M in toluene, 1.44 mmol) was added to a solution of **26** (0.53 g, 1.05 mmol) in toluene (20 mL) at room temperature. The reaction mixture was refluxed at 140 °C for 15 h. Volatiles were

removed under reduced pressure, and the residue was extracted with Et₂O. After filtration and concentration of the filtrate, **62** (0.12 g, 21.0%) was obtained as colorless crystals. M.p.: 266 °C. Elemental analysis (%) Calcd for C₅₈H₆₄N₂Al₂P₄S₂Si₂: C 64.07, H 5.94, N 2.58; Found: C 63.82, H 5.67, N 2.35. ¹H NMR (395.9 MHz, 25 °C, C₆D₆): δ 0.057 (s, 18H, SiMe₃), 0.17 (s, 6H, AlMe), 6.65-6.70 (m, 8H, Ph), 6.78-6.79 (m, 4H, Ph), 7.15-7.17 (m, 8H, Ph), 7.40-7.43 (m, 12H, Ph), 7.88-7.94 (m, 4H, Ph), 8.19-8.22 ppm (m, 4H, Ph). ¹³C{¹H} NMR (100.5 MHz, 25 °C, C₆D₆): δ 2.87 (SiMe₃), 2.90 (AlMe), 129.39, 130.22, 130.74, 130.80, 131.19, 131.29, 131.62, 131.73, 132.83, 133.54, 133.66, 137.24, 137.47, 138.09, 138.34, 138.71, 139.54 ppm (Ph). ³¹P{¹H} NMR (160.3 MHz, 25 °C, C₆D₆): δ 22.8, 25.9 ppm (d, ²J_{P-P} = 13.0 Hz). ²⁷Al NMR (104.1 MHz, 25 °C, C₆D₆): δ 54.6 ppm.

[CH(PPh₂=NSiMe₃)(PPh₂=S)SnCl] (63). ⁿBuLi (0.5 mL, 1 mmol) was added to the solution of [CH₂(PPh₂=NSiMe₃)(PPh₂=S)] (**26**) (0.50 g, 1 mmol) in THF at -78 °C. The resulting yellow solution was stirred at room temperature for 15 h. Volatiles were removed under reduced pressure and the resulting yellow solution of monolithium salt in Et₂O was added to SnCl₂ (0.19 g, 1 mmol) in Et₂O dropwise at -78 °C. The yellow suspension was stirred at room temperature for 1 day. Volatiles were removed by vacuum. The resulting orange residue was extracted by toluene. Colorless crystals of **63** (0.43 g, 65.1 %) were obtained after filtration and concentration. M.p.: 187.3 °C. Elemental analysis (%) calcd for C₂₈H₃₀ClNP₂SSiSn: C 51.20, H 4.60, N 2.13; Found: C 51.20, H 4.14, N 4.14. ¹H NMR (399.5 MHz, 25 °C, C₆D₆): δ 0.0103 (s, 9H, SiMe₃), 3.86 (dd, 1H, PCHP, ²J_{P-H} = 5.86 Hz, ²J_{P'-H} = 7.68 Hz), 6.87-7.05 (m, 12H, Ph),

7.66-7.86 (m, 8H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, 25°C, C_6D_6): δ 2.56 (SiMe_3), 30.26 (dd, PCP, $J_{\text{P-C}} = 56.24$, $J_{\text{P'-C}} = 73.40$ Hz), 131.33, 132.83, 136.92, 137.81 ppm (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, 25°C, C_6D_6): δ 32.0 ppm (t, $^2J_{\text{Sn-P}} = 43.59$ Hz), 35.0 ppm (t, $^2J_{\text{Sn-P'}} = 72.05$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (147.6 MHz, 25 °C, C_6D_6): δ 67.63 ppm (ABq, $J_{\text{P-Sn}} = 161.6$ Hz).

[HC{(PPh₂=NSiMe₃)(PPh₂=S)}SnN(SiMe₃)₂] (64). Toluene (20 mL) was added to a mixture of **26** (0.51 g, 1.01 mmol) and $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (0.88 g, 2.01 mmol) at ambient temperature. The resulting orange mixture was stirred for overnight. Volatiles were removed under reduced pressure. The residue was washed with hexane and then extracted with Et₂O. The insoluble precipitate was filtered off, and the orange filtrate was concentrated to yield colorless crystals of **64** (0.37 g, 46.9 %). M.p.: 130 °C. Elemental analysis (%) calcd for $\text{C}_{34}\text{H}_{48}\text{N}_2\text{P}_2\text{Si}_3\text{Sn}$: C 52.24, H 6.19, N 3.59; Found: C 51.94, H 6.01, N 3.37. ^1H NMR (395.9 MHz, 25 °C, C_6D_6): δ 0.072 (s, 9H, SiMe_3), 0.48 (s, 18H, $\text{N}(\text{SiMe}_3)_2$), 3.84 (dd, 1H, PCHP, $^2J_{\text{P-H}} = 10.9$ Hz), 6.89-7.08 (m, 15H, Ph), 7.49-8.22 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, 25 °C, C_6D_6): δ 3.53 (SiMe_3), 7.71 ($\text{N}(\text{SiMe}_3)_2$), 31.5 (d, PCP, $J_{\text{P-C}} = 55.9$ Hz), 129.5-135.5 ppm (m) (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, 25 °C, C_6D_6): δ 30.2 ppm (t, $^2J_{\text{Sn-P}} = 73.7$ Hz), 34.7 ppm (t, $^2J_{\text{Sn-P'}} = 39.0$ Hz). ^{119}Sn NMR (147.6 MHz, 25 °C, C_6D_6): δ -19.3 ppm.

[(PPh₂=NSiMe₃)(PPh₂=S)C=Sn:]₂ (65). Toluene (20 mL) was added to a mixture of **26** (0.50 g, 0.99 mmol) and $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (0.89 g, 2.03 mmol) at ambient temperature. The resulting orange mixture was refluxed for overnight. The solvent was removed under reduced pressure. The residue was washed with hexane and then

extracted by CH₂Cl₂. The insoluble precipitate was filtered off, and the orange filtrate was concentrated to yield yellow crystals of **65** (0.74 g, 30.1 %). M.p.: 180 °C (dec.). Elemental analysis (%) calcd for C₅₆H₅₈N₂P₄S₂Si₂Sn₂: C 54.21, H 4.72, N 2.26; Found: C 54.04, H 4.39, N 2.11. ¹H NMR (395.9 MHz, 25 °C, C₆D₆): δ 0.04 (s, 9H, SiMe₃), 6.64-7.12 (m, 15H, Ph), 7.18-7.42 (m, 2H, Ph), 7.86-8.04 (br s, 1H, Ph), 8.28-8.40 ppm (br s, 2H, Ph). ¹³C{¹H} NMR (99.5 MHz, 25 °C, C₆D₆): δ 2.30 (SiMe₃), 129.2-134.5 ppm (m) (Ph). ³¹P{¹H} NMR (161.7 MHz, 25 °C, C₆D₆): δ 20.5 ppm (d, ²J_{P-P} = 17.5 Hz), 27.4 ppm (d, ²J_{P-P} = 17.5 Hz). ¹¹⁹Sn NMR (147.6 MHz, 25 °C, C₆D₆): δ 132.1 ppm (dd, ²J_{Sn-P} = 177.1 Hz).

[(PPh₂=NSiMe₃)(PPh₂=S)C{C(O)N(Ad)Sn:}] (**66**). A solution of AdNCO (0.041 g, 0.23 mmol) in THF (5 mL) was added dropwise to **65** (0.14 g, 0.11 mmol) in THF (5 mL) at 0 °C. The yellow suspension stirred at room temperature and turned clear gradually. After stirring 34 h the reaction mixture was pale yellow clear solution. Volatiles were removed under reduced pressure and the residue was extracted with toluene. After filtration and concentration colorless crystals of **66** (0.068 g, 38.8 %) were obtained. M.p.: 217.3 °C (dec.). Elemental analysis (%) calcd for C₃₉H₄₄N₂OP₂SSiSn: C 58.73, H 5.56, N 3.51; Found: C 58.50, H 5.47, N 3.14. ¹H NMR (399.5 MHz, 25 °C, C₆D₆): δ -0.043 (s, 9H, SiMe₃), 1.59-1.66 (m, 6H, Ad), 1.87-1.89 (d, 3H, Ad), 1.96-2.00 (m, 6H, Ad), 6.99-7.03 (m, 12H, Ph), 7.35-7.40 (m, 2H, Ph), 8.15-8.18 (m, 4H, Ph), 8.80-8.86 (m, 2H, Ph). ¹³C{¹H} NMR (100.5 MHz, 25 °C, C₆D₆): δ 2.37 (SiMe₃), 30.57, 37.52, 43.51 (Ad), 56.70 (dd, PCP, J_{P-C} = 56.6 Hz, J_{P'-C} = 70.0 Hz), 127.11, 127.24, 128.22, 130.26, 130.28, 130.85, 130.88, 131.69,

131.72 (CH of Ph), 132.64 (dd, C_{ipso} of Ph, $J_{\text{P-C}} = 57.3$ Hz, $^3J_{\text{P'-C}} = 10.5$ Hz), 134.46 (dd, C_{ipso} of Ph, $J_{\text{P-C}} = 57.3$ Hz, $^3J_{\text{P'-C}} = 11.5$ Hz), 165.16 ppm (C=O). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, 25 °C, C_6D_6): δ 22.29 ppm (d, $^2J_{\text{P-P'}} = 15.2$ Hz, $^2J_{\text{Sn-P}} = 86.7, 121.4$ Hz), 41.23 ppm (d, $^2J_{\text{P-P'}} = 15.2$ Hz, $^2J_{\text{Sn-P}} = 47.7, 73.7$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (147.6 MHz, 25 °C, C_6D_6): δ -255.15 ppm (br).

[(PPh₂=NSiMe₃)(PPh₂=S)C⁻{C(O)N(Ar)}Sn⁺:] (67). A solution of ArNCO (0.05 mL, 0.2 mmol) in THF (5 mL) was added dropwise to **65** (0.14 g, 0.11 mmol) in THF (5 mL) at 0 °C. The yellow suspension stirred at room temperature and turned clear gradually. After stirring 15 h the reaction mixture was pale yellow clear solution. Volatiles were removed under reduced pressure and the residue was extracted with toluene. After filtration and concentration colorless crystals of **67** (0.066 g, 36.5%) were obtained. M.p.: 185.0 °C (dec.). Elemental analysis (%) calcd for C₄₁H₄₆N₂OP₂SSiSn: C 59.79, H 5.63, N 3.40; Found: C 59.53, H 5.57, N 3.32. ^1H NMR (399.5 MHz, 25 °C, C_6D_6): δ 0.21 (s, 9H, SiMe₃), 0.51 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 3H, CH(CH₃)₂), 0.67 (d, $^3J_{\text{H-H}} = 6.4$ Hz, 3H, CH(CH₃)₂), 1.20 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 3H, CH(CH₃)₂), 1.37 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CH(CH₃)₂), 2.26 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, CH(CH₃)₂), 3.03 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 1H, CH(CH₃)₂), 6.40-6.45 (m, 2H, Ph), 6.51-6.57 (m, 4H, Ph), 6.83-6.87 (m, 1H, Ph), 7.03-7.16 (m, 4H, Ph), 7.23-7.27 (m, 1H, Ph), 7.33-7.38 (m, 5H, Ph), 7.83-7.89 (m, 2H, Ph), 8.60-8.70 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, 25 °C, C_6D_6): δ 4.73 (SiMe₃), 24.29, 24.70, 25.99, 26.64 (CH(CH₃)₂), 28.87, 29.13 (CH(CH₃)₂), 40.64 (dd, PCP, $J_{\text{P-C}} = 56.6$ Hz, $J_{\text{P'-C}} = 74.3$ Hz), 123.86, 124.18, 126.72 (Ar), 127.78, 127.91, 128.84, 128.87, 128.98, 129.00,

130.56, 130.59, 131.36, 131.39 (CH of Ph), 132.22 (dd, C_{ipso} of Ph, $J_{\text{P-C}} = 79.4$ Hz, $^3J_{\text{P'-C}} = 11.5$ Hz), 134.20 (dd, C_{ipso} of Ph, $J_{\text{P-C}} = 75.8$ Hz, $^3J_{\text{P'-C}} = 10.5$ Hz), 140.56, 146.58, 146.77 (Ar), 166.82 ppm (C=O). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, 22 °C, C_6D_6): δ 27.79 ppm (d, $^2J_{\text{P-P'}} = 8.7$ Hz, $^2J_{\text{Sn-P}} = 69.4, 86.7$ Hz), 37.44 ppm (d, $^2J_{\text{P-P'}} = 8.7$ Hz, $^2J_{\text{Sn-P}} = 73.7, 134.4$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.0 MHz, 22 °C, C_6D_6): δ -129.25 ppm (br).

[(PPh₂=NSiMe₃)(PPh₂=S)C{Rh(cod)}(SnCl)] (68). A solution of $[\text{RhCl}(\text{cod})]_2$ (0.079 mL, 0.16 mmol) in THF (8.4 mL) was added dropwise to **65** (0.20 g, 0.16 mmol) in THF (8.4 mL) at 0 °C. The yellow suspension stirred at room temperature and turned clear and red gradually. After stirring 5 h, the reaction mixture turned to a red suspension with yellow solid. Volatiles were removed under reduced pressure and the residue was extracted with CH_2Cl_2 . After filtration and concentration red crystals of **68** (0.18 g, 55.4 %) were obtained. M.p.: 140.0 °C (dec.). Elemental analysis (%) calcd for $\text{C}_{36}\text{H}_{41}\text{ClNP}_2\text{RhSSiSn}$: C 49.87, H 4.77, N 1.62; Found: C 49.63, H 4.64, N 1.43. ^1H NMR (399.5 MHz, 25 °C, $\text{THF-}d_8$): δ 0.065 (s, 9H, SiMe₃), 1.57-2.61 (m, 8H, cod), 3.21 (m, 1H, cod), 4.14 (m, 1H, cod), 4.43 (m, 1H, cod), 4.91 (m, 1H, cod), 7.06-7.15 (m, 4H, Ph), 7.21-7.37 (m, 9H, Ph), 7.45-7.56 (m, 3H, Ph), 7.72-7.77 (m, 2H, Ph), 8.04-8.09 (m, 2H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, 25 °C, $\text{THF-}d_8$): δ 3.43 (SiMe₃), 29.04, 30.40, 32.89, 34.15 (sp^3 C of cod), 77.41 (d, sp^2 C of cod, $J_{\text{C-Rh}} = 11.1$ Hz), 81.68 (d, sp^2 C of cod, $J_{\text{C-Rh}} = 12.1$ Hz), 85.23 (d, sp^2 C of cod, $J_{\text{C-Rh}} = 10.1$ Hz), 87.11 (d, sp^2 C of cod, $J_{\text{C-Rh}} = 8.0$ Hz), 128.12, 128.23, 128.68, 128.81, 129.00, 129.13, 129.20, 129.31, 131.53, 132.12 (CH of Ph), 132.59 (dd, C_{ipso}

of Ph, $J_{\text{P-C}} = 57.3$ Hz, $^3J_{\text{P'-C}} = 12.5$ Hz), 133.91 ppm (dd, C_{ipso} of Ph, $J_{\text{P-C}} = 57.3$ Hz, $^3J_{\text{P'-C}} = 11.5$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, 25 °C, THF- d_8): δ 28.36 ppm (d, $^2J_{\text{P-P'}} = 26.0$ Hz), 37.86 ppm (dd, $^2J_{\text{P-P'}} = 26.0$ Hz, $^2J_{\text{P-Rh}} = 13.0$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.0 MHz, 25 °C, THF- d_8): δ 110.74 ppm (m).

$[\{(\mu\text{-S})\text{Sn}^{\text{IV}}\text{C}(\text{PPh}_2=\text{NSiMe}_3)(\text{PPh}_2=\text{S})\}_3\text{Sn}^{\text{II}}(\mu_3\text{-S})]$ (**69**). A solution of elemental sulfur (0.013 g, 0.05 mmol) in toluene (7 mL) was added dropwise at 0 °C to **65** (0.23 g, 0.19 mmol) in toluene (15 mL). The yellow suspension was raised to room temperature and stirred for 4 h. The solution became red and clear. Red crystals of **69** (0.058 g, 29.2 %) were obtained in C_6D_6 . M.p.: 186.7 °C (dec.). Elemental analysis (%) calcd for $\text{C}_{84}\text{H}_{87}\text{N}_3\text{P}_6\text{S}_7\text{Si}_3\text{Sn}_4$: C 47.86, H 4.16, N 1.99; Found: C 47.52, H 4.03, N 1.65. ^1H NMR (399.5 MHz, 21.8 °C, CD_2Cl_2): δ -0.29 (s, 27H, SiMe_3), 6.88-7.38 ppm (m, 60H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, 21.7 °C, CD_2Cl_2): δ 2.74 (SiMe_3), 128.45, 130.67, 130.85, 132.54-132.85 ppm (m) (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, 21.9 °C, CD_2Cl_2): δ 27.42, 30.07 ppm (d, $^2J_{\text{P-P'}} = 8.68$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.0 MHz, 21.8 °C, CD_2Cl_2): δ -242.1 ppm (m). ^{119}Sn CPMAS NMR (149.0 MHz, spinning speed = 9 kHz): δ_{iso} -260.3 (Sn^4), -232.3 ppm (Sn^{1-3}).

Crystal Structure Determinations of Compounds 61-69. 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 .⁴² 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.

Mössbauer spectroscopy of Compound 69. The air and moisture sensitive sample was received in a sealed ampoule which was opened in an inert atmosphere glove box and the powder transferred to an O-ring sealed Perspex sample holder which was immediately cooled to liquid nitrogen temperature. The sample was then transferred to the pre-cooled cryostat and examined in transmission geometry using a BaSnO₃ source at room temperature. Temperature control and monitoring was effected as described earlier⁴³ and all IS are referred to a BaSnO₃ room temperature reference spectrum. Spectrometer calibration was derived from an α -Fe absorption spectrum at room temperature.

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Chapter 3

Synthesis and Reactivity of Transition and Lanthanide Metal

(Iminophosphinoyl)(thiophosphinoyl)methanide and Methanediide Complexes

3.1 Introduction

The synthesis of group 4 metal bis(phosphinoyl)methanediides were initiated by Cavell *et al.* [$\{C(PPh_2=NSiMe_3)_2\}MCl_2$] ($M = Ti$ (**70**), Zr (**71**)) were prepared by the reaction of the dilithiated salt $[C(PPh_2=NSiMe_3)_2Li_2]$ (**7**) with the corresponding metal tetrahalides via LiCl elimination.¹ The hafnium analogue [$\{C(PPh_2=NSiMe_3)_2\}HfCl_2$] (**72**) was formed by the reaction of $[CH_2(PPh_2=NSiMe_3)_2]$ (**2**) with $[HfCl_2\{N(SiMe_3)_2\}_2]$ via amine elimination (Scheme 3.1).²

Scheme 3.1

Zirconium benzyl bis(iminophosphinoyl)methanediide complex

$[Zr\{C(PPh_2=NSiMe_3)_2\}(CH_2Ph)_2]$ (**73**) was prepared by alkane elimination reaction of $[CH_2(PMe_2=NSiMe_3)_2]$ (**2**) with $[Zr(CH_2Ph)_4]$.³ Adjusting stoichiometry of **2** and $[Zr(CH_2Ph)_4]$ in a ratio of 2:1 resulted in the synthesis of a novel zirconium bis(methanediide) complex $[Zr\{C(PPh_2=NSiMe_3)_2\}_2]$ (**74**) that contains a linear assembly of two metal–carbon multiple bond units which was also reported by Cavell *et al* (Scheme 3.2).⁴ The core structure of **74** consisted of two perpendicular

six-membered ring units. Each of them was formed from the two planar four-membered rings that share a common C=Zr double bond edge.

Scheme 3.2

Roesky *et al.* reported the synthesis of $[\text{ZrCpCl}\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\}]$ (**75**) by the reaction of zirconocene dichloride with $[\text{K}\{\text{CH}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\}]$ (**12**) via a concomitant elimination of KCl and C_5H_6 (Scheme 3.3).⁵

Scheme 3.3

The reactivity of zirconium and hafnium bis(iminophosphino)methanediide complexes **71** and **72** has been investigated. Three classes were involved:^{6, 7}

(i) base adduct formation (Scheme 3.4):

Scheme 3.4

The base adduct product **76** resulted from the addition of 2,6-dimethylphenyl isocyanide to **71**. The reaction between **72** and adamantyl cyanide or THF afforded the base adduct products **77** and **78**, respectively.

(ii) 1,2-addition across the M=C bond (Scheme 3.5):

Scheme 3.5

The addition of adamantyl alcohol to **71** afforded the 1,2-addition complex **79**.

Likewise, the reaction of **72** with *p*-tolylamine and methyl iodide afforded the 1,2 addition products **80** and **81** respectively. The regioselective nature of these 1,2-additions confirmed the nucleophilic nature of the methandiide centers.

(iii) cycloadditions across the M=C double bond (Scheme 3.6):

Scheme 3.6

Compounds **71** and **72** reacted with a range of unsaturated substrates to afford cycloaddition products. [2+2] cycloaddition of adamantyl isocyanate with **71** and **72** gave **82** and **85** respectively. [2 + 2] cycloaddition products **83** and **86** were obtained by the reaction of carbodiimides with **71** and **72**. The formation of **84** is from the addition of carbon dioxide to **72**.

Le Floch *et al.* reported three zirconium bis(thiophosphinoyl)methanediide complexes **87-89** (Scheme 3.7).⁸

Scheme 3.7

The reaction between zirconocene dichloride and the germinal dianion $[\text{Li}_2\{\text{C}(\text{PPh}_2=\text{S})_2\}]$ (**16**) afforded compound **87**. The dimeric complex **88** was prepared from the reaction of germinal dianion **16** with ZrCl_4 followed by addition of THF. Moreover the addition of pyridine to **88** afforded the monomeric complex **89**.

Bis(iminophosphinoyl)methanide complexes of group 11 metals have also been explored. Transmetalation of the potassium methanide complex, $[\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}]$ (**12**) with $[(\text{Ph}_3\text{P})_2\text{CuI}]$ afforded $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{CuPPh}_3]$ (**90**). Moreover, the reaction of **12** with $[(\text{Ph}_3\text{P})\text{AuCl}]$ gave the dinuclear gold complex $[(\text{Ph}_3\text{PAu})_2\{\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2\}]$ (**91**) (Scheme 3.8).⁹

Scheme 3.8

Silver complexes were obtained by the reaction of the *N*-thiophosphorylated bis(iminophosphinoyl)methane ligands with silver hexafluoroantimonate to afford $[\text{CH}_2[\text{P}\{\text{NP}(\text{S})(\text{OR})_2\}\text{Ph}_2]_2\text{Ag}][\text{SbF}_6]$ ($\text{R} = \text{Ph}$ (**92a**), Et (**92b**)) (Scheme 3.9).¹⁰

Scheme 3.9

Cavell *et al.* reported the copper(I) clusters $[\text{Cu}_6\text{L}_2\text{X}_2]$ ($\text{L} = \text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2^{2-}$; $\text{X} = \text{CH}_3^-$ (**93**), Cl^- (**94**), Br^- (**95**), I^- (**96**)) by reacting the corresponding Cu(I) precursors with **7** in either THF or Et_2O (Scheme 3.10).¹¹

Scheme 3.10

Lanthanide bis(iminophosphino) metal complex have been investigated comprehensively.¹² Samarium (**97**), dysprosium (**98**), erbium (**99**), ytterbium (**100**), lutetium (**101**), and yttrium (**102**) bis(iminophosphino)methanide dichlorides were prepared from the corresponding lanthanide trichlorides and **12** in THF.¹³ Additionally, treatment of **97** and **102** with potassium diphenylamide gave products **103**, **104**¹³ and treatment of **97** and **99** a with sodium cyclopentadienyl afforded the bis(cyclopentadienyl) derivatives **105-106**, respectively (Scheme 3.11).¹⁴

Scheme 3.11

The first samarium bis(iminophosphinoyl)methandiide complex **107** was reported by Cavell *et al.*^{12(a)} It was synthesized by the reaction of $[\text{Sm}(\text{NCy}_2)_3(\text{THF})]$ with **3**. Besides, the synthesis of samarium and thulium bis(iminophosphinoyl)methandiide complexes **108** and **109** by the reaction of the germinal dianion **16** with $[\text{LnI}_3(\text{THF})_{3.5}]$ ($\text{Ln} = \text{Sm}, \text{Tm}$) was reported by Le Floch *et al* (Scheme 3.12).^{15, 16}

Scheme 3.12

In Chapter 3, the synthesis of the zirconium and the hafnium (iminophosphinoyl)(thiophosphinoyl)methanide and methandiide complexes and their reactivity toward water are reported. The synthesis of Cu^{I}_6 and Ag^{I}_6 clusters stabilized by the (iminophosphinoyl)(thiophosphinoyl)methandiide ligand are described. The

synthesis of ytterbium (iminophosphinoyl)(thiophosphinoyl)methanide complex is also presented.

3.2 Results and Discussion

3.2.1 Synthesis of Zirconium (Iminophosphinoyl)(thiophosphinoyl)methanide

Complex

The zirconium (iminophosphinoyl)(thiophosphinoyl)methanide complex $[L_1'ZrCl_2\{N(SiMe_3)_2\}]$ (**110**) was synthesized by the reaction of **26**¹⁷ with $[ZrCl_2\{N(SiMe_3)_2\}_2]$ in refluxing toluene (Scheme 3.13).

Scheme 3.13

Compound **110** was isolated in CH_2Cl_2 as an air- and moisture-sensitive colorless crystalline solid in 68.2 % yield. It has been characterized by NMR spectroscopy and X-ray crystallography. The 1H NMR spectrum of **110** displays one doublet of doublets at δ 2.64 ppm (dd, $J_{P-H} = 5.25$ Hz, $J_{P'-H} = 1.36$ Hz) for the methine proton and resonances for the $SiMe_3$ and phenyl protons. The $^{31}P\{^1H\}$ NMR spectrum of **110** shows two singlets at δ 23.2, 34.5 ppm. The $^{13}C\{^1H\}$ NMR shows one doublet of doublets at δ 14.84 ppm (dd, $J_{P-C} = 57.4$ Hz, $J_{P'-C} = 73.8$ Hz) for the methanide carbon in **110**.

Figure 3.1 Molecular structure of **110** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)-C(1) 2.5376(15), Zr(1)-Cl(1) 2.4206(4), Zr(1)-Cl(2) 2.4452(4), Zr(1)-N(2) 2.0808(14), Zr(1)-N(1) 2.2611(14), Zr(1)-S(1) 2.7224(4), C(1)-P(1) 1.7706(17), C(1)-P(2) 1.7464(17), P(1)-N(1) 1.6016(13), P(2)-S(1) 1.9980(6); N(1)-Zr(1)-C(1) 66.50(5), C(1)-Zr(1)-S(1) 69.35(4), C(1)-Zr(1)-N(2) 93.28(5), C(1)-Zr(1)-Cl(1) 143.86(4), C(1)-Zr(1)-Cl(2) 117.36(4), P(1)-C(1)-P(2) 122.83(10).

The molecular structure of **110** is shown in Figure 3.1. Compound **110** is a monomer. It has an “open book” structure with the C(1)-Zr(1) bond lying on the spine. The thiophosphinoyl and iminophosphinoyl groups of the ligand are coordinated to the metal center. The Zr(1)-C(1) bond (2.5376(15) Å) in **110** is similar to the C-Zr single bonds in $[\text{ZrCl}_2(\text{OAd})\{\text{C}(\text{H})(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\}]$ (2.478(3) Å)⁶ and $[\text{ZrCl}_2\{\text{C}(\text{NCy})\text{N}(\text{Cy})\}\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]$ (2.467(4) Å).⁷ And it is obviously longer than the C=Zr double bonds of $[\{\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2\}\text{ZrCl}_2]$ (**71**) (2.190(8) Å),¹ $[\text{Zr}\{\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2\}(\text{CH}_2\text{Ph})_2]$ (**73**) (2.379(6) Å)³ and $[\{\text{C}(\text{PPh}_2=\text{S})_2\}\text{ZrCp}_2]$ (**87**) (2.251(2) Å).¹⁸ Therefore the carbon center is singly bonded to the zirconium atom. The P-C bonds are shortened and the P-N, P-S bonds are lengthened in **110** compared with those in **26**.¹⁷

3.2.2 Synthesis of Zirconium (Iminophosphinoyl)(thiophosphinoyl)methanediide Complexes

The zirconium (iminophosphinoyl)(thiophosphinoyl)methanediide complex $[L_1''Zr(NMe_2)_2]$ (**111**) was formed by the reaction of **26**¹⁷ with $[Zr(NMe_2)_4]$ in refluxing toluene. The X-ray crystallography shows that the C-Zr has some multiple bond character. Treatment of compound **111** with H_2O (0.042M in toluene) in toluene afforded the μ -oxo bridged zirconium (iminophosphinoyl)(thiophosphinoyl)methanediide complex $[\{\mu-L_1''Zr(NMe_2)_2\}_2O]$ (**112**) (Scheme 3.14). The X-ray crystallography shows that one of the C-Zr bonds is highly ionic.

Scheme 3.14

Compounds **111** and **112** were both isolated in Et_2O as an air- and moisture-sensitive colorless crystalline solid in 65.0 % yield and in 14.8 % yield respectively. They have been characterized by NMR spectroscopy and X-ray crystallography. The 1H NMR spectra of **111** and **112** display resonances for the $SiMe_3$, NMe_2 and phenyl protons. The $^{31}P\{^1H\}$ NMR spectrum of **111** shows only one singlet at δ 13.0 ppm. The lack of coupling of two nonequivalent phosphorus nuclei at room temperature is unusual. Thus $^{31}P\{^1H\}$ NMR spectrum at 0 $^{\circ}C$ was performed, which shows one AB quartet at δ 13.01 ppm (ABq, $^2J_{P-P'} = 43.35$ Hz). The $^{13}C\{^1H\}$ NMR spectrum of **111** shows one doublet of doublets for the methanediide carbon at δ 59.45 ppm (dd, PCP, $J_{P-C} = 139.93$ Hz, $J_{P'-C} = 142.33$ Hz) at room temperature. The $^{31}P\{^1H\}$ NMR spectrum of **112** at room temperature shows two doublets at δ 24.04, 25.61 ppm

(d, $^2J_{\text{P-P}} = 17.3$ Hz) due to two nonequivalent phosphorus nuclei, which shows a downfield shift compared with **111**. The $^{13}\text{C}\{^1\text{H}\}$ NMR signal for the methanediide carbon in **112** is not observed.

Figure 3.2 Molecular structure of **111** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)-C(1) 2.237(3), C(1)-P(1) 1.667(3), C(1)-P(2) 1.650(3), P(1)-N(1) 1.623(2), P(2)-S(1) 2.0370(10), Zr(1)-N(1) 2.241(2), Zr(1)-S(1) 2.6786(8), Zr(1)-N(2) 2.038(2), Zr(1)-N(3) 2.028(2); N(1)-Zr(1)-C(1) 69.29(9), P(2)-C(1)-P(1) 160.24(18), C(1)-Zr(1)-S(1), 72.02(7), N(1)-Zr(1)-S(1) 141.11(6).

The molecular structure of **111** is shown in Figure 3.2. Compound **111** adopts an “open book” structure with the C(1)-Zr(1) bond lying on the spine (P(2)-C(1)-P(1) (160.24(18)°). The thiophosphinoyl and iminophosphinoyl group of the ligand coordinate to the metal center. The sum of the angles around the C_{methanediide} atom (357.4°) shows the planar N-P-C-P-S core, which is comparable to that of **87**. The C-Zr bond (2.237(3) Å) in **111** is within the range of C=Zr double bonds in **71** (2.190(8) Å),¹ **73** (2.379(6) Å)³, **87** (2.251(2) Å) and **88** (2.180(3) Å).⁸ The P-C bonds are shortened and the P-N, P-S bonds are lengthened compared with those in **26**,¹⁷ which indicates the ligand backbone has the resonance structure as shown in Scheme 1.6.

Figure 3.3 Molecular structure of **112** with thermal ellipsoids at the 30% probability level. Phenyl substituents, hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)-Zr(1) 2.7167(17), C(1)-Zr(2) 2.4089(17), C(2)-Zr(1) 2.3965(17), C(2)-Zr(2) 2.7283(17), N(1)-Zr(1) 2.2020(16), S(2)-Zr(1) 2.6377(5), N(3)-Zr(2) 2.1816(16), S(1)-Zr(2) 2.6380(5), O(1)-Zr(1) 1.9586(14), O(1)-Zr(2) 1.9559(14); Zr(2)-C(1)-Zr(1) 73.82(5), Zr(1)-C(2)-Zr(2) 73.79(5), C(2)-Zr(1)-C(1) 81.89(6), C(1)-Zr(2)-C(2) 81.43(5), Zr(2)-O(1)-Zr(1) 104.17(5).

The molecular structure of **112** is shown in Figure 3.3. Compound **112** consists of a Zr-O-Zr skeleton, which is bridged between two (iminophosphinoyl)(thiophosphinoyl)methanediide ligands. Each Zr atom is bonded to two C_{methanediide} atoms and one amino group. It is also coordinated by the thiophosphinoyl and iminophosphinoyl group of the ligands. The Zr(1)-O(1), Zr(2)-O(1) bonds (1.9586(14), 1.9559(14) Å) are similar to those in [(((Me₃Si)₂N)₂ZrMe)₂O] (1.950(1) Å)¹⁸ and [Cp₂Zr(CH₃)₂(μ-O)] (1.948(1) Å).¹⁹ The Zr(1)-O-Zr(2) bond angle (104.17(5)°) is more acute than that of [(((Me₃Si)₂N)₂ZrMe)₂O] (180°).¹⁹ The C(1)···Zr(1), C(2)···Zr(2) distances (2.7167(17), 2.7283(17) Å) are significantly longer than the C-Zr single bonds in **110** (2.5376(15) Å), [ZrCl₂(OAd){C(H)(Ph₂P=NSiMe₃)₂}] (2.478(3) Å)⁷ and [ZrCl₂{C(NCy)N(Cy)}C(Ph₂P=NSiMe₃)₂] (2.467(4) Å)⁷ but it is shorter than the sum of van der Waals radii (*ca.* 3.70 Å). It indicates that there is a zwitterionic interaction

between the C(1)···Zr(1) and C(2)···Zr(2) atoms. The C(1)-Zr(2), C(2)-Zr(1) bonds (2.4089(17), 2.3965(17) Å) are comparable with the C-Zr single bonds in [ZrCl₂(OAd){C(H)(Ph₂P=NSiMe₃)₂}] (2.478(3) Å)⁷ and [ZrCl₂{C(NCy)N(Cy)}C(Ph₂P=NSiMe₃)₂] (2.467(4) Å)⁷.

3.2.3 Reactivity of μ -Oxo Bridged Zirconium

(Iminophosphinoyl)(thiophosphinoyl)methanediide Complex towards Adamantyl Isocyanate

The reaction of μ -oxo bridged zirconium (iminophosphinoyl)(thiophosphinoyl)methanediide complex [$\{L_1''Zr(NMe_2)_2O\}$] (**112**) with AdNCO in THF afforded **113**, in which AdNCO inserts into Zr-NMe₂ bond of **112** instead of C-Zr bonds (Scheme 3.15). The X-ray crystallography shows that the C-Zr bond in **113** has some multiple bond character.

Scheme 3.15

Compound **113** was isolated in toluene as air- and moisture-sensitive colorless crystalline solids in 35.2 % yield. It is stable in solid state in an inert atmosphere but unstable in solution. A freshly prepared solution of **113** in THF-*d*₈ was characterized by NMR spectroscopy. The ¹H NMR spectrum displays resonances for the SiMe₃, NMe₂, Ad and phenyl protons. The ³¹P{¹H} NMR spectrum of **113** in THF-*d*₈ shows

two doublets at δ 17.0, 36.4 ppm (d, $^2J_{\text{P-P}} = 21.5$ Hz) and signals for **26**. When the solution was placed at room temperature for ten days, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows **26** only, which indicates the instability of **113** in THF. It is noteworthy that the $^{13}\text{C}\{^1\text{H}\}$ NMR signal for the methanediide carbon in **113** is not observed.

Figure 3.4 Molecular structure of **113** with thermal ellipsoids at the 30% probability level. Phenyl substituents, hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)-Zr(1) 2.231(2), O(1)-Zr(2) 1.9428(16), O(1)-Zr(1) 1.9560(16), C(57)-Zr(1) 2.639(2), O(2)-Zr(1) 2.1749(17), N(3)-Zr(1) 2.2460(19), C(57)-O(2) 1.300(3), C(57)-N(3) 1.332(4), C(57)-N(5) 1.360(3), C(1)-P(1) 1.702(3), C(1)-P(2) 1.690(3), N(1)-P(1) 1.610(2), P(2)-S(1) 2.0283(11), C(2)-Zr(2) 2.240(2), C(70)-Zr(2) 2.645(2), N(4)-Zr(2) 2.2495(17), O(3)-Zr(2) 2.1920(17), C(70)-O(3) 1.298(3), C(70)-N(4) 1.330(3), C(70)-N(6) 1.369(3), C(2)-P(3) 1.691(2), C(2)-P(4) 1.691(2), N(2)-P(3) 1.616(2), P(4)-S(2) 2.0318(8); P(2)-C(1)-P(1) 132.10(14), P(2)-C(1)-Zr(1) 132.31(14), P(1)-C(1)-Zr(1) 94.11(11), O(1)-Zr(1)-C(57) 104.00(7), P(4)-C(2)-P(3) 133.74(14), P(4)-C(2)-Zr(2) 130.03(12), P(3)-C(2)-Zr(2), 94.20(9), O(1)-Zr(2)-C(70) 101.94(7), Zr(2)-O(1)-Zr(1) 147.67(8).

The molecular structure of **113** is shown in Figure 3.4. Each Zr atom is bonded with C_{methanediide}, S and N atoms. The ureate ligand is bonded to the Zr atom in a *N,O*-chelate fashion. The Zr(1)-O(1), Zr(2)-O(1) bonds (1.9428(16), 1.9560(16) Å) in **113** are comparable to those in **111** (1.9586(14), 1.9559(14) Å). The Zr(2)-O(1)-Zr(1) bond angle (147.67(8)°) is larger than that in **111** (104.17(5)°). The C(1)-Zr(1), C(2)-Zr(2) bonds (2.231(2), 2.240(2) Å) in **113** are comparable to the C=Zr double

bond (2.237(3) Å) in **111**. The C(57)-N(3), C(70)-N(4) bonds (1.332(4), 1.330(3) Å) and C(57)-O(2), C(70)-O(3) bonds (1.300(3), 1.298(3) Å) are intermediate between the single and double bond length, which indicate there is an electron delocalization along the O(2)-C(57)-N(3), O(3)-C(70)-N(4) skeletons. The Zr-N_{ureate} bonds (2.2460(19) Å, 2.2495(17) Å) and Zr-O_{ureate} bonds (2.1749(17) Å, 2.1920(17) Å) are comparable with those in η^2 -ureato-*N,O* complexes [(TTP)Zr(η^2 -NAr^{*i*Pr}C(=N^{*t*}Bu)O)] (TTP = *meso*-tetra-*p*-tolylporphyrinato dianion) (Zr-N: 2.1096(13) Å; Zr-O: 2.0677(12) Å) and [(TTP)Zr(η^2 -N^{*t*}BuC(=NAr^{*i*Pr})O)] (Zr-N: 2.137(3) Å; Zr-O: 2.066(3) Å).²⁰

3.2.4 Synthesis of Zirconium Bis(methanediide) Complex

The zirconium bis(methanediide) complex [(L^{1''})₂Zr] (**114**) was afforded from the reaction of **26**¹⁷ with two equivalents of [Zr(NMe₂)₄] in refluxing toluene (Scheme 3.16).

Scheme 3.16

Compound **114** was isolated in hexane as an air- and moisture-sensitive colorless crystalline solid in 48.2 % yield. It is soluble in toluene and THF and has been characterized by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectrum of **114** displays resonances for the SiMe₃ and phenyl protons. The ³¹P{¹H} NMR spectrum of **114** shows two doublets at δ 16.0, 17.6 ppm (d, ²*J*_{P-P'} = 56.4 Hz) due to two nonequivalent phosphorus nuclei, which show a downfield shift compared

to that of **111** [δ 12.8, 13.3 ppm (ABq, $^2J_{\text{P-P}} = 43.35$ Hz)]. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **114** shows one doublet of doublets for the methanediide carbon at δ 40.07 ppm (dd, PCP, $J_{\text{P-C}} = 66.72$ Hz, $J_{\text{P'-C}} = 43.85$ Hz).

Figure 3.5 Molecular structure of **114** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)-C(1) 2.261(2), Zr(1)-N(1) 2.207(2), Zr(1)-S(1) 2.6477(7), P(1)-S(1) 2.0341(9), P(2)-N(1) 1.638(2), P(1)-C(1) 1.651(3), P(2)-C(1) 1.661(2), P(1)-C(1)-P(2) 165.59(17), C(1)-Zr(1)-C(2) 164.17(9), N(1)-Zr(1)-N(2) 103.73(8), S(1)-Zr(1)-S(2) 93.79(2).

The molecular structure of **114** is shown in Figure 3.5. The core structure consists of two mutually perpendicular six-membered planes, each containing the tridentate pincer methanediide ligand moiety bound to the metal center. Each of the six-atom planes is formed from the two planar four-membered rings that share a common Zr-C edge. The sum of the angles around the $\text{C}_{\text{methanediide}}$ atom is 359.9° , which suggests it is planar. The C(1) atom adopts a T-shaped geometry (C(1)-Zr-C(2): $164.17(9)^\circ$). The C(1)-Zr(1), C(2)-Zr(1) bonds (2.261(2), 2.264(2) Å) in **114** are comparable with the C=Zr double bonds in **111** (2.237(3) Å) and **74** (2.288(3) Å).⁴ The P-N, P-S bonds are lengthened and the P-C bonds are shortened compared with those in **26**,¹⁷ which

indicates the ligand backbone has the resonance structure as shown in Scheme 1.6.

3.2.5 Synthesis of Hafnium (Iminophosphinoyl)(thiophosphinoyl)methanide

Complex

The hafnium (iminophosphinoyl)(thiophosphinoyl)methanide complex $[L_1'HfCl_2\{N(SiMe_3)_2\}]$ (**115**) was synthesized by the reaction of **26**¹⁷ with $[HfCl_2\{N(SiMe_3)_2\}_2]$ in refluxing toluene (Scheme 3.17).

Scheme 3.17

Compound **115** was isolated in CH_2Cl_2 as an air- and moisture-sensitive colorless crystalline solid in 45.6 % yield. It has been characterized by NMR spectroscopy and X-ray crystallography. The ^1H NMR spectrum of **115** displays a doublet of doublets at δ 2.67 ppm (dd, $^2J_{\text{P-H}} = 5.95$ Hz) for the methine proton and resonances for the SiMe_3 and phenyl protons. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **115** shows two doublets at δ 21.5, 32.9 ppm (d, $^2J_{\text{P-P}} = 21.7$ Hz) due to two nonequivalent phosphorus nuclei. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the methanide carbon was not observed.

Figure 3.6 Molecular structure of **115** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Hf(1)-C(1) 2.5090(10), Hf(1)-Cl(1) 2.4246(3), Hf(1)-Cl(2) 2.4064(3), Hf(1)-N(2) 2.0831(9), Hf(1)-N(1) 2.2509(9), Hf(1)-S(1) 2.7012(3), C(1)-P(1) 1.7681(10), C(1)-P(2) 1.7544(10), P(1)-N(1) 1.6018(9), P(2)-S(1) 2.0005(4); N(1)-Hf(1)-C(1) 66.91(3), C(1)-Hf(1)-S(1) 70.14(2), C(1)-Hf(1)-N(2) 93.86(3), C(1)-Hf(1)-Cl(1) 115.30(2), C(1)-Hf(1)-Cl(2) 145.15(2), P(1)-C(1)-P(2) 122.36(6).

The molecular structure of **115** is shown in Figure 3.6. Compound **115** displays as a monomer. It has an “open book” structure with the C(1)-Hf(1) bond lying on the spine. The thiophosphinoyl and iminophosphinoyl groups of the ligand are coordinated to the metal center. The Hf(1)-C(1) bond (2.5090(10) Å) in **115** is similar to the Hf-C single bonds in $[\text{HfCl}_2(\text{HN}(p\text{-tolyl}))\{\text{HC}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_{2-k}\text{C}_k^2\text{N},\text{N}'\}]$ (2.437(6) Å)⁷ and $[\text{HfCl}_2\{(\text{C}(\text{O})\text{N}(\text{Ad})\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2)\}]$ (2.431(6) Å).⁷ It is longer than the C=Hf bonds in $[\text{HfCl}_2\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_{2-k}\text{C}_k^3\text{N},\text{N}'\}]$ (**72**) (2.162(6) Å)² and $[\text{Hf}(\text{AdCN})\text{Cl}_2\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_{2-k}\text{C}_k^2\text{N},\text{N}'\}]$ (**77**) (2.211(6) Å).⁷ Therefore the carbon center is singly bonded to the hafnium atom. The P-C bonds are shortened and the P-N, P-S bonds are lengthened in **115** compared with those in **26**.¹⁷

3.2.6 Synthesis of Hafnium (Iminophosphinoyl)(thiophosphinoyl)methanediide

Complexes

The hafnium (iminophosphinoyl)(thiophosphinoyl)methanediide complex $[L_1''Hf(NMe_2)_2]$ (**116**) was afforded by the reaction of **26**¹⁷ with $[Hf(NMe_2)_4]$ in refluxing toluene. The X-ray crystallography shows that the C-Hf has some multiple bond character. Treatment of **116** with H_2O (0.042M in toluene) in toluene afforded the μ -oxo bridged hafnium (iminophosphinoyl)(thiophosphinoyl)methanediide complex $[\{\mu-L_1''Hf(NMe_2)\}_2O]$ (**117**) (Scheme 3.18). The X-ray crystallography shows that one of the C-Hf bonds in **117** is highly ionic.

Scheme 3.18

Compounds **116** and **117** were air- and moisture-sensitive colorless crystalline solids. **116** was isolated in hexane in 61.3 % yield and **117** was isolated in toluene in 10.5 % yield. They have been characterized by NMR spectroscopy and X-ray crystallography. The 1H NMR spectra of **116** and **117** display resonances for the $SiMe_3$, NMe_2 and phenyl protons. The $^{31}P\{^1H\}$ NMR spectrum of **116** shows two doublets at δ 10.4, 11.1 ppm (d, $^2J_{P-P'} = 52.0$ Hz) due to two nonequivalent phosphorus nuclei. The $^{31}P\{^1H\}$ NMR spectrum of **117** [δ 22.8, 23.2 ppm (d, $^2J_{P-P'} = 21.7$ Hz)] shows a downfield shift compared with **116**. The $^{13}C\{^1H\}$ NMR spectrum of **116** shows one doublet of doublets for the methanediide carbon at δ 55.97 ppm (dd, PCP, $J_{P-C} = 144.89$ Hz, $J_{P'-C} = 129.44$ Hz). The $^{13}C\{^1H\}$ NMR spectrum of **117** shows one doublet of doublets for the methanediide carbon at δ 40.17 ppm (dd, PCP, $J_{P-C} = 29.55$ Hz, $J_{P'-C} = 65.78$ Hz). The upfield shift of $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR of **117**

compared with those of **116** indicates the existence of zwitterionic C $\cdots$ Hf interaction in **117**.

Figure 3.7 Molecular structure of **116** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Hf(1)-C(1) 2.218(2), C(1)-P(1) 1.667(2), C(1)-P(2) 1.647(2), P(1)-N(1) 1.628(2), P(2)-S(1) 2.0376(8), Hf(1)-N(1) 2.2125(19), Hf(1)-S(1) 2.6565(6); N(1)-Hf(1)-C(1) 70.06(7), P(2)-C(1)-P(1) 160.15(16), N(2)-Hf(1)-C(1) 118.94(8), C(1)-Hf(1)-S(1), 72.42(6), N(3)-Hf(1)-S(1) 98.22(6), N(2)-Hf(1)-C(1) 118.94(8), N(3)-Hf(1)-C(1) 126.23(9), N(1)-Hf(1)-S(1) 142.20(5).

The molecular structure of **116** is shown in Figure 3.7. Compound **116** adopts an “open book” structure with the C(1)-Hf(1) bond lying on the spine (P(2)-C(1)-P(1) (160.15(16)°). The thiophosphinoyl and iminophosphinoyl group of the ligand coordinate to the metal center. The sum of the angles around the C_{methanediide} atom is 357.12°, which suggests the planar N-P-C-P-S core. The C-Hf bond (2.218(2) Å) in **116** is similar to the C=Hf bonds in [HfCl₂{C(Ph₂P=NSiMe₃)_{2-k}C_k²N,N'}] (**72**) (2.162(6) Å)² and [Hf(AdCN)Cl₂{C(Ph₂P=NSiMe₃)_{2-k}C_k²N,N'}] (**77**) (2.211(6) Å).⁷ The P-C bonds are shortened and the P-N, P-S bonds are lengthened compared with those in **26**,¹⁷ which indicates the ligand backbone has the resonance structure as shown in Scheme 1.6.

Figure 3.8 Molecular structure of **117** with thermal ellipsoids at the 30% probability level. Phenyl substituents, hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)-Hf(1) 2.388(5), C(1)-Hf(2) 2.707(4), C(2)-Hf(1) 2.725(4), C(2)-Hf(2) 2.363(4), N(2)-Hf(1) 2.162(4), S(1)-Hf(1) 2.6183(14), N(1)-Hf(2) 2.178(4), S(2)-Hf(2) 2.6207(14), O(1)-Hf(1) 1.956(4), O(1)-Hf(2) 1.958(4), Hf(1)-Hf(2) 3.0648(3); Hf(2)-C(1)-Hf(1) 73.82(5), Hf(1)-C(2)-Hf(2) 73.70(12), C(2)-Hf(1)-C(1) 81.16(14), C(1)-Hf(2)-C(2) 82.00(14), Hf(2)-O(1)-Hf(1) 103.07(13).

The molecular structure of **117** is shown in Figure 3.8. Compound **117** consists of a Hf-O-Hf skeleton, which is bridged between two (iminophosphinoyl)(thiophosphinoyl)methanediide ligands. Each Hf atom is bonded to two C_{methanediide} atoms and one amino group. It is also coordinated by the thiophosphinoyl and iminophosphinoyl group of the ligands. The Hf(1)-O(1), Hf(2)-O(1) bonds (1.958(4), 1.956(4) Å) are similar to that of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)]_2\text{O}$ (1.941(3) Å).²¹ The Hf(1)-O-Hf(2) bond angle (103.07(13)°) is more acute than that of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)]_2\text{O}$ (173.9(3)°).²¹ The C(1)⋯Hf(2), C(2)⋯Hf(1) distances (2.707(4), 2.725(4) Å) are significantly longer than the C=Hf double bonds in **116** (2.218(2) Å), $[\text{HfCl}_2\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}k^3\text{C},\text{N},\text{N}^*\}]$ (**72**) (2.162(6) Å)² and $[\text{Hf}(\text{AdCN})\text{Cl}_2\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}k^2\text{C}_k\text{N},\text{N}^*\}]$ (**77**) (2.211(6) Å)⁷, but it is shorter than the sum of van der Waals radii (*ca.* 3.31 Å). It indicates that there is a zwitterionic interaction between the C(1)⋯Hf(2), C(2)⋯Hf(1) atoms. The C(1)-Hf(1), C(2)-Hf(2)

bonds (2.388(5), 2.363(4) Å) are comparable with those C-Hf single bonds in $[\text{HfCl}_2(\text{HN}(p\text{-tolyl}))\{\text{HC}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}^k\text{C}_k^2\text{N},\text{N}^{\circ}\}]$ (**80**) (2.437(6) Å) and $[\text{HfCl}_2\{(\text{C}(\text{O})\text{N}(\text{Ad}))(\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2)\}]$ (**85**) (2.431(6) Å).⁷

3.2.7 Proposed Mechanism

Scheme 3.19

Firstly, one amino group of **111** and **116** reacts with H_2O to generate the corresponding hydroxides **B**. Then the HNMe_2 elimination during the reaction of **B** with another molecule of **A** leads to the formation of **C** (Scheme 3.19).

3.2.8 Synthesis of Copper (iminophosphinoyl)(thiophosphinoyl)methanediide

Complex

The reaction of **26** with one equivalent of $^n\text{BuLi}$ in THF, followed by the treatment with CuI afforded the copper (iminophosphinoyl)(thiophosphinoyl)methanediide $(\text{L}_1'\text{Cu}_2)_3$ (**118**), **26** and one unidentified minor product, which was confirmed by NMR spectroscopy (Scheme 3.20). The reaction probably proceeds through the formation of a copper (iminophosphinoyl)(thiophosphinoyl)methanide intermediate “ $(\text{L}_1'\text{Cu})$ ”, which then be deprotonated by $[\text{Li}(\text{L}_1')]$ (**27**) to form **118** and **26**.

Scheme 3.20

The Cu^{I}_6 cluster consists of a puckered $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ ring core with two bridging Cu^{I} and Cu^{II} atoms at the opposite edge. Three $\text{C}_{\text{methanediide}}$ atoms are bridged at the three edges of the $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ ring. The structure of **118** is different from that of $[(\text{PPh}_2=\text{NSiMe}_3)_2\text{CCu}_2]_2 \cdot (\text{CuX})_2$ ($\text{X} = \text{Cl}$ (**94**), Br (**95**) or I , (**96**)) (Scheme 3.10) supported by “ $\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2$ ” ligand.¹¹ $[(\text{PPh}_2=\text{NSiMe}_3)_2\text{CCu}_2]_2 \cdot (\text{CuX})_2$ (**94-96**) has a capped boat-shaped Cu_6 cluster which is formed by the coordination of $[(\text{PPh}_2=\text{NSiMe}_3)_2\text{CCu}_2]_2$ with two CuX moieties. It was synthesized by the reaction of $[\text{Li}_2(\text{PPh}_2=\text{NSiMe}_3)_2]$ (**7**) with $[\text{Cu}_2(\text{cod})_2\text{X}_2]$. In contrast, the reaction of $[\text{LiCH}(\text{PPh}_2=\text{NSiMe}_3)_2]$ (**6**) with $[(\text{Ph}_3\text{P})\text{CuI}]$ afforded the copper bis(iminophosphinoyl)methanide $[\text{HC}(\text{PPh}_2=\text{NSiMe}_3)_2\text{Cu}(\text{PPh}_3)]$ (**90**).⁹

Compound **118** was isolated in $\text{Et}_2\text{O}/\text{THF}$ as a highly air- and moisture-sensitive yellow crystalline solid in 32.1 % yield. It is soluble in THF and CH_2Cl_2 , but it decomposes slowly in solution to give **26**, which is confirmed by NMR spectroscopy. It is stable in the solid state at room temperature in an inert atmosphere. In this regard, a solution of **118** in $\text{THF-}d_8/\text{CDCl}_3$ was freshly prepared and characterized by NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows six doublets at 24.60 ($^2J_{\text{P-P}} = 13.1$ Hz), 27.97 ($^2J_{\text{P-P}} = 26.2$ Hz), 30.53 ($^2J_{\text{P-P}} = 30.6$ Hz), 33.71 ($^2J_{\text{P-P}} = 30.6$ Hz), 35.22

($^2J_{\text{P-P}'} = 26.2$ Hz), 36.06 ppm ($^2J_{\text{P-P}'} = 17.5$ Hz) due to non-equivalent phosphorus nuclei. The results are consistent with the crystallographic data that the phosphorus nuclei have different chemical environments. Moreover, compound **118** retains its solid state structure in solution. The UV-Vis spectrum of **118** in THF shows two absorption bands at 310 nm in the ultraviolet region and 420 nm in the visible light region, which are assigned to the Cu(3d)→Cu(4p) transition and ligand to metal charge transfer. The results are comparable with those in [(PPh₂=NSiMe₃)₂CCu₂]₂·(CuX)₂. (**94-96**).¹¹

Figure 3.9 Molecular structure of **118** with thermal ellipsoids at the 30% probability level. Phenyl substituents, hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu(1)-C(1) 1.984(4), Cu(1)-S(2) 2.1450(13), Cu(1)-Cu(2) 2.5386(8), Cu(1)-Cu(6) 2.6125(9), Cu(1)-Cu(4) 2.6396(8), Cu(2)-C(1) 2.011(4), Cu(2)-C(51) 2.034(4), Cu(2)-Cu(5) 2.5358(7), Cu(2)-Cu(6) 2.6968(9), Cu(2)-Cu(4) 3.0343(8), Cu(3)-N(2) 1.904(4), Cu(3)-S(3) 2.1637(13), Cu(3)-Cu(5) 2.6595(8), Cu(3)-Cu(4) 2.7244(8), Cu(4)-N(1) 1.949(4), Cu(4)-C(26) 1.980(4), Cu(4)-Cu(5) 2.5926(7), Cu(5)-C(26) 1.979(4), Cu(5)-C(51) 1.990(4), Cu(6)-N(3) 1.922(4), Cu(6)-S(1) 2.1501(14), C(1)-P(1) 1.726(5), C(1)-P(2) 1.740(5), C(26)-P(3) 1.752(4), C(26)-P(4) 1.761(5), C(51)-P(5) 1.728(5), C(51)-P(6) 1.761(5), N(1)-P(2) 1.658(4), N(2)-P(4) 1.608(4), N(3)-P(6) 1.612(4), P(1)-S(1) 2.0359(17), P(3)-S(2) 2.0334(16), P(5)-S(3) 2.0387(17); P(1)-C(1)-P(2) 125.5(3), Cu(1)-C(1)-Cu(2) 78.90(16), P(3)-C(26)-P(4) 120.8(2), Cu(5)-C(26)-Cu(4) 81.81(16), P(5)-C(51)-P(6) 124.1(3), Cu(5)-C(51)-Cu(2) 78.12(16).

The molecular structure of **118** is shown in Figure 3.9. Three C_{methanediide} atoms (C(1), C(26) and C(51)) of the (iminophosphinoyl)(thiophosphinoyl)methanediide ligands are geminally bonded to four Cu^I (Cu(1), Cu(2), Cu(4) and Cu(5)) atoms, which constitute a puckered four-membered ring. The Cu(3) and Cu(6) atoms are bridged the opposite edge (Cu(4)-C(5) and Cu(1)-Cu(2) bonds) of the Cu(1)Cu(2)Cu(5)Cu(4) four-membered ring to form a Cu₆^I cluster. The Cu(1), Cu(3), Cu(4) and Cu(6) atoms are also coordinated with the iminophosphinoyl and thiophosphinoyl substituents. The C_{methanediide}-Cu bond lengths (1.980(4) – 2.034(4) Å) are not equal and they are comparable with those in [(PPh₂=NSiMe₃)₂CCu₂]₂·(CuX)₂ (**94-96**) (X = Cl: average 1.960 Å; Br: average: 1.962 Å; I: 1.965 Å).¹¹ Similarly, the C-P, P-N, P-S bond lengths of the (iminophosphinoyl)(thiophosphinoyl)methanediide ligands are slightly different, which lead to six non-equivalent phosphorus environments. The results are consistent with the ³¹P{¹H} NMR spectroscopy. The Cu-Cu bond lengths (2.5358(7) - 2.7244(8) Å) in **118** are comparable with those in [(PPh₂=NSiMe₃)₂CCu₂]₂·(CuX)₂ (**94-96**) (X = Cl: average 2.7296 Å; Br: average: 2.7251 Å; I: 2.6956 Å).¹¹ The Cu(2)···Cu(4) (3.0343(8) Å) and Cu(1)-Cu(5) (3.194(8) Å) distances are longer than the sum of the van der Waals radii (*ca* 2.80 Å), which indicate that there is no interaction among these atoms. The Cu(1)-S(2) (2.1450(13) Å), Cu(3)-S(3) (2.1637(13) Å), Cu(6)-S(1) (2.1501(14) Å) bonds are significantly shorter than those in [Cu₂{(SPh₂P)₂CSSC(PPh₂S₂)₂}] (average 2.24 Å)²² and [H₂C(PPh₂S)₂CuI] (2.259(2), 2.321(2) Å).²³ The Cu(3)-N(2) (1.904(4) Å), Cu(4)-N(1) (1.949(4) Å) and Cu(6)-N(3) (1.922(4) Å) are shorter than those in

$[(PPh_2=NSiMe_3)C(CuPPh_3)_2]$.⁹ Moreover, the P-C bonds are shortened and the P-N/S bonds are lengthened compared with **26**.¹⁷

3.2.9 Synthesis of Gold (Iminophosphinoyl)(thiophosphinoyl)methanediide

Complex

The reaction of **26**¹⁷ with one equivalents of $nBuLi$ in THF, followed by the treatment with $[Au(PPh_3)Cl]$ in the absence of light afforded $[L_1''Au_2(PPh_3)_2]$ (**119**) in Et₂O (Scheme 3.21). Silimar phosphine-stabilized gold(I) bis(iminophosphinoyl)methanediide complex $[(PPh_2=NSiMe_3)_2C(AuPPh_3)_2]$ (**91**) has been reported.

Scheme 3.21

Compound **119** was isolated in Et₂O as an air- and moisture-sensitive colorless crystalline solid in 55.6 % yield. It has been characterized by NMR spectroscopy and X-ray crystallography. The 1H NMR spectrum of **119** displays resonances for the SiMe₃ and phenyl protons. The $^{13}C\{^1H\}$ NMR signal shows one doublet of doublets at δ 71.22 ppm (dd, $J_{P-C} = 24.9$ Hz, $J_{P'-C} = 64.3$ Hz) for the methanediide carbon. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at δ 6.80, 37.0 ppm (d, $^2J_{P-P'} = 30.3$ Hz) for the methanediide carbon and one AB quartet at δ 49.42 ppm (ABq, $^3J_{P-P'} = 54.59$ Hz) for the PPh₃ substituents due to three nonequivalent phosphorus nuclei.

Figure 3.10 Molecular structure of **119** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Au(1)-Au(2) 2.9010(15), Au(1)-C(1) 2.12(2), Au(2)-C(1) 2.092(19), Au(1)-P(1) 2.278(6), Au(2)-P(2) 2.251(7), N(1)-P(4) 1.519(18), S(1)-P(3) 1.979(9), C(1)-P(3) 1.79(2), C(1)-P(4) 1.78(2); Au(1)-C(1)-Au(2) 87.1(7), C(1)-Au(1)-P(1) 176.9(6), C(1)-Au(2)-P(2) 173.4(6), P(3)-C(1)-Au(1) 109.5(9), P(3)-C(1)-Au(2) 107.2(11), P(4)-C(1)-Au(2) 119.1(9), P(4)-C(1)-Au(1) 110.0(11), P(3)-C(1)-P(4) 118.5(11).

The molecular structure of **119** is shown in Figure 3.10. It is comparable with that of $[(\text{Ph}_3\text{PAu})_2\{\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2\}]$ (**91**). The iminophosphinoyl or thiophosphinoyl substituents are not coordinated to the gold(I) center. The C(1) atom is geminally bonded to Au(1) and Au(2) atoms. The C-Au bonds (2.12(2) Å, 2.092(19) Å) are comparable with those of $[(\text{Ph}_3\text{PAu})_2\{\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2\}]$ (**91**) (2.105(2) Å, 2.099(3) Å).⁹ The Au(1)···Au(2) (2.9010(15) Å) distance is shorter than the sum of van der Waals radii (*ca.* 3.32 Å). This indicates that there is an interaction between these two gold atoms. Moreover, the P-C bonds are shortened and the P-N/S bonds are lengthened compared with **26**,¹⁷ which indicates the ligand backbone has the resonance structure as shown in Scheme 1.6.

3.2.10 Synthesis of Silver (Iminophosphinoyl)(thiophosphinoyl)methanediide

Complex

The reaction of **26** with one equivalent of $^n\text{BuLi}$ in THF, followed by the treatment with AgCl in the absence of light afforded a mixture of the silver (iminophosphinoyl)(thiophosphinoyl)methanediide $(\text{L}_1''\text{Ag}_2)_3$ (**120**), $[(\text{L}_1''\text{Ag}_2)_2(\text{AgL}_1')]$ (**121**), black precipitates and unidentified products, which was confirmed by NMR spectroscopy (Scheme 3.22). The black precipitates could be silver metal.

Scheme 3.22

A mixture of compounds **120** and **121** was isolated as a cocrystal in a ratio of 3:2 by recrystallization in $\text{Et}_2\text{O}/\text{THF}$ in 25.6 % yield. An attempt to separate **120** and **121** by recrystallization failed. Similar to compound **118**, the reaction probably proceeds through the formation of a silver (iminophosphinoyl)(thiophosphinoyl)methanide intermediate “ $(\text{L}_1'\text{Ag})$ ”, which then be deprotonated by $[\text{Li}(\text{L}_1')]$ (**27**) to form **120**. Compound **120** is a trimer of “ $(\text{L}''\text{Ag}_2)$ ”, which contains a Ag_6^{I} cluster coordinated

with three methanediide ligands (L’’). It is isostructural with **118**. Compound **120** comprises two “(L’Ag₂)” moieties coordinating with a “(L’Ag)” moiety. Compound **121** can be considered as an intermediate during the formation of **120**. In this regard, the reaction of two equivalent of [Li(L₁’)] (**27**) with AgCl in THF in the absence of light was performed in order to afford **120** as a sole product. However, only black precipitate was observed.

A mixture of compounds **120** and **121** was isolated a highly air- and moisture-sensitive colorless cocrystalline solid. It is slightly soluble in organic solvents and unstable in solution to give black precipitates. In this regard, a solution of the mixture in THF-*d*₈/CDCl₃ was freshly prepared and characterized by NMR spectroscopy. The ³¹P{¹H} NMR spectrum of the mixture shows twelve multiples at δ 13.15, 15.36, 18.61, 19.39, 22.89, 23.51, 32.03, 35.06, 36.81, 39.68, 42.60, 46.88 (m) ppm due to coupling with the non-equivalent phosphorous, ¹⁰⁷Ag, ¹⁰⁹Ag nuclei. The ¹H NMR shows one AB quartet at δ 2.95 ppm (²J_{P-H} = 6.8 Hz) for the methine proton in **121**.

Figure 3.11 Molecular structures of **120** with thermal ellipsoids at the 50% probability level. Phenyl substituents, hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ag(1)-C(1) 2.205(5), Ag(1)-C(2) 2.266(5), Ag(1)-Ag(2) 2.8523(5),

Ag(1)-Ag(5) 2.9089(11), Ag(1)-Ag(6) 2.8984(10), Ag(1)-Ag(3) 3.2329(5), Ag(2)-C(2) 2.184(5), Ag(2)-C(3) 2.191(5), Ag(2)-Ag(4) 2.8680(6), Ag(2)-Ag(3) 2.8893(5), Ag(3)-N(1) 2.147(4), Ag(3)-C(3) 2.164(5), Ag(3)-Ag(6) 2.8535(10), Ag(3)-Ag(4) 2.9635(6), Ag(4)-N(3) 2.130(4), Ag(4)-S(2) 2.3723(13), Ag(5)-N(2) 2.174(5), Ag(5)-S(1) 2.361(5), Ag(5)-Ag(6) 2.8948(13), Ag(6)-C(1) 2.123(5), Ag(6)-S(3) 2.355(5), S(3)-P(6) 2.025(5), C(1)-P(1) 1.762(5), C(1)-P(2) 1.767(11), C(2)-P(4) 1.725(6), C(2)-P(3) 1.747(6), C(3)-P(6) 1.739(5), C(3)-P(5) 1.752(5), P(2)-S(1) 2.018(10), N(1)-P(1) 1.600(4), N(2)-P(3) 1.595(5), N(3)-P(5) 1.614(5), P(4)-S(2) 2.051(2); P(1)-C(1)-P(2) 122.2(5), Ag(6)-C(1)-Ag(1) 84.07(18), P(4)-C(2)-P(3) 126.5(3), Ag(2)-C(2)-Ag(1) 79.71(16), P(6)-C(3)-P(5) 124.2(3), Ag(3)-C(3)-Ag(2) 83.14(16).

The molecular structure of **120** is shown in Figure 3.11. It is isostructural with compound **118**. Three C_{methanediide} atoms C(1-3) are geminally bonded to four Ag^I (Ag(1), Ag(2), Ag(3) and Ag(6)) atoms, which constitute a puckered four-membered ring. The Ag(4) and Ag(5) atoms are bridged the opposite edge (Ag(1)-Ag(6) and Ag(2)-Ag(3) bonds) of the four-membered ring to form a Ag₆^I cluster. In addition, the Ag(1)⋯Ag(3) distance (3.2329(5) Å) is shorter than the sum of the van der Waals radii of two Ag atoms (*ca.* 3.44 Å). This indicates that there is an interaction between the Ag(1) and Ag(3) atoms. The Ag(3)-Ag(4) bond (2.9635 Å) is slightly longer than other Ag-Ag bonds (2.8523(5) - 2.9089(11) Å). They are comparable with those in Ag cluster compounds (2.740 - 3.278 Å).²⁴ The C_{methanediide}-Ag bond lengths are not equal with one slightly longer than the other one (C(1)-Ag: 2.123(5), 2.205(5); C(2)-Ag: 2.184(5), 2.266(5); C(3)-Ag: 2.164(5), 2.191(5) Å). They are slightly shorter than the C_{methanediide}-Ag bond (2.289(11) Å) in [Ag₂(PPh₃)₂(SPhPh₂CHPPh₂CHCO₂Me)]ClO₄·4CH₂Cl₂.²⁵ The Ag(4)-S(2) (2.3723(13) Å), Ag(5)-S(1) (2.361(5) Å), Ag(6)-S(3) (2.355(5) Å) bonds are significantly shorter than those in the silver(I) (thiophosphinoyl)methanide [HC(PPh₂=S)₃AgP(ⁿBu)₃] (2.585(2) - 2.670(2) Å).²⁶ They are comparable with those in [Ag₂{(PPh₂S)₂CSeSeC(PPh₂S)₂}] (2.400(2), 2.420(2) Å).²² The Ag(3)-N(1) (2.147(4)

Å), Ag(4)-N(3) (2.130(4) Å) and Ag(5)-N(2) (2.174(5) Å) are shorter than that in $[(PPh_2=NSiMe_3)CGe(Ag)(Cl)]_2$ (2.158(9) Å).²⁷ Moreover, the P-C bonds are shortened and the P-N/S bonds are lengthened compared with **26**,¹⁷ which indicates the ligand backbone has the resonance structure as shown in Scheme 1.6.

Figure 3.12 Molecular structures of **121** with thermal ellipsoids at the 50% probability level. Phenyl substituents, hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)-H(1) 1.0001, Ag(1)-C(1) 2.205(5), Ag(2)-C(2) 2.184(5), Ag(1)-C(2) 2.266(5), Ag(2)-C(3) 2.191(5), Ag(3)-C(3) 2.164(5), Ag(1)-Ag(2) 2.8523(5), Ag(1)-Ag(3) 3.2329(5), Ag(2)-Ag(3) 2.8893(5), Ag(2)-Ag(4) 2.8680(6), Ag(2)-Ag(3) 2.8893(5), Ag(3)-Ag(4) 2.9635(6), Ag(1)-Ag(5A) 2.8816(8), Ag(2)-Ag(5A) 2.8984(8), Ag(3)-N(1) 2.147(4), Ag(4)-N(3) 2.130(4), Ag(4)-S(2) 2.3723(13), Ag(5A)-N(2) 2.255(4), Ag(5A)-S(3A) 2.454(3), Ag(5A)-S(1A) 2.657(4), C(1)-P(2A) 1.756(9), C(1)-P(1) 1.762(5), P(2A)-S(1A) 1.999(8), N(1)-P(1) 1.600(4), C(2)-P(4) 1.725(6), C(2)-P(3) 1.747(6), N(2)-P(3) 1.595(5), P(4)-S(2) 2.051(2), C(3)-P(6) 1.739(5), C(3)-P(5) 1.752(5), N(3)-P(5) 1.614(5), S(3A)-P(6) 2.055(4); P(4)-C(2)-P(3) 126.5(3), Ag(2)-C(2)-Ag(1) 79.71(16), P(6)-C(3)-P(5) 124.2(3), Ag(3)-C(3)-Ag(2) 83.14(16), P(2A)-C(1)-P(1) 129.6(4), Ag(1)-C(1)-H(1) 100.6.

Compound **121** comprises three fused Ag_3 rings. In addition, the $C_{methanediide}$ (C(1)) atom is bonded to the Ag(1) atom and the $C_{methanediide}$ atoms (C(2), C(3)) are geminally bonded to Ag(1-3) atoms. Moreover, the Ag(3) atom is coordinated with the iminophosphinoyl substituent, while the Ag(4) and Ag(5a) atoms are coordinated with the iminophosphinoyl and thiophosphinoyl substituents. The $C_{methanediide}$ -Ag (Ag1)-C(1): 2.205(5) Å) and $C_{methanediide}$ -Ag (C(2)-Ag: 2.184(5), 2.266(5); C(3)-Ag: 2.164(5), 2.191(5) Å) and Ag-Ag bonds (2.8523(5)-3.2329(5) Å) are comparable to

120.

3.2.11 Synthesis of Ytterbium (Iminophospinoyl)(thiophosphinoyl)methanide Complex

The reaction of **26**¹⁷ with ⁿBuLi in THF, followed by the treatment with YbCl₃ afforded the ytterbium (iminophospinoyl)(thiophosphinoyl)methanide complex [(L1')₂YbCl] (**122**) (Scheme 3.23).

Scheme 3.23

Compound **122** was isolated in THF/hexane as an air- and moisture-sensitive red crystalline solid in 68.2 % yield. It has been characterized by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectrum of **122** displays resonances for the SiMe₃ and phenyl protons. The ³¹P{¹H} NMR spectrum of **122** shows two doublets at δ 172.4, 180.2 ppm (d, ²J_{P-P'} = 21.5 Hz) due to two nonequivalent phosphorus nuclei. It is noteworthy that the ¹³C{¹H} NMR signal for the methanide carbon in **122** is not observed.

Figure 3.12 Molecular structure of **122**. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)-Yb(1) 2.742(6), C(2)-Yb(1) 2.714(7), Yb(1)-Cl(1) 2.5469(19), Yb(1)-N(1) 2.378(5), Yb(1)-S(1) 2.7526(16), Yb(1)-N(2) 2.421(5), Yb(1)-S(2) 2.7796(16), P(1)-N(1) 1.601(6), C(1)-P(1) 1.729(6), C(1)-P(2) 1.756(6), P(2)-S(1) 2.007(2), P(3)-N(2) 1.592(6), C(2)-P(3) 1.727(7), C(2)-P(4) 1.749(6), P(4)-S(2) 2.001(2); P(1)-C(1)-P(2) 126.5(4), C(1)-Yb(1)-Cl(1) 134.30(15), C(1)-Yb(1)-N(1) 63.27(19), C(1)-Yb(1)-S(1) 68.53(13), P(3)-C(2)-P(4) 123.3(4), C(2)-Yb(1)-Cl(1) 142.27(14), C(2)-Yb(1)-N(2) 62.7(2), C(2)-Yb(1)-S(2) 67.84(14), C(1)-Yb(1)-C(2) 82.34(18).

The molecular structure of **122** is shown in Figure 3.12. The two (iminophosphinoyl)(thiophosphinoyl)methanide ligands act as tridentate donors. The C-Yb bonds (2.742(6), 2.714(7) Å) are within the range of C-Yb bonds in reported ytterbium methanide analogues (2.592(2) - 2.786(4) Å).²⁸ The Yb-Cl bond (2.5469(19) Å) is also comparable with reported analogues containing Yb-Cl bonds (2.5208(7) - 2.677(2) Å).²⁸ The P-C bonds are shortened and the P-N/S bonds are lengthened compared with those in **26**.¹⁷

3.3 Conclusion

In summary, the zirconium and the hafnium (iminophosphinoyl)(thiophosphinoyl)methanide and methanediide complexes **110-112** and **115-117** have been synthesized. The reactivity of μ -oxo bridged zirconium (iminophosphinoyl)(thiophosphinoyl)methanediide complex [$\{\mu\text{-L}_1''\text{Zr}(\text{NMe}_2)\}_2\text{O}$]

(**112**) with AdNCO (Ad = adamantyl) has been investigated. The X-ray crystallography shows the insertion of AdNCO into the Zr-NMe₂ bond. The zirconium bis(methanediide) complex [(L₁')₂Zr] (**114**) was also synthesized. The synthesis of copper, gold and silver (iminophosphinoyl)(thiophosphinoyl)methanediide complexes (L₁'Cu₂)₃ (**118**), [L₁'Au₂(PPh₃)₂] (**119**) and (L₁'Ag₂)₃ (**120**) has been presented. The X-ray crystallography shows that **118** and **119** consist of the unusual Cu₆^I and Ag₆^I cluster structures. The ytterbium (iminophosphinoyl)(thiophosphinoyl)methanide complex [(L₁')₂YbCl] (**122**) was also reported.

Since the bis(phosphinoyl)methane containing two donor sites of different hardness displays extraordinary coordination chemistry, its ability of stabilizing variety of metals could be expanded extensively toward more kinds of elements e.g. the silicon chemistry.

3.4 Experimental Section

All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled over Na/K alloy prior to use. The ¹H, ¹³C, ³¹P and ¹¹⁹Sn NMR spectra and CPMAS spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to SiMe₄ for ¹H and ¹³C, 85% H₃PO₄ for ³¹P, adamantane for ¹H CPMAS, hexa-methylbenzene for ¹³C CPMAS and ammonium dihydrogen phosphorus for ³¹P 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.

26 was prepared as described in Chapter 1.

[CH(PPh₂=NSiMe₃)(PPh₂=S)Zr{N(SiMe₃)₂}Cl₂] (110). Toluene (15 mL) was added to a mixture of [CH₂(PPh₂=NSiMe₃)(PPh₂=S)] (**26**) (0.52 g, 1 mmol) and [ZrCl₂{N(SiMe₃)₂}₂] (0.48 g, 1 mmol) at room temperature. The reaction mixture was then refluxed for 12 h to give a pale yellow solution with white precipitate. Volatiles were removed under reduced pressure. The resulting white residue was extracted by CH₂Cl₂. Colorless crystals of **110** (0.56 g, 68.2 %) were obtained after filtration and concentration. M.p.: 253.3 °C. Elemental analysis (%) calcd for C₃₄H₄₈Cl₂N₂P₂SSi₃Zr·2CH₂Cl₂: C 43.45, H 5.27, N 2.82; Found: C 44.84, H 5.25, N 3.00. ¹H NMR (399.5 MHz, 25°C, C₆D₆): δ 0.10 (s, 9H, SiMe₃), 0.37 (s, 18H, N(SiMe₃)₂), 2.64 (dd, 1H, PCHP, ²J_{P-H} = 5.25 Hz, ²J_{P'-H} = 1.36 Hz), 6.47-6.55 (m, 4h, Ph), 6.60-6.63 (m, 2H, Ph), 6.96-6.98 (m, 7H, Ph), 7.18-7.20 (m, 1H, Ph), 7.36-7.42 (m, 2H, Ph), 7.80-7.85 (m, 2H, Ph), 8.03-8.08 (m, 2H, Ph). ¹³C{¹H} NMR (100.5 MHz, 25°C, CDCl₃): δ 3.83, 3.86 (SiMe₃), 14.84 (dd, PCP, J_{P-C} = 57.4 Hz, J_{P'-C} = 73.8 Hz), 127.74 (d, C_{meta} of Ph, ³J_{P-C} = 12.07 Hz), 128.31 (d, C_{meta} of Ph, ²J_{P-C} = 12.07 Hz), 128.81 (d, C_{para} of Ph, ⁴J_{P-C} = 8.05 Hz), 128.87 (d, C_{para} of Ph, ⁴J_{P-C} = 7.04 Hz), 129.15 (d, C_{ortho} of Ph, ²J_{P-C} = 11.06 Hz), 130.12 (d, C_{ortho} of Ph, ²J_{P-C} = 11.06 Hz), 131.73 (dd, C_{ipso} of Ph, J_{P-C} = 37.0 Hz, ³J_{P-C} = 3.47 Hz), 132.38 ppm (d, C_{ipso} of Ph, J_{P-C} = 11.07 Hz). ³¹P{¹H} NMR (161.7 MHz, C₆D₆, 25°C): δ 23.2, 34.5 ppm.

[C(PPh₂=NSiMe₃)(PPh₂=S)Zr(NMe₂)₂] (111). Toluene (15 mL) was added to a mixture of [CH₂(PPh₂=NSiMe₃)(PPh₂=S)] (**26**) (0.49g, 1mmol) and [Zr(NMe₂)₄] (0.28 g, 1 mmol) at room temperature. The reaction mixture was then refluxed for 12 h to give a yellow solution. Volatiles were removed under reduced pressure. The resulting yellow residue was extracted by Et₂O. Colorless crystals of **111** (0.43 g, 65.0

%) were obtained after filtration and concentration. M.p.: 244.3 °C. Elemental analysis (%) calcd for $C_{32}H_{41}ZrN_3P_2SSi$: C 56.44, H 6.07, N 6.17; Found: C 56.25, H 6.01, N 6.08. 1H NMR (399.5 MHz, 25°C, C_6D_6): δ 0.057 (s, 9H, $SiMe_3$), 3.16 (s, 12H, NMe_2), 6.91-6.96 (m, 6H, Ph), 7.04-7.09 (m, 6H, Ph), 7.69-7.74 (m, 8H, Ph). $^{13}C\{^1H\}$ NMR (100.5 MHz, 25°C, C_6D_6): δ 3.16 ($SiMe_3$), 41.59 (NMe_2), 59.45 (dd, PCP, $J_{P-C} = 139.93$ Hz, $J_{P'-C} = 142.33$ Hz), 129.69 (C_{para} of Ph), 130.16 (C_{para} of Ph), 130.40 (t, C_{ortho} of Ph, $^2J_{P-C} = 5.74$ Hz), 131.05 (t, C_{ortho} of Ph, $^2J_{P-C} = 5.74$ Hz), 137.07-138.48 (m, C_{ipso} of Ph), 139.07-140.42 ppm (m, C_{ipso} of Ph). $^{31}P\{^1H\}$ NMR (161.7 MHz, 0°C, C_6D_6): δ 13.01 ppm (ABq, $^2J_{P-P'} = 43.35$ Hz).

[$C(PPh_2=NSiMe_3)(PPh_2=S)Zr(NMe_2)_2O$] (112). Toluene (0.042M H_2O in toluene, 58 mL) was added to the yellow solids of $[C(PPh_2=NSiMe_3)(PPh_2=S)Zr(NMe_2)_2]$ (0.68 g, 1 mmol) (**111**). The yellow solution was stirred at room temperature for 12 h. Volatiles were removed under reduced pressure. The resulting yellow residue was extracted by Et_2O . Colorless crystals of **112** (0.098 g, 14.8 %) were obtained after filtration and concentration. M.p.: 206.2 °C. Elemental analysis (%) calcd for $C_{64.90}H_{79.40}N_4O_{1.70}P_4S_2Si_2Zr_2$: C 56.92, H 5.84, N 4.09; Found: C 57.01, H 6.15, N 4.15. 1H NMR (395.9 MHz, 25°C, C_6D_6): δ 0.183 (s, 9H, $SiMe_3$), 3.29 (s, 6H, NMe_2), 6.49-6.62 (m, 4H, Ph), 6.76 (s, 4H, Ph), 6.87-6.92 (m, 2H, Ph), 7.01-7.11 (m, 4H, Ph), 7.31-7.36 (m, 2H, Ph), 7.54-7.60 (m, 2H, Ph), 7.93-7.98 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (99.5 MHz, 25°C, C_6D_6): δ 3.60 ($SiMe_3$), 47.09 (NMe_2), 127.02-127.27 (m, C_{meta} of Ph), 129.64 (d, C_{para} of Ph, $^4J_{P-C} = 2.45$ Hz), 130.08 (d, C_{para} of Ph, $^4J_{P-C} = 3.65$ Hz), 132.08 (d, C_{ortho} of Ph, $^2J_{P-C} = 7.83$ Hz), 132.86-132.99 (m, C_{ortho} & C_{ipso} of Ph), 133.88

ppm (d, C_{ipso} of Ph, $J_{\text{P-C}} = 9.04$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, 25°C, C_6D_6): δ 24.0, 25.6 ppm (d, $^2J_{\text{P-P}'} = 17.3$ Hz).

[(PPh₂=NSiMe₃)(PPh₂=S)CZr{N(Ad)C(NMe₂)O}]₂O (113). AdNCO (0.046 g, 0.26 mmol) in THF was added dropwise to **112** (0.18 g, 0.13 mmol) in THF at 0 °C. The yellow solution was stirred at room temperature for 15 h. Volatiles were removed under reduced pressure. The resulting residue was extracted by toluene. Colorless crystals of **113** (0.078 g, 35.2 %) were obtained after filtration and concentration. M.p.: 145.7 °C. Elemental analysis (%) calcd for $\text{C}_{91}\text{H}_{110}\text{N}_4\text{O}_3\text{P}_4\text{S}_2\text{Si}_2\text{Zr}_2 \cdot (\text{C}_2\text{H}_7\text{N}) \cdot 15\text{H}_2\text{O} \cdot 4\text{O}_2$: C 51.29, H 6.80, N 3.22; Found: C 51.66, H 6.41, N 3.66. ^1H NMR (395.9 MHz, 0 °C, THF- d_8): δ 0.33 (s, 18H, SiMe₃), 1.59-1.70 (m, 6H, Ad), 1.80-1.96 (m, 14H, Ad), 1.96-2.00 (s, 10H, Ad), 2.95 (s, 6H, NMe₂), 3.77 (s, 6H, NMe₂), 7.03-8.43 (m, 40H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, 25°C, C_6D_6): δ 4.93 (SiMe₃), 30.65 (Ad), 36.37 (Ad), 37.42 (Ad), 40.83 (NMe₂), 43.31 (Ad), 44.82 (NMe₂), 127.96 (d, C_{meta} of Ph, $^3J_{\text{P-C}} = 12.39$ Hz), 131.29 (d, C_{para} of Ph, $^4J_{\text{P-C}} = 3.81$ Hz), 131.59 (d, C_{para} of Ph, $^4J_{\text{P-C}} = 2.86$ Hz), 131.93 (d, C_{ortho} of Ph, $^2J_{\text{P-C}} = 9.53$ Hz), 132.67-133.18 (m, C_{ipso} and C_{ortho} of Ph), 134.44 (dd, C_{ipso} of Ph, $J_{\text{P-C}} = 40.04$ Hz, $^3J_{\text{P'-C}} = 10.49$ Hz), 157.41 ppm (NCO). $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, 0 °C, THF- d_8): δ 17.0, 36.4 ppm (d, $^2J_{\text{P-P}'} = 21.5$ Hz).

[[C(PPh₂=NSiMe₃)(PPh₂=S)]₂Zr] (114). Toluene (15 mL) was added to a mixture of $[\text{CH}_2(\text{PPh}_2=\text{NSiMe}_3)(\text{PPh}_2=\text{S})]$ (**26**) (0.49g, 1mmol) and two equivalents of $[\text{Zr}(\text{NMe}_2)_4]$ (1.3 g, 2 mmol) at room temperature. The reaction mixture was then refluxed for 12 h to give a yellow solution. Volatiles were removed under reduced

pressure. The resulting yellow residue was extracted by hexane. Colorless crystals of **114** (0.28 g, 48.2 %) were obtained after filtration and concentration. M.p.: 231.5 °C. Elemental analysis (%) calcd for $C_{56}H_{58}N_2P_4S_2Si_2Zr \cdot 6H_2O \cdot 2(C_6H_{14})$: C 56.09, H 6.09, N 1.92; Found: C 55.64, H 6.31, N 2.16. 1H NMR (399.5 MHz, C_6D_6 , 25°C): δ 0.18 (s, 9H, SiMe₃), 6.90-7.06 (m, 12H, Ph), 7.37-7.43 (m, 1H, Ph), 7.70-7.75 (m, 2H, Ph), 7.81-7.90 (m, 4H, Ph), 7.96-8.02 (m, 1H, Ph). $^{13}C\{^1H\}$ NMR (100.5 MHz, 25°C, C_6D_6): δ 4.72 (SiMe₃), 40.07 (dd, PCP, J_{P-C} = 66.72 Hz, $J_{P'-C}$ = 43.85 Hz), 130.25 (s, C_{para} of Ph), 130.75 (s, C_{para} of Ph), 131.32 (d, C_{meta} of Ph, $^3J_{P-C}$ = 3.81 Hz), 131.72 (d, C_{meta} of Ph, $^3J_{P-C}$ = 4.76 Hz), 131.96 (d, C_{ortho} of Ph, $^2J_{P-C}$ = 10.48 Hz), 133.15 (d, C_{ortho} of Ph, $^2J_{P-C}$ = 10.48 Hz), 135.50 (dd, C_{ipso} of Ph, J_{P-C} = 166.82 Hz, $^3J_{P-C}$ = 82.93 Hz), 140.26 ppm (dd, C_{ipso} of Ph, J_{P-C} = 152.52 Hz, $^3J_{P-C}$ = 80.08 Hz). $^{31}P\{^1H\}$ NMR (161.7 MHz, C_6D_6 , 25°C): δ 16.0, 17.6 ppm (d, $^2J_{P-P'}$ = 56.4 Hz).

[CH(PPh₂=NSiMe₃)(PPh₂=S)Hf{N(SiMe₃)₂}Cl₂] (115). Toluene (15 mL) was added to a mixture of [CH₂(PPh₂=NSiMe₃)(PPh₂=S)] (**26**) (0.52 g, 1 mmol) and [HfCl₂{N(SiMe₃)₂}₂] (0.56 g, 1 mmol) at room temperature. The reaction mixture was then refluxed for 12 h to give a pale yellow solution with white precipitate. Volatiles were removed under reduced pressure. The resulting white precipitate was extracted by CH₂Cl₂. Colorless crystals of **115** (0.41 g, 45.6 %) were obtained after filtration and concentration. M.p.: 259.4 °C. Elemental analysis (%) calcd for $C_{34}H_{48}Cl_2HfN_2P_2SSi_3$: C 44.76, H 5.30, N 3.07; Found: C 44.84, H 5.25, N 3.00. 1H NMR (399.5 MHz, 25°C, C_6D_6): δ 0.10 (s, 9H, SiMe₃), 0.37 (s, 18H, N(SiMe₃)₂), 2.67 (dd, 1H, PCHP, $^2J_{P-H}$ = 5.95 Hz), 6.45-6.55 (m, 3H, Ph), 6.59-6.63 (m, 1H, Ph), 6.87-6.91 (m, 1H, Ph),

6.94-6.96 (m, 3H, Ph), 7.79-7.84 (m, 1H, Ph), 8.04-8.09 (m, 1H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, 25°C, C_6D_6): δ 3.26 ($\text{N}(\text{SiMe}_3)_2$), 4.63 (SiMe_3), 127.79 (s, CH of Ph), 129.29 (s, CH of Ph), 129.61 (dd, C_{ipso} of Ph, $J_{\text{P-C}} = 21.09$, $^3J_{\text{P'-C}} = 10.54$ Hz), 130.61 (d, C_{ortho} of Ph, $^2J_{\text{P-C}} = 10.54$ Hz), 132.22 (s, CH of Ph), 133.11 (s, CH of Ph), 133.38 ppm (d, C_{ortho} of Ph, $^2J_{\text{P-C}} = 10.54$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, 25°C, C_6D_6): δ 21.5, 32.9 ppm (d, $^2J_{\text{P-P'}} = 21.7$ Hz).

[C(PPh₂=NSiMe₃)(PPh₂=S)Hf(NMe₂)₂] (116). Toluene (15 mL) was added to a mixture of $[\text{CH}_2(\text{PPh}_2=\text{NSiMe}_3)(\text{PPh}_2=\text{S})]$ (**26**) (0.52 g, 1 mmol) and $[\text{Hf}(\text{NMe}_2)_4]$ (0.25 g, 1.2 mmol) at room temperature. The reaction mixture was then refluxed for 12 h to give a pale yellow solution. Volatiles were removed under reduced pressure. The resulting yellow residue was extracted by hexane. Colorless crystals of **116** (0.28 g, 61.3 %) were obtained after filtration and concentration. M.p.: 207.5 °C. Elemental analysis (%) calcd for $\text{C}_{32}\text{H}_{41}\text{HfN}_3\text{P}_2\text{SSi}\cdot 6\text{H}_2\text{O}$: C 42.97, H 4.85, N 4.70; Found: C 42.81, H 3.92, N 1.79. ^1H NMR (395.9 MHz, 25 °C, C_6D_6): δ 0.064 (s, 9H, SiMe_3), 3.24 (s, 12H, NMe_2), 6.91-6.94 (m, 6H, Ph), 7.02-7.08 (m, 6H, Ph), 7.67-7.76 ppm (m, 8H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, 25 °C, C_6D_6): δ 3.63 (SiMe_3), 42.02 (NMe_2), 55.97 (dd, PCP, $J_{\text{P-C}} = 144.89$ Hz, $J_{\text{P'-C}} = 129.44$ Hz), 130.59 (s, C_{para} of Ph), 131.06 (s, C_{para} of Ph), 131.16 (d, C_{ortho} of Ph, $^2J_{\text{P-C}} = 12.39$ Hz), 131.85 (d, C_{ortho} of Ph, $^2J_{\text{P-C}} = 11.44$ Hz), 138.16 (dd, C_{ipso} of Ph, $J_{\text{P-C}} = 84.67$ Hz, $^3J_{\text{P-C}} = 84.83$ Hz), 140.41 ppm (dd, C_{ipso} of Ph, $J_{\text{P-C}} = 75.30$ Hz, $^3J_{\text{P-C}} = 80.07$ Hz) $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, 25°C, C_6D_6): δ 10.4, 11.1 ppm (d, $^2J_{\text{P-P'}} = 52.0$ Hz).

[{C(PPh₂=NSiMe₃)(PPh₂=S)Hf(NMe₂)₂O}] (117). Toluene (0.042M H_2O in toluene,

58 mL) was added to yellow solid of $[\text{C}(\text{PPh}_2=\text{NSiMe}_3)(\text{PPh}_2=\text{S})\text{Hf}(\text{NMe}_2)_2]$ (**116**) (0.77 g, 1 mmol). The yellow solution was refluxed for 12 h. Volatiles were removed under reduced pressure. The resulting yellow residue was extracted by toluene. Colorless crystals of **117** (0.066 g, 10.5 %) were obtained after filtration and concentration. M.p.: 192.1 °C. Elemental analysis (%) calcd for $\text{C}_{64}\text{H}_{80}\text{Hf}_2\text{N}_4\text{O}_2\text{P}_4\text{S}_2\text{Si}_2$: C 49.96, H 5.24, N 3.64; Found: C 50.21, H 5.16, N 3.84. ^1H NMR (395.9 MHz, 25 °C, C_6D_6): δ 0.19 (s, 9H, SiMe_3), 0.27 (s, 12H, NMe_2), 6.50-6.52 (m, 2H, Ph), 6.60-6.61 (m, 1H, Ph), 6.77 (s, 3H, Ph), 6.87-6.92 (m, 2H, Ph), 7.01-7.05 (m, 2H, Ph), 7.10-7.12 (m, 2H, Ph), 7.34-7.38 (m, 3H, Ph), 7.60-7.65 (m, 2H, Ph), 7.89-7.94 (m, 3H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, 25°C, C_6D_6): δ 4.37 (SiMe_3), 40.17 (dd, PCP, $J_{\text{P-C}} = 29.55$ Hz, $J_{\text{P'-C}} = 65.78$ Hz), 48.16 (NMe_2), 126.51 (d, C_{meta} of Ph, $^3J_{\text{P-C}} = 10.48$ Hz), 128.10 (d, C_{meta} of Ph, $^3J_{\text{P-C}} = 10.48$ Hz), 129.87 (s, C_{para} of Ph), 130.40 (s, C_{para} of Ph), 133.01 (d, C_{ortho} of Ph, $^2J_{\text{P-C}} = 12.38$ Hz), 133.70 ppm (dd, C_{ipso} of Ph, $J_{\text{P-C}} = 12.38$ Hz, $^3J_{\text{P'-C}} = 6.67$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, 25°C, C_6D_6): δ 22.8, 23.2 ppm (d, $^2J_{\text{P-P'}} = 21.7$ Hz).

$[(\text{PPh}_2=\text{NSiMe}_3)(\text{PPh}_2=\text{S})\text{CCu}_2]_3$ (**118**). $^n\text{BuLi}$ (0.5 mL, 1 mmol) was added to a solution of $[\text{CH}_2(\text{PPh}_2=\text{NSiMe}_3)(\text{PPh}_2=\text{S})]$ (**26**) (0.50 g, 1 mmol) in THF (10 mL) at room temperature. The reaction was stirred for 15 h. The reaction mixture was then added to a solution of CuI (0.19 g, 1 mmol) in THF (10 mL) at -78 °C. The reaction mixture was warmed to room temperature and then stirred for 6 h to give a dark green suspension. Volatiles were removed under reduced pressure. The resulting residue was extracted by $\text{Et}_2\text{O}/\text{THF}$. Yellow crystals of copper

[(PPh₂=NSiMe₃)(PPh₂=S)CCu₂]₃ (**118**) (0.21 g, 32.1 %) were obtained after filtration and concentration. M.p.: 232.3 °C. Elemental analysis (%) calcd for C₈₆H₉₂Cu₆N₃O_{0.50}P₆S₃Si₃: C 53.71, H 4.82, N 2.18; Found: C 51.22, H 5.82, N 1.42. ¹H NMR (395.9 MHz, 25 °C, THF-*d*₈/CDCl₃ (3:2 ratio)): δ -1.18 - -1.16 (d, 2H, SiMe₃), -0.76 - -0.75 (d, 2H, SiMe₃), -0.54 - -0.52 (d, 5H, SiMe₃), 6.56-6.78 (m, 4H, Ph), 6.91-7.00 (m, 9H, Ph), 7.14-7.19 (m, 5H, Ph), 7.50-7.55 (m, 2H, Ph). ¹³C NMR (99.5 MHz, 25°C, THF-*d*₈/CDCl₃ (3:2 ratio)): δ 2.62 (SiMe₃), 3.04 (SiMe₃), 4.05 (SiMe₃), 14.70, 127.02-127.78, 130.78-130.91, 131.48-131.58 ppm (Ph). ³¹P{¹H} NMR (160.3 MHz, 25°C, THF-*d*₈/CDCl₃ (3:2 ratio)): δ 24.60 ppm (²J_{P-P'} = 13.1 Hz); 27.97 ppm (²J_{P-P'} = 26.2 Hz); 30.53 ppm (²J_{P-P'} = 30.6 Hz); 33.71 ppm (²J_{P-P'} = 30.6 Hz); 35.22 ppm (²J_{P-P'} = 26.2 Hz); 36.06 ppm (²J_{P-P'} = 17.5 Hz).

[C(PPh₂=NSiMe₃)(PPh₂=S)Au₂(PPh₃)₂] (**119**). ⁿBuLi (0.49 mL, 1 mmol) was added to [CH₂(PPh₂=NSiMe₃)(PPh₂=S)] (**26**) (0.49 g, 1 mmol) in THF (10 mL) at -78 °C. The yellow solution was stirred at room temperature for 15 h in the absence of light. The resulting yellow solution was added dropwise to [AuCl(PPh₃)] (0.46 g, 1 mmol) in THF (10 mL) at -78 °C. The yellow suspension was stirred at room temperature for 12 h in the absence of light. Volatiles were removed under reduced pressure. The resulting yellow residue was extracted by Et₂O. Colorless crystals of **119** (0.77 g, 55.6 %) were obtained after filtration and concentration. M.p.: 228.5 °C. Elemental analysis (%) calcd for C₆₄H₅₉Au₂NP₄SSi: C 54.13, H 4.19, N 0.99; Found: C 52.90, H 4.54, N 1.06. ¹H NMR (395.9 MHz, 25 °C, C₆D₆): δ 0.35 (s, 9H, SiMe₃), 6.76-6.79 (m, 4H, Ph), 6.89-7.00 (m, 20H, Ph), 7.03-7.06 (m, 2H, Ph), 7.46-7.51 (m, 14H, Ph),

8.17-8.23 (m, 5H, Ph), 8.92-8.98 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, 25°C, C_6D_6): δ 5.32 (SiMe_3), 71.22 (dd, PCP, $J_{\text{P-C}} = 64.3$ Hz, $J_{\text{P'-C}} = 24.9$ Hz), 127.41 (ABq, C_{ipso} of Ph, $J_{\text{p-c}} = 12.34$ Hz), 129.54 (dd, PPh_3 , $J_{\text{p-c}} = 23.74$ Hz, $^3J_{\text{p'-c}} = 18.04$ Hz), 131.40 (s, CH of Ph), 132.27 (s, CH of Ph), 132.78 (s, CH of Ph), 133.66 (d, C_{ortho} of Ph, $^2J_{\text{p-c}} = 9.49$ Hz), 134.63 (d, C_{ortho} of Ph, $^2J_{\text{p-c}} = 10.43$ Hz), 135.18 ppm (dd, PPh_3 , $J_{\text{p-c}} = 14.24$ Hz, $^3J_{\text{p'-c}} = 6.65$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, 25°C, C_6D_6): δ 6.80, 37.0 ppm (d, PCP, $^2J_{\text{P-P'}} = 30.3$ Hz); δ 49.42 ppm (ABq, PPh_3 , $^3J_{\text{P-P'}} = 54.59$ Hz).

$^n\text{BuLi}$ (0.71 mL, 1.5 mmol) was added to a solution of $[\text{CH}_2(\text{PPh}_2=\text{NSiMe}_3)(\text{PPh}_2=\text{S})]$ (**26**) (0.72 g, 1.5 mmol) in THF (10 mL) at room temperature. The reaction was stirred for 15 h. The reaction mixture was then added to a solution of AgCl (0.21 g, 1.5 mmol) in THF (10 mL) at -78 °C. The reaction mixture was warmed to room temperature and then stirred for 12h in the absence of light to give a dark brown suspension. Volatiles were removed under reduced pressure. The resulting residue was extracted by $\text{Et}_2\text{O}/\text{THF}$. Colorless cocrystals (0.26 g, 25.6 %) of $[(\text{PPh}_2=\text{NSiMe}_3)(\text{PPh}_2=\text{S})\text{CAg}_2]_3$ (**120**) and $[\{(\text{PPh}_2=\text{NSiMe}_3)(\text{PPh}_2=\text{S})\text{CAg}_2\}_2\{\text{AgCH}(\text{PPh}_2=\text{NSiMe}_3)(\text{PPh}_2=\text{S})\}]$ (**121**) were obtained after filtration and concentration in the absence of light. M.p.: 223.0 °C. Elemental analysis (%) calcd for $\text{C}_{86}\text{H}_{92.58}\text{Ag}_{5.42}\text{N}_3\text{O}_{0.50}\text{P}_6\text{S}_3\text{Si}_3$: C 48.56, H 4.39, N 1.98; found: C 46.47, H 4.52, N 1.84. ^1H NMR (395.9 MHz, 25 °C, CDCl_3): δ -0.23 (s, 9H, SiMe_3), 0.10 (s, 6H SiMe_3), 3.68 (ABq, 0.4H, PCHP of **121**, $^2J_{\text{P-H}} = 14.05$ Hz), 6.74-7.01 (m, 12H, Ph), 7.11-7.20 (m, 12H, Ph), 7.21-7.56 (m, 12H, Ph), 7.69-7.75 (m,

4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum can't be afforded due to the decomposition in THF-*d*₈/CDCl₃ overnight. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, 25°C, THF-*d*₈/CDCl₃ (3:2 ratio)): δ 13.15, 15.36, 18.61, 19.39, 22.89, 23.51, 32.03, 35.06, 36.81, 39.68, 42.60, 46.88 (m) ppm.

[{CH(PPh₂=NSiMe₃)(PPh₂=S)}₂YbCl] (122). ⁿBuLi (0.7 mL, 1.5 mmol) was added to a solution of [CH₂(PPh₂=NSiMe₃)(PPh₂=S)] (**26**) (0.65 g, 1.5 mmol) in THF (10 mL) at -78 °C. The resulting yellow solution was stirred at room temperature for 15 h then it was added dropwise to a solution of YbCl₃ (0.36 g, 1.5 mmol) in THF (10 mL) at -78 °C. The yellow suspension was stirred at room temperature for 1 day and turned red. Volatiles were removed by reduced pressure. The resulting red residue was extracted by THF/hexane. Red crystals of **122** (0.42 g, 68.2 %) were obtained after filtration and concentration. M.p.: 319.0 °C. Elemental analysis (%) calcd for C₅₆H₆₁ClN₂P₄S₂Si₂Yb: C 55.37, H 5.06, N 2.31; Found: C 51.87, H 5.42, N 2.08. ^1H NMR (399.5 MHz, 25°C, CDCl₃): δ -0.59 (s, 3H, SiMe₃), 3.71 (br, 1H, PCHP), 5.50-5.72 (d, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, 25°C, CDCl₃): δ 3.84 (SiMe₃), 126.10 (s, CH of Ph), 128.79 (s, CH of Ph), 131.16 (dd, C_{ipso} of Ph, $J_{\text{P-C}}$ = 26.84 Hz, $^3J_{\text{P'-C}}$ = 16.30 Hz), 132.45 ppm (d, C_{ortho} of Ph, $^2J_{\text{P-C}}$ = 11.50 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, 25°C, CDCl₃): δ -172.4, 180.2 ppm (d, $^2J_{\text{P-P'}}$ = 21.5 Hz).

Crystal Structure Determinations of Compounds 110-122. 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 .²⁹

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 isotropic thermal parameters and included in the structure-factor calculations.

References of Chapter 3

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Appendix

Table 1. Crystallographic Data for Compounds 26-28, 30-31

Table 2. Crystallographic Data for Compounds 61-65

Table 3. Crystallographic Data for Compounds 66-69, 110

Table 4. Crystallographic Data for Compounds 111-115

Table 5. Crystallographic Data for Compounds 116-121

Table 6. Crystallographic Data for Compound 122

Table 1. Crystallographic Data for Compounds 26-28, 30-31

	26	27	28	30	31
formula	C _{31.5} H ₃₅ NP ₂ SSi	C ₃₆ H ₄₆ LiNO ₂ P ₂ SSi	C ₆₃ H ₇₃ Li ₄ N ₂ OP ₄ S ₂ Si ₂	C ₂₅ H ₂₅ BOP ₂	C ₅₄ H ₅₆ B ₂ MgO ₃ P ₄
formula weight	549.70	653.77	1146.17	414.20	922.80
color	colorless	colorless	colorless	colorless	colorless
crystal system	monoclinic	triclinic	monoclinic	orthorhombic	triclinic
space group	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>P2(1)2(1)2(1)</i>	<i>P</i> $\bar{1}$
<i>a</i> / Å	36.025(2)	10.234(4)	41.092(2)	8.869(5)	9.7685(4)
<i>b</i> / Å	15.835(6)	13.653(5)	12.539(5)	11.116(6)	13.5091(6)
<i>c</i> / Å	11.096(4)	13.805(5)	27.462(1)	22.260(12)	19.1449(8)
α / deg	90.00	80.61(2)	90.00	90	77.945(2)
β / deg	106.50(4)	73.13(2)	114.82(3)	90	85.880(2)
γ / deg	90.00	82.87(2)	90.00	90	81.847(2)
<i>V</i> / Å ³	6069.1(4)	1815.0(1)	12842.5(11)	2194(2)	2443.42(18)
<i>Z</i>	8	2	8	4	2
<i>d</i> _{calcd} / mg cm ⁻³	1.203	1.196	1.186	1.254	1.254
μ / mm ⁻¹	0.272	0.241	0.260	0.212	0.210
<i>F</i> (000)	2328	696	4840	872	972
crystal size / mm ³	0.34 x 0.30 x 0.02	0.54 x 0.52 x 0.50	0.40 x 0.10 x 0.06	0.10 x 0.04 x 0.02	0.40 x 0.40 x 0.28
Index ranges	-44 ≤ <i>h</i> ≤ 44 -19 ≤ <i>k</i> ≤ 19 -13 ≤ <i>l</i> ≤ 13	-13 ≤ <i>h</i> ≤ 13 -18 ≤ <i>k</i> ≤ 18 -18 ≤ <i>l</i> ≤ 18	-48 ≤ <i>h</i> ≤ 49 -14 ≤ <i>k</i> ≤ 14 -32 ≤ <i>l</i> ≤ 32	-11 ≤ <i>h</i> ≤ 11 -13 ≤ <i>k</i> ≤ 13 -27 ≤ <i>l</i> ≤ 27	-14 ≤ <i>h</i> ≤ 14 -20 ≤ <i>k</i> ≤ 20 -28 ≤ <i>l</i> ≤ 28
no. of rflns collected	45386	37909	43672	23762	73378
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0467, 0.1218	0.0646, 0.1713	0.0674, 0.1723	0.0834, 0.1487	0.0406, 0.1120
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0735, 0.1607	0.1086, 0.2597	0.1522, 0.2477	0.1863, 0.1972	0.0540, 0.1293
goodness of fit., <i>F</i> ²	1.152	1.137	1.000	0.978	1.074
no. of data/restraints/params	5996 / 200 / 368	9595 / 39 / 492	11367 / 474 / 811	4471 / 9 / 271	16961 / 168 / 647
largest diff peak, hole/eÅ ⁻³	0.531, -0.686	0.648, -1.255	1.190, -0.774	0.431, -0.413	1.005, -0.447

Table 2. Crystallographic Data for Compounds 61-65

	61	62	63	64	65
formula	C ₅₆ H ₅₈ Mg ₂ N ₂ P ₄ S ₂ Si ₂ ·0.5(C ₇ H ₈)	C ₆₆ H ₈₄ Al ₂ N ₂ O ₂ P ₄ S ₂ Si ₂	C ₂₈ H ₃₀ CINP ₂ SSiSn	C ₃₆ H ₅₃ N ₂ O _{0.50} P ₂ SSi ₃ Sn	C ₅₆ H ₅₈ N ₂ P ₄ S ₂ Si ₂ Sn ₂
formula weight	1097.91	1235.49	656.76	818.76	1240.60
color	colorless	colorless	colorless	colorless	yellow
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2(1)	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> / Å	13.4186(4)	10.99060(10)	11.2790(4)	9.2762(3)	10.6210(2)
<i>b</i> / Å	24.1503(6)	20.9657(3)	11.3253(4)	40.3235(12)	12.6848(3)
<i>c</i> / Å	19.3995(5)	15.5840(2)	13.5636(8)	11.5632(3)	20.9770(5)
α / deg	90	90	108.595(2)	90	90
β / deg	107.751(2)	108.7800	96.036(2)	110.8640(10)	101.3440(10)
γ / deg	90	90	115.3860(10)	90	90
<i>V</i> / Å ³	5987.4(3)	3399.78(7)	1423.16(11)	4041.6(2)	2770.92(11)
<i>Z</i>	4	2	2	4	2
<i>d</i> _{calcd} /mg cm ⁻³	1.218	1.207	1.533	1.346	1.487
μ / mm ⁻¹	0.295	0.276	1.238	0.880	1.174
<i>F</i> (000)	2308	1312	664	1700	1256
crystal size / mm ³	0.34 x 0.32 x 0.30	0.30 x 0.28 x 0.18	0.40 x 0.30 x 0.26	0.40 x 0.14 x 0.10	0.38 x 0.36 x 0.28
index ranges	-17 ≤ <i>h</i> ≤ 17 -30 ≤ <i>k</i> ≤ 30 -25 ≤ <i>l</i> ≤ 24	-17 ≤ <i>h</i> ≤ 17 -32 ≤ <i>k</i> ≤ 31 -24 ≤ <i>l</i> ≤ 22	-15 ≤ <i>h</i> ≤ 15 -15 ≤ <i>k</i> ≤ 15 -19 ≤ <i>l</i> ≤ 19	-11 ≤ <i>h</i> ≤ 11 -51 ≤ <i>k</i> ≤ 50 -14 ≤ <i>l</i> ≤ 14	-21 ≤ <i>h</i> ≤ 11 -25 ≤ <i>k</i> ≤ 23 -39 ≤ <i>l</i> ≤ 41
no. of rflns collected	70498	69211	27778	46207	116621
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0526, 0.1394	0.0415, 0.1113	0.0229, 0.0571	0.0367, 0.0683	0.0268, 0.0667
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0857, 0.1937	0.0702, 0.1373	0.0266, 0.0589	0.0495, 0.0750	0.0431, 0.0793
goodness of fit., <i>F</i> ²	1.173	1.120	1.044	1.043	1.121
no. of data/restraints/params	13374 / 373 / 728	13555 / 0 / 367	8230 / 0 / 319	17778 / 6 / 841	23274 / 0 / 310
largest diff peak, hole/e Å ⁻³	0.841, -0.733	0.638, -0.709	0.485, -0.331	0.863, -1.403	0.922, -1.548

Table 3. Crystallographic Data for Compounds 66-69, 110

	66	67	68	69	110
formula	C ₃₉ H ₄₄ N ₂ OP ₂ SSiSn	C ₄₁ H ₄₆ N ₂ OP ₂ SSiSn	C _{37.50} H ₄₇ Cl ₄ NP ₂ RhSSiSn	C ₁₀₈ H ₈₇ D ₂₄ N ₃ P ₆ S ₇ Si ₃ Sn ₄	C ₃₄ H ₄₈ Cl ₂ N ₂ P ₂ SSi ₃ Zr
formula weight	797.54	823.58	997.25	2444.41	825.13
color	colorless	colorless	red	orange	colorless
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	<i>C2/c</i>	<i>P2(1)/c</i>	<i>P2(1)/n</i>	<i>P2(1)/c</i>	<i>P$\bar{1}$</i>
<i>a</i> / Å	30.8813(11)	9.4127(3)	11.7899(2)	16.4619(10)	10.0221(2)
<i>b</i> / Å	11.1580(4)	21.5662(6)	16.7568(3)	33.693(2)	10.1870(2)
<i>c</i> / Å	22.3386(8)	19.0244(5)	20.4015(3)	19.8683(12)	19.9255(3)
α / deg	90	90	90	90	102.4530(10)
β / deg	104.853(2)	95.3480(10)	97.5720(10)	92.672(4)	94.4990(10)
γ / deg	90	90	90	90	94.9080(10)
<i>V</i> / Å ³	7440.1(5)	3845.07(19)	3995.39(11)	11008.1(12)	1969.31(6)
<i>Z</i>	8	4	4	4	2
<i>d</i> _{calcd} / mg cm ⁻³	1.424	1.423	1.658	1.475	1.392
μ / mm ⁻¹	0.895	0.868	1.497	1.196	0.667
<i>F</i> (000)	3280	1696	2008	4896	856
crystal size / mm ³	0.34 x 0.28 x 0.26	0.34 x 0.30 x 0.16	0.40 x 0.34 x 0.30	0.20 x 0.10 x 0.10	0.30 x 0.20 x 0.12
Index ranges	-44 ≤ <i>h</i> ≤ 44 -16 ≤ <i>k</i> ≤ 13 -32 ≤ <i>l</i> ≤ 32	-15 ≤ <i>h</i> ≤ 15 -32 ≤ <i>k</i> ≤ 34 -30 ≤ <i>l</i> ≤ 29	-19 ≤ <i>h</i> ≤ 17 -27 ≤ <i>k</i> ≤ 27 -32 ≤ <i>l</i> ≤ 32	-21 ≤ <i>h</i> ≤ 21 -44 ≤ <i>k</i> ≤ 45 -25 ≤ <i>l</i> ≤ 26	-12 ≤ <i>h</i> ≤ 12 -12 ≤ <i>k</i> ≤ 12 -24 ≤ <i>l</i> ≤ 24
no. of rflns collected	76461	73823	74292	147130	27251
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0612, 0.1625	0.0333, 0.0779	0.0290, 0.0657	0.0770, 0.1862	0.0243, 0.0609
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0948, 0.1916	0.0507, 0.0928	0.0412, 0.0704	0.1327, 0.2238	0.0286, 0.0631
goodness of fit., <i>F</i> ²	1.351	1.082	1.045	1.176	1.063
no. of data/restraints/params	11810 / 623 / 639	17312 / 0 / 449	17658 / 3 / 457	27312 / 404 / 1235	8089 / 0 / 415
largest diff peak, hole/e Å ⁻³	0.665, -1.421	0.831, -0.750	1.436, -1.100	1.860, -1.998	0.370, -0.338

Table 4. Crystallographic Data for Compounds 111-115

	111	112	113	114	115
formula	C ₃₂ H ₄₁ N ₃ P ₂ SSiZr	C _{64.90} H _{79.40} N ₄ O _{1.70} P ₄ S ₂ Si ₂ Zr ₂	C ₈₉ H ₁₀₈ N ₆ O ₃ P ₄ S ₂ Si ₂ Zr ₂	C ₆₀ H ₆₉ N ₂ OP ₄ S ₂ Si ₂ Zr	C ₃₄ H ₄₈ Cl ₂ HfN ₂ P ₂ SSi ₃
formula weight	680.99	1369.34	1736.43	1169.57	912.40
color	colorless	colorless	colorless	colorless	colorless
crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> / Å	9.6234(2)	12.6988(5)	12.7258(8)	13.6793(3)	10.0221(3)
<i>b</i> / Å	18.0821(3)	17.7746(7)	12.7610(9)	14.0728(3)	10.1736(3)
<i>c</i> / Å	19.4580(3)	14.4923(6)	29.211(2)	15.6590(3)	19.9931(7)
α / deg	87.0260(10)	90	80.011(4)	93.1900(10)	102.563(2)
β / deg	89.2870(10)	92.501(2)	89.827(4)	91.9080(10)	94.634(2)
γ / deg	87.7320(10)	90	67.807(3)	99.5520(10)	94.794(2)
<i>V</i> / Å ³	3378.52(10)	3268.0(2)	4315.4(5)	2965.28(11)	1972.45(11)
<i>Z</i>	4	2	2	2	2
<i>d</i> _{calcd} / mg cm ⁻³	1.339	1.392	1.336	1.310	1.536
μ / mm ⁻¹	0.543	0.563	0.444	0.445	3.032
<i>F</i> (000)	1416	1421	1816	1222	920
crystal size / mm ³	0.34 x 0.20 x 0.02	0.40 x 0.36 x 0.08	0.20 x 0.16 x 0.08	0.20 x 0.16 x 0.06	0.22 x 0.18 x 0.16
Index ranges	-14 ≤ <i>h</i> ≤ 14 -26 ≤ <i>k</i> ≤ 27 -24 ≤ <i>l</i> ≤ 29	-21 ≤ <i>h</i> ≤ 21 -30 ≤ <i>k</i> ≤ 25 -24 ≤ <i>l</i> ≤ 22	-16 ≤ <i>h</i> ≤ 18 -16 ≤ <i>k</i> ≤ 18 -42 ≤ <i>l</i> ≤ 42	-19 ≤ <i>h</i> ≤ 19 -20 ≤ <i>k</i> ≤ 20 -22 ≤ <i>l</i> ≤ 22	-16 ≤ <i>h</i> ≤ 16 -17 ≤ <i>k</i> ≤ 17 -33 ≤ <i>l</i> ≤ 33
no. of rflns collected	109036	69745	161184	69650	96947
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0503, 0.0913	0.0346, 0.0856	0.0454, 0.1114	0.0437, 0.1031	0.0184, 0.0432
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1172, 0.1216	0.0439, 0.1005	0.0794, 0.1381	0.0867, 0.1367	0.0210, 0.0444
goodness of fit., <i>F</i> ²	1.018	1.097	1.093	1.063	1.057
no. of data/restraints/params	23481 / 36 / 775	30455 / 1 / 785	28597 / 92 / 1104	18982 / 0 / 657	19761 / 0 / 415
largest diff peak, hole/e Å ⁻³	0.608, -0.957	0.953, -1.362	0.926, -1.507	1.306, -1.439	1.631, -0.548

Table 5. Crystallographic Data for Compounds 116-121

	116	117	118	119	120-121
formula	C ₃₂ H ₄₁ HfN ₃ P ₂ SSi	C ₆₄ H ₈₀ Hf ₂ N ₄ O ₂ P ₄ S ₂ Si ₂	C ₈₆ H ₉₂ Cu ₆ N ₃ O _{0.50} P ₆ S ₃ Si ₃	C ₆₄ H ₅₉ Au ₂ NP ₄ SSi	C ₈₆ H _{92.58} Ag _{5.42} N ₃ O _{0.50} P ₆ S ₃ Si ₃
formula weight	768.26	1538.48	1923.14	1420.09	2127.14
color	colorless	colorless	yellow	colorless	colorless
crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> / Å	9.6249(3)	12.7016(5)	15.5149(7)	11.6417(11)	15.6169(4)
<i>b</i> / Å	18.0474(6)	17.7710(6)	21.6790(10)	11.9398(11)	21.9768(6)
<i>c</i> / Å	19.5069(6)	14.4417(5)	24.9801(13)	21.313(2)	25.2698(6)
α / deg	86.597(2)	90	90	95.271(5)	90
β / deg	89.237(2)	92.436(2)	91.755(3)	93.307(5)	92.3010(10)
γ / deg	87.933(2)	90	90	101.522(5)	90
<i>V</i> / Å ³	3380.05(19)	3256.8(2)	8398.1(7)	2881.8(5)	8665.8(4)
<i>Z</i>	4	2	4	2	4
<i>d</i> _{calcd} /mg cm ⁻³	1.510	1.569	1.521	1.637	1.630
μ / mm ⁻¹	3.303	3.430	1.771	5.294	1.473
<i>F</i> (000)	1544	1544	3948	1396	4273
crystal size / mm ³	0.40 x 0.40 x 0.20	0.30 x 0.23 x 0.12	0.12 x 0.06 x 0.06	0.02 x 0.02 x 0.02	0.20 x 0.06 x 0.04
Index ranges	-13 ≤ <i>h</i> ≤ 14 -24 ≤ <i>k</i> ≤ 26 -28 ≤ <i>l</i> ≤ 28	-18 ≤ <i>h</i> ≤ 18 -23 ≤ <i>k</i> ≤ 25 -20 ≤ <i>l</i> ≤ 20	-18 ≤ <i>h</i> ≤ 18 -23 ≤ <i>k</i> ≤ 25 -20 ≤ <i>l</i> ≤ 20	-14 ≤ <i>h</i> ≤ 12 -14 ≤ <i>k</i> ≤ 14 -25 ≤ <i>l</i> ≤ 25	-22 ≤ <i>h</i> ≤ 22 -31 ≤ <i>k</i> ≤ 31 -36 ≤ <i>l</i> ≤ 33
no. of rflns collected	90062	79840	146983	31925	129199
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0276, 0.0578	0.0325, 0.0650	0.0587, 0.1566	0.0807, 0.1752	0.0517, 0.1124
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0397, 0.0619	0.0471, 0.0893	0.1258, 0.1975	0.2632, 0.2799	0.1234, 0.1636
goodness of fit., <i>F</i> ²	1.043	1.080	1.062	0.967	1.033
no. of data/restraints/params	21814 / 83 / 805	20147 / 1 / 733	26761 / 31 / 1002	10242 / 1060 / 723	27518 / 654 / 1096
largest diff peak, hole/e Å ⁻³	0.951, -0.990	1.532, -2.718	4.038, -2.229	1.316, -3.741	1.264, -2.422

Table 6. Crystallographic Data for Compound 122

122	
formula	C ₅₆ H ₆₁ ClN ₂ P ₄ S ₂ Si ₂ Yb
formula weight	1214.74
color	red
crystal system	triclinic
space group	<i>P</i> $\bar{1}$
<i>a</i> / Å	12.0816(4)
<i>b</i> / Å	12.6340(4)
<i>c</i> / Å	19.6428(8)
α / deg	99.202(2)
β / deg	96.781(2)
γ / deg	109.039(2)
<i>V</i> / Å ³	2750.81(17)
<i>Z</i>	2
<i>d</i> _{calcd} / mg cm ⁻³	1.467
μ / mm ⁻¹	2.023
<i>F</i> (000)	1236
crystal size / mm ³	0.20 x 0.16 x 0.10
Index ranges	-16 ≤ <i>h</i> ≤ 17 -17 ≤ <i>k</i> ≤ 18 -17 ≤ <i>l</i> ≤ 27
no. of rflns collected	16579
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0602, 0.1390
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0976, 0.1744
goodness of fit., <i>F</i> ²	1.045
no. of data/restraints/params	16579 / 0 / 619
largest diff peak, hole/e Å ⁻³	2.152, -2.105