

Syntheses, Structures and Reactivities of Bis(thiophosphinoyl) Metal Complexes

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A Thesis Submitted in Partial Fulfillment
of the Requirement for the Degree of
Master of Philosophy
in
Chemistry

The Chinese University of Hong Kong
September 2009



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Acknowledgements

I wish to express my sincere gratitude to my supervisor, Prof. Kevin W.-P. Leung, for his invaluable guidance, continuous encouragement and enthusiasm throughout the course of my research and the preparation of this thesis.

I am indebted to Prof. Thomas C. W. Mak and Miss H.-S. Chan for carrying out X-ray structure analysis. Thanks are also given to Mr. K.-W. Kwong and Miss H.-Y. Ng for their assistance in recording the multinuclear NMR spectra.

I would also like to express my thanks to Prof. H.-K. Lee, Prof. C.-W. So, Dr. K.-W. Kan and all my colleagues for their assistance and helpful discussions.

Financial support from The Chinese University of Hong Kong in the form of Postgraduate Studentship is gratefully acknowledged.

September 2009

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Abstract

This thesis is focused on three areas: (i) the synthesis of lithium and magnesium bis(thiophosphinoyl) complexes and their role as ligand transfer reagents; (ii) the synthesis and reactivities of group 13 and 14 bis(thiophosphinoyl) metal complexes and (iii) the synthesis of group 4 early transition metal bis(thiophosphinoyl) complexes.

Chapter 1 begins with an introduction on the development of thiophosphinoyl metal complexes. The synthesis of lithium complex $[\text{Li}\{(\text{S}=\text{PPh}_2)_2\text{CH}\}(\text{THF})(\text{Et}_2\text{O})]$ (**42**) and magnesium methanediide complex $[\text{MgC}(\text{PPh}_2=\text{S})_2(\text{THF})_2]$ (**43**) from bis(thiophosphinoyl)methane, $(\text{S}=\text{PPh}_2)_2\text{CH}_2$ (**4**) were described. They can act as ligand transfer reagents in the synthesis of metal complexes. Structural characterization of these two compounds by X-ray crystallography are also presented.

Chapter 2 describes the synthesis and reactivities of group 14 metal bis(thiophosphinoyl) complexes. 1,3-Dimetallacyclobutanes $[\text{M}\{\mu^2\text{-C}(\text{Ph}_2\text{P}=\text{S})_2\}]_2\cdot\text{THF}$ ($\text{M} = \text{Sn}$ (**74**), Pb (**75**)) were prepared from **4** and $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$ ($\text{M} = \text{Sn}$, Pb) by amine elimination. Compound **75** further reacts with chalcogens (S and Se) to give two $\text{Pb}(\text{II})$ complexes, $[\text{PbE}\{\text{C}(\text{Ph}_2\text{P}=\text{S})_2\}]$ ($\text{E} = \text{S}$ (**78**), Se (**79**)). Chlorogermylene $[\text{GeCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$ (**80**) and chlorostannylene $[\text{SnCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$ (**81**) can be obtained from the metathesis reaction of **2** with MCl_2 ($\text{M} = \text{Ge}$, Sn). Reaction of **80** with sulfur gave the *trans*-dithiagermetane $[\text{GeCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}(\mu\text{-S})_2]$ (**82**) while that of

$[\text{SnCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$ (**81**) with half equivalents of $\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2$ afforded **74**.

Chapter 3 deals with the synthesis and characterization of group 13 metal bis(thiophosphinoyl) complexes $[\text{MCl}\{\text{C}(\text{PPh}_2=\text{S})_2\}]_2$ ($\text{M} = \text{Al}$ (**108**), Ga (**109**), In (**110**)). These compounds have been characterized by single X-ray crystallography and are shown to be dimeric in nature.

Chapter 4 describes the preparation and characterization of group 4 bis(thiophosphinoyl) metal complexes. Ligand **4** reacts with $\text{M}(\text{NMe}_2)_4$ ($\text{M} = \text{Zr}, \text{Hf}$) to give (dimethyl)amido metal complexes $[\text{M}(\text{NMe}_2)_3\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$ ($\text{M} = \text{Zr}$ (**125**), Hf (**126**)). Two group 4 metal carbene complexes, $[\text{Cp}_2\text{M}=\text{C}(\text{Ph}_2\text{P}=\text{S})_2]$ ($\text{M} = \text{Ti}$ (**127**), Zr (**128**)) were formed respectively from the reaction of **43** with Cp_2MCl_2 ($\text{M} = \text{Ti}, \text{Zr}$).

摘要

本論文工作主要包括三個方面：(i) 金屬鋰和鎂的雙膦亞硫配合物的合成以及它們作為配體轉移試劑的研究；(ii) 第十三及第十四主族金屬的雙膦亞硫配合物的合成和反應研究 和 (iii) 第四族過渡金屬的雙膦亞硫配合物的合成。

第一章介紹了雙膦亞硫配合物的發展。並描述了從膦亞硫配體 $(S=PPh_2)_2CH_2$ (4) 出發合成鋰化合物 $[Li\{(S=PPh_2)_2CH\}(THF)(Et_2O)]$ (42) 和鎂配合物 $[Mg=C\{(PPh_2=S)_2\}(THF)]_2$ (43)；在金屬配合物的合成中，它們可以充當配體轉移試劑；對這兩個化合物都做了 X - 射綫單晶衍射表征。

第二章描述了第十四族金屬雙膦亞硫配合物合成和反應。從化合物 4 和 $M\{N(SiMe)_2\}_2$ ($M = Sn, Pb$) 出發，通過脫胺反應分別合成了低價態 1,3-雙錫化環丁烷 74 及 1,3-雙鉛化環丁烷 75。化合物 75 進一步和硫族元素單質反應生成二價鉛化合物 $[PbE\{C(Ph_2P=S)_2\}]$ ($E = S$ (78), Se (79))。雙膦亞硫配位體的二價銻氯化物 $[GeCl\{CH(PPh_2=S)_2\}]$ (80) 和二價錫氯化物 $[SnCl\{CH(PPh_2=S)_2\}]$ (81) 可以由化合物 42 和第十四族金屬氯化物的復分解反應得到。化合物 80 跟硫反應生成 $[GeCl\{CH(PPh_2=S)_2\}(\mu-S)]_2$ (82)，而化合物 81 和一半當量的 $Pb\{N(SiMe_3)_2\}_2$ 反應產生了 74。

第三章介紹雙膦亞硫的第十三族有機金屬化合物 $[MCl\{C(PPh_2=S)_2\}]_2$ ($M = Al$ (108), Ga (109), In (110)) 的合成與結構研究。從這些化合物的 X - 射綫單晶衍射表征可以看到它們是以二聚體的形式存在。

第四章介紹雙膦亞硫的第四族金屬配合物的合成和表征。配體 **4** 和 $M(\text{NMe}_2)_4$ ($M = \text{Zr, Hf}$) 反應給出 $[M(\text{NMe}_2)_3\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$ ($M = \text{Zr}$ (**125**), Hf (**126**))。同時，鎂配合物 **43** 跟 Cp_2MCl_2 ($M = \text{Ti, Zr}$) 產生反應，生成了第四族金屬的卡賓配合物 $[\text{Cp}_2\text{M}=\text{C}(\text{Ph}_2\text{P}=\text{S})_2]$ ($M = \text{Ti}$ (**127**), Zr (**128**))。

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List of Compounds Synthesized in This Work

Compound	Number	Page	
		Syn.	Struc.
[Li{(S=PPh ₂) ₂ CH}(THF)(Et ₂ O)]	42	17	13
[MgC(PPh ₂ =S) ₂ (THF)] ₂ ·2THF	43	18	16
[Sn{μ ² -C(Ph ₂ P=S) ₂ }] ₂ ·THF	74	54	35
[Pb{μ ² -C(Ph ₂ P=S) ₂ }] ₂ ·THF	75	55	37
[Ge{N(SiMe ₃) ₂ }(μ-S)] ₂	77	55	
[PbS{C(PPh ₂ =S) ₂ }] ₂ · ⁵ / ₄ THF	78	56	41
[PbSe{C(PPh ₂ =S) ₂ }]	79	56	42
[GeCl{CH(PPh ₂ =S) ₂ }]	80	57	47
[SnCl{CH(PPh ₂ =S) ₂ }]	81	58	47
[GeCl{CH(PPh ₂ =S) ₂ }(μ-S)] ₂ ·4THF	82	59	52
[AlCl{C(PPh ₂ =S) ₂ }] ₂	108	79	76
[GaCl{C(PPh ₂ =S) ₂ }] ₂	109	79	76
[InCl{C(PPh ₂ =S) ₂ }] ₂	110	80	77
[Zr(NMe ₂) ₃ {CH(PPh ₂ =S) ₂ }]	125	97	
[Hf(NMe ₂) ₃ {CH(PPh ₂ =S) ₂ }]	126	98	95
[Cp ₂ Ti=C(PPh ₂ =S) ₂]	127	98	
[Cp ₂ Zr=C(PPh ₂ =S) ₂]	128	99	

Abbreviation

Anal.	analytically
Ar	2,6-diisopropylphenyl
Bbt	2,6-bis(bis(trimethylsilyl)methyl)-4-(tris(trimethylsilyl)methyl)phenyl
Bu ⁱ	isobutyl
Bu ⁿ	butyl
Bu ^t	<i>tert</i> -butyl
Br	broad (spectral)
Bz	benzyl
Calcd.	calculated
Cp	cyclopentadienyl
d	doublet (spectral)
dec	decomposed
DME	dimethoxyethane
Et ₂ O	diethyl ether
<i>fac</i>	facial
Hz	hertz
<i>J</i>	coupling constant
m	multiplet (spectral)
Me	methyl
Mes	2,4,6-trimethylphenyl
Mp.	melting point
MHz	megahertz
NMR	nuclear magnetic resonance
Ph	phenyl

Pr ⁱ	isopropyl
Pr ⁿ	propyl
Py	pyridyl
s	singlet (spectral)
t	triplet (spectral)
Tbt	2,4,6-tris(bis(trimethylsilyl)methyl)phenyl
THF	tetrahydrofuran
Tip	2,4,6-triisopropylphenyl
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
Tol	toluene
tz	1,2,3-triazole

Chapter 1 Synthesis of Group 1 and 2 Metal Bis(thiophosphinoyl) Complexes

1.1 Introduction

1.1.1 General Aspects of Thiophosphinoyl Ligands

The chemistry of phosphoranoimine ($R_3P=NR'$) has attracted much attention and has been studied extensively in recent years.¹ In contrast, only moderate work has been done with phosphoranosulfide ($R_3P=S$). As a sulfur analogue of phosphoranoimine, phosphoranosulfide can also act as neutral or anionic ligands in coordination chemistry. The highly polar P–S bond features a multiple bond character, relating to two resonance structures from cationic phosphonium and anionic sulfide centers **I** to doubly bonded P=S species **II** (Fig. 1.1).²



Fig. 1.1

Phosphoranosulfides can be prepared by direct oxidation of the corresponding phosphines with elemental sulfur.³ Since 1970s, phosphoranosulfides have been used as ligands in coordination and organometallic chemistry. A variety of coordination modes is possible and complexes involving monodentate *S*, bidentate *S,S*, and bridging *S,S*,

have all been reported. Several examples of phosphoranosulfide ligands are shown in Fig. 1.2.

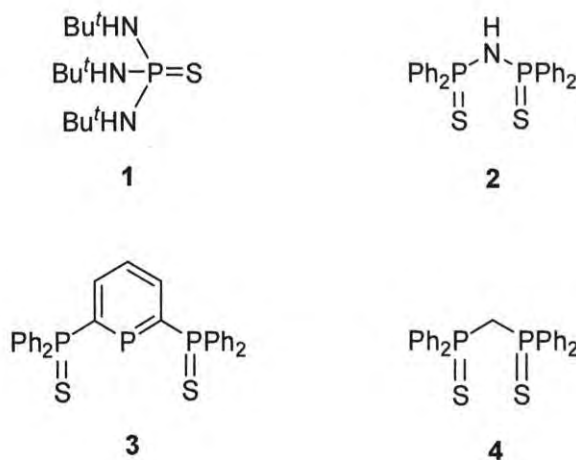


Fig. 1.2

Phosphoranosulfide can act as a neutral ligand by using the lone pair of electrons at the sulfur atom to form transition metal complexes. For example, $[\text{Ph}_3\text{P}=\text{S}]$ was used to prepare *cis*- $[\text{Pt}(\text{Ph}_3\text{P}=\text{S})\text{RCl}_2]$ ($\text{R} = \text{SOMe}_2, (\text{S})\text{-Me-}p\text{-TolSO}$) (**5**),⁴ $[\text{Cu}(\mu\text{-I})(\text{Ph}_3\text{P}=\text{S})(\text{MeCN})_2]$ (**6**)⁵ and $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{Ph}_3\text{P}=\text{S})_2]$ (**7**).⁶ Group 10 metal adducts $[\text{CuX}\{\text{CH}_2(\text{Ph}_3\text{P}=\text{S})_2\}]$ ($\text{X} = \text{Cl}, \text{I}$) (**8**)⁷ and $[(\text{C}_6\text{F}_5)\text{Au}(\text{S}=\text{PPh}_2\text{CH}_2\text{PPh}_2=\text{S})\text{Au}(\text{C}_6\text{F}_5)]$ (**9**)⁸ have been reported. Compound **9** is the first example of gold complex containing $(\text{S}=\text{PPh}_2)_2\text{CH}_2$ as bridging ligand (Fig. 1.3).

Protons at the $\alpha\text{-C}$ or $\alpha\text{-N}$ positions of phosphoranosulfides can be deprotonated to give monoanionic or dianionic ligands. They can serve as chelating agents for transition metals and lanthanides.

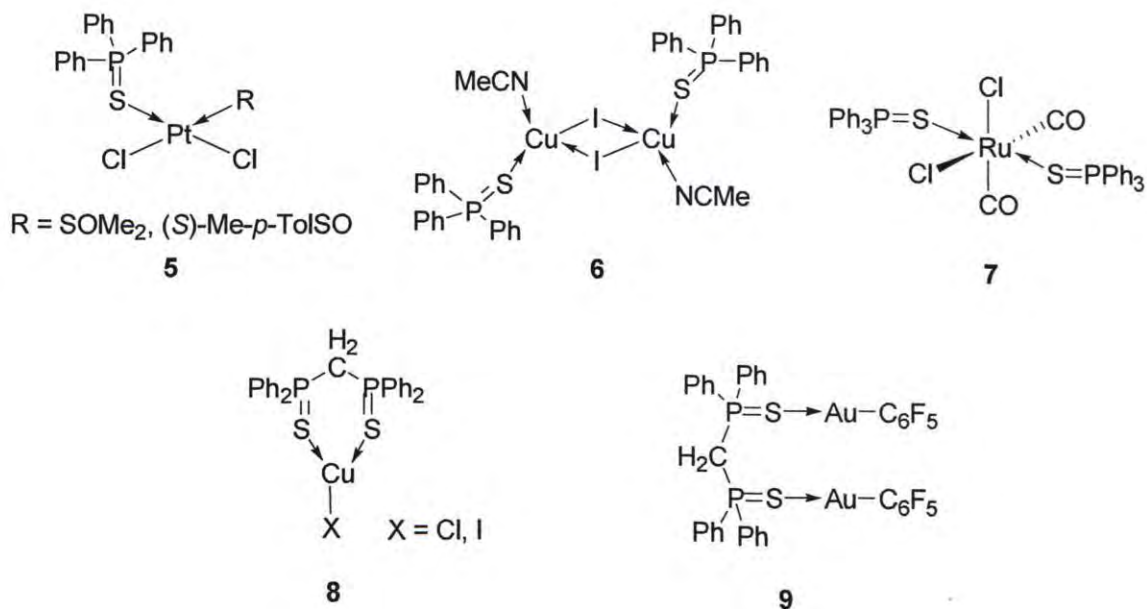


Fig. 1.3

Lithiation of compound **1** by Bu^tLi afforded $[(\text{THF})\text{Li}\{(\text{NBu}^t)\text{SP}(\text{NHBu}^t)_2\}]$ (**10**).⁹ Further reaction of **10** with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and $[\text{NiBr}_2(\text{DME})]$ gave the corresponding tris(tert-butylamido)orthothiophosphates **11** and **12**, respectively (Fig. 1.4). Two zinc complexes $[\text{MeZn}(\mu\text{-S})(\mu\text{-NBu}^t)\text{P}(\text{NHBu}^t)_2]_2$ (**13**) and $[\text{Zn}\{\text{S}(\text{NBu}^t)\text{P}(\text{NHBu}^t)_2\}_2]$ (**14**) were also synthesized from the reaction of **1** with ZnMe_2 in 1:1 and 2:1 ratio, respectively.¹⁰

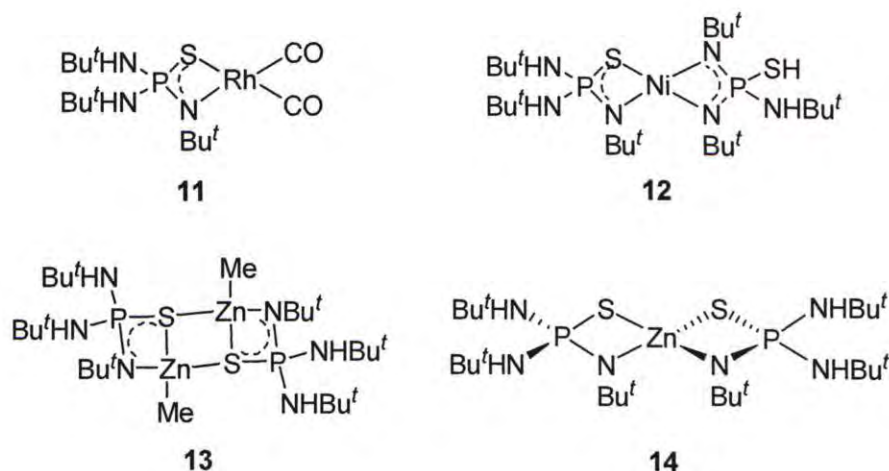


Fig. 1.4

The deprotonated iminobis(phosphoranosulfide) **2** acts as a versatile monoanionic ligand for transition metals, lanthanides and actinides. For examples, $[M\{N(SPh_2)_2\}_2]$ ($M = Mn$ (**15a**), Co (**15b**)),^{11,12} ($M = Ni$ (**16a**), Pd (**16b**)),^{13,14} $[AuI_2\{N(SPh_2)_2\}]$ (**17**),¹⁵ $[Cp_2Yb\{N(SPh_2)_2\}]$ (**18**),¹⁶ and $[M\{N(SPh_2)_2\}_3]$ ($M = La$ (**19a**), Ce (**19b**), U (**19c**), Pu (**19d**))¹⁷ have been reported (Fig. 1.5). The X-ray structures of these compounds indicate that the transition metal centers accommodate η^2 -coordination from the ligand while the larger rare earth elements show η^3 -coordination.

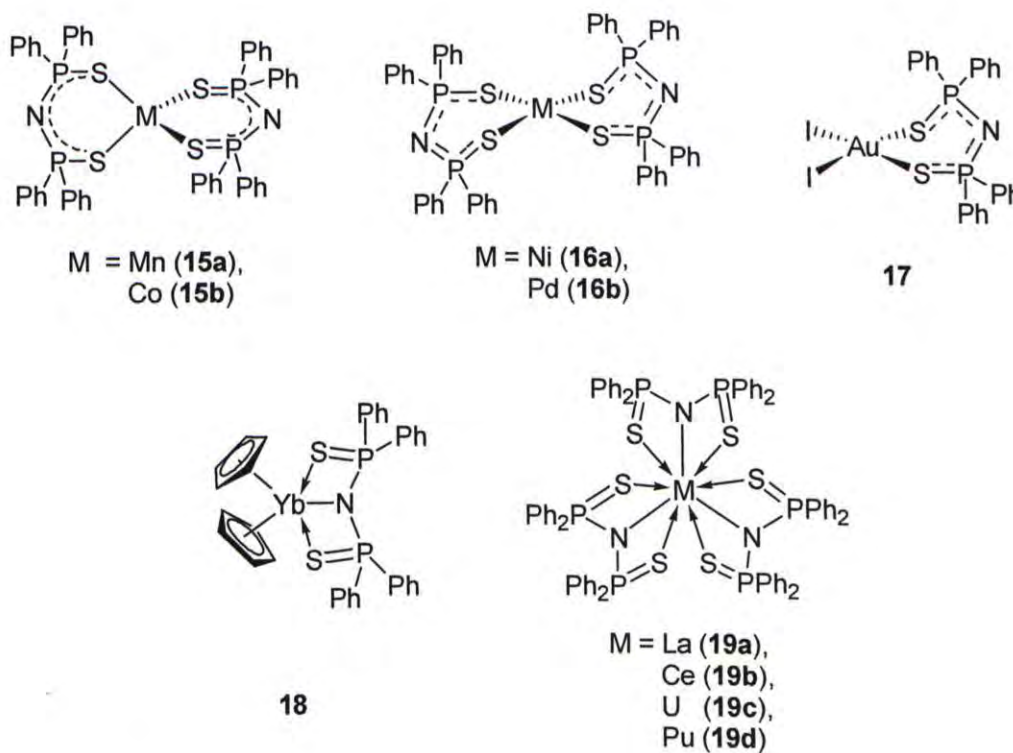


Fig. 1.5

The chemistry of pincer ligands has undergone a rapid development in the past decade after seminal report by Shaw in the 1970s.¹⁸ They have found many applications in coordination chemistry and catalysis. Le Floch's group has developed a

new class of monoanionic S–P–S and dianionic S–C–S system from ligands **3** and **4**.¹⁹ Reaction of **3** with charged nucleophiles such as MeLi and BuⁿLi has led to the formation of anions **20** (Fig. 1.6).²⁰ Palladium(II) complex (**21**)²¹ and rhodium(I) complex (**22**)²² were obtained by treating anions **20** with the corresponding metal precursors. Compound **21** was proved to be a very efficient catalysis in C–C (Suzuki) and C–B (Suzuki-Miyaura) coupling reactions,²³ meanwhile compound **22** reacts in a regioselective way with small molecules (O₂, SO₂, CS₂, MeI).^{22,24}

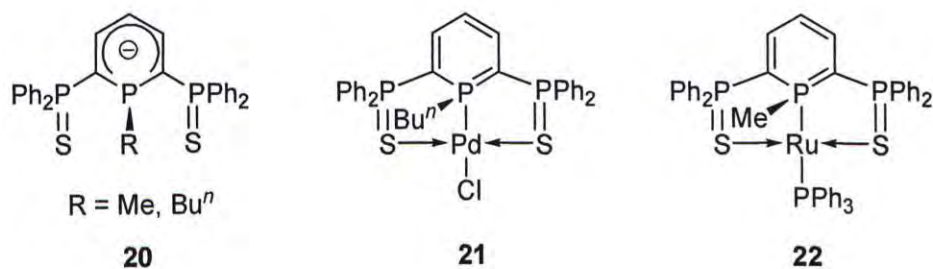


Fig. 1.6

Following a similar strategy employed by Cavell et al., and Stephan et al. for the synthesis of bis(iminophosphorane)methanediide ligands,²⁵ Le Floch's group have reported the corresponding dianionic ligand from compound **4**. This dianionic ligand was used as a precursor to synthesize a series of transition metal and rare earth metal carbene complexes (Fig. 1.7). Theoretical calculations on compounds **23-25** revealed that the double-bond character is weak and the formal π -bond is strongly polarized toward the carbon atom. These result in relatively long M–C bond lengths.²⁶ The nucleophilicity of the rare earth metal complexes have been demonstrated by their

reaction toward benzophenone.²⁷

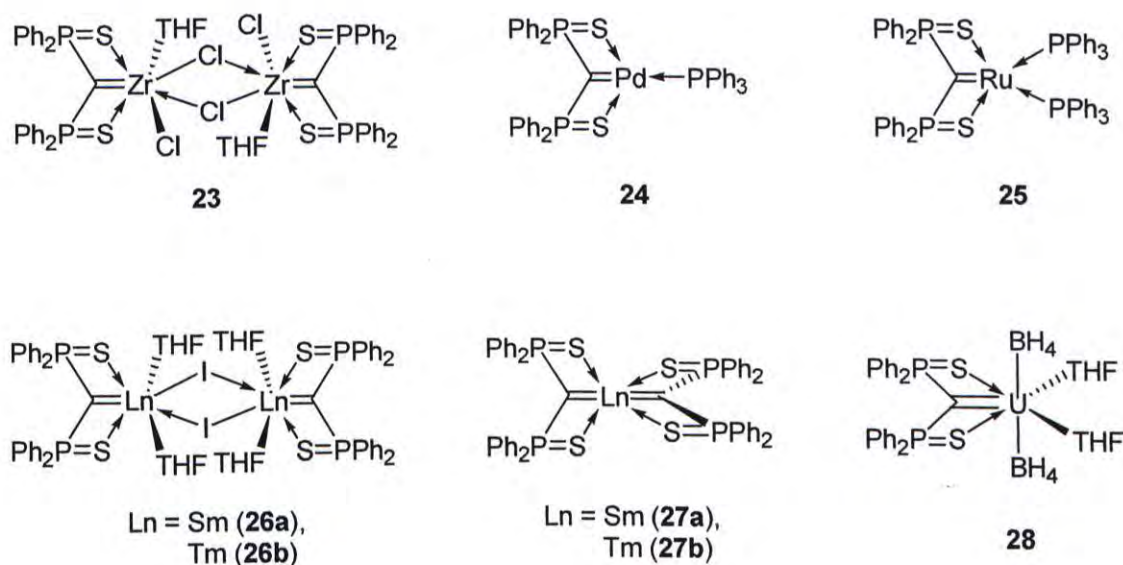


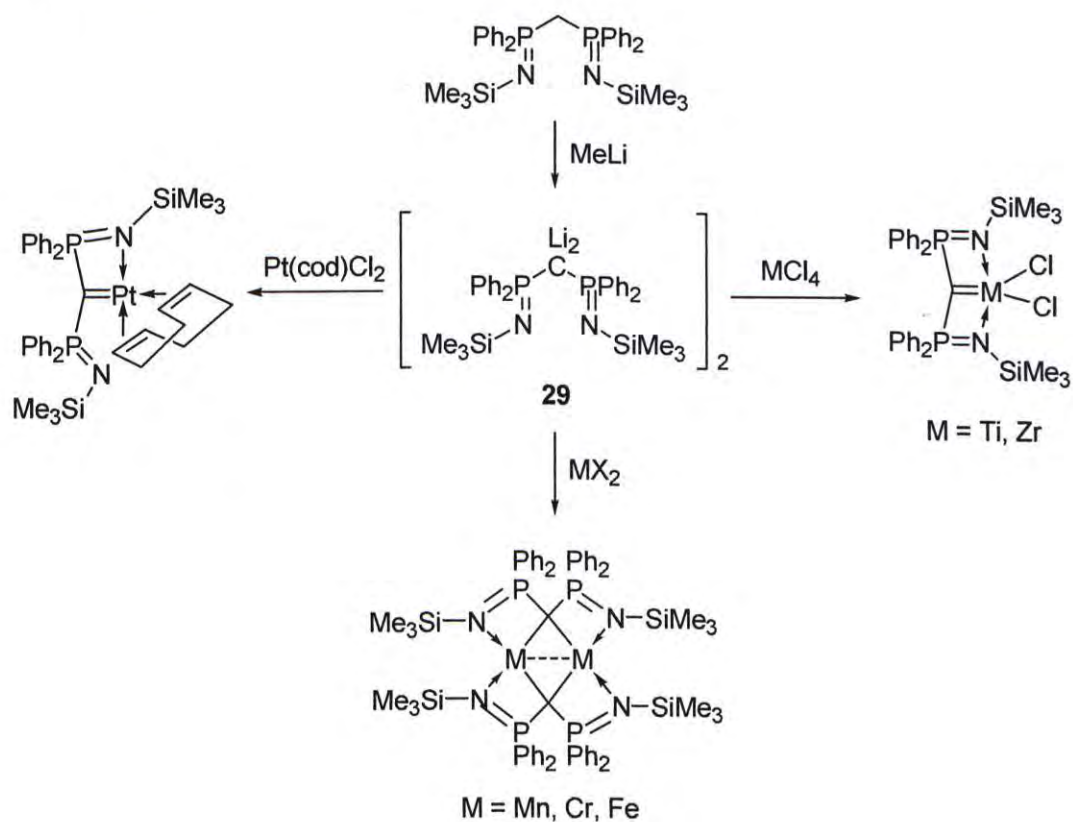
Fig. 1.7

1.1.2 General Aspects of Group 1 and 2 Thiophosphinoyl Metal Complexes

Alkali metal and alkaline earth metal compounds are generally used as transfer reagents in preparative main-group and transition metal chemistry. Syntheses and structures of this class of complexes have been reviewed.²⁸ For the doubly oxidized derivatives of bisphosphine compound, anionic ligands can be prepared by the reaction of organo alkali metal reagent or Grignard reagent with the neutral ligands. In general, they are prepared in situ for subsequent use in transmetallation reaction, without isolation.

Nevertheless, recent interest has focused on the structures and bonding in these species. Numerous group 1 and 2 metal complexes have been synthesized and structurally characterized. The doubly deprotonated methylenebis(phosphinimine)

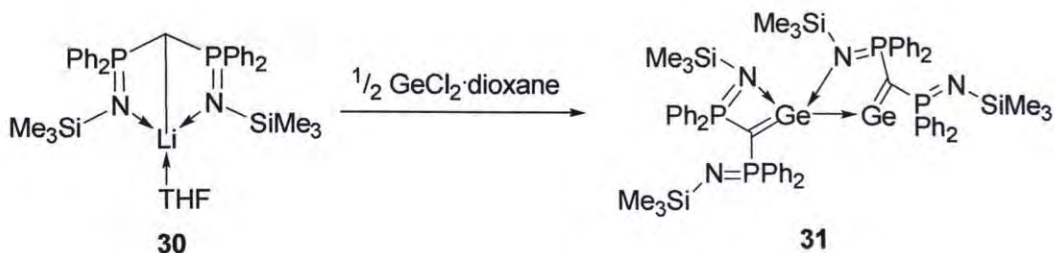
ligand (**29**) in the form of the dilithiated salt has been reported²⁵ and Cavell's group have further developed the transition metal chemistry from this deprotonated ligand (**Scheme 1.1**).²⁹



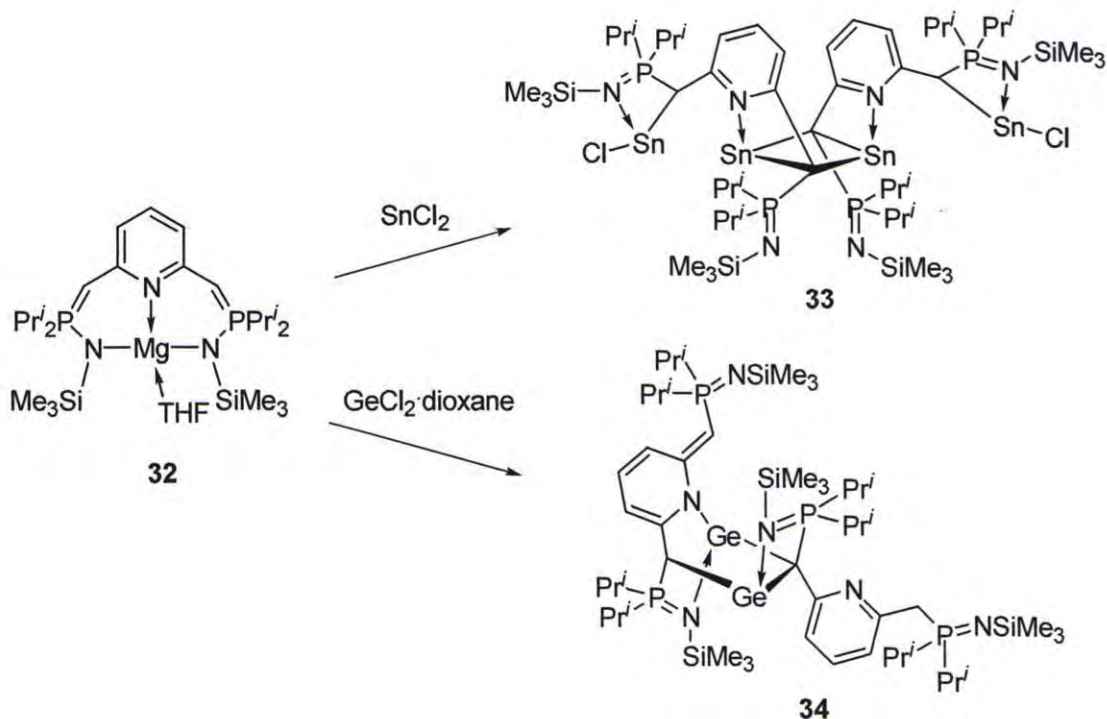
Scheme 1.1

Our group has also synthesized the monolithium salt $[\text{LiCH}(\text{PPh}_2=\text{NSiMe}_3)_2(\text{THF})]$ (**30**)³⁰ from the same ligand. Compound **30** was used as a precursor in the synthesis of bisgermavinylidene **31** (**Scheme 1.2**).³¹

Dianionic magnesium complex $[\text{Mg}\{(\text{Me}_3\text{SiN}=\text{PPr}'_2\text{CH})\text{C}_5\text{H}_3\text{N}-2,6\}\text{THF}]$ (**32**) can be obtained by the metalation of 2,6-lutidine-functionalized bis(phosphoranimines) $(\text{Me}_3\text{SiNdPPr}'_2\text{CH}_2)_2\text{C}_5\text{H}_3\text{N}-2,6$ with MgBu_2 . Bivalent group 14 metal complexes **33-34** were synthesized from compound **32** (**Scheme 1.3**).³²



Scheme 1.2



Scheme 1.3

There are relatively fewer structural reports on alkali and alkaline earth metal complexes of bis(thiophosphinoyl) ligands. Several alkali metal salts **35-37** were prepared by treating compound **2** with Bu^nLi or corresponding alkali metal hydroxides.³³ Reaction of neutral ligand **2** with barium metal in the presence of gaseous NH_3 gave compound **38**.³⁴ The structures of these compounds are shown in Fig. 1.8.

Le Floch and coworkers have reported the first example of geminal dianionic bis(thiophosphinoyl) species $[\text{Li}_2\text{C}(\text{Ph}_2\text{P}=\text{S})_2]$ (**39**) from reaction of **4** with MeLi . Two

1.1.3 Objectives of This Work

A series of thiophosphinoyl transition metal, lanthanide and actinide complexes have been studied. In addition, the coordination chemistry of bis(thiophosphinoyl)methane has been explored more than 30 years.^{2,7,8,27,35,37} But the main group metal compounds bearing bis(thiophosphinoyl) ligand are scarcely found. This work aims to prepare some main-group metal complexes derived from bis(thiophosphinoyl)methane ligand. This ligand not only acts as a neutral ligand (**III**), but it can also behave as a monoanionic (**IV**) or dianionic ligand (**V**) in forming metal complexes due to the acidity of the methylene protons (Fig. 1.11).

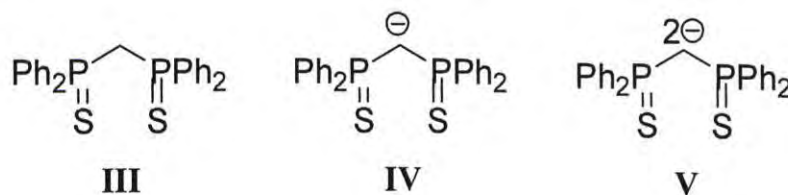


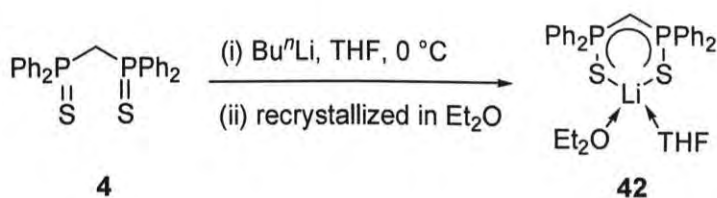
Fig. 1.11

In this chapter, the preparation of monoanionic lithium and dianionic magnesium complexes from bis(thiophosphinoyl)methane will be described and their structural characterization will be presented. They will be further used as ligand transfer reagents to prepare some main group 13 and 14 metal complexes in the following chapters.

1.2 Results and Discussion

1.2.1.1 Synthesis of Monoanionic Bis(thiophosphinoyl) Lithium Complex

Bis(thiophosphinoyl)methane [(S=PPh₂)₂CH₂] (**4**) was prepared according to the literature procedures.³⁵ Treatment of **4** with one equivalent of BuⁿLi in THF and then recrystallization in Et₂O afford bis(thiophosphinoyl) monolithium complex [Li{(S=PPh₂)₂CH}(THF)(Et₂O)] (**42**) (Scheme 1.4).



Scheme 1.4

1.2.1.2 Spectroscopic Properties of **42**

Compound **42** is an extremely air and moisture sensitive colorless crystalline solid. It is soluble in THF, Et₂O and sparingly soluble in toluene. It has been characterized by NMR spectroscopy and elemental analysis.

The ¹H NMR and ¹³C NMR spectra of **42** displayed signals assignable to the bis(thiophosphinoyl)methanide ligand, solvated THF and Et₂O molecules. The ¹H NMR spectrum of **42** showed a triplet at δ 2.23 ppm (*J*_{P-H} = 1.8 Hz) for the methanide proton on P-C-P backbone with coupling to two equivalent phosphorus nuclei. These indicate considerable delocalization throughout the SPCPS backbone of the ligand. This is also consistent with the ¹³P NMR which showed one singlet at δ 37.61 ppm. The ¹³C NMR

spectrum of **42** is normal.

1.2.1.3 Molecular Structure of [Li{(S=PPh₂)₂CH}(THF)(Et₂O)] (**42**)

The molecular structure of **42** is shown in Fig. 1.12. Selected bond distances (Å) and angles (deg) of **42** are listed in Table 1.1. Compound **42** is a monomeric lithium complex. The Li(1) coordinates to the ligand in *S,S'*-chelation to form a six-membered ring. The lithium is bonded to a THF and a Et₂O molecules to adopt a tetrahedral geometry. The Li–S bond distances of 2.422(1) Å and 2.421(1) Å in **42** are comparable to those of 2.474(8) Å and 2.473(8) Å in [Li{(S=PPh₂)₂N}(THF)₂].^{33a} The P–S bond distances [1.993(2), 1.993(2) Å] and the P–C bond distances [1.712(4), 1.711(4) Å] in **42** are different from those of (S=PPh₂)₂CH₂ (**4**) [P–S: 1.944 Å; P–C: 1.829 Å].³⁸ These suggest a charge delocalization within the SPCPS skeleton. The P(2)–C(13)–P(1) angle of 126.8(3)° is larger than that of 118.4(2)° in **4**.

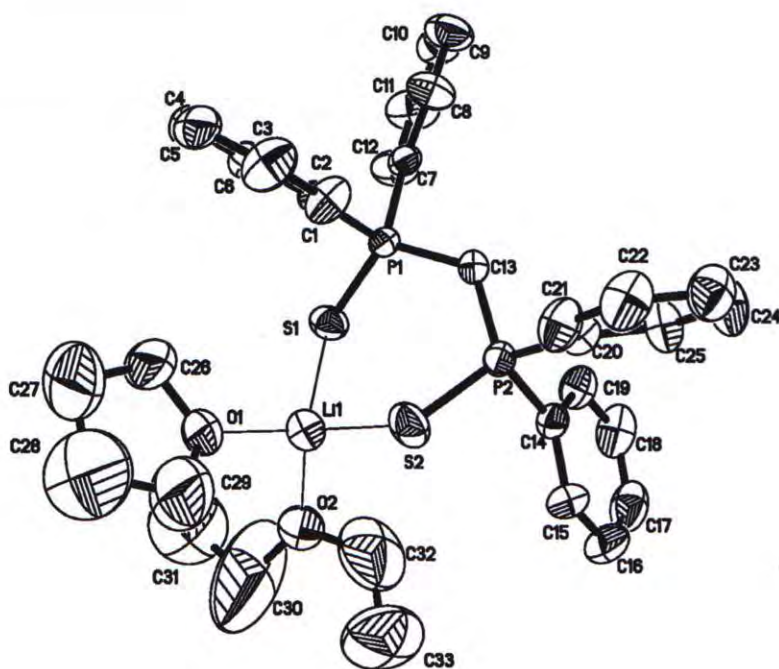


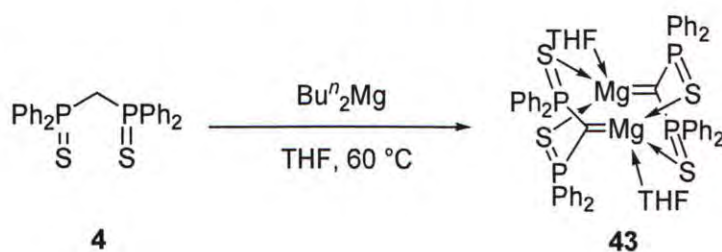
Fig. 1.12 Molecular structure of $[\text{Li}\{(\text{S}=\text{PPh}_2)_2\text{CH}\}(\text{THF})(\text{Et}_2\text{O})]$ (**42**) (30% probability ellipsoids)

Table 1.1 Selected Bond Distances (Å) and Angles (deg) for Compound 42

Li(1)-O(1)	1.941(1)	P(1)-C(13)	1.712(4)
Li(1)-O(2)	1.960(1)	P(1)-S(1)	1.993(2)
Li(1)-S(1)	2.422(1)	P(2)-C(13)	1.711(4)
Li(1)-S(2)	2.421(1)	P(2)-S(2)	1.993(2)
O(1)-Li(1)-O(2)	101.9(5)	C(13)-P(1)-S(1)	118.6(2)
O(1)-Li(1)-S(1)	117.3(5)	C(13)-P(2)-S(2)	117.1(2)
O(1)-Li(1)-S(2)	104.7(5)	P(1)-S(1)-Li(1)	102.9(2)
O(2)-Li(1)-S(1)	108.5(5)	P(2)-S(2)-Li(1)	106.6(3)
O(2)-Li(1)-S(2)	116.5(5)	P(2)-C(13)-P(1)	126.8(3)
S(2)-Li(1)-S(1)	108.1(4)		

1.2.2.1 Synthesis of Dianionic Bis(thiophosphinoyl) Magnesium Complex

The reaction of **4** with one equivalent of Bu^n_2Mg in THF afforded $[\text{MgC}(\text{PPh}_2=\text{S})_2(\text{THF})]_2$ (**43**) in 66% yield (**Scheme 1.5**). It is formed through a double deprotonation of the methylene group in the ligand. Similar reaction using MeLi as the metallating reagent gave the dilithiomethanediide complex at low temperature has been reported by Le Floch and co-workers.³⁵



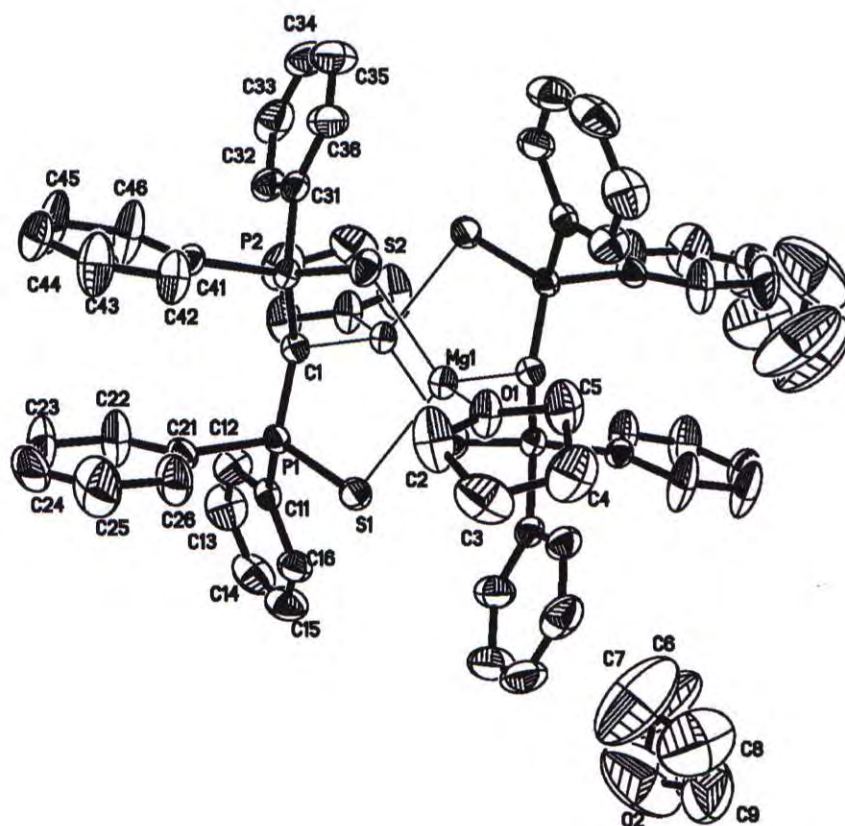
Scheme 1.5

1.2.2.2 Spectroscopic Properties of **43**

Compound **43** was isolated as an extremely air-sensitive yellow crystalline solid; soluble in THF only. It has been characterized by NMR spectroscopy and elemental analysis. Although no signal is observed for the carbenic carbon in the ^{13}C NMR spectrum of **43**, the absence of signals due to the methylene protons in compound **43** was confirmed by ^1H NMR spectroscopy. The ^{31}P NMR spectrum of **43** displays two singlets at δ 14.05 and 34.96 ppm, which does not correspond to the solid-state X-ray structure. This may be due to the existence of equilibrium between a monomer and a dimer of **43** in solution.

1.2.2.3 Molecular Structure of $[\text{MgC}(\text{PPh}_2=\text{S})_2(\text{THF})_2]_2 \cdot 2\text{THF}$ (**43**)

The molecular structure of **43** is shown in Fig. 1.13. Selected bond distances (Å) and angles (deg) of **43** are listed in Table 1.2. Compound **43** is a dimeric species with two magnesiummethanediide molecules bonded side-by-side via the sulfur atoms in a head-to-tail fashion. The magnesium metal center is bonded to the methanediide carbon atom, two thio sulfur atoms from adjacent ligand, and a THF molecule to give a tetrahedral geometry. The angles at the three coordinated methanediide carbon atom [119.0(3), 115.4(2), 115.0(2)°; \sum bond angles = 349.4°] supports the existence of a sp^2 hybridized carbon. The Mg(1)–C(1A) bond distance of 2.156(5) Å is significantly shorter than those reported Mg–C single bond distance of 2.460(8) Å in $[\text{HC}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{Mg}(\mu\text{-Cl})_2]$ ³⁹ and that of 2.573(6) Å in $\text{HC}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{MgI}(\text{THF})$.³⁹ This value also shows good agreement with the calculated Mg–C bond (2.08–2.10 Å) of $\text{Mg}=\text{CH}_2$.⁴⁰ The Mg–S bond distances of 2.455(2) and 2.459(2) Å is comparable to the averaged Mg–S bond distance of 2.518 Å in $[\text{Mg}(\text{S}=\text{PPr}'_2\text{CH})_2\text{C}_5\text{H}_3\text{N-2,6}]$.³⁶ The relative short P–C bond length of 1.705 Å suggests that the thiophosphinoyl arms help to stabilize the electron density on the carbon center.



1.3 Experimental for Chapter 1

Materials:

(S=PPh₂)₂CH₂ was prepared according to the literature procedures.³⁵ BuⁿLi (1.6 M in hexane) and Buⁿ₂Mg (1.0 M in heptane) were purchased from Aldrich Chemical Co. and used without further purification.

[Li{(S=PPh₂)₂CH}(THF)(Et₂O)] (**42**).

BuⁿLi (4.40 ml, 7.04 mmol, 1.6 M solution in hexane) was added slowly to a solution of (S=PPh₂)₂CH₂ (3.12 g, 6.96 mmol) in THF (50 ml) at 0 °C. The temperature of the reaction mixture was raised to ambient temperature and stirred for 15 h. Volatiles were removed under reduced pressure and the residue was extracted with Et₂O. After filtration and concentration of filtrate, **42** was obtained as colorless crystals. Yield: 3.48 g (83%). Mp: 169.2-172.1 °C. Anal. Found: C, 65.36; H, 6.54. Calcd for C₃₃H₃₉LiO₂P₂S₂: C, 65.99; H, 6.54. ¹H NMR (400 MHz, C₆D₆): δ = 1.05 (t, 3H, Et₂O, *J* = 7.0 Hz), 1.17-1.20 (m, 4H, THF), 2.23 (t, 1H, CH, *J*_{P-H} = 1.8 Hz), 3.19-3.25 (q, 2H, Et₂O, *J* = 7.0 Hz), 3.39-3.42, (m, 4H, THF), 6.97-7.05 (m, 12H, Ph), 8.15-8.20 (m, 8H, Ph). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ = 15.68 (Et₂O), 20.05 (t, PCP, *J*_{P-C} = 101.0 Hz), 25.65 (THF), 66.15 (Et₂O), 68.55 (THF), 128.17 (*m*-Ph), 129.88 (*p*-Ph), 132.18 (t, *o*-Ph, *J*_{P-C} = 5.4 Hz), 140.49 (d, *ipso*-Ph, *J*_{P-C} = 93.3 Hz). ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 37.61.

[MgC(PPh₂=S)₂(THF)]₂·2THF (43).

Buⁿ₂Mg (1.33 ml, 1.33 mmol, 1.0 M solution in heptane) was added slowly to a solution of (S=PPh₂)₂CH₂ (0.60 g, 1.33 mmol) in THF (70 ml). The reaction mixture was stirred at 60 °C for 15 h. The precipitate was filtered. The yellow filtrate was concentrated under reduced pressure to yield yellow crystals of **43**. Yield: 0.54 g (66%). Mp: 208 °C (dec). Anal. Found: C, 63.87; H, 6.08. Calcd for C₅₈H₅₆Mg₂O₂P₄S₄·THF: C, 64.31; H, 5.58. ¹H NMR (300 MHz, THF-*d*₈): δ = 6.98-7.27 (m, 24H, Ph), 7.72-7.82 (m, 16H, Ph). ¹³C{¹H} NMR (75.5 MHz, THF-*d*₈): δ = 26.39 (THF), 68.23(THF), 127.36, 127.44, 127.52, 128.22, 128.63, 130.25, 131.84, 132.20, 139.53, 140.77 (Ph). ³¹P{¹H} NMR (121.5 MHz, THF-*d*₈): δ = 14.05, 34.98.

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Chapter 2 Synthesis and Reactivity of Group 14 Metal Bis(thiophosphinoyl) Complexes

2.1 Introduction

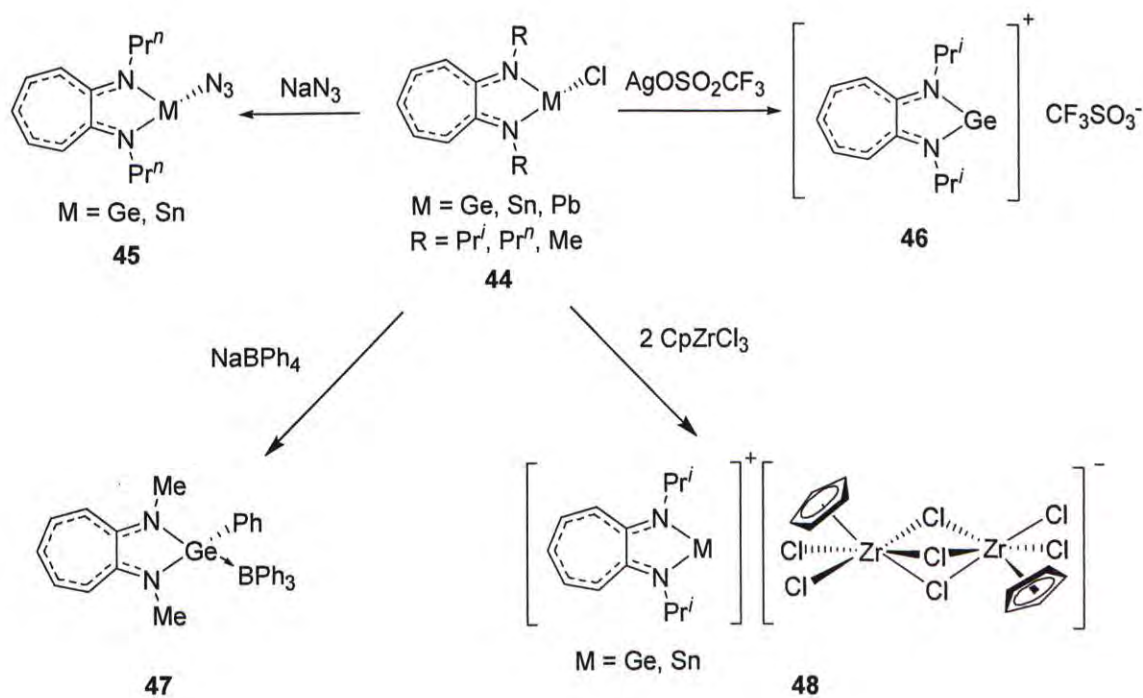
2.1.1 General Aspects of Low Valent Group 14 Organometallic Compounds

Group 14 elements usually have the oxidation state of +2 or +4. The stability of M(II) increases in the sequence of Ge<Sn<Pb, because of the “inert pair effect”. Divalent germanium, tin and lead compounds can be regarded as carbene analogues. These carbene analogues are very reactive species that form cyclic, linear or branched oligomers easily. Nevertheless, Lappert and coworkers have reported the first series of group 14 metal alkyl $[M\{CH(SiMe_3)_2\}_2]$ (M = Ge, Sn and Pb) in 1976.¹ After that, the chemistry of heavier congeners of carbene analogues remains an area of active research interest in the past few decades.²

In general, low-valent group 14 carbene analogues can be stabilized either kinetically by bulky substituents, and/or thermodynamically by coordination of donor atoms such as nitrogen and phosphorus. In the past decades, ligands with N-donor have particularly been useful in the synthesis of this species.

For example, aminotroponimate ligand (ATI) was used to prepare several low valent group 14 compounds bearing heterobicyclic 10- π -electron ring systems. $[(R_2ATI)MCl]$ (M = Ge, Sn, Pb; R = Prⁱ, Prⁿ, Me; ATI = aminotroponimate) (**44**) can

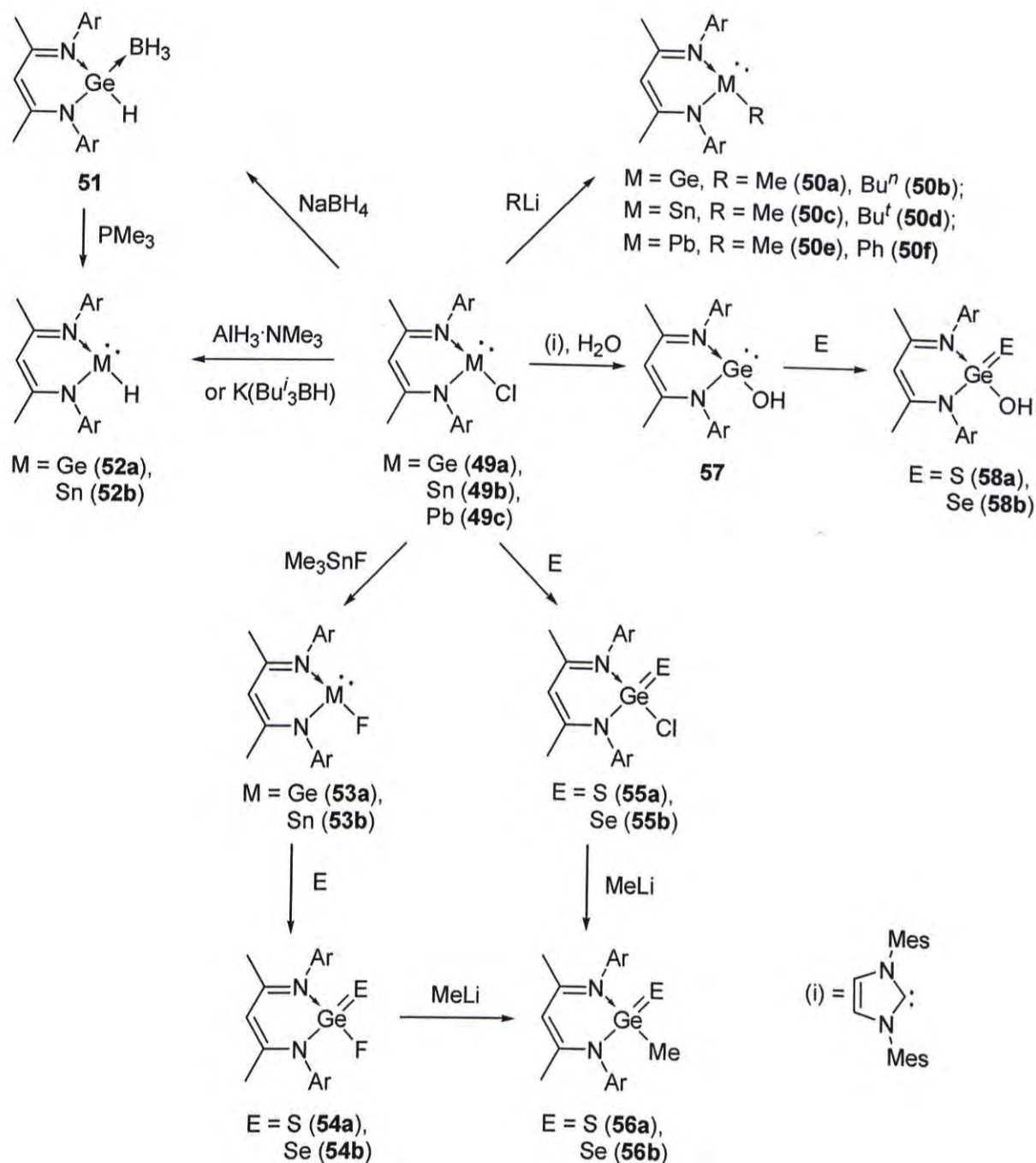
be obtained by the reaction between MCl_2 and $[(R_2ATI)Li]$ in 1:1 ratio.^{3,4,5} The chloride in **44** can be replaced by azide or trifluoromethanesulfonate. Compound **45** and **46** were synthesized by treating **44** with NaN_3 and $AgOSO_2CF_3$ respectively.^{3,6} The reaction between $[(Me_2ATI)GeCl]$ and $NaBPh_4$ resulted in the formation of a phenyl group transferred product $[(Me_2ATI)GePh \cdot BPh_3]$ (**47**).³ Dias and coworkers also reported the synthesis of two novel cationic Ge(II) and Sn(II) species. Treatment of $[(Pr^i_2ATI)MCl]$ ($M = Ge, Sn$) with two equivalents of $CpZrCl_3$ gave **48** as product.^{3,4} $CpZrCl_3$ serves as a chloride abstracting agent in these reactions. The synthesis of compound **44-48** was summarized in **Scheme 2.1**.



Scheme 2.1

β -Diketiminato ligand is a versatile ligand for stabilizing group 14 metal centers with low-valence states. The synthesis and structural characterization of the

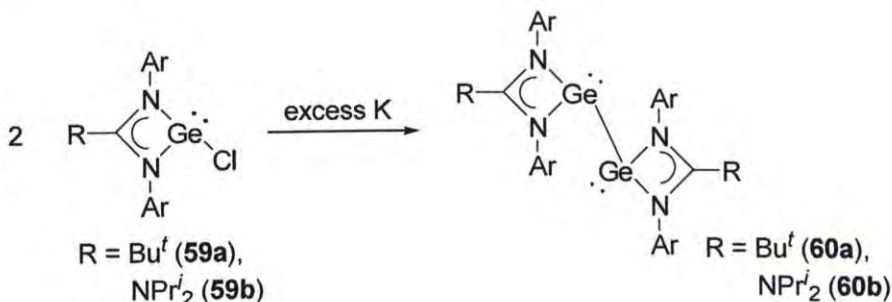
β -diketiminato group 14 metal(II) chloride [$\{\text{HC}(\text{CMeNAr})_2\}\text{MCl}$] (M = Ge (**49a**), Sn (**49b**), Pb (**49c**)) have been described.^{7,8} Compound **49a-c** were found to be useful precursors for preparing heteroleptic group 14 carbene analogues. Treating **49** with corresponding organolithium reagent, group 14 metal(II) species with small alkyl substituents **50a-f** were formed.^{7,9,10,11} Monomeric low-valent group 14 metal hydride, fluoride and hydroxide are scarcely found. By utilizing compound **49** as starting materials, Roesky's group reported the first example of stable group 14 metal(II) hydride [$\{\text{HC}(\text{CMeNAr})_2\}\text{MH}$] (M = Ge (**52a**), Sn (**52b**)),^{12,13} fluoride [$\{\text{HC}(\text{CMeNAr})_2\}\text{MF}$] (M = Ge (**53a**), Sn (**53b**))^{10,12} and hydroxide [$\{\text{HC}(\text{CMeNAr})_2\}\text{GeOH}$] (**57**).¹⁴ Compound **52a,b** can be prepared by reacting **49a,b** with $\text{AlH}_3\cdot\text{NMe}_3$ ¹³ or potassium triisobutylborohydride.^{15,16} [$\{\text{HC}(\text{CMeNAr})_2\}\text{GeH}$] may also be formed by the reaction of PMe_3 with **51**, which was synthesized from **49a** and NaBH_4 .¹² Compound **49** was treated with Me_3SnF to afford **53** or with water in the presence of 1,3-dimesitylimidazole-2-ylidene) to give **57**. Compound **49**, **53** and **57** serve as a synthon in the synthesis of heavier chalcogen analogues of alkanoyl halides [$\{\text{HC}(\text{CMeNAr})_2\}\text{Ge}(\text{X})=\text{E}$] (X = F, Cl; E = S, Se)^{17,18} and heavier analogues of carboxylic acid [$\{\text{HC}(\text{CMeNAr})_2\}\text{Ge}(\text{E})\text{OH}$] (E = S, Se).^{19,20} Furthermore, the reaction of **54** and **55** with MeLi gave the methylgermanethione **56a** and methgermaneselone **56b**.^{9,17,18} The reactions mentioned above are summarized in **Scheme 2.2**.



Scheme 2.2

Recently, Jones and coworker have investigated the coordination chemistry of amidinato- and guanidinogermylene chloride **59**. Reduction of **59** with potassium in toluene at room temperature afforded germanium(I) dimers **60** (Scheme 2.3).²¹ They are thermally stable compounds with the Ge–Ge bond length (2.6380(8) Å for $\text{R} = \text{Bu}^t$,

2.6721(13) Å for R = NPr^t₂) in the normal region for averaged single Ge–Ge interactions (2.61 Å). Theoretical calculations on **60** revealed that there are no multiple bond characters in the Ge–Ge bonds.



Scheme 2.3

Using bulky 1-azaallyl ligands, a series of homoleptic and heteroleptic metal complexes (**61-64**) were reported by our group recently (Fig. 2.1).^{22,23} In these compounds, the low-valent metal centers are stabilized by the nitrogen donor and the steric demanding substituents. Moreover, the reactivity of [Ge{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}Cl] (**64a**) has been investigated and reviewed.²⁴

Phosphoranoimines can serve as supporting ligands for main group metal complexes via the sterically demanding side arm. We have reported the synthesis and structure of various divalent group 14 complexes derived from phosphoranoimino ligands, including rare bisgermavinylidene and novel 1,3-dimetallacyclobutanes.^{25,26} Some examples of compounds derived from phosphoranoimines are shown on Fig. 2.2.

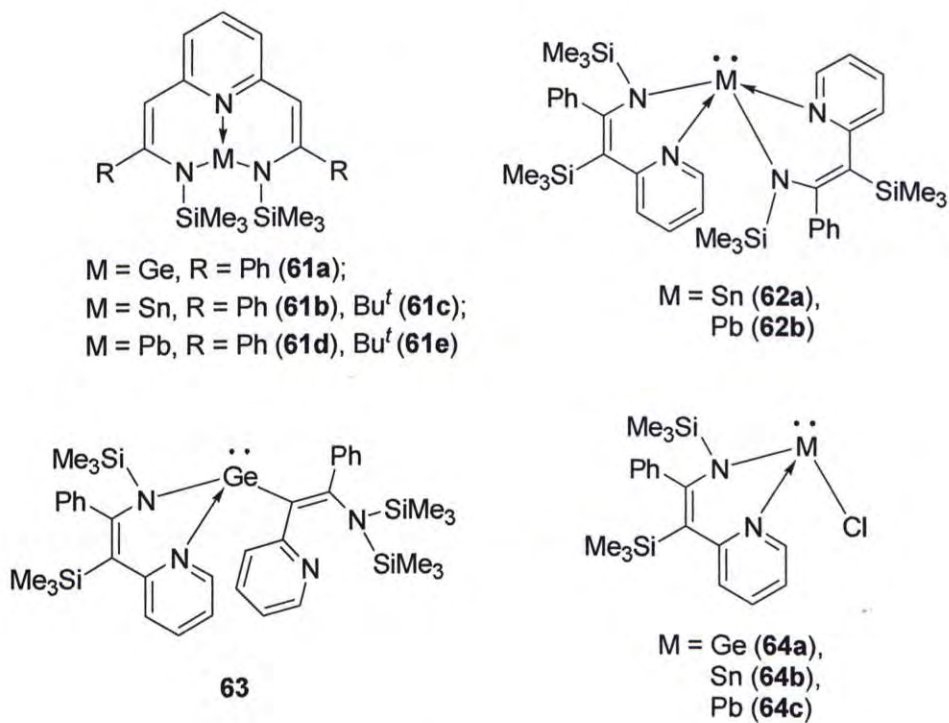


Fig. 2.1

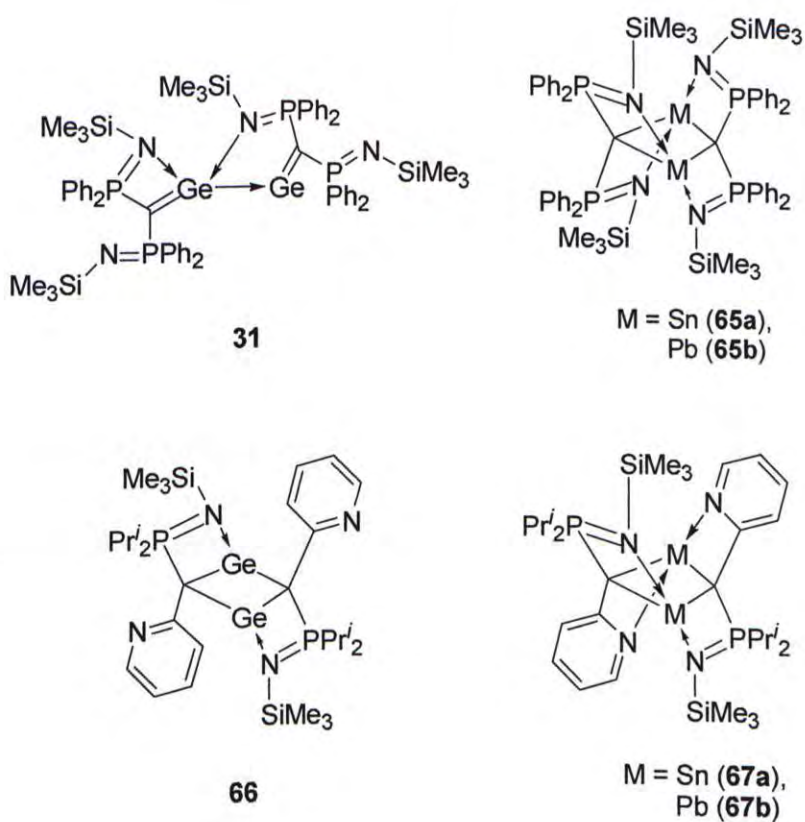


Fig. 2.2

In contrast, only a handful of divalent group 14 metal compounds bearing phosphoranosulfides have been reported in the literature. A lead(II) complex $[\text{Pb}(\text{NPPh}_2\text{S})_2]$ (**68**)²⁷ was synthesized from iminobis(phosphoranosulfide) ligand. With the same ligand, a tetravalent tin complex $[\text{Me}_2\text{Sn}(\text{NPPh}_2\text{S})_2]$ (**69**) was also prepared.²⁸ They have been characterized by X-ray structure analysis. Both compounds contain inorganic carbon-free $\text{MS}_2\text{P}_2\text{N}$ chelate rings (Fig. 2.3).

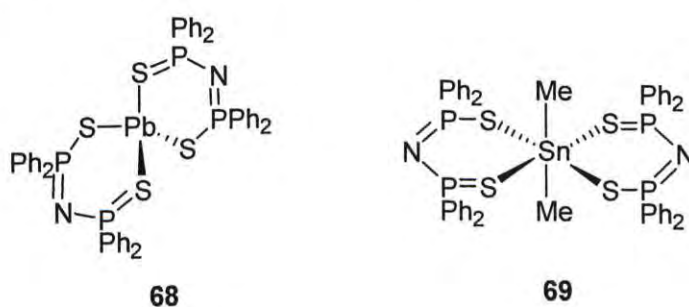


Fig. 2.3

We have recently developed a new phosphoranosulfide ligand with 2,6-lutidine as the ligand backbone. It was used to prepare thiophosphinoyl group 14 metal compounds. Two 1,3-dimetallacyclobutanes (**70,71**), a novel digermylgermylene (**72**) and an ionic tin(II) complex (**73**) were obtained.²⁹ The structures of these compounds are illustrated in Fig. 2.4.

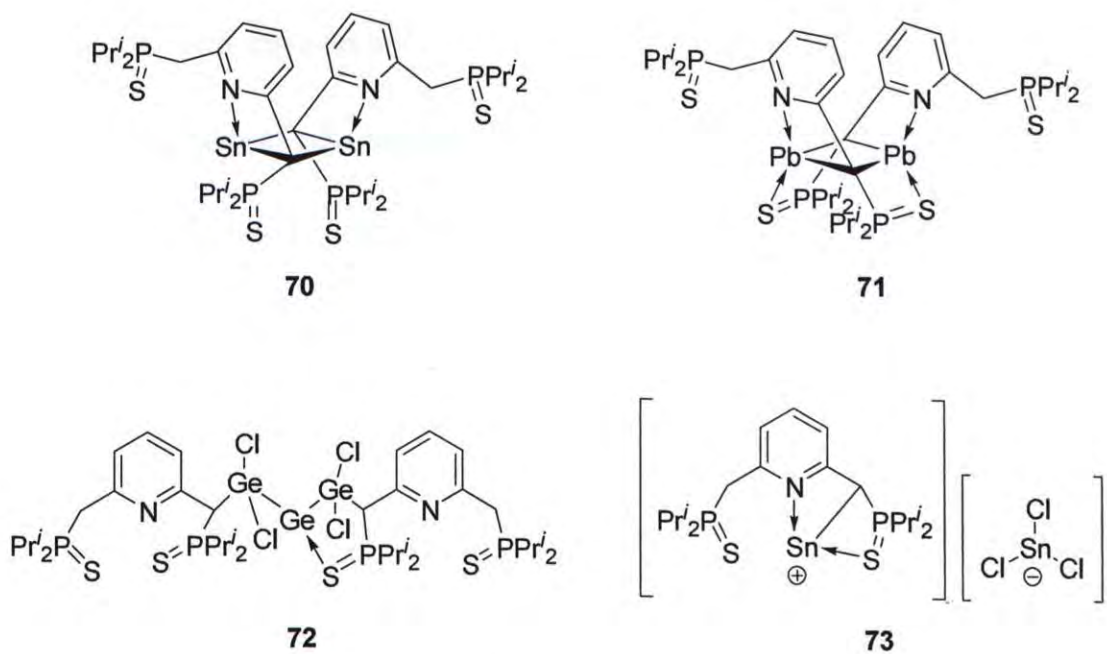


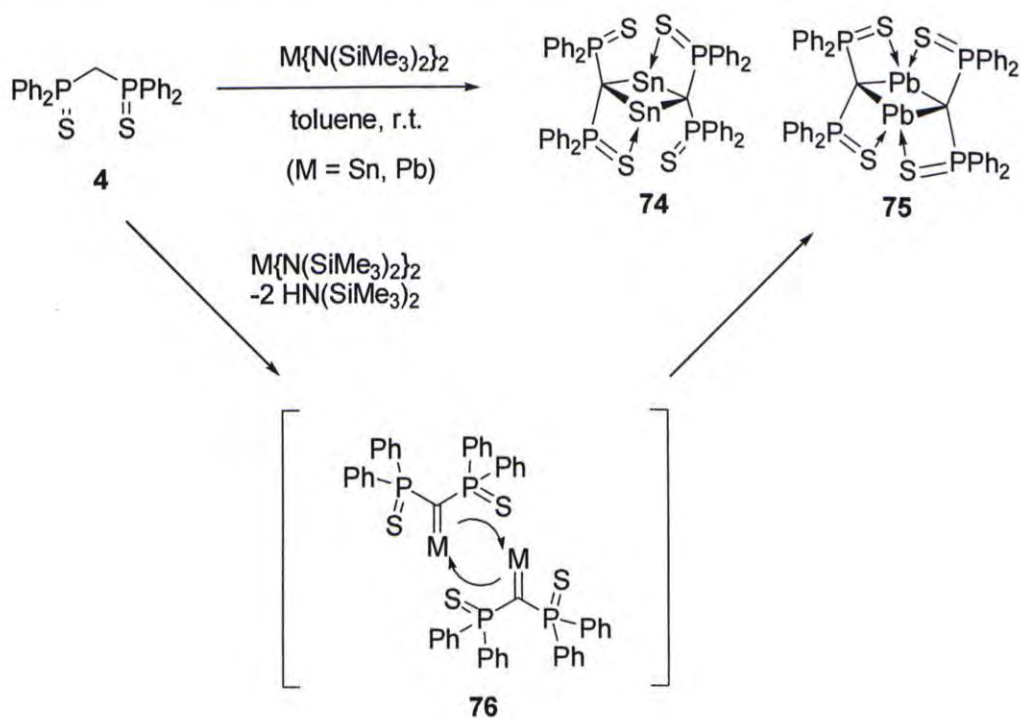
Fig. 2.4

In previous chapter, the preparation and structural characterization of $[\text{Li}\{(\text{S}=\text{PPh}_2)_2\text{CH}\}(\text{THF})(\text{Et}_2\text{O})]$ (**42**) have been reported. Compound **42** as well as the neutral ligand **4** can be used as starting materials in the synthesis of low-valent group 14 metal complexes. In this chapter, the preparation of a series of group 14 metal compounds and their reactivity are reported.

2.2 Results and Discussion

2.2.1.1 Synthesis of 1,3-Distannacyclobutane and 1,3-Diplumbacyclobutane

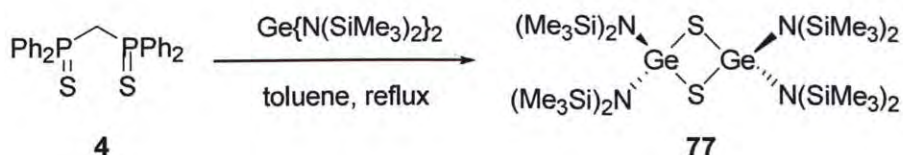
The reaction of $(S=PPh_2)_2CH_2$ with equimolar of $M\{N(SiMe_3)_2\}_2$ ($M = Sn, Pb$) afforded 1,3-distannacyclobutane $[Sn\{\mu^2-C(Ph_2P=S)_2\}]_2$ (74) and 1,3-diplumbacyclobutane $[Pb\{\mu^2-C(Ph_2P=S)_2\}]_2$ (75), respectively (Scheme 2.4). From the X-ray structures of the products, it is suggested that the reaction undergoes the elimination of hexamethyldisilazane to form a metallavinylidene intermediate $[:M=C(Ph_2P=S)_2]$ ($M = Sn, Pb$) (76). It is then followed by a head-to-tail cyclodimerization of unstable metallavinylidene intermediate to form the 1,3-dimetallacyclobutanes. Similar reaction has been found in the synthesis of $[\{2-\{M\{C(Pr^i_2P=S)\}\}-6-\{CH_2(Pr^i_2P=S)\}\}C_5H_3N\}_2]$ ($M = Sn, Pb$).²⁹



Scheme 2.4

However, there is no reaction between **4** and $\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}_2$ at room temperature.

When the reaction mixture was allowed to reflux for 18 hours, the oxidative product $[\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-S})_2]$ (**77**) was obtained (**Scheme 2.5**).³⁰ Compound **4** acted as sulfurization agent in this reaction.



Scheme 2.5

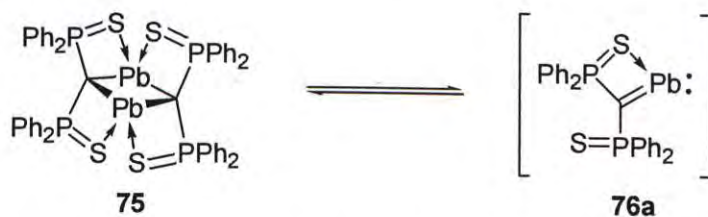
2.2.1.2 Spectroscopic Properties of **74** and **75**

Compounds **74** and **75** were isolated as air and moisture sensitive yellow crystalline solids. They are soluble in THF, CH_2Cl_2 and sparingly soluble in toluene. They have been characterized by NMR spectroscopy and elemental analysis.

The ^1H NMR and ^{13}C NMR spectra of **74** displayed one set of signal due to bis(thiophosphinoyl)methanediide ligand. The ^{31}P NMR spectrum of complex **74** showed a singlet at δ 32.01 ppm which may be due to fluxional coordination of the thio sulfur atoms at tin centers in solution.

However, the ^1H NMR and ^{13}C NMR spectra of **75** showed a different pattern. Two sets of signal assignable to ligand backbone can be found. And the ^{31}P NMR spectra of **75** displayed two singlets (δ 33.83, 35.72 ppm) due to two different phosphorus

environments. These do not correspond to the solid-state structure. One possible reason is that compound **75** exists in an equilibrium between plumbacyclobutane and plumbavinylidene in the solution (**Scheme 2.6**).



Scheme 2.6

2.2.1.3 Molecular Structures of $[\text{Sn}\{\mu^2\text{-C}(\text{Ph}_2\text{P}=\text{S})_2\}]_2\cdot\text{THF}$ (**74**) and $[\text{Pb}\{\mu^2\text{-C}(\text{Ph}_2\text{P}=\text{S})_2\}]_2\cdot\text{THF}$ (**75**)

The molecular structure of **74** is shown in Fig. 2.5. Selected bond distances (Å) and angles (deg) are listed in Table 2.1. In compound **74**, two tin metal centers are bridged by two methanediide carbon atoms to form a planar 1,3- Sn_2C_2 four-membered ring. Additional coordination to the trigonal pyramidal tin center from the thio sulfur atoms of the ligand form SnCPS four-membered rings. These SnCPS rings together with the Sn_2C_2 ring, as the base, form a “step-like” structure framework.

The averaged $\text{Sn}-\text{C}$ bond distances of 2.421 Å is comparable to that of 2.376 Å in $[\text{Sn}\{\mu^2\text{-C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\}]_2$ ²⁵ The $\text{Sn}-\text{Sn}$ distance is too long to consider the presence of bonding interaction. The averaged $\text{P}-\text{S}$ bond distances of 2.010 Å is slightly longer than that in neutral ligand **4** (1.944 Å)³¹ and similar to that in $[\{2\text{-}\{\text{Sn}\{\text{C}(\text{Pr}'_2\text{P}=\text{S})\}\}-6\text{-}\{\text{CH}_2(\text{Pr}'_2\text{P}=\text{S})\}\}\text{C}_5\text{H}_3\text{N}\}_2$ (**70**) (1.964 Å).²⁹

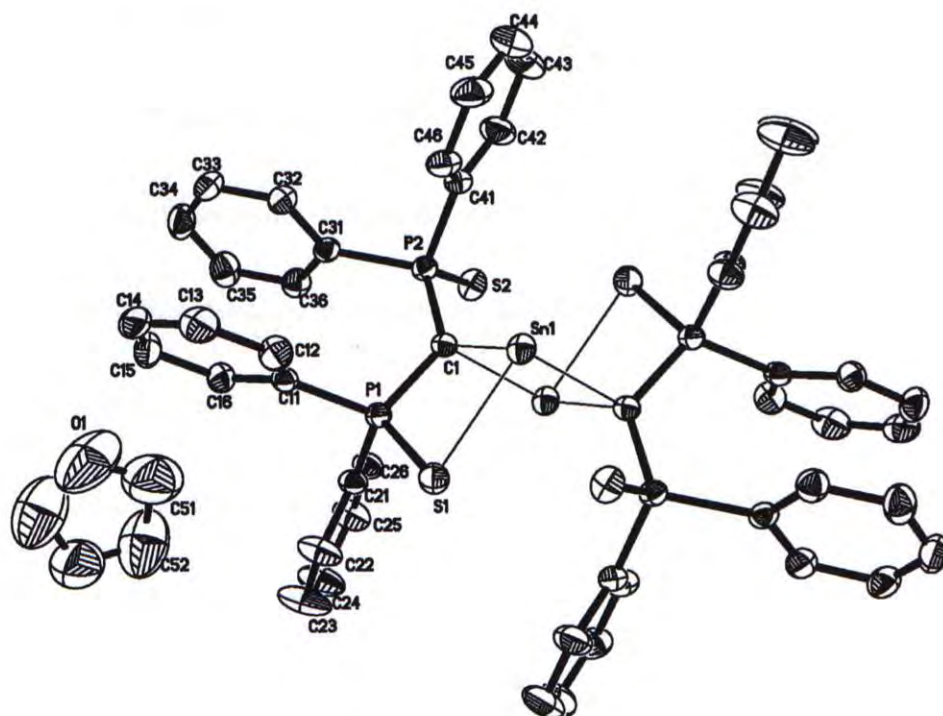


Fig. 2.5 Molecular structure of $[\text{Sn}\{\mu^2\text{-C}(\text{Ph}_2\text{P}=\text{S})_2\}]_2 \cdot \text{THF}$ (74) (30% probability ellipsoids)

Table 2.1 Selected Bond Distances (Å) and Angles (deg) for Compound 74

Sn(1)-C(1A)	2.327(3)	P(1)-C(1)	1.741(3)
Sn(1)-C(1)	2.514(3)	P(1)-S(1)	2.026(1)
Sn(1)-S(1)	2.618(1)	P(2)-C(1)	1.758(3)
		P(2)-S(2)	1.994(1)
C(1A)-Sn(1)-C(1)	91.2(1)	P(1)-C(1)-P(2)	125.4(2)
C(1A)-Sn(1)-S(1)	92.7(1)	P(1)-C(1)-Sn(1A)	110.3(1)
C(1)-Sn(1)-S(1)	70.6(1)	P(2)-C(1)-Sn(1A)	102.9(1)
C(1)-P(1)-S(1)	103.6(1)	P(1)-C(1)-Sn(1)	94.4(1)
C(1)-P(2)-S(2)	110.0(1)	P(2)-C(1)-Sn(1)	128.9(1)
P(1)-S(1)-Sn(1)	84.95(4)	Sn(1A)-C(1)-Sn(1)	88.8(1)

Symmetry transformations used to generate equivalent atoms: 1A: $-x+1/2, -y+3/2, -z+1$;
2A: $-x+1, y, -z+1/2$

The molecular structure of **75** is shown in Fig. 2.6. Selected bond distances (Å) and angles (deg) of **75** are listed in Table 2.2. Compound **75** consists of two lead atoms bridged by two methanediide carbon atom to form a 1,3-Pb₂C₂ four-membered planar ring. Two thio sulfur atoms of the ligand are bonded to each lead center, forming PbCPS four-membered rings. These PbCPS rings with the Pb₂C₂ as the base, result in a “step-like” structure framework. This is different from the “open-box” like structure of [Pb{μ²-C(Ph₂P=NSiMe₃)₂}]₂.²⁵ The lead center is tetracoordinated with distorted square pyramidal geometry.

The averaged Pb–C bond distances of 2.506 Å is comparable to that of 2.473 Å in [Pb{μ²-C(Ph₂P=NSiMe₃)₂}]₂.²⁵ The Pb–Pb distance is too long to consider the presence of bonding interaction. The averaged P–S bond distances of 2.010 Å is slightly longer than that in neutral ligand **4** (1.944 Å)³¹ and comparable to the coordinated P–S bond in [{2-{Pb{C(Prⁱ₂P=S)}}-6-{CH₂(Prⁱ₂P=S)}}C₅H₃N]₂ (**71**) (1.995 Å).²⁹ This can be explained by the reduced electron density of P–S bond resulted from S→Pb donar bond.

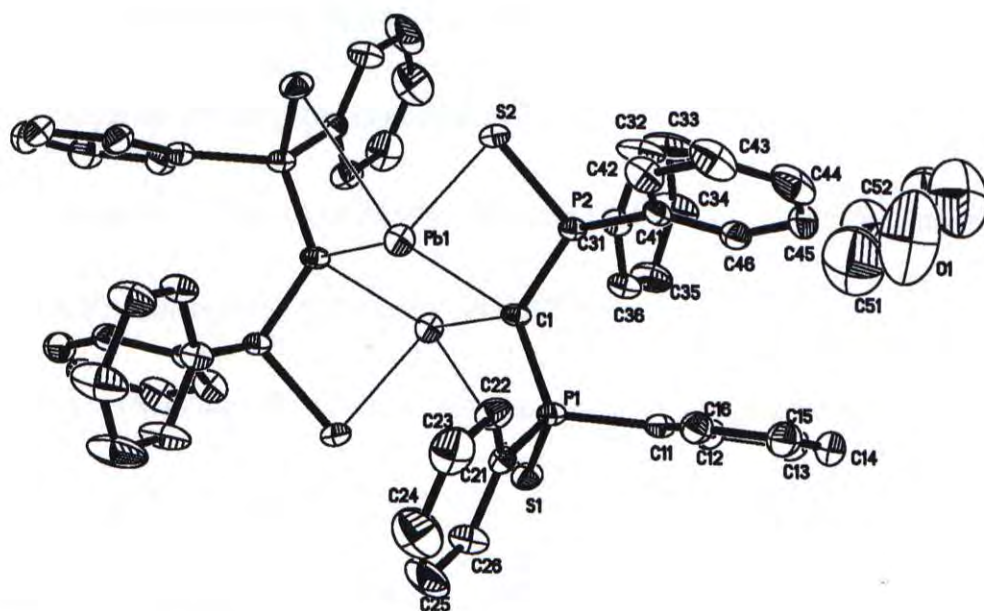


Fig. 2.6 Molecular structure of $[\text{Pb}\{\mu^2\text{-C}(\text{Ph}_2\text{P}=\text{S})_2\}]_2\cdot\text{THF}$ (**75**) (30% probability ellipsoids)

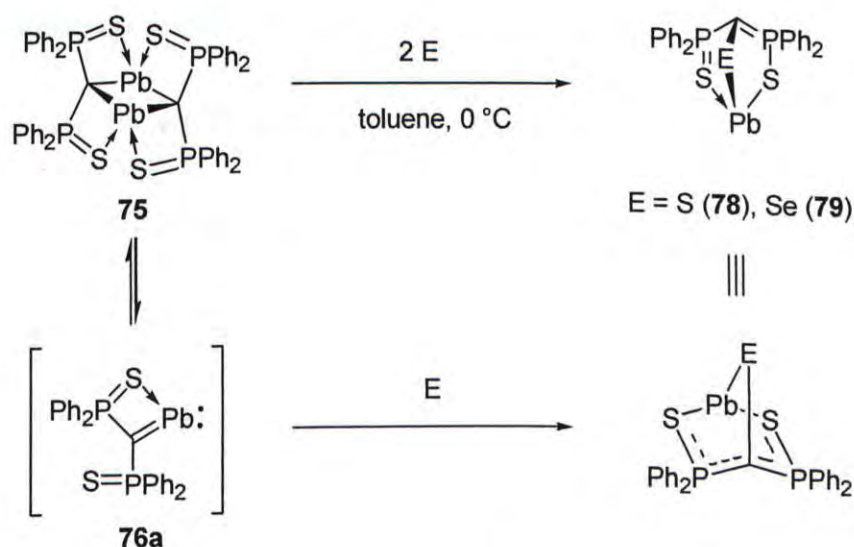
Table 2.2 Selected Bond Distances (Å) and Angles (deg) for Compound 75

Pb(1)-C(1A)	2.419(6)	P(1)-C(1)	1.749(6)
Pb(1)-C(1)	2.593(7)	P(1)-S(1)	2.000(2)
Pb(1)-S(2)	2.726(2)	P(2)-C(1)	1.741(6)
Pb(1)-S(1A)	3.085(2)	P(2)-S(2)	2.020(3)
C(1A)-Pb(1)-C(1)	91.8(2)	P(1)-S(1)-Pb(1A)	76.9(1)
C(1A)-Pb(1)-S(2)	91.9(2)	P(2)-S(2)-Pb(1)	85.4(1)
C(1)-Pb(1)-S(2)	68.1(1)	P(2)-C(1)-P(1)	126.8(4)
C(1A)-Pb(1)-S(1A)	67.2(2)	P(2)-C(1)-Pb(1A)	108.6(3)
C(1)-Pb(1)-S(1A)	135.1(1)	P(1)-C(1)-Pb(1A)	102.3(3)
S(2)-Pb(1)-S(1A)	73.2(1)	P(2)-C(1)-Pb(1)	95.5(3)
C(1)-P(1)-S(1)	111.2(2)	P(1)-C(1)-Pb(1)	128.1(3)
C(1)-P(2)-S(2)	104.7(3)	Pb(1A)-C(1)-Pb(1)	88.2(2)

Symmetry transformations used to generate equivalent atoms: 1A: $-x+3/2, -y+1/2, -z+1$;
2A: $-x+1, y, -z+3/2$

2.2.2.1 Reaction of 1,3-Diplumbacyclobutane with Chalcogens

Treatment of **75** with stoichiometric amounts of elemental chalcogens in toluene did not give group 14 ketone or ketene analogues ($R_2Pb=E$ or $>C=Pb=E$). Instead, two novel lead(II) chalcogenate complexes $[PbE\{C(Ph_2P=S)_2\}]$ ($E = S$ (**78**), and Se (**79**)) were obtained (**Scheme 2.7**). It is believed that chalcogen inserted between $C=Pb:$ bond to form a $>C-E-Pb:$ moiety. This result differs markedly from the synthesis of group 14 dialkylmetal chalcogenones $R_2M=E$ ($R = CH(SiMe_3)C_9H_6N-8$ or $CPh(SiMe_3)C_5H_4N-2$; $M = Ge$ or Sn)³² and chalcogen-bridged dimers of germaketene analogues $[(Me_3SiN=PPh_2)_2C=Ge(\mu-E)]_2$ ($E = S, Se,$ and Te).³³ It may be explained by the “inert pair effect” which makes the electron pair on the lead(II) center less favor for bond formations. Compound **79** is light sensitive and turns black on exposure to light, therefore it was prepared in the absence of light.



Scheme 2.7

2.2.2.2 Spectroscopic Properties of **78** and **79**

Compounds **78** and **79** were isolated as air and moisture sensitive red crystalline solids. They are only soluble in THF and CH₂Cl₂. They have been characterized by NMR spectroscopy and elemental analysis.

The ¹H and ¹³C NMR spectra of **78** and **79** are normal and showed signals assignable to the ligand backbone. Two singlets [δ 31.87, 57.73 (**78**); δ 31.86, 59.39 ppm (**79**)] were observed in their ³¹P NMR spectra. It indicated two phosphorous are in different environments, consistent with the solid-state structures.

The ⁷⁷Se NMR spectrum of compound **79** was obtained and displayed a singlet at δ 893.34 ppm. To our knowledge, it is the first report of ⁷⁷Se NMR chemical shift for lead(II) chalcogenate compounds.

2.2.2.3 Molecular Structures of [PbE{C(PPh₂=S)₂}] (E = S (**78**), Se (**79**))

Compounds **78** and **79** are isostructural monomeric complexes. Their molecular structures are shown in Fig. 2.8 and Fig. 2.9. Selected bond distances (Å) and angles (deg) are listed in Table 2.3.

Both compounds have a three-coordinated lead center, with a chalcogen atom and two thio sulfur atoms from the ligand. The bond angles around the Pb(II) center [83.7(1), 82.6(1), 91.4 (1)°, $\sum \angle = 257.7^\circ$ (**78**); 83.0(1), 84.6(1), 93.1(1)°, $\sum \angle = 260.7^\circ$ (**79**)]

suggest a trigonal pyramidal geometry and support the presence of a stereochemically active lone pair.

It is worth to note that the C(1) atom in compounds **78** and **79** are distorted from the expected trigonal planar structure. This can be indicated by the sum of angles around the carbon center [$\sum \angle = 339.5^\circ$ (**78**), $\sum \angle = 339.1^\circ$ (**79**)]. This may be resulted from the unusual cage formed.

A six-membered $\text{PbS}_2\text{P}_2\text{C}$ metallacycle with a boat conformation, as shown in Fig. 2.7, is found. P(1), S(1), P(2) and S(2) lie in a plane, with C(1) and Pb(1) above the plane. The chalcogen locked the boat conformation by bridging C(1) and Pb(1). The CEPb plane is almost perpendicular to the P_2S_2 plane. The P–C bond distances [1.748(8), 1.725(8) (**78**); 1.749(1), 1.741(1) Å (**79**)] and P–S bond distances [2.031(3), 2.045(3) (**78**); 2.019(6), 2.060(6) Å (**79**)] in two compounds are very similar, suggesting considerable delocalization throughout the six-membered ring.

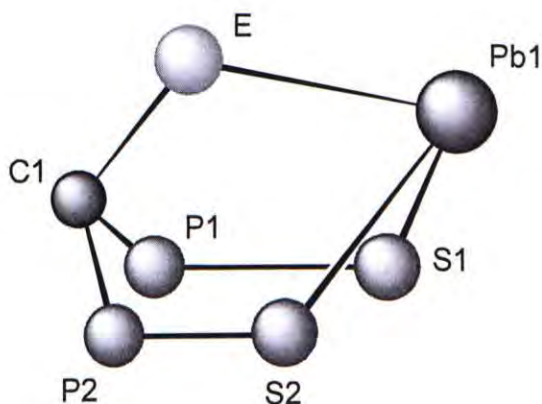


Fig. 2.7

The lead-chalcogen bond [2.632(2) (**78**); 2.727(2) Å (**79**)] and carbon-chalcogen bond distances [1.801(8) (**78**); 1.917(1) Å (**79**)] increases with the size of chalcogens. The C–E bond distances in both compounds are closer to the C–E single bonds distances [C–S: 1.81; C–Se: 1.94 Å] than the C–E double bond distances [C–S: 1.61; C–Se: 1.74 Å].³⁴

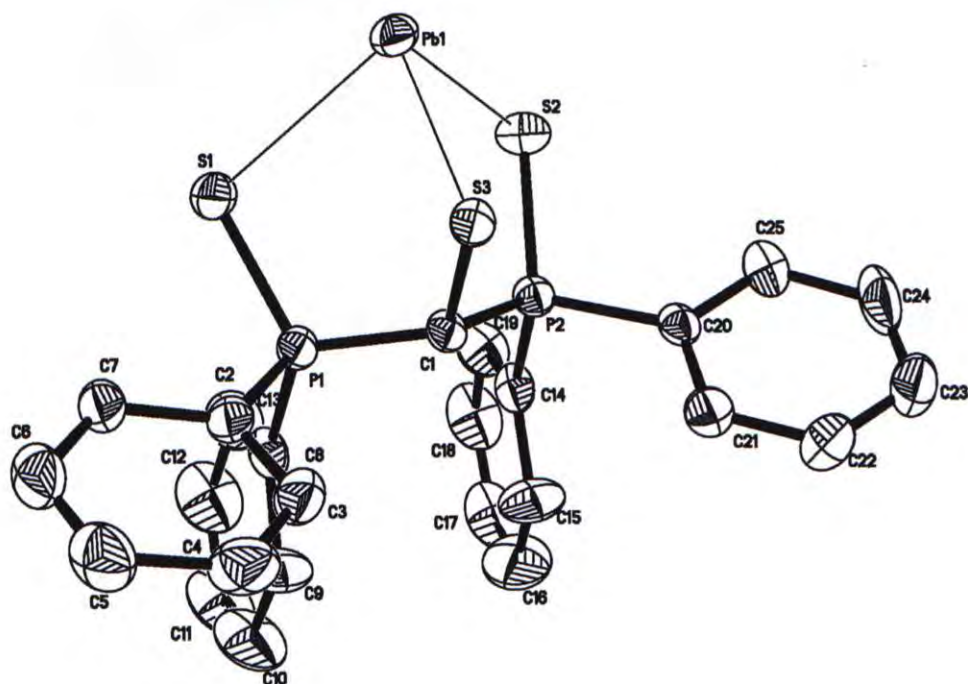


Fig. 2.8 Molecular structure of [PbS{C(PPh₂=S)₂}] (**78**); cocrystallized THF molecule is omitted for clarity (30% probability ellipsoids)

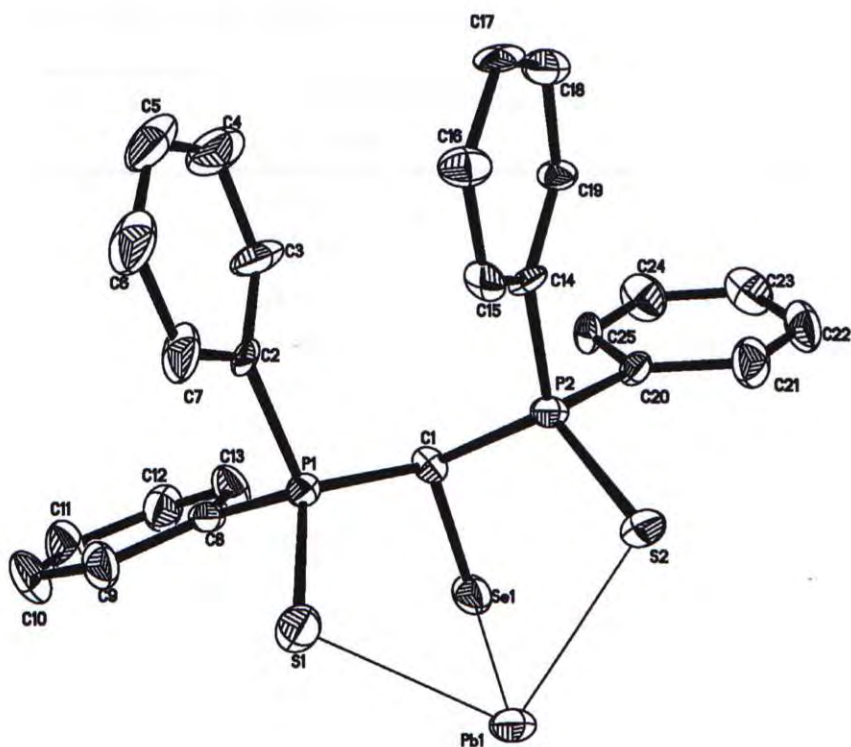


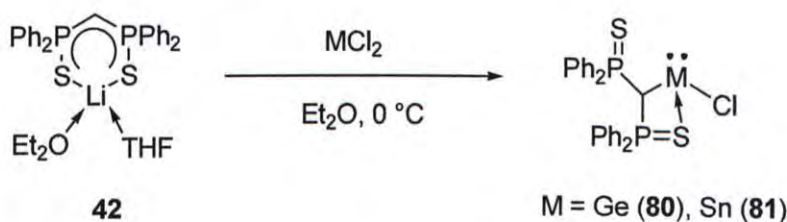
Fig. 2.9 Molecular structure of $[\text{PbSe}\{\text{C}(\text{PPh}_2=\text{S})_2\}]$ (**79**) (30% probability ellipsoids)

Table 2.3 Selected Bond Distances (Å) and Angles (deg) for Compounds 78 and 79

[PbE{C(PPh ₂ =S) ₂ }]		
	E = S (78)	E = Se (79)
Pb(1)-E	2.632(2)	2.727(2)
Pb(1)-S(2)	2.736(3)	2.750(4)
Pb(1)-S(1)	2.830(2)	2.813(4)
P(1)-C(1)	1.748(8)	1.749(1)
P(1)-S(1)	2.031(3)	2.019(6)
P(2)-C(1)	1.725(8)	1.741(1)
P(2)-S(2)	2.045(3)	2.060(6)
E-C(1)	1.801(8)	1.917(1)
E-Pb(1)-S(2)	83.7(1)	83.0(1)
S(3)-Pb(1)-S(1)	82.6(1)	84.6(1)
S(2)-Pb(1)-S(1)	91.4(1)	93.1(1)
C(1)-P(1)-S(1)	114.6(3)	116.3(5)
C(1)-P(2)-S(2)	115.6(3)	115.7(5)
P(1)-S(1)-Pb(1)	96.2(1)	96.9(2)
P(2)-S(2)-Pb(1)	96.7(1)	97.6(2)
C(1)-E-Pb(1)	96.0(3)	92.1(4)
P(2)-C(1)-P(1)	122.6(5)	121.8(7)
P(2)-C(1)-E	108.9(4)	107.5(7)
P(1)-C(1)-E	108.0(4)	109.8(7)

2.2.3.1 Synthesis of Chlorogermylene and Chlorostannylene

Metathesis reaction of **42** with one equivalent of MCl_2 ($M = Ge, Sn$) in Et_2O afforded $[MCl\{CH(PPh_2=S)_2\}]$ ($M = Ge$ (**80**), Sn (**81**)) (Scheme 2.8). From the X-ray structures obtained, MCPS four-membered rings were observed. It shows deviation from the structures of $[MCl\{(PPh_2=NSiMe_3)_2CH\}]$ ($M = Ge, Sn$) reported by our group,^{29,33} in which no interactions between the metal centers and the methanide carbons result in six-membered rings. It is because the less bulky sulfur atom from the ligand makes the coordination to the metal easier.



Scheme 2.8

2.2.3.2 Spectroscopic Properties of **80** and **81**

Compounds **80** and **81** were isolated as air and moisture sensitive colorless crystalline solids. They are soluble in THF and CH_2Cl_2 only. They have been characterized by NMR spectroscopy and elemental analysis. The 1H NMR spectra of **80** and **81** both displayed one set of signals due to the ligand backbone. A triplet [δ 3.83 (br) (**80**); δ 4.20 ppm ($J_{P-H} = 13.5$ Hz) (**81**)] was observed for the methanide proton on the P-C-P backbone.

The ^{13}C NMR spectra of **80** and **81** are normal. The ^{31}P NMR spectra showed two singlets [δ 33.81, 39.95 (**80**); δ 33.82, 37.63 ppm (**81**)] due to two different phosphorus environments, consistent with the solid-states structures. It indicates that the coordination of the thio sulfur atoms to the metal centers in **80** and **81** are non-fluxional in the solution.

The ^{119}Sn spectrum of compound **81** displayed one triplet at δ -129.58 ($^2J_{\text{Sn-P}} = 169$ Hz) ppm which is comparable to that of δ -139.21 ppm in $[\text{SnCl}\{(\text{PPh}_2=\text{NSiMe}_3)_2\text{CH}\}]^{29}$, δ -197.95 ppm in $[\text{Sn}\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)-(\text{C}_5\text{H}_4\text{N}-2)\}\text{Cl}]^{23}$ and δ -224 ppm in $[\{\text{HC}(\text{CMeNAr})_2\}\text{SnCl}]$.⁷ This indicates that the tin metal center is probably three coordinate in solution as well.

2.2.3.3 Molecular Structures of $[\text{MCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$ (M = Ge (**80**), Sn (**81**))

The molecular structures of **80** and **81** are illustrated in Fig. 2.10 and 2.11. Selected bond distances (Å) and angles (deg) of **80** and **81** are given in Table 2.4. Compounds **80** and **81** are heteroleptic germylene and stannylene, respectively. The metal center is bonded to the ligand via a *C,S*-chelate fashion and displays a trigonal pyramidal geometry. The angle sum at the germanium and tin centers are 271.7° and 254.2° , respectively, consistent with a stereochemically active electron pair at the metal centers. The MCPS four-membered rings are nearly planar as indicated by the sum of bond angles (360.0° (**80**); 359.3° (**81**)). The coordinated P–S bond distances [2.007(3) (**80**);

2.017(1) Å (**81**)] are slightly longer than the non-coordinated ones [1.954(2) (**80**); 1.959(1) (**81**) Å] as the electron density of P–S bonding is reduced by S→M bond.

The Ge–C bond distance of 2.153(6) Å in **80** is similar to the Ge–C single bond distance of 2.127(4) Å in $[\text{Ge}\{\text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2\}_2]$ ³⁵ and 2.135(4) Å in $[\text{Ge}\{\text{CPh}(\text{SiMe}_3)\text{C}_5\text{H}_4\text{N}-2\}_2]$.³⁶ The Ge–Cl bond distances of 2.288(2) Å is comparable to that of 2.334(2) Å in $[\text{GeCl}\{(\text{PPh}_2=\text{NSiMe}_3)_2\text{CH}\}]$ ³³ and 2.295(12) Å in $[\{\text{HC}(\text{CMeNAr})_2\}\text{GeCl}]$.⁷ The Ge–S bond (2.479(2) Å) is significantly shorter than that in $\text{Ge}[\text{GeCl}_2\{(\text{S}=\text{PPr}'_2\text{CH})(\text{S}=\text{PPr}'_2\text{CH}_2)\text{C}_5\text{H}_3\text{N}-2,6\}]_2$ (2.675(1) Å).²⁹

The Sn–C bond distance of 2.374(2) Å in **81** is very close to the Sn–C single bond distance of 2.35(2) Å in $[\text{Sn}\{\text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-2\}_2]$ ^{37,38} and 2.329(4) Å in $[\text{Sn}\{\text{CPh}(\text{SiMe}_3)\text{C}_5\text{H}_4\text{N}-2\}_2]$.³⁶ The Sn–Cl bond distances of 2.521(1) Å agrees very well with the corresponding distances of 2.540(1) Å in $[\text{SnCl}\{(\text{PPh}_2=\text{NSiMe}_3)_2\text{CH}\}]$ ²⁹ and 2.473(9) Å in $[\{\text{HC}(\text{CMeNAr})_2\}\text{SnCl}]$.⁷ The Sn–S distance of 2.636(1) Å is shorter than the averaged Sn–S distance of 2.735 Å in $[\text{Me}_2\text{Sn}\{(\text{SPPH}_2)_2\text{N}\}_2]$.²⁸

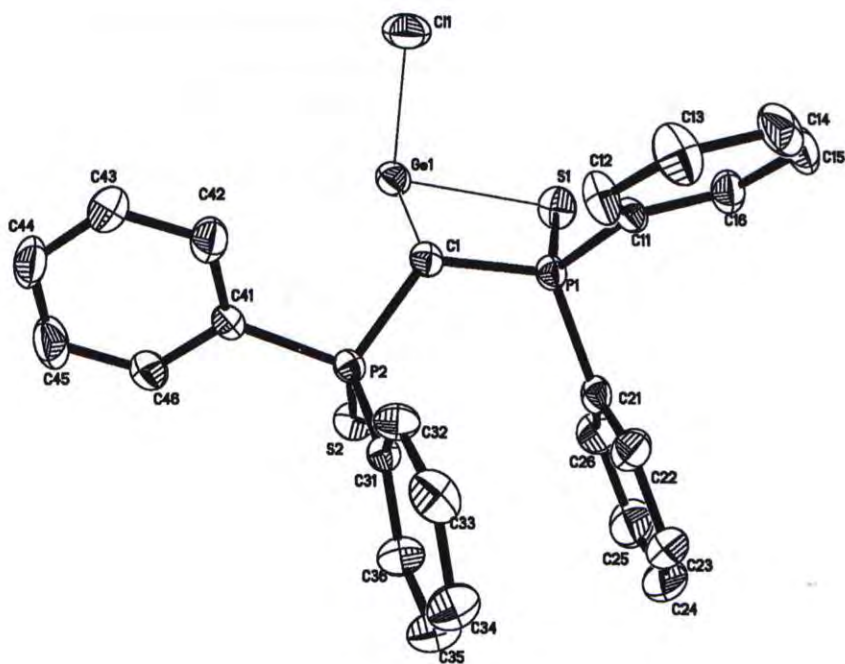


Fig. 2.10 Molecular structure of $[\text{GeCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$ (**80**) (30% probability ellipsoids)

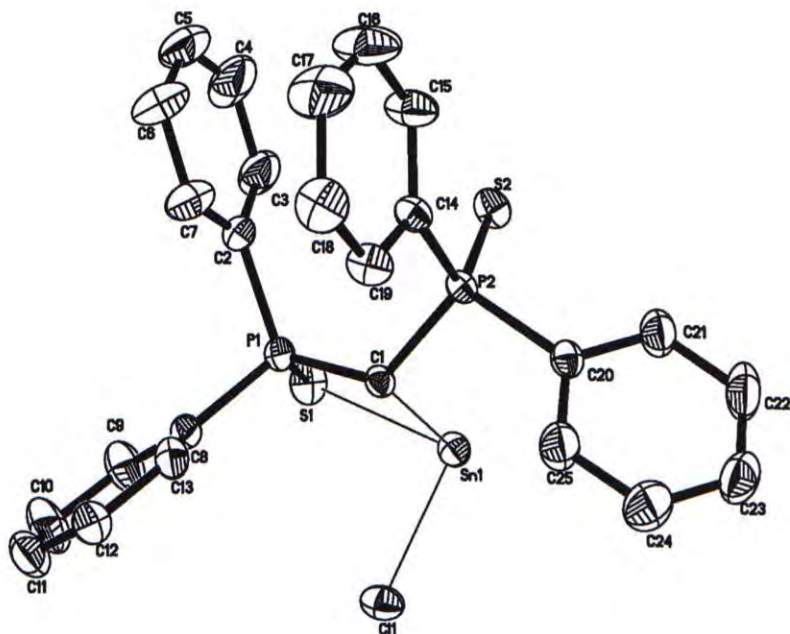


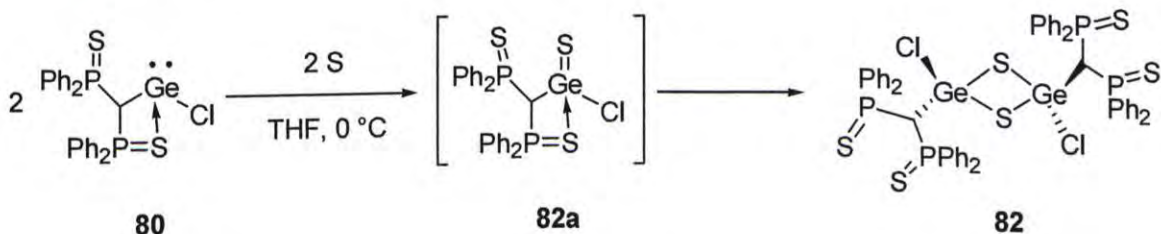
Fig. 2.11 Molecular structure of $[\text{SnCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$ (**81**) (30% probability ellipsoids)

Table 2.4 Selected Bond Distances (Å) and Angles (deg) for Compounds 80 and 81

	[MCl{CH(PPh ₂ =S) ₂ }]	
	M = Ge (80)	M = Sn (81)
M(1)-C(1)	2.153(6)	2.374(2)
M(1)-Cl(1)	2.288(2)	2.521(1)
M(1)-S(1)	2.479(2)	2.636(1)
P(1)-C(1)	1.786(6)	1.769(2)
P(1)-S(1)	2.007(3)	2.017(1)
P(2)-C(1)	1.803(6)	1.782(2)
P(2)-S(2)	1.954(2)	1.959(1)
C(1)-M(1)-Cl(1)	94.6(2)	86.35(6)
C(1)-M(1)-S(1)	79.8(2)	74.56(6)
Cl(1)-M(1)-S(1)	97.3(1)	93.29(3)
C(1)-P(1)-S(1)	103.5(2)	106.7(1)
C(1)-P(2)-S(2)	111.7(2)	112.1(1)
P(1)-S(1)-M(1)	80.9(1)	82.31(3)
P(1)-C(1)-P(2)	119.8(4)	122.0(1)
P(1)-C(1)-M(1)	95.8(3)	95.7(1)
P(2)-C(1)-M(1)	107.2(3)	102.7(1)

2.2.4.1 Reaction of Chlorogermylene with Chalcogens

The oxidation of germylene chloride (**80**) with equimolar amount of sulfur in THF gave the *trans*-dithiagermetane $[\text{GeCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}(\mu\text{-S})_2]$ (**82**) (**Scheme 2.9**) as confirmed by X-ray structure analysis. It is believed that the germathiocarbonyl chloride (**82a**) was formed as intermediate. This intermediate exists between resonance forms **A** and **B** in the mixture (**Scheme 2.10**). The $\text{>Ge}=\text{S}$ is so polar that cannot be stabilized kinetically by the ligand, i.e. resonance form **B** contributes more. The intermediate **82a** underwent head-to-tail dimerization to give the product. Only *trans*-compound was isolated. It may be because the extremely bulky ligands make the formation of *trans*-isomer be more favorable.



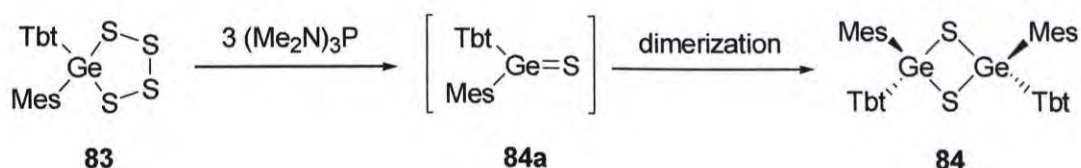
Scheme 2.9



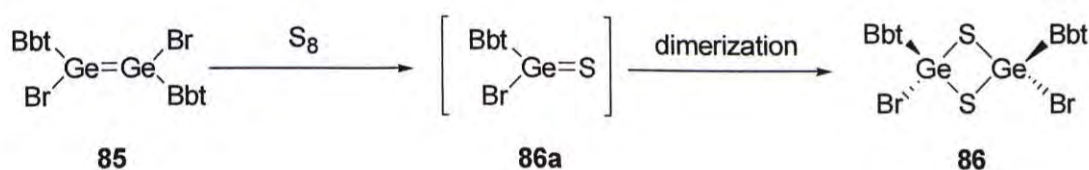
Scheme 2.10

Similar structure of dithiagermetanes $[(\text{Tbt})(\text{Mes})\text{Ge}(\mu\text{-S})_2]$ (**84**)³⁹ and $[(\text{Bbt})(\text{Br})\text{Ge}(\mu\text{-S})_2]$ (**86**)⁴⁰ have been reported from the desulfurization of tetrathiagermolane and sulfurization of digermene, respectively. It was suggested that

they were also formed by the rapid dimerization of the intermediary germanethione **84a** or germathiocarbonyl bromide **86a** (Scheme 2.11 and 2.12). But X-ray structure analysis indicated the *cis*-configuration with folded rhombic Ge₂S₂ ring in these two compounds.



Scheme 2.11



Scheme 2.12

2.2.4.2 Spectroscopic Properties of **82**

Compound **82** is an air-sensitive colorless crystalline solid that is soluble in THF, and sparingly soluble in toluene. It has been characterized by NMR spectroscopy and elemental analysis.

The ¹H and ¹³C NMR spectra of **82** are normal and displayed signals assignable to the ligand. There is a sharp singlet at δ 36.78 ppm in ³¹P NMR spectrum of **82** which indicates all phosphorus atoms share the same chemical environment in solution. This agrees with the X-ray structure.

2.2.4.3 Molecular Structure of $[\text{GeCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}(\mu\text{-S})]_2\cdot 4\text{THF}$ (**82**)

The molecular structure of **82** is illustrated in Fig. 2.12. Selected bond distances (Å) and angles (deg) of **82** are listed in Table 2.5. X-ray analysis revealed the *trans*-configuration of **82** with a Ge_2S_2 planar ring. The S-Ge-S' angles ($96.25(4)^\circ$) are larger than the Ge-S-Ge angles ($83.75(4)^\circ$). The two thio sulfur atoms of the ligand remain uncoordinated. The tetracoordinated germanium adopts a tetrahedral geometry.

The averaged Ge–S bond distance of 2.218 Å is longer than that of 2.056(6) Å in $[\text{Ge}(\text{S})\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)(\text{C}_5\text{H}_4\text{N-2})\}\text{Cl}]^{41}$ and 2.063(3) Å in $[(\text{Tbt})(\text{Tip})\text{Ge}=\text{S}]$, but is within the typical Ge–S single bond range (2.17–2.25 Å).⁴²

The germanium carbon bond distance of 2.010(4) Å and germanium chloride bond distance of 2.133(1) Å are shorter than those found in the starting material **80** [Ge–C: 2.153(6); Ge–Cl: 2.288(2) Å]. This is expected for the higher oxidation state germanium center in **82**. The Ge–C bond distance of 2.010(4) Å is similar to the Ge(IV)–C bond distances of 1.94(1) Å in $[(\text{MesGe})_2\text{S}_2\text{Cl}_2]$,⁴³ 1.959(8) Å in $[\text{GeH}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)_3]$,⁴⁴ and 1.970(7) Å in $[\text{Ge}(\text{C}_6\text{H}_5)_3\text{Cl}]$.⁴⁵ The Ge–Cl bond distance shows good agreement with those in $[(\text{MesGe})_2\text{S}_2\text{Cl}_2]$ (2.183(2) Å),⁴³ $[\{\text{HC}(\text{CMeNAr})_2\}\text{Ge}(\text{S})\text{Cl}]$ (2.195(7) Å),^{17,18} and $[\text{Ge}(\text{S})\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)(\text{C}_5\text{H}_4\text{N-2})\}\text{Cl}]$ (2.180(2) Å).⁴¹

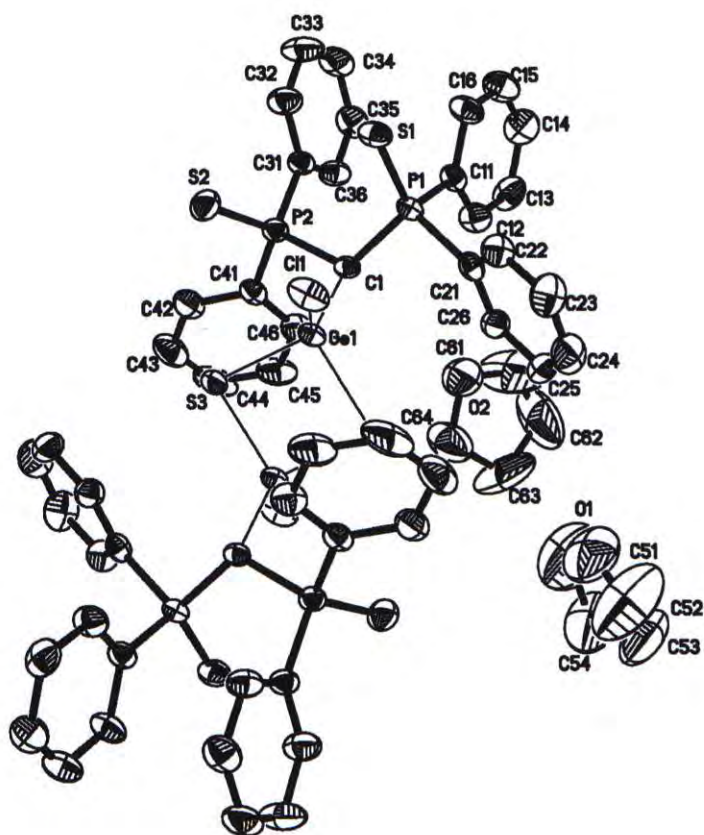


Fig. 2.12 Molecular structure of $[\text{GeCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}(\mu\text{-S})_2]\cdot 4\text{THF}$ (**82**) (30% probability ellipsoids)

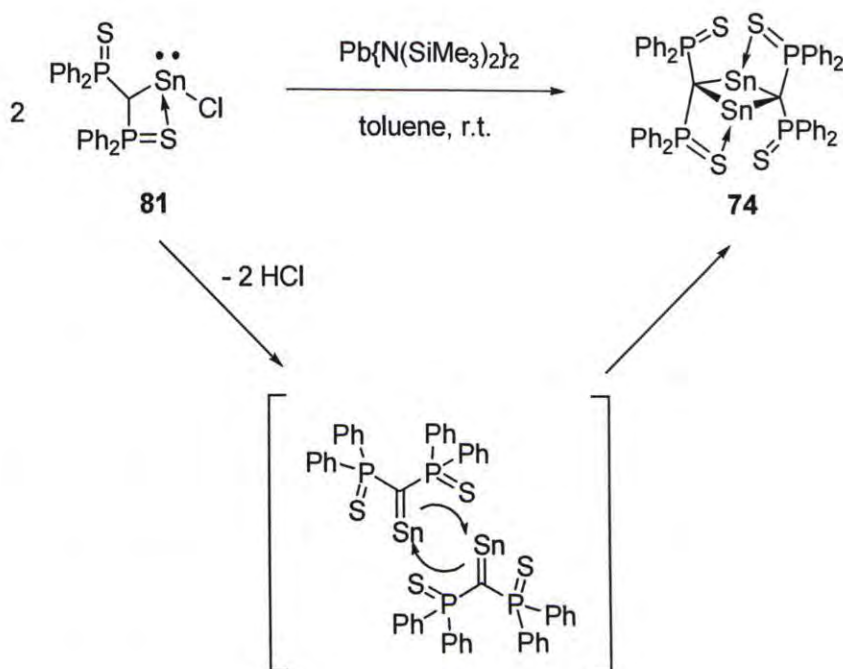
Table 2.5 Selected Bond Distances (Å) and Angles (deg) for Compound 82

Ge(1)-C(1)	2.010(4)	P(1)-C(1)	1.851(4)
Ge(1)-Cl(1)	2.133(1)	P(1)-S(1)	1.934(2)
Ge(1)-S(3)	2.209(1)	P(2)-C(1)	1.845(4)
Ge(1)-S(3A)	2.226(1)	P(2)-S(2)	1.939(2)
C(1)-Ge(1)-Cl(1)	112.1(1)	Ge(1)-S(3)-Ge(1A)	83.75(4)
C(1)-Ge(1)-S(3)	118.0(1)	C(1)-P(1)-S(1)	115.8(2)
Cl(1)-Ge(1)-S(3)	108.5(1)	C(1)-P(2)-S(2)	110.9(2)
C(1)-Ge(1)-S(3A)	111.9(1)	P(2)-C(1)-P(1)	117.2(2)
Cl(1)-Ge(1)-S(3A)	108.9(1)	P(2)-C(1)-Ge(1)	106.7(2)
S(3)-Ge(1)-S(3A)	96.25(4)	P(1)-C(1)-Ge(1)	113.3(2)

Symmetry transformations used to generate equivalent atoms: 1A: $-x+3/2, -y+3/2, -z+2$

2.2.4.4 Reaction of Chlorostannylene with $\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2$

Treatment of $[\text{SnCl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$ (**81**) with $\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2$ in 2:1 ratio afforded the 1,3-distannacyclobutane $[\text{Sn}\{\mu^2\text{-C}(\text{Ph}_2\text{P}=\text{S})_2\}]_2$ (**74**) (Scheme 2.13). It is proposed that **81** was dehydrochlorinated by $\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2$ to form the unstable stannavinylidene intermediate $[\text{:Sn}=\text{C}(\text{Ph}_2\text{P}=\text{S})_2]$. This intermediate then underwent “head-to-tail” cycloaddition to form **74**. This result is different from the synthesis of the mixed-metal 1,3-stanna-plumbacyclobutane $[1\text{-Sn}\{\text{C}(\text{Pr}'_2\text{P}=\text{NSiMe}_3)(2\text{-Py})\}3\text{-Pb}\{\text{C}(\text{Pr}'_2\text{P}=\text{NSiMe}_3)2\text{-Py}\}]$ from the reaction of $[\text{Sn}\{\text{CH}(\text{Pr}'_2\text{P}=\text{NSiMe}_3)(2\text{-Py})\}\text{Cl}]$ with $\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2$.²⁶



Scheme 2.13

2.3 Experimental for Chapter 2

Materials:

(S=PPh₂)₂CH₂,⁴⁶ Sn{N(SiMe₃)₂}₂,⁴⁷ Pb{N(SiMe₃)₂}₂⁴⁷ were prepared according to the literature procedures. S, Se, GeCl₂·dioxane and SnCl₂ were purchased from Aldrich Chemical Co. and used without further purification.

[Sn{μ²-C(Ph₂P=S)₂}]₂ (74).

Method 1: A mixture of (S=PPh₂)₂CH₂ (1.19 g, 2.65 mmol) and Sn{N(SiMe₃)₂}₂ (1.17g, 2.66mmol) in toluene (20 ml) was stirred at room temperature for 3 days. Volatiles were removed under reduced pressure. The residue was extracted with THF and filtered. The yellow filtrate was concentrated and allowed to stand for 3 days. Bright yellow crystals of **74** were obtained. Yield: 0.79 g (50%).

Method 2: A solution of Pb{N(SiMe₃)₂}₂ (0.16 g, 0.30 mmol) in toluene (20 ml) was slowly added to a solution of **81** (0.34 g, 0.56 mmol) in toluene (10 ml) at room temperature. The reaction mixture was stirred for 2 days. Volatiles were removed under reduced pressure and the residue was extracted with THF. After filtration and concentration, the mixture was allowed to stand for 3 days to give bright yellow crystals of *title* compounds. Yield: 0.23 g (67%). Mp: 152.7 °C (dec). Anal. Found: C, 53.62; H, 4.11. Calcd for C₅₀H₄₀P₄S₄Sn₂·THF: C, 53.94; H, 4.02. ¹H NMR (300 MHz, THF-*d*₈): δ

= 7.28-7.41 (m, 24H, Ph), 7.89-7.97 (m, 16H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, THF- d_8):
 δ = 128.68 (t, *m*-Ph, $^3J_{\text{P-C}}$ = 6.3 Hz), 131.73 (*p*-Ph), 132.60 (t, *o*-Ph, $^2J_{\text{P-C}}$ = 5.4 Hz),
134.35 (d, *ipso*-Ph, $^1J_{\text{P-C}}$ = 85.8 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, THF- d_8): δ = 32.01.

[Pb $\{\mu^2\text{-C}(\text{Ph}_2\text{P}=\text{S})_2\}_2$] (75).

A mixture of (S=PPh₂)₂CH₂ (1.30 g, 2.90 mmol) and Pb{N(SiMe₃)₂}₂ (1.54 g, 2.91 mmol) in toluene (20 ml) was stirred at room temperature for 3 days. Volatiles were removed under reduced pressure, and the residue was extracted with THF. After filtration and concentration of the filtrate, compound **75** was obtained as yellow crystals. Yield: 1.28 g (64%). Mp: 155 °C (dec). Anal. Found: C, 46.49; H, 3.38. Calcd for C₅₀H₄₀P₄Pb₂S₄· $\frac{1}{2}$ THF: C, 46.49; H, 3.30. ^1H NMR (300 MHz, THF- d_8): δ = 7.10-7.41 (m, 24H, Ph), 7.69-7.97 (m, 16H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, THF- d_8): δ = 128.45-128.72 (m, *m*-Ph), 130.92 (*p*-Ph), 131.71 (*p*-Ph), 131.90 (t, *o*-Ph, $^2J_{\text{P-C}}$ = 5.5 Hz), 132.58 (t, *o*-Ph, $^2J_{\text{P-C}}$ = 5.4 Hz), 134.48 (d, *ipso*-Ph, $^1J_{\text{P-C}}$ = 85.9 Hz), 138.57 (d, *ipso*-Ph, $^1J_{\text{P-C}}$ = 89.6 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, THF- d_8): δ = 33.83, 35.72.

[Ge{N(SiMe₃)₂}₂(μ -S)]₂ (77).³⁰

A mixture of (S=PPh₂)₂CH₂ (0.63 g, 1.40 mmol) and Ge{N(SiMe₃)₂}₂ (0.53 g, 1.35 mmol) in toluene (20 ml) was refluxed at 120 °C for 18 h. Volatiles were removed under

reduced pressure. The residue was extracted with THF and filtered. The yellow filtrate was concentrated and cooled to yield colorless crystals of **77**. Yield: 0.20 g (35%). Spectroscopy data as literature reported.

[PbS{C(PPh₂=S)₂}] (78).

A solution of **75** (1.27 g, 0.92 mmol) in toluene (20 ml) was added slowly to the solution of powdered sulfur (0.06 g, 1.87 mmol) in toluene (20 ml) at 0 °C with stirring.

The resultant red suspension was raised to ambient temperature and stirred for 18 h.

Volatiles were removed under reduced pressure, and the residue was extracted with THF. After filtration and concentration of the filtrate, compound **78** was obtained as red crystals. Yield: 0.19 g (14%). Mp: 129.8 °C (dec). Anal. Found: C, 46.03; H, 3.76.

Calcd for C₂₅H₂₀P₂PbS₃·THF: C, 45.96; H, 3.72. ¹H NMR (400 MHz, THF-*d*₈): δ = 1.69 (s, 2.5H, 0.75 THF), 3.54 (s, 2.5H, 0.75 THF), 7.19-7.46 (m, 12H, Ph), 7.87-7.92 (m, 8H, Ph). ¹³C{¹H} NMR (75.5 MHz, THF-*d*₈): δ = 26.39 (THF), 68.22 (THF), 128.67, 130.87, 131.72, 132.52, 132.60, 132.67, 134.67, 135.48 (Ph). ³¹P{¹H}NMR (162.0 MHz, THF-*d*₈): δ = 31.87, 57.73.

[PbSe{C(PPh₂=S)₂}] (79).

A solution of **75** (1.82 g, 1.32 mmol) in toluene (20 ml) was added slowly to the

solution of powdered selenium (0.24 g, 3.05 mmol) in toluene (20 ml) at 0 °C with stirring in the absence of light. The resultant dark brown suspension was raised to ambient temperature and stirred for 2 days. Volatiles were removed under reduced pressure, and the residue was extracted with THF. The insoluble precipitate was filtered off. The filtrate was concentrated to give red crystals of **79**. Yield: 0.48 g (25%). Mp: 150.6-151.1 °C (dec). Anal. Found: C, 41.17; H, 2.75. Calcd for C₂₅H₂₀P₂PbS₂Se: C, 40.98; H, 2.75. ¹H NMR (400 MHz, THF-*d*₈): δ = 7.30-7.40 (m, 12H, Ph), 7.90-7.96 (m, 8H, Ph). ¹³C{¹H} NMR (75.5 MHz, THF-*d*₈): δ = 128.59, 128.68, 128.76, 131.72, 132.52, 132.60, 132.67, 134.35, 135.49. ³¹P{¹H}NMR (162.0 MHz, THF-*d*₈): δ = 31.86, 59.39. ⁷⁷Se NMR (THF-*d*₈): δ = 893.34.

[GeCl{CH(PPh₂=S)₂}] (80).

A solution of **42** (3.36 g, 5.59 mmol) in Et₂O (20 ml) was added slowly to the solution of GeCl₂·dioxane (1.28 g, 5.55 mmol) in Et₂O (20 ml) at 0 °C with stirring. The resultant white suspension was raised to ambient temperature and stirred for 18 h. Volatiles were removed under reduced pressure. The residue was extracted with CH₂Cl₂ and filtered. Addition of THF to filtrate and concentration give **80** as colorless crystals. Yield: 2.17 g (70%). Mp: 175.2-175.6 °C (dec after melting). Anal. Found: C, 54.00; H, 3.78. Calcd for C₂₅H₂₁ClGeP₂S₂: C, 54.04; H, 3.81. ¹H NMR (400 MHz, THF-*d*₈): δ =

3.83 (br t, 1H, CH), 7.29-7.40 (m, 12H, Ph), 7.85-7.95 (m, 8H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, THF- d_8): δ = 37.49 (t, PCP, $J_{\text{P-C}}$ = 46.8 Hz), 128.60, 128.66, 128.73, 128.80, 131.72, 132.44, 132.52, 132.57, 132.63, 132.71, 134.47 (d, J = 85.5 Hz) (Ph). $^{31}\text{P}\{^1\text{H}\}$ (121.5 MHz, THF- d_8): δ = 33.81, 39.95.

[SnCl{CH(PPh₂=S)₂}] (81).

A solution of **42** (1.64 g, 2.73 mmol) in Et₂O (20 ml) was added slowly to the solution of SnCl₂ (0.58 g, 3.06 mmol) in Et₂O (20 ml) at 0 °C with stirring. The resultant white suspension was raised to ambient temperature and stirred for 18h. Volatiles were removed under reduced pressure. The residue was extracted with CH₂Cl₂ and filtered. The filtrate was added with THF and concentrated to give **81** as colorless crystals. Yield: 0.97 g (60%). Mp: 106.2 °C (dec). Anal. Found: C, 49.66; H, 3.51. Calcd for C₂₅H₂₁ClP₂S₂Sn: C, 49.91; H, 3.52. ^1H NMR (400 MHz, THF- d_8): δ = 4.20 (t, 1H, CH, $J_{\text{P-H}}$ = 13.5 Hz), 7.27-7.40 (m, 12H, Ph), 7.72-7.96 (m, 8H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, THF- d_8): δ = 37.62 (t, PCP, $J_{\text{P-C}}$ = 47.3 Hz), 128.67 (t, *m*-Ph, $^3J_{\text{P-C}}$ = 7.0 Hz), 131.72 (s, *p*-Ph), 132.58 (t, *o*-Ph, $^2J_{\text{P-C}}$ = 5.0 Hz), 134.47 (d, *ipso*-Ph, $^1J_{\text{P-C}}$ = 86.5 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, THF- d_8): δ = 33.82, 37.63. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.1 MHz, THF- d_8): δ = -129.58 (t, $^2J_{\text{Sn-P}}$ = 169 Hz).

[GeCl{CH(PPh₂=S)₂}(μ-S)]₂ (82**).**

A solution of **80** (0.50 g, 0.90 mmol) in THF (20 ml) was added to the solution of sulfur (0.04 g, 1.25 mmol) in THF (10 ml) at 0 °C with stirring. The resultant pale yellow suspension was raised to ambient temperature and stirred for 48 h. It was filtered and concentrated, yielding colorless crystals of **82**. Yield: 0.14 g (21 %). Mp: 139.2 °C (dec).

Anal. Found: C, 52.47; H, 4.43. Calcd for C₅₀H₄₂Cl₂Ge₂P₄S₆·2THF: C, 52.79; H, 4.43.

¹H NMR (300 MHz, THF-*d*₈): δ = 1.69 (4H, THF), 3.54 (4H, THF), 4.17 (t, 2H, CH, *J*_{P-H} = 13.5 Hz), 6.99-7.18 (m, 4H, Ph), 7.26-7.54 (m, 20H, Ph), 7.64-7.93 (m, 12H, Ph),

7.96-8.04 (m, 4H, Ph). ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈): δ = 26.38 (THF), 68.22 (THF), 128.24-129.19 (m, Ph), 131.71(Ph), 132.44-133.11 (m, Ph), 134.48 (d, *ipso*-Ph,

¹*J*_{P-C} = 85.6 Hz). ³¹P{¹H} (162.0 MHz, THF-*d*₈): δ = 36.78.

2.4 References for Chapter 2

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Chapter 3 Synthesis of Group 13 Metal Bis- (thiophosphinoyl) Complexes

3.1 Introduction

3.1.1 General Aspects of Group 13 Organometallic Chemistry

Among the group 13 elements, alkylaluminium compounds have been extensively investigated on account of their uses as alkene polymerization catalysts and chemical intermediates. For examples, they can be employed as activators of group 4 complexes in Zeigler-Natta system. Comparatively, gallium and indium complexes remain less explored due to less industrial applications. Nevertheless, this situation changes due to the potential application of these organometallic compounds in the production of semiconductors.

One general feature of group 13 organometallic compounds is their electron deficient character. This type of complexes, in monomeric form, has only three pairs of electrons in the valance shell. They exhibit trigonal planar configuration with three sp^2 hybrid orbitals of the metal and a vacant p -orbital perpendicular to the trigonal plane (Fig. 3.1). Such molecules with only six electrons in the valance shell are obviously coordinatively unsaturated.

As a result, trivalent group 13 complexes are often Lewis acids and combine easily with Lewis base to form tetrahedral species. It might be noted that when forming

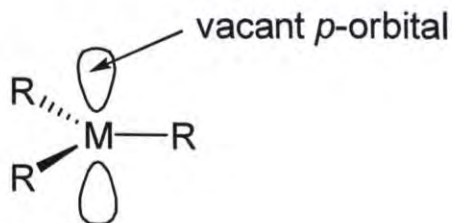


Fig. 3.1

tetrahedral complex, the group 13 elements change from sp^2 hybridized to sp^3 hybridized. Coordination numbers higher than four are also possible due to the presence of vacant d -orbital in the valence shells. Besides, they can increase their coordination number by oligomerization. The strength of these trivalent compounds to form adducts or oligomerize decrease in the sequence of $Al > Ga > In$. Tri-organogallium and organoindium compounds are less likely to associate through the electron deficient MCM bridges than the organoaluminum one. For example, Me_3M ($M = Ga, In$) are monomeric in vapor phase and in solution, while trimethylaluminum is dimeric even in vapor phase by forming two electron-three center Al-C-Al bonds (Fig. 3.2).^{1,2} With very bulky groups, for instance, trimesitylaluminum is a monomer.³

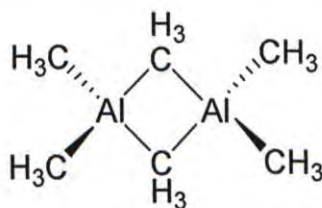


Fig. 3.2

Group 13 organometallic compounds are thermodynamically unstable and are easily oxidized or hydrolyzed. To enhance the stability of these complexes, bulky

substituents or coordination from donor atoms to the electron deficient metal center can be the effective method.

3.1.2 General Aspects of Group 13 Metal Complexes Bearing Phosphoranoimine or Phosphoranosulfide Ligands

The synthesis of group 13 organometallic compounds, especially organoaluminium ones, containing N-donors has attracted considerable interest in past decades. A range of ligands have been used and monofunctional amides, *N,N*-amidates, guanidates and β -diketiminates are the most prevalent.⁴ Utilization of phosphoranoimine ligands has also been widely studied.

Phosphoranoimine ligand can stabilize group 13 centers via sterically hindered substituents and nitrogen coordination. Cavell's group synthesized the first example of group 13 bis(iminophosphorano)methane complexes of aluminium. Both a single and the rare double deprotonation of the methylene backbone of the ligand to a monometallic alkyl methanide $[\text{AlMe}_2\{\text{HC}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2-\kappa^2\text{N},\text{N}'\}]$ (**87**) and to a bimetallic bridging methandiide $[(\text{AlMe}_2)_2\{\mu_2\text{-C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2-\kappa^4\text{C},\text{C}',\text{N},\text{N}'\}]]$ (**88**) were observed (Fig. 3.3).⁵ Later, they reported three more alkyl aluminium complexes **89-91** from the same ligand. The catalytic activity of this family of aluminium bis(iminophosphorano)methanide and methandiide complexes (**87-91**) toward olefin polymerization has also been evaluated.⁶ It was found that the dialuminium complexes

88 and **91** are much more effective catalysts than the single metal species **87**, **89** and **90**.

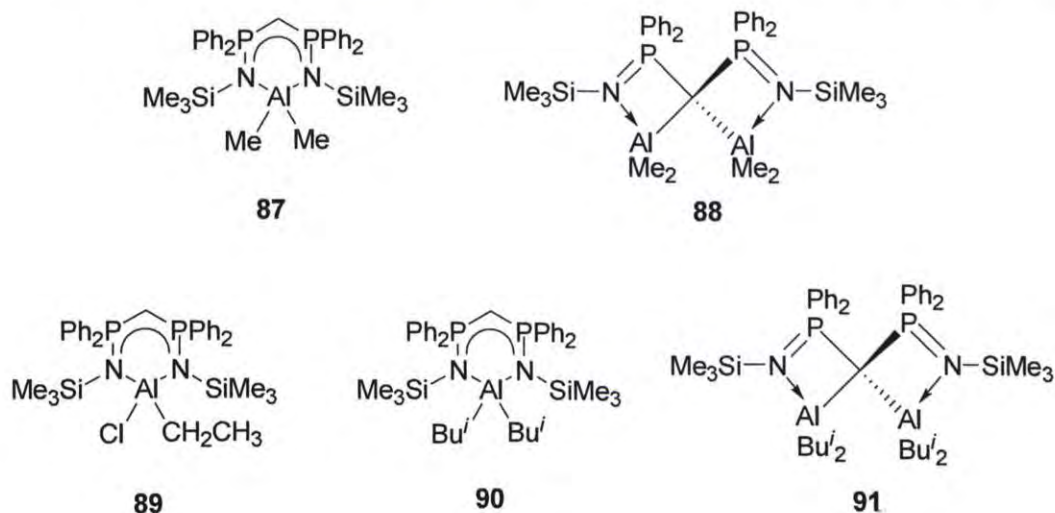


Fig. 3.3

Stephan et al. and Hill et al. have also prepared a series of group 13 metal complexes **92**⁷ and **93**⁸ from the same ligand system $[\text{CH}_2(\text{PPh}_2=\text{NR})_2]$ ($\text{R} = \text{SiMe}_3$, Mes). In all of these compounds, the metal center is bonded to ligand in N,N' -chelating fashion and adopts a tetrahedral geometry (Fig. 3.4).

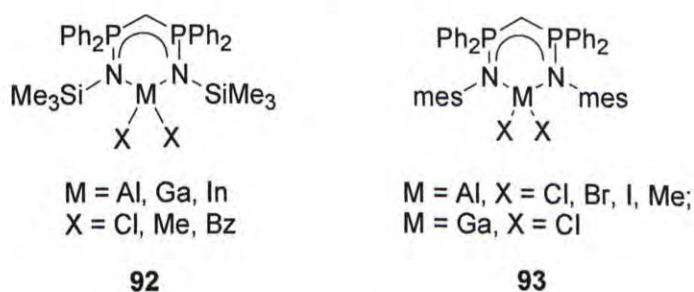


Fig. 3.4

Later on, different functionalized phosphoranoimines of group 13 metal complexes have been synthesized and structural characterized. For example, $[\text{In}(o\text{-C}_6\text{H}_4\text{PPh}_2=\text{NSiMe}_3)_3]$ (**94**),⁹ $[(\text{AlMe}_2)_2\{\text{C}(\text{Ph}_2\text{P}=\text{NBu}')(2\text{-R-8-quinolylyl})\}]$ ($\text{R} = \text{Me}, \text{H}$) (**95**),¹⁰ $[\{1\text{-NAr-2-(PPh}_2=\text{NMes})\text{C}_6\text{H}_4\}\text{AlR}_2]$ ($\text{R} = \text{Me}, \text{H}$) (**96**),¹¹

$[\{(ArN)C(Me)CHPPh_2=NAr\}MR_2]$ ($M = Al, R = Me, H; M = Ga, R = Me$) (**97**),¹²

$[\{MX_2(Me_3SiNPPr^i_2CH)\}_2C_4H_2N_2-2,3]$ ($M = Al, X = Cl, Me; M = Ga, X = Me$) (**98**),¹³

and $[AlEt_2\{2-(Me_3SiN=PPh_2)-6-(Me_3SiN=PPh_2CH)C_5H_3N\}]$ (**99**)¹⁴ were reported

(Fig. 3.5).

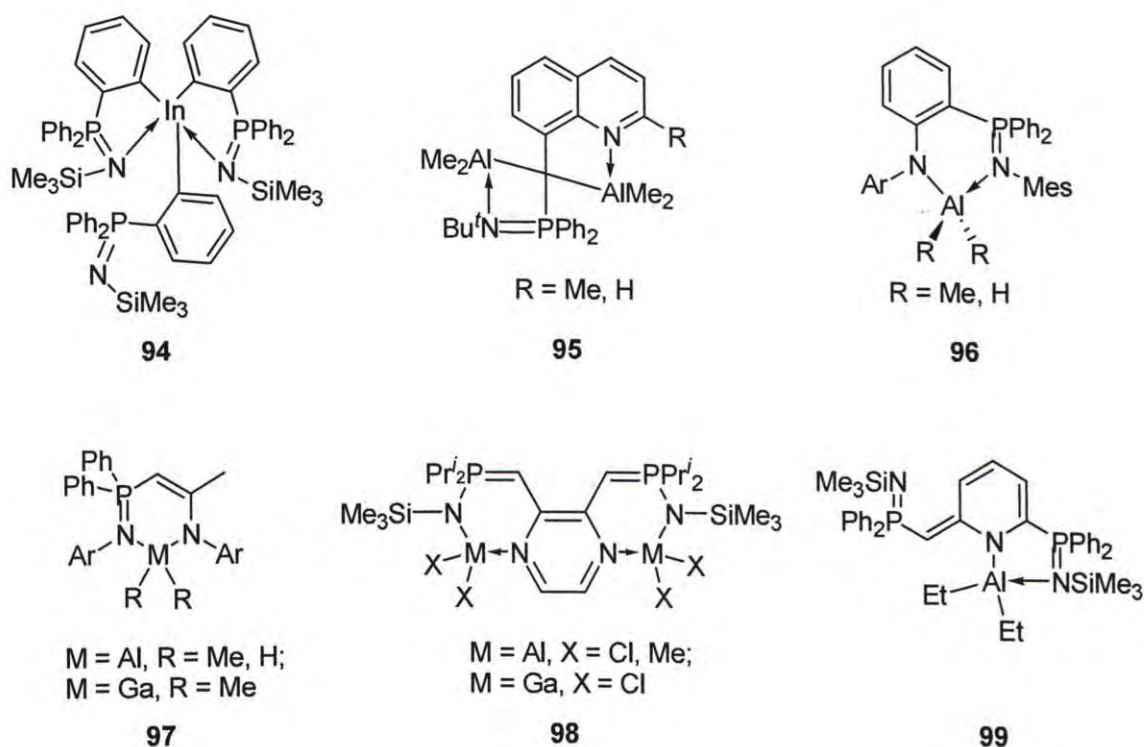


Fig. 3.5

In spite of extensive studies on phosphoranoimido group 13 metal complexes, only little efforts have been done on the chemistry of group 13 metal thiophosphinoyl ones. It is believed that the isoelectronic phosphoranosulfide can also enhance the stability of the metal centers by bulky substituents and sulfur donor atoms.

Sangkokya and coworkers reported the synthesis of two bis(thiophosphinoyl) aluminium complexes in 1990. Reaction of trimethylaluminum with bis(diphenylthio-

phosphinoyl)methane and bis(diphenylthiophosphinoyl)ethane in 2:1 ratio afforded $[\text{Al}(\text{Me}_2)\text{C}(\text{PPh}_2=\text{S})(\text{PPh}_2=\text{S}\rightarrow\text{AlMe}_3)]$ (**100**) and $[(\text{AlMe}_3)_2\{(\text{S}=\text{PPh}_2)_2\text{CH}_2\text{CH}_2\}]$ (**101**) respectively.¹⁵ X-ray analysis revealed that compound **100** is a condensation product while **101** is only the addition product (Fig. 3.6).

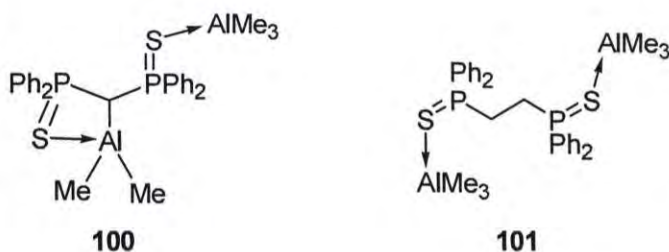


Fig. 3.6

Muñoz-Hernández's group has explored the incorporation of iminobis(phosphoranosulfide) ligand on organogallium centers. They reported the synthesis and characterization of several gallium complexes $[\text{GaXX}'\{(\text{SPPH}_2)_2\text{N}\}]$ ($\text{X} = \text{Cl}, \text{Me}; \text{X}' = \text{Cl}, \text{Me}$) (**102**).¹⁶ Uhl's group also used this ligand to prepare a organogallium complex $[\text{Ga}\{\text{CH}(\text{SiMe}_3)_2\}\{(\text{SPPH}_2)_2\text{N}\}]_2$ (**103**) which has a Ga–Ga bond. The bond length of 2.490 Å is consistent with Ga–Ga single bond.¹⁷

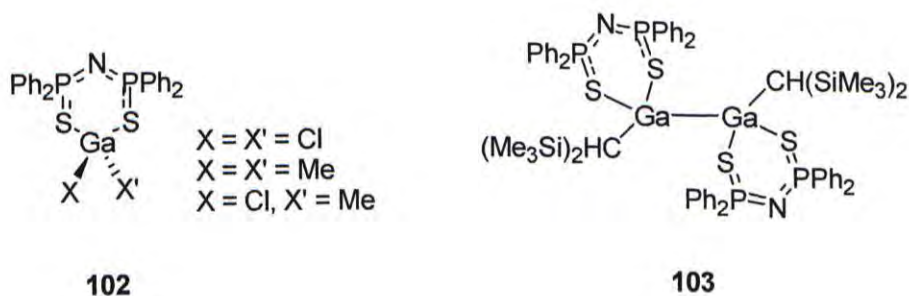


Fig. 3.7

With the same ligand system, $L_n\text{InX}_{(3-n)}$ [$L = \{\text{N}(\text{PR}_2=\text{S})_2\}^-$ ($\text{R} = \text{Ph}$ or Pr^i); $\text{X} = \text{Cl}$

or I] (**104-106**) were synthesized.^{18,19,20} The coordination number of indium increases from 4 to 6 as n increase from 1 to 3. The indium centers in **104-106** exhibit tetrahedral, trigonal-bipyramidal and octahedral coordination geometry, respectively (Fig. 3.8).

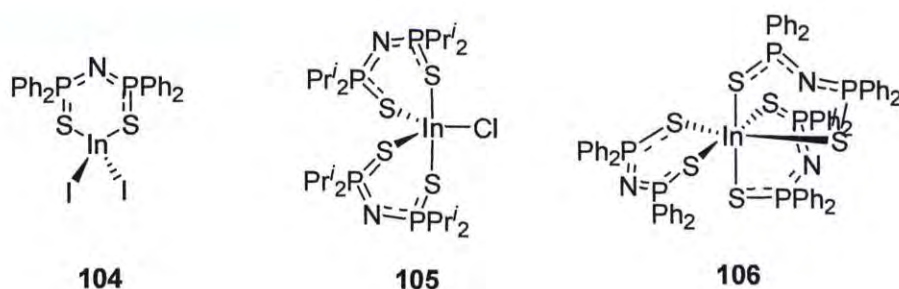


Fig. 3.8

Moya-Cabrera et al. reported the synthesis and structural characterization of an In(III) complex $[\kappa^3-N,N',S-\{4,5-(P(S)Ph_2)_2(\mu-tz)\}InMe_2]_2$ (**107**).²¹ Compound **107** was found to be a dimeric-like arrangement with a planar In_2N_4 core (Fig. 3.9).

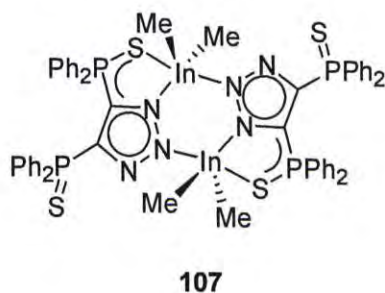


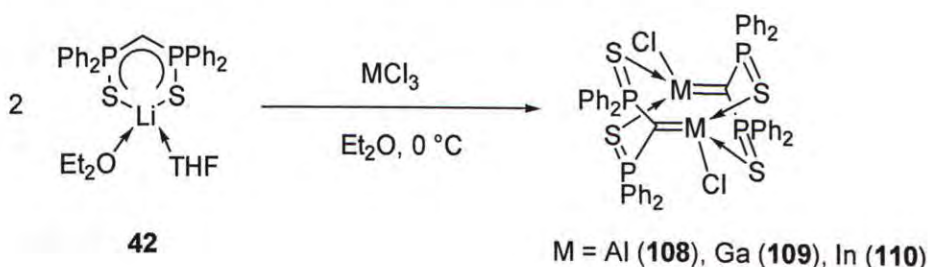
Fig. 3.9

In this chapter, the preparation of Group 13 bis(thiophosphinoyl) complexes from the lithiated salt (**42**) will be described. The X-ray structures of these metal complexes will also be presented.

3.2 Results and Discussion

3.2.1 Synthesis of Group 13 Metal Bis(thiophosphinoyl) Complexes

The reaction of MCl_3 ($M = Al, Ga, In$) with two equivalents of **42** gave bis(thiophosphinoyl)methandiide metal chlorides $[MCl\{C(PPh_2=S)_2\}]_2$ ($M = Al$ (**108**), Ga (**109**), In (**110**)) (Scheme 3.1). It is proposed that the intermediate $[MCl_2\{CH(PPh_2=S)_2\}]$ formed underwent further dehydrochlorination to form **108-110**. The monolithium complex acts both as a ligand transfer reagent and as a base for dehydrochlorination. The by-product, neutral bis(thiophosphinoyl)methane was confirmed by the signal of methylene protons in 1H NMR spectrum.



Scheme 3.1

Similar dehydrochlorination has been reported in the synthesis of bisgermavinylidene $[(Me_3SiN=PPh_2)_2C=Ge \rightarrow Ge=C(PPh_2=NSiMe_3)_2]$ from the reaction of $GeCl_2 \cdot dioxane$ with $[Li\{CH(PPh_2=NSiMe_3)_2\}(THF)]$.²²

3.2.2 Spectroscopic Properties of 108-110

Compounds **108-110** are air and moisture sensitive colorless crystalline solids.

They are soluble in THF and CH₂Cl₂ only. They have been characterized by NMR spectroscopy and elemental analysis.

The ¹H and ¹³C NMR spectra of **108-110** showed a similar pattern and displayed one set of signal due to the ligand. There is one sharp singlet [δ 32.24 (**108**); δ 31.86 (**109**); δ 31.87 ppm (**110**)] in all of their ³¹P NMR spectra. This indicates that the phosphorus atoms in these compounds are in the same environment.

3.2.3 Molecular Structures of [MCl{C(PPh₂=S)₂}]₂ (M = Al (**108**), Ga (**109**), In (**110**))

Compounds **108-110** are isostructural and their molecular structures are illustrated in Fig. 3.10 to 3.12. Selected bond distances (Å) and angles (deg) are shown in Table 3.2. All of **108-110** are dimeric species bearing structural resemblance similar to [MgC(PPh₂=S)₂(THF)]₂ (**43**) (see Chapter 1). The metal center is bonded to chloride atom instead of a THF molecule, methanediide carbon and two thio sulfur atoms from adjacent ligand leading to a tetrahedral environment. It is noteworthy that compound **108-110** possesses an inversion center *i*, so that the half of the structures is centrosymmetric to another half. The angle sum ($\sum \angle$) of 351.9°, 350.4° and 352.4° in **108**, **109** and **110** around C(1) atom is indicative of a *sp*² carbon.

The averaged metal-sulfur bond and metal-chloride bond distances increase down

the group [M–S: 2.286 (**108**), 2.298 (**109**), 2.480 (**110**); M–Cl: 2.169(1) (**108**), 2.219(2) (**109**), 2.410(1) Å (**110**)]. There is an interesting trend in the M–C contact lengths. Al–C bond distance [1.975(2) Å] and Ga–C bond distance [1.972(4) Å] are very close to each other while In–C bond distance [2.173(3) Å] is much longer. These M–C bond distances are in between the M–C single and double bond length values [M–C: 2.032 (Al), 2.032 (Ga), 2.212 (In); M=C: 1.927 (Al), 1.927 (Ga), 2.107 Å (In)].²³ In addition, they are relatively shorter than the similar M–C bond in N-heterocyclic carbene complexes [Al–C: 2.031–2.124, Ga–C: 2.071–2.131, In–C: 2.200–2.267 Å].²⁴ Also, the Al–C bond distance is shorter than the Al–C single bond distance of 2.119 Å in [(AlMe₂)₂{μ²-C(Ph₂P=NSiMe₃)₂-κ⁴C,C',N,N'}]⁵ and that of 2.097(4) Å in [Al(Me₂)C(PPh₂=S)(PPh₂=S→AlMe₃)].¹⁵

In compound **108**, the averaged Al–S bond distance of 2.286 Å is comparatively shorter than those in [{Me₂Si(μ-NBu')₂P=S(NPh)-κN-κS}AlMe₂] (2.352(1) Å),²⁵ [Al(Me₂)C(PPh₂=S)(PPh₂=S→AlMe₃)] (2.388(2), 2.460(2) Å)¹⁵ and [(AlMe₃)(S=PPh₂CH₂CH₂PPh₂=S)(AlMe₃)] (2.506(3) Å).¹⁵ The Al–Cl bond distance of 2.169(1) Å is comparable to those of 2.126 Å in [{HC(CMeNAr)₂}AlCl₂],^{4m} 2.152(1) Å in [{(Me₃SiNCH₂CH₂)₂NMe}AlCl],²⁶ and 2.149 Å in [{HC(Ph₂P=NMe)₂}AlCl₂].⁸

The averaged Ga–S bond distance of 2.298 Å in **109** is similar to that of 2.273 Å in [GaCl₂{N(Ph₂P=S)₂}]^{16c} but shorter than those of 2.398 Å in [GaMe₂{N(Ph₂P=S)₂}]^{16b}

and 2.3886(9) Å in [GaMe₂{(S=PPh₂)N(C₉H₁₀NC=S)}].^{16b} The Ga–Cl bond (2.219(2) Å) has similar bond length with the corresponding bond in [GaCl₂{N(Ph₂P=S)₂}] (2.169 Å),^{16c} [{CH(Ph₂P=NSiMe₃)₂}GaCl₂] (2.200 Å),⁷ and [{HC(CMeNAr)₂}GaCl₂] (2.223 Å).^{4m}

In the case of **110**, the averaged In–S bond distance of 2.481 Å agrees well with that of 2.485 Å in [InI₂{N(Ph₂P=S)₂}]²⁰ but shorter than those in [InCl{N(Pr'₂P=S)₂}₂] (2.5715 Å)¹⁹ and [κ^3 -*N,N',S*-{4,5-P(S)Ph₂}₂(μ -tz)]InMe₂]₂] (2.780(1) Å).²¹ It is believed that higher indium coordination number in the latter two compounds lengthen the In–S bond. The In–Cl bond distance of 2.410(1) Å is comparable to those of 2.410(2) Å in [InCl{N(Pr'₂P=S)₂}₂]¹⁹ and 2.396 Å in [{HC(CMeNAr)₂}InCl₂].^{4m}

In these three compounds, the P–S bonds [2.062 (**108**), 2.053 (**109**), 2.058 Å (**110**)] are lengthened and the P–C bonds [1.723 (**108**), 1.715 (**109**), 1.721 Å (**110**)] are shortened relative to the free ligand [(S=PPh₂)₂CH₂], this is consistent with π -delocalization around the MS₂P₂C ring.

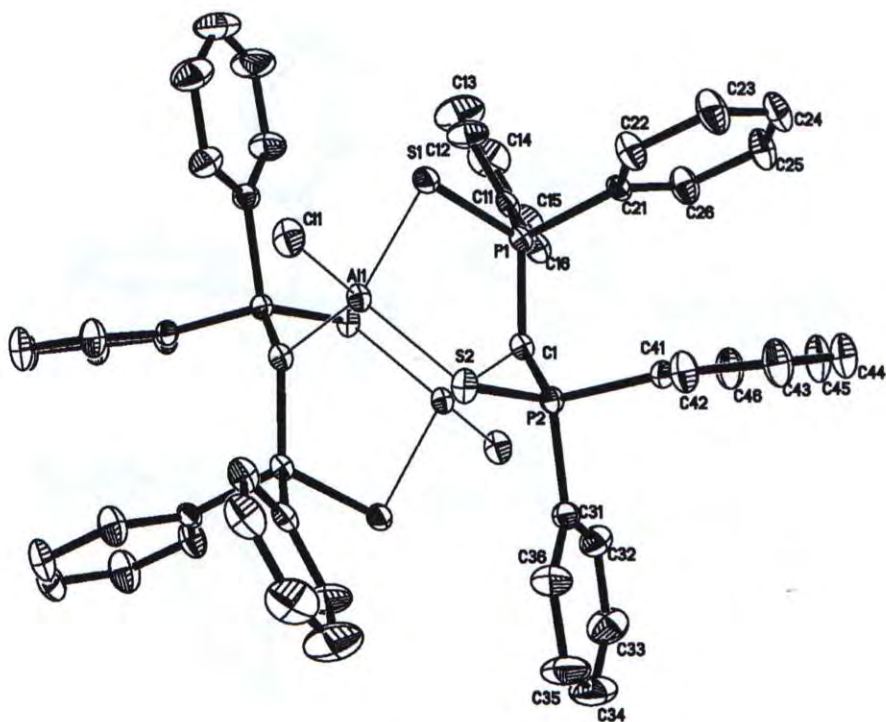


Fig. 3.10 Molecular structure of $[\text{AlCl}\{\text{C}(\text{PPh}_2=\text{S})_2\}]_2$ (**108**) (30% probability ellipsoids)

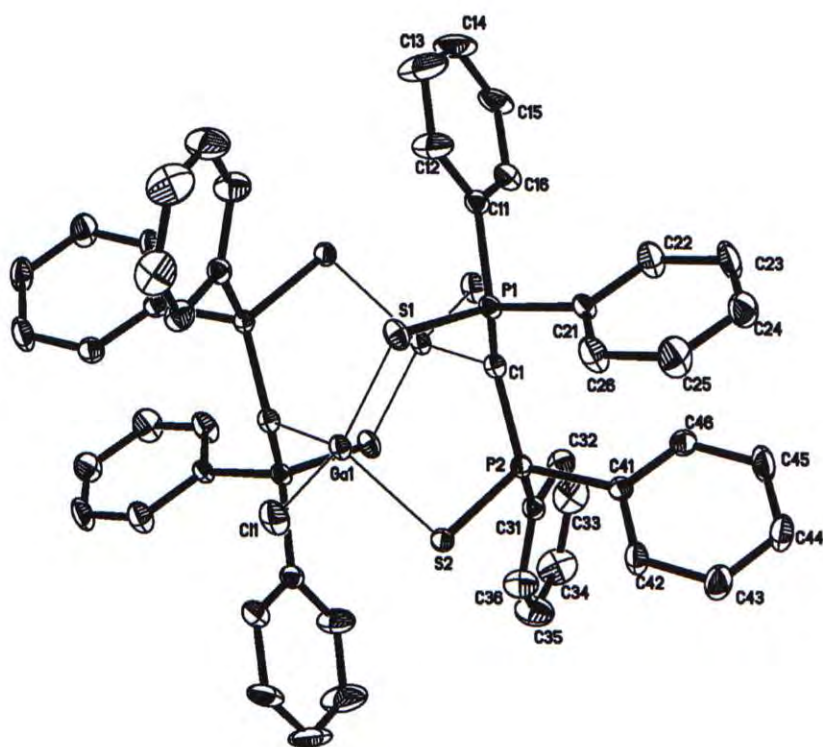


Fig. 3.11 Molecular structure of $[\text{GaCl}\{\text{C}(\text{PPh}_2=\text{S})_2\}]_2$ (**109**) (30% probability ellipsoids)

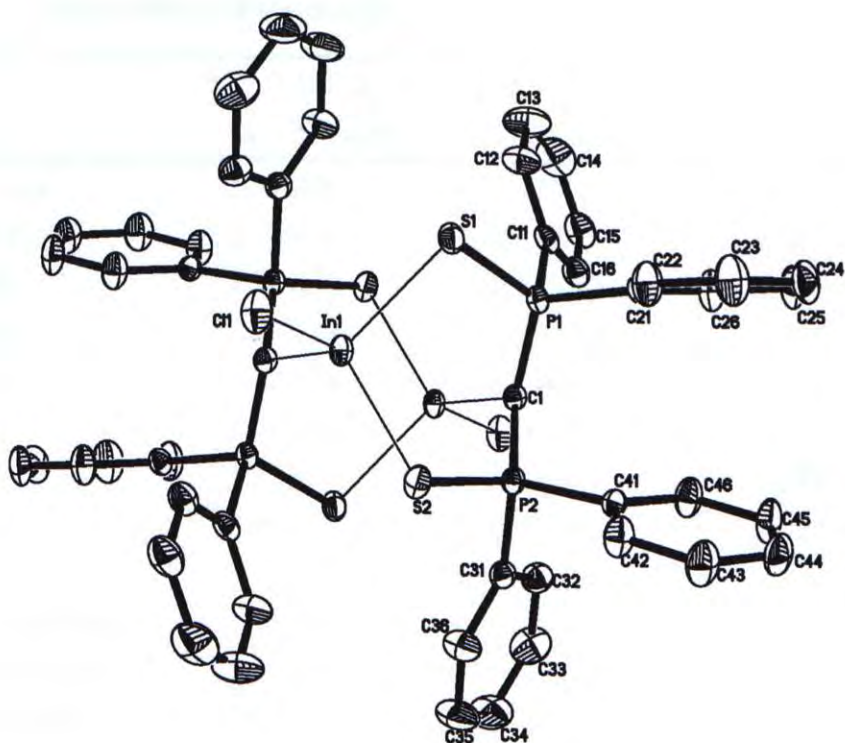


Fig. 3.12 Molecular structure of $[\text{InCl}\{\text{C}(\text{PPh}_2=\text{S})_2\}]_2$ (**110**) (30% probability ellipsoids)

Table 3.2 Selected Bond Distances (Å) and Angles (deg) for Compounds 108-110

	[MCl{C(PPh ₂ =S) ₂ }] ₂		
	M = Al (108)	M = Ga (109)	M = In (110)
M(1)-C(1A)	1.975(2)	1.972(4)	2.173(3)
M(1)-Cl(1)	2.169(1)	2.219(2)	2.410(1)
M(1)-S(1)	2.281(1)	2.294(2)	2.477(1)
M(1)-S(2)	2.291(1)	2.302(2)	2.485(1)
P(1)-C(1)	1.722(2)	1.710(5)	1.723(3)
P(1)-S(1)	2.062(1)	2.054(2)	2.059(1)
P(2)-C(1)	1.724(2)	1.720(5)	1.718(3)
P(2)-S(2)	2.062(1)	2.051(2)	2.057(1)
C(1A)-M(1)-Cl(1)	112.58(8)	112.0(1)	112.2(1)
C(1A)-M(1)-S(1)	116.03(7)	117.4(1)	119.1(1)
Cl(1)-M(1)-S(1)	100.81(4)	99.94(7)	99.68(3)
C(1A)-M(1)-S(2)	116.95(8)	117.9(1)	119.19(8)
Cl(1)-M(1)-S(2)	100.29(4)	99.60(6)	99.61(3)
S(1)-M(1)-S(2)	107.91(4)	107.12(6)	103.70(3)
C(1)-P(1)-S(1)	115.69(8)	116.3(2)	116.9(1)
C(1)-P(2)-S(2)	114.99(9)	115.4(2)	116.5(1)
P(1)-S(1)-M(1)	101.27(4)	101.05(8)	99.14(4)
P(2)-S(2)-M(1)	101.71(3)	101.73(7)	99.41(4)
P(1)-C(1)-P(2)	116.8(1)	117.8(3)	121.1(2)
P(1)-C(1)-M(1A)	118.0(1)	116.9(2)	115.4(2)
P(2)-C(1)-M(1A)	117.1(1)	115.7(2)	115.8(2)

Symmetry transformations used to generate equivalent atoms: 1A (Al, In): -x,-y,-z-1

1A (Ga): -x+1,-y+1,-z+1

3.3 Experimental for Chapter 3

Materials:

AlCl_3 , GaCl_3 and InCl_3 were purchased from Aldrich Chemical Co. and used without further purification.

$[\text{AlCl}\{\text{C}(\text{PPh}_2=\text{S})_2\}]_2$ (**108**).

A solution of **42** (0.63 g, 1.05 mmol) in Et_2O (20 ml) was added slowly to the solution of AlCl_3 (0.07 g, 0.52 mmol) in Et_2O (20 ml) at 0 °C with stirring. The resultant white suspension was raised to ambient temperature and stirred for 48 h. Volatiles were removed under reduced pressure. The residue was extracted with CH_2Cl_2 and filtered.

Addition of THF to filtrate and concentration give **108** as colorless crystals. Yield: 0.25 g (93 %). Mp: 244.2 °C (dec). Anal. Found: C, 57.95; H, 3.79. Calcd for $\text{C}_{25}\text{H}_{20}\text{AlClP}_2\text{S}_2 \cdot \frac{1}{6}\text{CH}_2\text{Cl}_2$: C, 57.78; H, 3.92. ^1H NMR (300 MHz, $\text{THF}-d_8$): δ = 7.29-7.39 (m, 12H, Ph), 7.90-7.97 (m, 8H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, $\text{THF}-d_8$): δ = 128.66 (t, *m*-Ph, $^3J_{\text{P-C}}$ = 6.3 Hz), 131.71 (s, *p*-Ph), 132.58 (t, *o*-Ph, $^2J_{\text{P-C}}$ = 5.3 Hz), 134.34 (d, *ipso*-Ph, $^1J_{\text{P-C}}$ = 85.3 Hz). $^{31}\text{P}\{^1\text{H}\}$ (121.5 MHz, $\text{THF}-d_8$): δ = 32.24.

$[\text{GaCl}\{\text{C}(\text{PPh}_2=\text{S})_2\}]_2$ (**109**).

A solution of **42** (0.63 g, 1.05 mmol) in Et_2O (20 ml) was added slowly to the solution

of GaCl₃ (0.10 g, 0.57 mmol) in Et₂O (20 ml) at 0 °C with stirring. The resultant white suspension was raised to ambient temperature and stirred for 48 h. Volatiles were removed under reduced pressure. The residue was extracted with CH₂Cl₂ and filtered. After adding THF to the filtrate, it was concentrated and allowed to stand for a week to give the *title* compound as colorless crystals. Yield: 0.06 g (21 %). Mp: 279.7 °C (dec). Anal. Found: C, 53.95; H, 3.95. Calcd for C₅₀H₄₀Ga₂Cl₂P₄S₄·¹/₄CH₂Cl₂: C, 53.67 ; H, 3.63. ¹H NMR (400 MHz, THF-*d*₈): δ = 7.29-7.40 (m, 12H, Ph), 7.90-7.95 (m, 8H, Ph). ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈): δ = 128.66 (t, *m*-Ph, ³J_{P-C} = 6.3 Hz), 131.71 (s, *p*-Ph), 132.58 (t, *o*-Ph, ²J_{P-C} = 5.4 Hz), 134.48 (d, *ipso*-Ph, ¹J_{P-C} = 85.6 Hz). ³¹P{¹H} (162.0 MHz, THF-*d*₈): δ = 31.86.

[InCl{C(PPh₂=S)₂}]₂ (110).

A solution of **42** (0.66 g, 1.10 mmol) in Et₂O (20 ml) was added slowly to the solution of InCl₃ (0.11 g, 0.53 mmol) in Et₂O (20 ml) at 0 °C with stirring. The resultant white suspension was raised to ambient temperature and stirred for 48 h. Volatiles were removed under reduced pressure. The residue was extracted with CH₂Cl₂ and filtered. Addition of THF to filtrate and concentration give **110** as colorless crystals. Yield: 0.20 g (64 %). Mp: 227.5 °C (dec). Anal. Found: C, 49.04; H, 3.27. Calcd for C₂₅H₂₀InClP₂S₂·¹/₄CH₂Cl₂: C, 49.07; H, 3.34. ¹H NMR (400 MHz, THF-*d*₈): δ =

7.08-7.41 (m, 12H, Ph), 7.90-7.96 (m, 8H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, THF- d_8): δ
= 128.66 (t, *m*-Ph, $^3J_{\text{P-C}} = 6.4$ Hz), 131.71 (s, *p*-Ph), 132.58 (t, *o*-Ph, $^2J_{\text{P-C}} = 5.4$ Hz),
134.47 (d, *ipso*-Ph, $^1J_{\text{P-C}} = 85.9$ Hz). $^{31}\text{P}\{^1\text{H}\}$ (162.0 MHz, THF- d_8): $\delta = 31.87$.

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Chapter 4 Synthesis of Group 4 Metal Bis- (thiophosphinoyl) Complexes

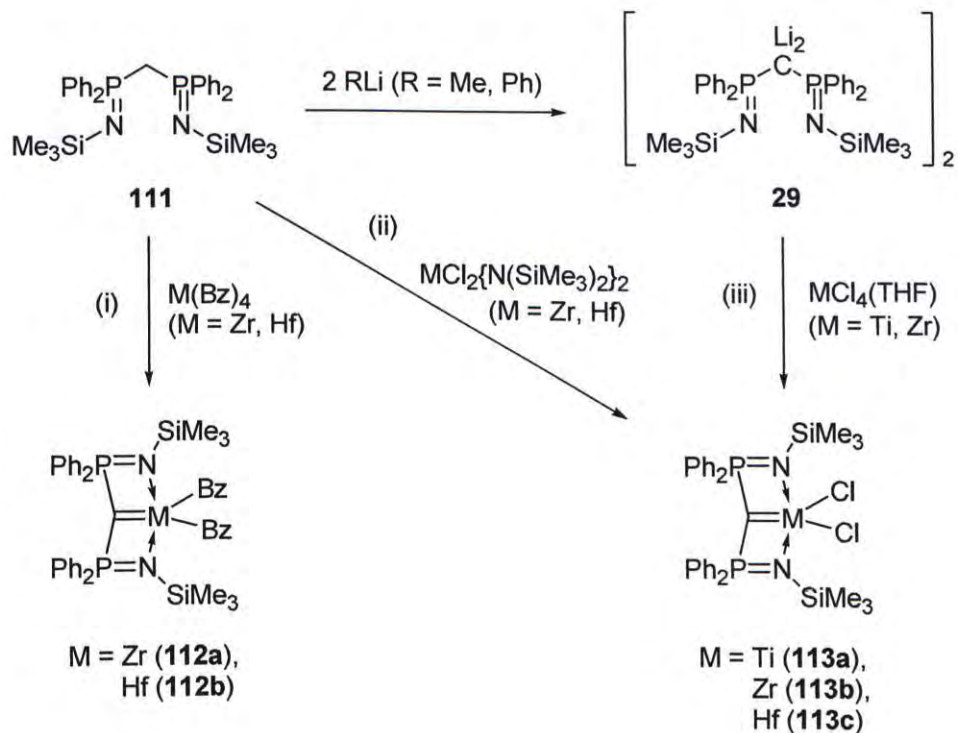
4.1 Introduction

4.1.1 General Aspects of Group 4 Early Transition Metal Complexes

Breslow and coworkers reported on the catalytic activity of bis(cyclopentadienyl)titanium dichloride in Ziegler-Natta polymerization in 1957.¹ This has spurred studies of early metal metallocene catalysts for more than 20 years. Over the past two decades, systems incorporating noncyclopentadienyl ancillary ligands have been studied intensively.² The electronic and steric analogies between phosphinimide ligands and cyclopentadienyl were described by Dehnicke et al.³ and Stephan et al.,⁴ respectively. As the alternatives to the cyclopentadienyl ligands, numerous group 4 early transition metal complexes bearing phosphoranoimine ligand have been reported.

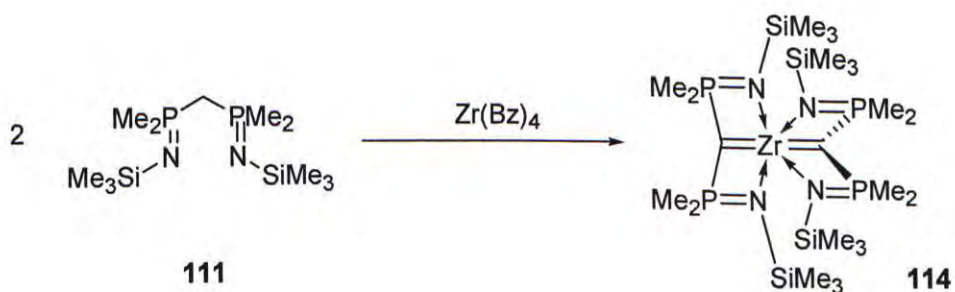
Utilizing bis(phosporanoimido)methane as supporting ligand, Cavell and coworkers have synthesized a series of group 4 metal complexes by (i) alkane elimination, (ii) hexamethyldisilazane elimination and (iii) metathesis reaction (Scheme 4.1).^{5,6}

The acidity of the methylene proton in **111** is enhanced by the strongly electron-withdrawing phosphoranoimine groups and therefore compound **111** can be deprotonated by $M(\text{Bz})_4$ and $M\text{Cl}_2\{\text{N}(\text{SiMe}_3)_2\}_2$ to give $[\text{MBz}_2\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\}]$



Scheme 4.1

(M = Zr (**112a**), Hf (**112b**)) and $[\text{MCl}_2\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\}]$ (M = Zr (**113b**), Hf (**113c**)), respectively.^{7,8} Later, by changing the phenyl substituent into less bulky methyl group, a biscarbene complex $[\text{Zr}\{\text{C}(\text{Me}_2\text{P}=\text{NSiMe}_3)_2\}_2]$ (**114**) was prepared from the reaction between $\text{Zr}(\text{Bz})_4$ and **111** in 1:2 ratio (**Scheme 4.2**).⁹ This result suggested that steric factors play an important role in the formation of the biscarbene complex.



Scheme 4.2

Due to the low thermal stability of titanium precursor, the titanium complex was not accessible by the above synthetic routes. Nevertheless, the dilithium salt of bis(phosphoranoimido)methane **29** was isolated successfully.¹⁰ After that, $[\text{MCl}_2\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\}]$ ($\text{M} = \text{Ti}$ (**113a**), Zr (**113b**)) can be synthesized from the metathesis reaction of the dilithium salt and MCl_4 ($\text{M} = \text{Ti}, \text{Zr}$).¹¹

Our group is interested in the synthetic and catalytic studies of group 4 organometallic complexes. Using different phosphoranoimine ligand, we have synthesized various group 4 metal complexes. For example, $[\text{Zr}\{(\text{Me}_3\text{SiNPPh}_2\text{C})-(\text{Me}_3\text{SiN}=\text{PPh}_2\text{CH}_2)\text{C}_5\text{H}_3\text{N}-2,6\}(\text{NMe}_2)_2]$ (**115**),¹² $[\text{M}\{\text{CH}(\text{R}_2\text{PNSiMe}_3)(2\text{-Py})\}_2\text{Cl}]^+_2$ $[\text{MCl}_6]^{2-}$ ($\text{M} = \text{Zr}, \text{R} = \text{Ph}$ (**116a**), Pr^i (**116b**); $\text{M} = \text{Hf}, \text{R} = \text{Ph}$ (**116c**), Pr^i (**116d**)),¹³

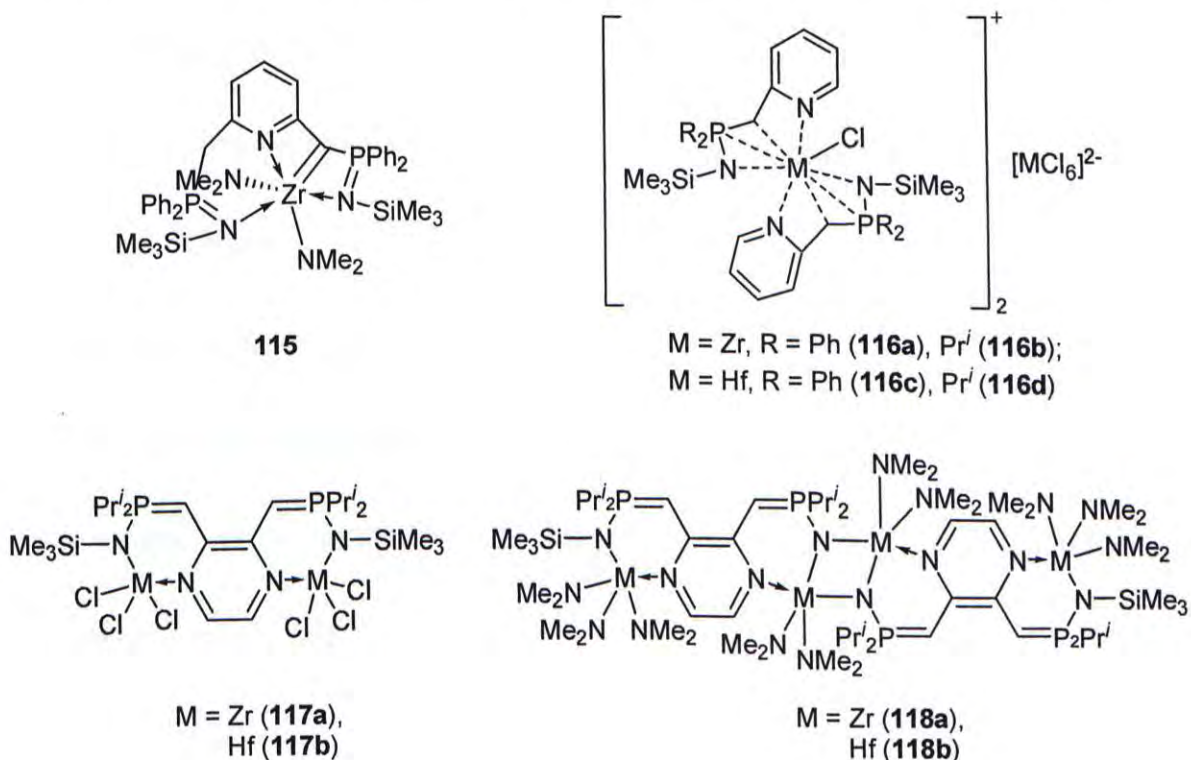
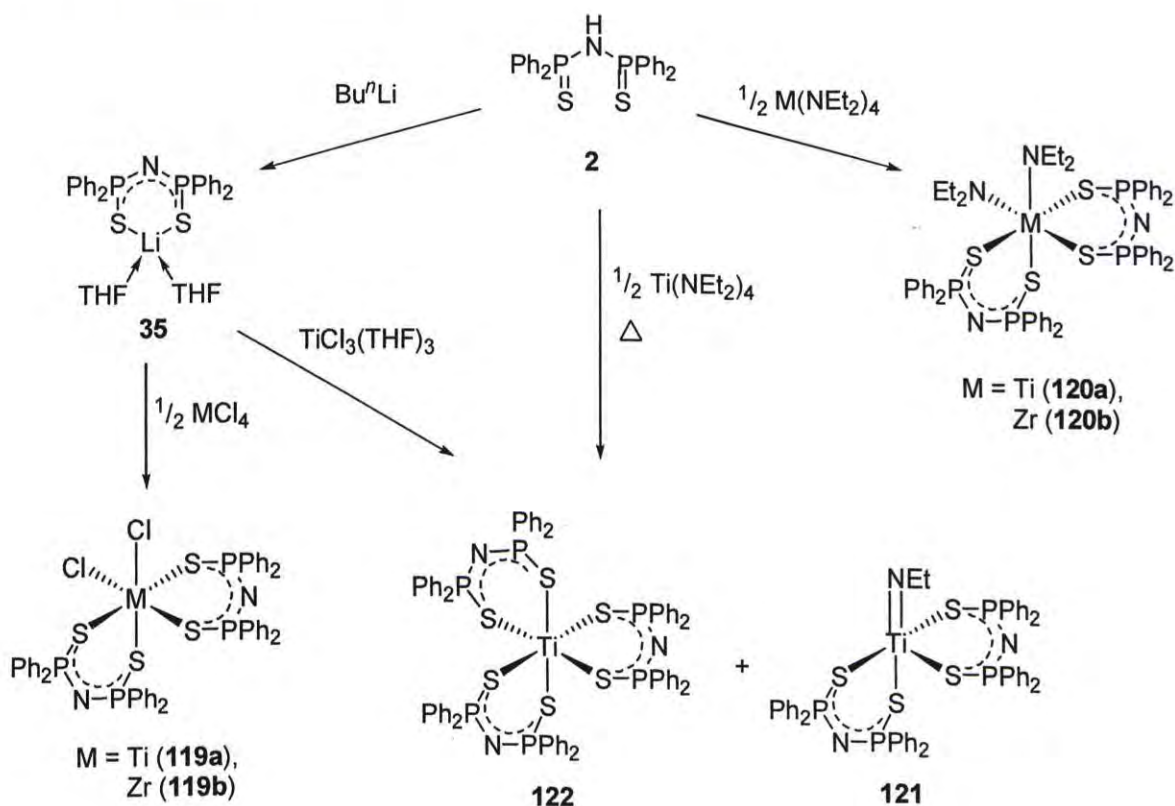


Fig. 4.1

$[\{MCl_3(Me_3SiNPPr'_2CH)\}_2C_4H_2N_{2-2,3}]$ (M = Zr (**117a**), Hf (**117b**)), and $[\mu-M(NMe_2)_2(NPPr'_2CH)C_4H_2N_{2-2,3}(CHPPr'_2NSiMe_3)M(NMe_2)_3]_2$ (M = Zr (**118a**), Hf (**118b**))¹⁴ were reported (Fig 4.1). The catalytic activities of **116-118** towards ethylene polymerization were also investigated.

Recently, the synthetic approach has been extended to the phosphoranosulfides. Esien and coworkers described the synthetic method of a series of group 4 complexes containing different coordination numbers of imidodithiodiphosphinate ligands.¹⁵ The metathesis reaction of lithium salt **35** with half equivalent of MCl_4 (M = Ti, Zr) afforded the disubstituted group 4 metal dichlorides complexes $[\{(Ph_2PS)_2N\}_2MCl_2]$ (M = Ti (**119a**), Zr (**119b**)). In addition, $[\{(Ph_2PS)_2N\}_2M(NEt_2)_2]$ (M = Ti (**120a**), Zr (**120b**)), were obtained from the amine elimination of neutral ligand **2** with half equivalent of $M(NEt_2)_4$. When the reaction of **2** with 0.5 equivalent of $Ti(NEt_2)_4$ was carried out in refluxing toluene, two unexpected products were found. They were bis(imidodithiodiphosphinate)titanium(IV) ethylimido complex (**121**) (major product) and tris(imidodithiodiphosphinate)titanium(III) complex (**122**). It is proposed that **121** was formed via the metathesis elimination of an ethyl moiety of the corresponding bisamido complex and then eliminate NEt_3 . On the other hand, **122** was presumably formed in two steps. Firstly, redistribution of ancillary ligands occurred at high temperature and then followed by reduction of the metal center. Compound **122** may

also be obtained in good yield from the reaction of $\text{TiCl}_3(\text{THF})_3$ with 3 equivalent of lithium salt **35** in THF at reflux temperature. The synthesis of **119-122** is summarized in **Scheme 4.3**. Their catalytic activity in the polymerization of ethylene and propylene was also studied.



Scheme 4.3

Zirconium complexes **123** and **124** derived from bis(diphenylthiophosphino) methane and 1,3-bis(diphenylthiophosphino)indene were reported by Le Floch et al. and Bourissou et al., respectively.^{16,17} In these two compounds, the metal is bonded to the ligands with *S,C,S'*-chelating fashion. DFT calculations revealed that there is a weak π -interaction between Zr and C in **123** and even none in **124**. The Zr–C bond is highly

polarized toward the carbon atom.

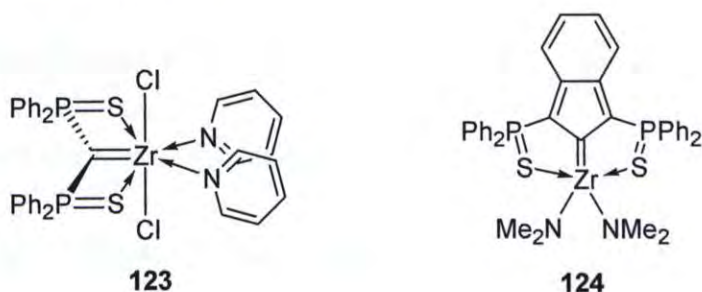


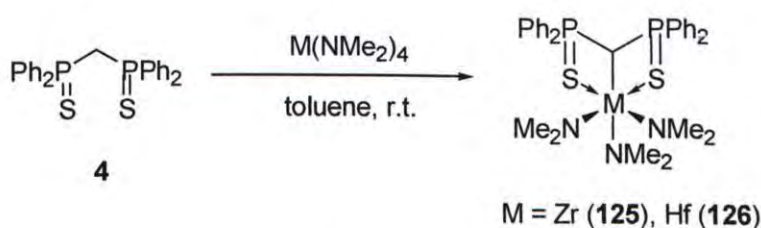
Fig. 4.2

The development of thiophosphinoyl complexes of group 4 early transition metal has been known only a few years ago. Like phosphoranoimines, thiophosphinoyl ligands are able to stabilize the metal center by donation from sulfur atoms. In the coming section, the synthesis of several group 4 metal complexes from the neutral ligand **4** and the dianionic ligand **43** will be presented.

4.1 Results and Discussion

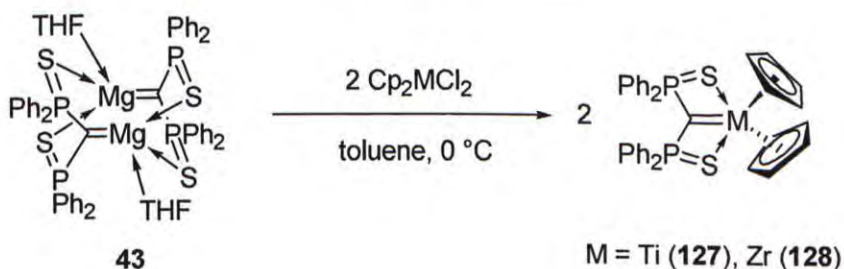
4.1.2 Synthesis of Group 4 Metal Bis(thiophosphinoyl) Complexes

Metalation of the neutral ligand **4** with equimolar amount of $M(\text{NMe}_2)_4$ ($M = \text{Zr}, \text{Hf}$) yielded group 4 (dimethyl)amido complexes $[M(\text{NMe}_2)_3\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$ ($M = \text{Zr}$ (**125**), Hf (**126**)), respectively (**Scheme 4.4**). The products were formed via the elimination of one equivalent of HNMe_2 .



Scheme 4.4

Metathesis reaction of **43** with two equivalents of Cp_2MCl_2 ($M = \text{Ti}, \text{Zr}$) afforded titanium and zirconium carbene complex $[\text{Cp}_2\text{M}=\text{C}(\text{PPh}_2=\text{S})_2]$ ($M = \text{Ti}$ (**127**), Zr (**128**)) (**Scheme 4.5**). In this reaction, compound **43** acts as a carbene ligand transfer reagent. Compound **128** can also be prepared from dianionic lithium salt.¹⁶ The structure of **128** has been confirmed by X-ray crystallography,¹⁸ however attempts to isolate single crystals of **127** for X-ray structure analysis were unsuccessful.



Scheme 4.5

4.1.3 Spectroscopic Properties of 125-128

Compounds **125-128** are air and moisture sensitive crystalline solids. Compounds **125**, **126** and **128** are yellow, and compound **127** is deep red. Compounds **125** and **126** are soluble in THF but sparingly soluble in toluene while compound **127** and **128** are soluble in THF, CH₂Cl₂, Et₂O, and toluene. They have been characterized by NMR spectroscopy and elemental analysis.

A very similar pattern was observed for the ¹H and ¹³C NMR spectra of **125** and **126**. They displayed signals assignable to the bis(thiophosphinoyl)methanide ligand and (dimethyl)imido groups. The ¹H NMR spectra showed a triplet at δ 2.81 ppm ($J_{P-H} = 4.4$ Hz) for **125** and δ 2.83 ppm ($J_{P-H} = 4.8$ Hz) for **126** for the methanide proton. These chemical shift values appear more upfielded than that in neutral ligand (δ 3.97 ppm). This is indicative of interaction between CH and the metal. One sharp singlet was observed for (dimethyl)imido groups in ¹H NMR [δ 2.62 (**125**); δ 2.65 (**126**)] and ¹³C NMR [δ 44.20 (**125**); δ 43.86 ppm (**126**)] spectra. It reveals the three (dimethyl)imido groups having the same environment.

The ¹³C NMR spectra of **125** and **126** are normal. The ³¹P NMR spectra displayed one signal [δ 32.85 (**125**); δ 31.97 ppm (**126**)] for these two compounds, which is consistent with one phosphorus environment in the solid-state structure.

In addition, the ¹H and ¹³C NMR spectra of **127** and **128** in C₆D₆ have been

obtained and showed a very similar pattern of signal due to ligand backbone. Surprisingly, the signals of both carbenic carbon [δ 57.58 ppm, $J_{P-C} = 74.7$ Hz (**127**); δ 32.47 ppm, $J_{P-C} = 87.2$ Hz (**128**)] are much more upfield than those recorded for carbene complexes of titanium (260-300 ppm)¹⁹ and zirconium (230-300 ppm).²⁰

The symmetrical structures of **127** and **128** were confirmed by ³¹P NMR data which displayed one sharp signal [δ 15.58 (**127**); δ 20.06 ppm (**128**)].

4.1.4 Molecular Structures of [Hf(NMe₂)₃{CH(PPh₂=S)₂}] (**126**)

The molecular structure of **126** is shown in Fig. 4.3. Selected bond distances (Å) and angles (deg) are listed in Table 4.1. In compound **126**, the ligand bonded to hafnium in a tridentate manner through coordination of the methanide carbon and two thio sulfur atoms. The hafnium environment is highly distorted octahedral which be presumably because of the constrained *fac* coordination of the ligand. The two strained four-membered (Hf, C(1), P(1), S(1) and Hf, C(1), P(2), S(2)) rings has a dihedral angle of $\sim 105^\circ$. The Hf–C bond distance of 2.524(10) Å is longer than that of 2.437(6) Å in [HfCl₂(HN(*p*-tolyl)) {HC(Ph₂P=NSiMe₃)₂- κ C, κ^2 N,N'}] and those in other hafnium hydrocarbyl complexes (averaged Hf–C distances: 2.300 {Hf-CH₂(R)}; 2.387 Å {Hf-CH(R₂)}).²¹ The reason may be the delocalization of electrons within the four-membered rings which is indicative of the difference of P–C and P–S bond lengths

from the neutral ligand **4**.²²

The three Hf–N bonds distances are very similar and the averaged value of 2.043 Å is close to those in [Me₂NHf(Me₃SiNCH₂CH₂)₃N] (2.048(6) Å)²³ and [Hf{η²-(Pr^tN)₂CNMe₂}₂(NMe₂)₂] (2.078 Å).²⁴ The averaged Hf–S bond distance of 2.852 Å agrees well with that of 2.8741 Å in [Bz₂Hf{(SCH₂S)(4,6-But₂-C₆H₂O)₂}]²⁵ and that of 2.798 Å in [Hf(μ-tbop-κ³O,S,O)₂Me₂(AlMe₂)₂] where tbopH₂ = 2,2'-thiobis{4-(1,1,3,3-tetramethylbutyl)phenol}.²⁶

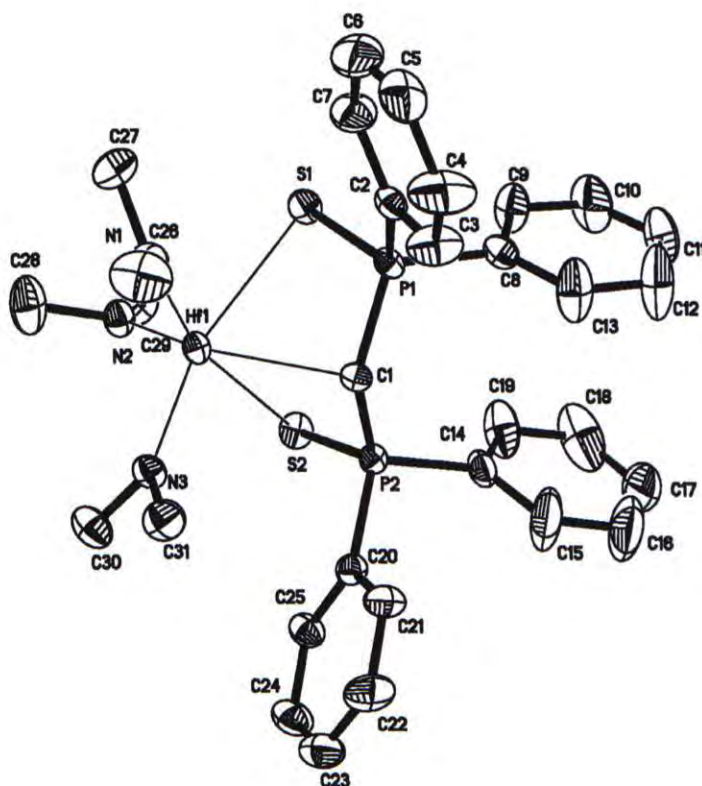


Fig. 4.3 Molecular structure of [Hf(NMe₂)₃{CH(PPh₂=S)₂}] (**126**) (30% probability ellipsoids)

Table 4.1 Selected Bond Distances (Å) and Angles (deg) for Compound 126

Hf(1)-N(2)	2.040(9)	Hf(1)-C(1)	2.524(1)
Hf(1)-N(3)	2.043(8)	P(1)-C(1)	1.769(9)
Hf(1)-N(1)	2.046(9)	P(1)-S(1)	1.984(4)
Hf(1)-S(1)	2.831(3)	P(2)-C(1)	1.758(1)
Hf(1)-S(2)	2.873(3)	P(2)-S(2)	1.976(4)
C(1)-Hf(1)-S(1)	69.3(2)	P(1)-S(1)-Hf(1)	81.2(1)
C(1)-Hf(1)-S(2)	67.6(2)	P(2)-S(2)-Hf(1)	80.5(1)
S(1)-Hf(1)-S(2)	79.8(1)	P(2)-C(1)-P(1)	122.2(5)
C(1)-P(1)-S(1)	108.9(3)	P(2)-C(1)-Hf(1)	95.3(4)
C(1)-P(2)-S(2)	107.7(4)	P(1)-C(1)-Hf(1)	94.6(4)

4.2 Experimental for Chapter 4

Materials:

(S=PPh₂)₂CH₂ was prepared according to the literature procedures.²⁷ Zr(NMe₂)₄, Hf(NMe₂)₄, Cp₂TiCl₂ and Cp₂ZrCl₂ were purchased from Aldrich Chemical Co. and used without further purification.

[Zr(NMe₂)₃{CH(PPh₂=S)₂}] (125).

A solution of Zr(NMe₂)₄ (0.47 g, 1.75 mmol) in toluene (10 ml) was added slowly to a solution of (S=PPh₂)₂CH₂ (0.77 g, 1.71 mmol) in toluene (10 ml). The reaction mixture was stirred at room temperature for 3 days. Volatiles were removed under reduced pressure and the residue was extracted with THF. After filtration and concentration of filtrate, **125** was obtained as pale yellow crystals. Yield: 0.72 g (63%). Mp: 179.2-180.4 °C. Anal. Found: C, 55.03; H, 5.49; N, 6.23. Calcd for C₃₁H₃₉N₃P₂S₂Zr: C, 55.49; H, 5.86; N, 6.26. ¹H NMR (400 MHz, THF-*d*₈): δ = 2.62 (s, 18H, NMe₂), 2.81 (t, 1H, CH, *J*_{P-H} = 4.4 Hz), 7.15-7.24 (m, 12H, Ph), 7.68-7.74 (m, 8H, Ph). ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈): δ = 13.51 (t, PCP, *J*_{P-C} = 51.3 Hz), 44.20 (NMe₂), 128.62, 128.74, 131.13, 131.19, 131.24, 131.42, 131.49, 131.61, 135.78-136.62 (dd, *J* = 79.3 Hz, *J* = 5.2 Hz) (Ph). ³¹P{¹H} NMR (162.0 MHz, THF-*d*₈): δ = 32.85.

[Hf(NMe₂)₃{CH(PPh₂=S)₂}] (126).

A solution of Hf(NMe₂)₄ (0.88 g, 2.48 mmol) in toluene (10 ml) was added slowly to a solution of (S=PPh₂)₂CH₂ (1.19 g, 2.65 mmol) in toluene (10 ml). The reaction mixture was stirred at room temperature for 3 days. Volatiles were removed under reduced pressure and the residue was extracted with THF. After filtration and concentration of filtrate, **126** was obtained as pale yellow crystals. Yield: 1.36 g (72%). Mp: 190.3-193.2 °C. Anal. Found: C, 49.39; H, 5.35; N, 5.58. Calcd for C₃₁H₃₉HfN₃P₂S₂: C, 49.11; H, 5.18; N, 5.54. ¹H NMR (400 MHz, THF-*d*₈): δ = 2.65 (s, 18H, NMe₂), 2.83 (t, 1H, CH, *J*_{P-H} = 4.8 Hz), 7.15-7.25 (m, 12H, Ph), 7.68-7.73 (m, 8H, Ph). ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈): δ = 13.19 (t, PCP, *J*_{P-C} = 48.1 Hz), 43.86 (NMe₂), 128.66, 128.78, 131.06, 131.17, 131.23, 131.72, 132.53, 132.59, 135.92-136.76 (dd, *J* = 79.1 Hz, *J* = 5.2 Hz) (Ph). ³¹P{¹H} NMR (162.0 MHz, THF-*d*₈): δ = 31.97.

[Cp₂Ti=C(PPh₂=S)₂] (127).

A solution of **43** (1.02 g, 0.82 mmol) in toluene (20 ml) was added to a solution of Cp₂TiCl₂ (0.20 g, 0.80 mmol) in toluene (10 ml) at 0 °C. The resultant deep red suspension was stirred at ambient temperature for 48 h. The precipitate was filtered. Adding CH₂Cl₂ (*ca.* 5 ml) to the filtrate, followed by concentration yield **127** as red crystalline solids. Yield: 0.16 g (33%). Mp: 156.2 °C (dec). Anal. Found: C, 66.17; H,

5.22. Calcd for $C_{35}H_{30}P_2S_2Ti^{1/8}$ toluene: C, 66.42; H, 4.80. 1H NMR (400 MHz, C_6D_6): $\delta = 6.18$ (s, 10H, Cp-*H*), 6.93-6.95 (m, 8H, Ph), 7.58-7.95 (m, 12H, Ph); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): $\delta = 57.58$ (t, PCP, $J_{P-C} = 74.7$ Hz), 116.44 (Cp-C), 128.34, 130.21, 131.36 (t, $J = 6.0$ Hz), 140.18 (d, $J = 73.4$) (Ph); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): $\delta = 15.58$.

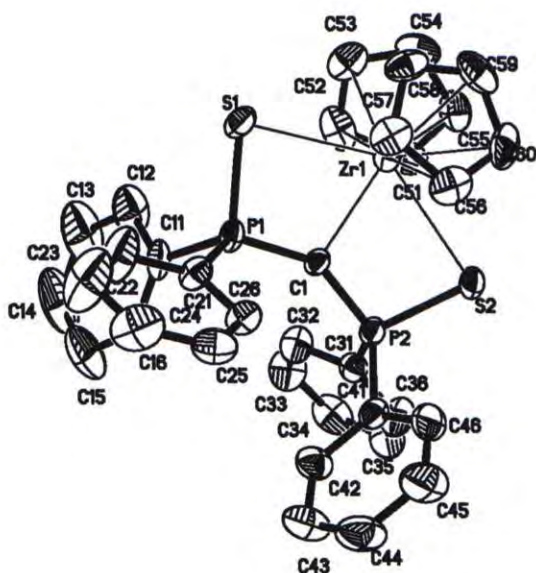
[Cp₂Zr=C(PPh₂=S)₂] (128).

A solution of **43** (0.54 g, 0.44 mmol) in toluene (20 ml) was added to a solution of Cp₂ZrCl₂ (0.24 g, 0.82 mmol) in toluene (10 ml) at 0 °C. The resultant yellow suspension was stirred at ambient temperature for 48 h. The precipitate was filtered. Adding CH₂Cl₂ (ca. 5 ml) to the filtrate, followed by concentration yield yellow crystals of **128**. Yield: 0.46 g (84%). Mp: 228.9-232.5 °C. Anal. Found: C, 64.70; H, 4.94. Calcd for $C_{35}H_{30}P_2S_2Zr^{1/2}$ toluene: C, 64.77; H, 4.80. 1H NMR (300 MHz, C_6D_6): $\delta = 6.12$ (s, 10H, Cp-*H*), 6.93-6.98 (m, 8H, Ph), 7.56-7.62 ppm (m, 12H, Ph); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): $\delta = 32.47$ (t, PCP, $J_{P-C} = 87.2$ Hz), 113.19 (Cp-C), 128.52, 130.45, 130.87 (d, $J = 12.3$ Hz), 140.17 (d, $J = 72.7$ Hz) (Ph); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): $\delta = 20.06$.

4.3 References for Chapter 4

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- 18 Crystal data for **128** (C₃₅H₃₀P₂S₂Zr): *M* = 667.87, crystal size 0.40 × 0.30 × 0.20 mm, monoclinic, space group C2/c, *a* = 18.077(6), *b* = 15.860(5), *c* = 38.750(12) Å, β = 102.166(6)°, *V* = 10860(6) Å³, *Z* = 12, *d*_{calc} = 1.255 g cm⁻³, μ = 0.528 mm⁻¹, *2* θ range = 1.08 to 25.00°, *F*(000) = 4104, 9566 independent reflections [*R*_{int} = 0.0673], *R*1 = 0.0567, *wR*2 = 0.1400 (*I* > 2 σ (*I*)), largest diff. peak and hole 0.510 and -3.579 eÅ⁻³.
- Molecular Structure is shown as follow.



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Appendix I

A. General Procedures

All experiments were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over and freshly distilled, under nitrogen, from CaH₂ (hexane, CH₂Cl₂), sodium benzophenone ketyl (THF, Et₂O), sodium/potassium alloy (pentane, toluene) and degassed twice by freeze-thaw cycle prior to use.

B. Physical and Analytical Measurements

(i) *Spectroscopic Measurements*

¹H NMR spectra were recorded at 300.13 MHz using a Brüker DPX-300 spectrometer or at 400.13 MHz using a Brüker DPX-400 spectrometer. Chemical shifts were referenced to δ 7.15 ppm for CDCl₃, δ 7.26 ppm for C₆D₆ and δ 3.58 ppm for THF-*d*₈.

¹³C{¹H} NMR spectra were recorded at 75.49 MHz using a Brüker DPX-300 spectrometer or at 100.62 MHz using a Brüker DPX-400 spectrometer.. Chemical shifts were referenced to δ 128.00 ppm for C₆D₆ and δ 67.40 ppm for THF-*d*₈.

³¹P{¹H} NMR spectra were recorded at 121.49 MHz using a Brüker DPX-300 spectrometer or at 161.98 MHz using a Brüker DPX-400 spectrometer.. Chemical shifts were referenced to δ 0.00 ppm for 85% H₃PO₄.

$^{77}\text{Se}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra were recorded using Varian Inova 400 spectrometer at 76.28 MHz and 149.14 MHz, respectively and chemical shifts were referenced to δ 0.00 ppm for Me_2Se and δ 0.00 ppm for SnMe_4 , respectively.

(ii) *Microanalysis*

Elemental (C, H, N) analysis was performed by MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, Middlesex, U.K.

(iii) *Melting Point Measurements*

Melting points were recorded on an Electrochemical Melting Point Apparatus and were uncorrected.

C. X-ray Crystallographic Determination

All single crystals were sealed in Lindemann glass capillaries under nitrogen.

X-ray data of **42-43**, **74-75**, **78-82**, **108-110** and **126** were collected at 293 K on a Brüker SMART CCD diffractometer using Mo $K\alpha$ radiation. An empirical absorption correction was applied using the SADABS program.¹ The structures were solved by direct methods, and non-hydrogen atoms were located from difference-Fourier maps and refined anisotropically by full-matrix least-squares on F^2 using the SHELX-TL

program package.² Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factor calculations. Crystal data are summarized in Appendix II.

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Appendix II

Table A.1. Selected Crystallographic Data for Compounds **42**, **43**, **74** and **75**

Table A.2. Selected Crystallographic Data for Compounds **78-81**

Table A.3. Selected Crystallographic Data for Compounds **82**, **108-110** and **126**

Table A.1. Selected Crystallographic Data for Compounds 42, 43, 74 and 75

	42	43	74	75
Formula	$C_{33}H_{39}LiO_2P_2S_2$	$C_{66}H_{72}Mg_2O_4P_4S_4$	$C_{54}H_{48}OP_4S_4Sn_2$	$C_{54}H_{48}OP_4Pb_2S_4$
Fw	600.64	1229.98	1202.42	1379.42
Color	Colorless	Yellow	Yellow	Yellow
Cryst. Syst.	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	P $\bar{1}$	P2 $_1$ /c	C2/c	C2/c
<i>a</i> (Å)	10.4369(18)	10.420(4)	19.962(3)	19.971(4)
<i>b</i> (Å)	10.6649(18)	13.181(5)	10.1888(16)	10.1578(18)
<i>c</i> (Å)	17.073(3)	23.464(9)	25.461(4)	25.641(5)
α (deg)	81.831(4)	90	90	90
β (deg)	73.596(3)	96.986	94.424(3)	94.569(5)
γ (deg)	69.205(3)	90	90	90
<i>V</i> (Å ³)	1702.4(5)	3199(2)	5163.0(14)	5185.0(17)
<i>Z</i>	2	2	4	4
<i>d</i> _{calcd} (g cm ⁻³)	1.172	1.277	1.547	1.767
μ (mm ⁻¹)	0.277	0.315	1.292	6.808
F(000)	636	1296	2416	2672
Cryst size (mm)	0.50 × 0.40 × 0.30	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.30	0.50 × 0.40 × 0.40
2 θ range (deg)	1.24 to 25.00	1.75 to 28.05	1.60 to 28.04	1.59 to 25.00
Index range	-12 ≤ <i>h</i> ≤ 9, -12 ≤ <i>k</i> ≤ 12, -20 ≤ <i>l</i> ≤ 20	-13 ≤ <i>h</i> ≤ 13, -16 ≤ <i>k</i> ≤ 17, -26 ≤ <i>l</i> ≤ 30	-26 ≤ <i>h</i> ≤ 26, -13 ≤ <i>k</i> ≤ 13, -27 ≤ <i>l</i> ≤ 33	-22 ≤ <i>h</i> ≤ 23, -12 ≤ <i>k</i> ≤ 12, -30 ≤ <i>l</i> ≤ 25
No. of rflns collected	9291	21358	17047	13384
No. of indep rflns	5975	7736	6212	4559
R1, wR2 (<i>I</i> > 2(σ)/ <i>I</i>)	0.0785, 0.2216	0.0666, 0.1645	0.0373, 0.0850	0.0456, 0.1189
R1, wR2 (all data)	0.1015, 0.2406	0.1906, 0.2355	0.0615, 0.0974	0.0563, 0.1267
Goodness of fit, <i>F</i> ²	1.075	1.012	1.049	1.003
No. of data/restraints/params	5975 / 9 / 361	7736 / 10 / 361	6261 / 0 / 294	4559 / 0 / 294
Largest diff peaks, eÅ ⁻³	0.739 to -0.426	0.468 to -0.302	0.930 to -0.324	3.117 to -2.297

Table A.2. Selected Crystallographic Data for Compounds 78-81

	78	79	80	81
Formula	C ₃₀ H ₃₀ O _{1.25} P ₂ PbS ₃	C ₂₅ H ₂₀ P ₂ PbS ₂ Se	C ₂₅ H ₂₁ ClGeP ₂ S ₂	C ₂₅ H ₂₁ ClP ₂ S ₂ Sn
Fw	775.85	732.62	555.52	601.62
Color	Red	Red	Colorless	Colorless
Cryst. Syst.	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	C2/c	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
<i>a</i> (Å)	18.988(5)	13.3170(19)	16.213(3)	16.563(3)
<i>b</i> (Å)	18.080(4)	10.7311(15)	8.9053(14)	8.7424(14)
<i>c</i> (Å)	22.732(6)	18.023(3)	18.961(3)	18.206(3)
α (deg)	90	90	90	90
β (deg)	111.820(4)	107.877(3)	113.280(3)	99.773(3)
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	7245(3)	2451.3(6)	2514.8(7)	2598.0(7)
<i>Z</i>	8	4	4	4
<i>d</i> _{calcd} (g cm ⁻³)	1.423	1.985	1.467	1.538
μ (mm ⁻¹)	4.938	8.680	1.629	1.381
F(000)	3040	1392	1128	1200
Cryst size (mm)	0.50 × 0.40 × 0.30	0.20 × 0.20 × 0.10	0.30 × 0.20 × 0.20	0.40 × 0.30 × 0.20
2 θ range (deg)	1.61 to 25.00	1.68 to 25.00	1.40 to 28.02	1.54 to 28.04
Index range	-22 ≤ <i>h</i> ≤ 22, -16 ≤ <i>k</i> ≤ 21, -26 ≤ <i>l</i> ≤ 26	-15 ≤ <i>h</i> ≤ 14, -12 ≤ <i>k</i> ≤ 12, -18 ≤ <i>l</i> ≤ 21	-18 ≤ <i>h</i> ≤ 21, -11 ≤ <i>k</i> ≤ 11, -24 ≤ <i>l</i> ≤ 24	-19 ≤ <i>h</i> ≤ 21, -11 ≤ <i>k</i> ≤ 11, -23 ≤ <i>l</i> ≤ 24
No. of rflns collected	19229	13056	16730	16985
No. of indep rflns	6378	4312	6055	6258
R1, $wR2$ (<i>I</i> > 2(σ)/ <i>I</i>)	0.0453, 0.1478	0.0559, 0.1153	0.0639, 0.1833	0.0340, 0.0840
R1, $wR2$ (all data)	0.0711, 0.1665	0.1539, 0.1635	0.1579, 0.2348	0.0474, 0.0940
Goodness of fit, <i>F</i> ²	1.106	0.992	1.079	1.029
No. of data/restraints/params	6378 / 90 / 393	4312 / 6 / 280	6055 / 0 / 280	6258 / 0 / 281
Largest diff peaks, eÅ ⁻³	1.182 to -1.002	1.292 to -1.018	0.739 to -0.517	1.105 to -0.747

Table A.3. Selected Crystallographic Data for Compounds 82, 108-110 and 126

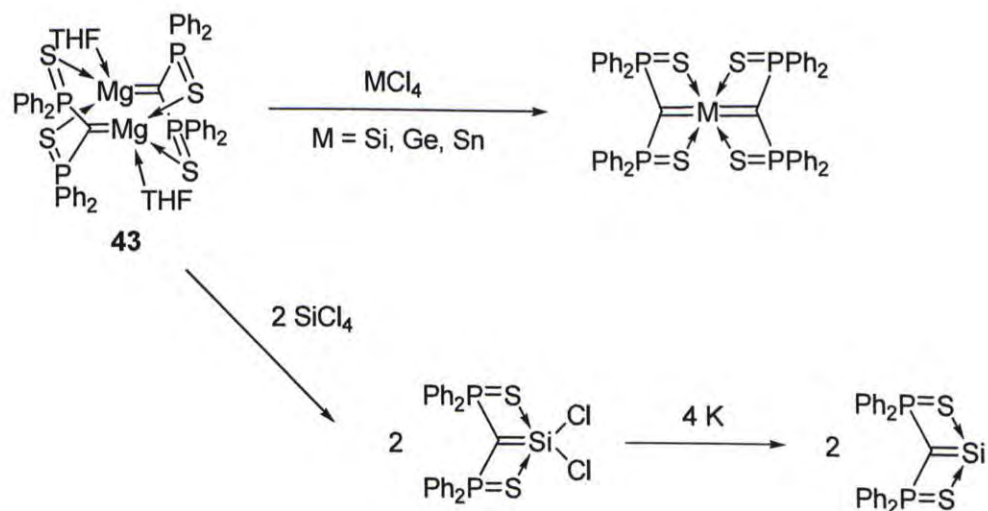
	82	108	109	110	126
Formula	$C_{66}H_{74}Cl_2Ge_2O_4P_4S_6$	$C_{25}H_{20}AlClP_2S_2$	$C_{50}H_{40}Cl_2Ga_2P_4S_4$	$C_{25}H_{20}ClInP_2S_2$	$C_{31}H_{39}HN_3P_2S_2$
Fw	1463.57	508.90	1103.28	596.74	758.20
Color	Colorless	Colorless	Colorless	Colorless	Pale yellow
Cryst. Syst.	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space Group	C2/c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	Pbca
<i>a</i> (Å)	19.263(3)	11.5467(16)	11.557(8)	11.6775(17)	13.034(6)
<i>b</i> (Å)	13.8672(19)	19.957(3)	19.892(14)	20.458(3)	35.031(15)
<i>c</i> (Å)	28.132(4)	12.4806(17)	12.418(8)	12.5404(19)	14.336(6)
α (deg)	90	90	90	90	90
β (deg)	93.501(3)	105.873(2)	106.293(11)	108.184(2)	90
γ (deg)	90	90	90	90	90
<i>V</i> (Å ³)	7500.8(18)	2766.4(6)	2740(3)	2846.3(7)	6545(5)
<i>Z</i>	4	4	2	4	8
d_{calc} (g cm ⁻³)	1.296	1.222	1.337	1.393	1.539
μ (mm ⁻¹)	1.167	0.447	1.381	1.193	3.437
F(000)	3024	1048	1120	1192	3040
Cryst size (mm)	$0.40 \times 0.30 \times 0.20$	$0.40 \times 0.30 \times 0.20$	$0.40 \times 0.30 \times 0.20$	$0.40 \times 0.30 \times 0.20$	$0.40 \times 0.30 \times 0.20$
2 θ range (deg)	1.45 to 28.03	1.83 to 25.00	1.84 to 25.00	1.84 to 25.00	1.84 to 25.00
Index range	$-25 \leq h \leq 20$	$-10 \leq h \leq 13$	$-13 \leq h \leq 13$	$-13 \leq h \leq 13$	$-15 \leq h \leq 15$,
	$-18 \leq k \leq 18$	$-19 \leq k \leq 23$	$-23 \leq k \leq 23$	$-20 \leq k \leq 24$	$-41 \leq k \leq 41$,
	$-30 \leq l \leq 37$	$-14 \leq l \leq 14$	$-14 \leq l \leq 8$	$-14 \leq l \leq 14$	$-17 \leq l \leq 13$
No. of rflns collected	25404	14857	14297	15234	32336
No. of indep rflns	9094	4867	4819	5013	5755
R1, $wR2$ ($I > 2(\sigma)I$)	0.0573, 0.1366	0.0388, 0.0973	0.0524, 0.1126	0.0323, 0.0785	0.0636, 0.1519
R1, $wR2$ (all data)	0.1410, 0.1598	0.0537, 0.1036	0.0875, 0.1235	0.0425, 0.0826	0.0880, 0.1710
Goodness of fit, F^2	0.829	0.993	0.901	0.978	1.076
No. of data/restraints/params	9094 / 0 / 379	4867 / 0 / 280	4819 / 0 / 280	5013 / 0 / 280	5755 / 0 / 352
Largest diff peaks, eÅ ⁻³	0.529 to -0.436	0.458 to -0.233	0.834 to -0.523	0.805 to -0.386	2.087 to -4.712

Appendix III

A. Future Work

A.1 Synthesis of Group 14 Metal Complexes from Magnesium Dianion

The magnesium complex (**43**) is the first compound with a Mg=C interaction. Also two group 4 metal carbene complexes $[\text{Cp}_2\text{M}=\text{C}(\text{PPh}_2=\text{S})_2]$ (M = Ti (**127**), Zr (**128**)) were synthesized from it (**Scheme 4.5**). It is suggested that compound **43** can be a precursor for preparing group 14 2-metalalene (**Scheme A.1**). Moreover, metathesis reaction of **43** with two equivalents of SiCl_4 and then reduction by potassium may lead to the formation of silavinylidene.

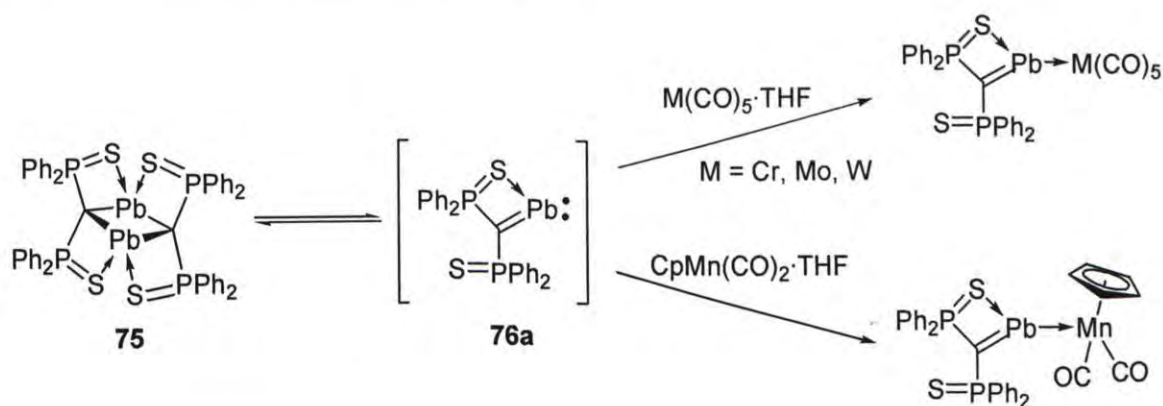


Scheme A.1

A.2 Reaction of 1,3-Diplumbacyclobutane with Transition Metal Carbonyls

From the NMR studies (P.33-34) and the reaction of 1,3-diplumbacyclobutane **75**

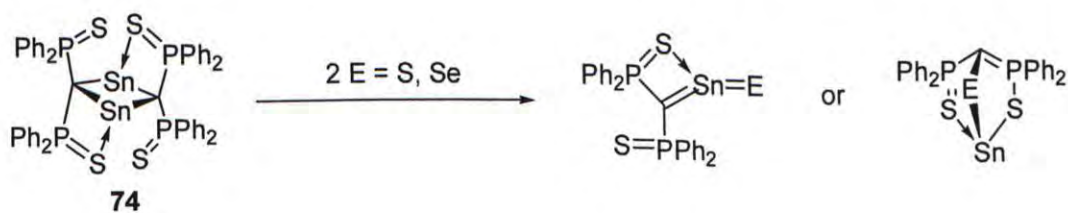
with chalcogens (**Scheme 2.6**), it is proposed that plumbavinylidene may exist in the solution. To demonstrate this, reaction of compound **75** with various transition metal carbonyls should be conducted (**Scheme A.2**).



Scheme A.2

A.3 Reaction of 1,3-Distannacyclobutane with Chalcogens

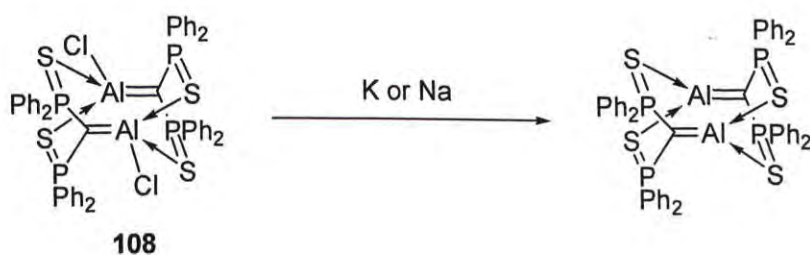
The reaction of 1,3-diplumbacyclobutane **75** with elemental chalcogens gave two lead(II) chalcogenate complexes $[PbE\{C(Ph_2P=S)_2\}]$ ($E = S$ (**78**), Se (**79**)) instead of group 14 ketone or ketene analogues ($R_2Pb=E$ or $>C=Pb=E$) (**Scheme 2.6**). This may be due to the “inert pair effect”. Similar reaction should be performed on 1,3-distannacyclobutane **74** (**Scheme A.3**) and comparison can then be made.



Scheme A.3

A.4 Reduction of Group 13 Metal Complexes

Aluminium bis(thiophosphinoyl)methanediide chloride (**108**) was synthesized from the reaction of AlCl_3 with lithium salt **42** in 1:2 ratio. Further reduction of compound **108** should be carried out. It is potential precursor for aluminium(II) compound as the proposed product can gain extra stability from the conjugated double bonds (**Scheme A.4**).



Scheme A.4

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