Synthesis of base-stabilized heavier low valent group 14 complexes

Chia, Siew Peng

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**SYNTHESIS OF BASE-STABILIZED HEAVIER LOW
VALENT GROUP 14 COMPLEXES**

CHIA SIEW PENG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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VALENT GROUP 14 COMPLEXES**

CHIA SIEW PENG

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School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
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Abbreviations

Ad	adamantyl
Ar	2,6-diisopropylphenyl
br	broad
calcd	calculated
Cp	cyclopentadienyl
d	doublet
dec.	decomposed
DME	dimethoxyethane
Et	ethyl
Et ₂ O	diethyl ether
<i>i</i> Pr	isopropyl
IR	infrared
m	multiplet
Mamx	2,4-di- <i>tert</i> -butyl-6-(<i>N,N</i> -dimethylaminomethyl)phenyl
Me	methyl
MeLi	methyllithium
Mes	2,4,6-trimethylphenyl
M.p.	melting point
<i>n</i> BuLi	<i>n</i> -butyllithium
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
<i>t</i> Bu	<i>tert</i> -butyl
s	singlet

t	triplet
<i>t</i>	tert
THF	tetrahydrofuran
sept	septet
UV-vis	ultraviolet-visible
Å	Angstrom
δ	chemical shift
λ_{max}	maximum wavelength

List of Synthesized Compounds

Formula	Numbering Scheme	Page	Structure
$C_{29}H_{43}ClGeN_2O_{0.33}$	1	19
$C_{29}H_{43}ClN_2Sn$	2	19
$C_{70}H_{92}Cl_2Ge_2N_4$	3	24
$C_{56}H_{78}Ge_2N_4$	4	24
$C_{28}H_{39}ClN_2Sn$	6	27
$C_{32}H_{39}ClGeN_2$	7	43
$C_{16}H_2ClN_2Sn$	8	43
$C_{32}H_{39}BrN_2Pb$	9	43

Formula	Numbering Scheme	Page	Structure
$C_{64}H_{78}Ge_2N_4$	10	47	
$C_{32}H_{46}N_4Sn_2$	11	47	
$C_{38}H_{55}GeKN_4$	12	53	
$C_{20}H_{31}KN_2OSn$	13	53	
$C_{48}H_{71}LiN_2O_4Pb$	14	59	
$C_{64}H_{78}N_4Pb_2$	15	59	
$C_{136}H_{138}Ge_2N_4P_4Pd_2$	18	65	
$C_{38}H_{58}Cl_2GeN_2OSn_2$	19	89	

Formula	Numbering Scheme	Page	Structure
$C_{32}H_{39}GeN_5$	20	91	
$C_{43}H_{54}GeN_5P$	21	93	

General Introduction

Stable heavier group 14 alkyne analogues of composition REER (R = bulky terphenyl or silyl ligand; E = Si, Ge, Sn, Pb) have attracted much attention in the past decades due to their unique structures and reactivities.^[1] Recent theoretical studies and UV/Vis spectroscopy showed that they adopt a multiply bonded structure **M** in solution (Chart 2.1).^[2] Reduction of heavier group 14 alkyne analogues is one of the well-studied reactivities.

Recently, a series of novel base-stabilized group 14 element(I) dimers [R $\ddot{\text{E}}$ - $\ddot{\text{E}}$ R] (E = Si, Ge, Sn, R = amidinate, guanidinate, β -diketiminato, N-functionalized aryl etc.) was synthesized.^[3] They comprise a $\ddot{\text{E}}$ - $\ddot{\text{E}}$ single bond and a lone pair of electrons on each E atom. Their structures resemble the singly bonded structure **S** (Chart 2.1). Thus, they are considered as base-stabilized heavier alkyne analogues. However reduction of these complexes is rare.

The fact that heavier group 14 alkyne analogues can be singly or doubly reduced prompted us to investigate the reduction of intramolecular base-stabilized group 14 element(I) dimers. Two ligands: 1) 1,4-diaza-2,3-dimethyl-1,3-butadiene (DAB) ligand and 2) 2,6-diiminophenyl ligand were targeted for the synthesis of new base-stabilized group 14 element(I) dimers. DAB ligand is tunable and has flexible coordination mode while 2,6-diiminophenyl ligand is a NCN pincer ligand with two imino moieties used as donor groups. These two ligands have been widely utilized in transition metals,^[4] hence we believe they are potential to be useful ligand for stabilizing main-group elements.

Beside investigating on the reduction of base-stabilized group 14 element(I) dimers, we are also interested in isolating other functionalized germylenes.

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Abstract

This thesis describes the synthesis of heavier low valent group 14 complexes stabilized by 1,4-diaza-2,3-dimethyl-1,3-butadiene (**L**¹ and **L**²) and 2,6-diiminophenyl (**L**³ and **L**⁴).

Chapter 1 describes the syntheses and structures of heteroleptic germanium(II) and tin(II) chlorides supported by derived anionic ligands of 1,4-diaza-2,3-dimethyl-1,3-butadiene (**L**¹ and **L**²). The reaction of **L**¹ with GeCl₂·dioxane or SnCl₂, afforded [L¹ECl] [**L**¹ = ArN=C(Me)C(Me)₂-NAr; Ar = 2,6-diisopropylphenyl, E = Ge (**1**), Sn (**2**)]. The reaction of **L**² with GeCl₂·dioxane in Et₂O afforded [{C(=CH)-NAr}{C(Me)=NAr}]₂(GeCl)₂ (**3**). In contrast, the reaction of **L**² with SnCl₂, afforded [L²SnCl] (**4**).

Chapter 2 describes the synthesis and the structures of group 14 element(I) dimers $[L'EEL']$ [$L' = L^3$, $E = \text{Ge}$ (**10**), Pb (**15**); $L' = L^4$, $E = \text{Sn}$ (**11**)] and their reduction to afford the respective group 14 element(I) anions **12**, **14** and **13**. The treatment of **10** and **11** with excess KC_8 , afforded the germylidenide anion $[\text{L}^3\text{GeK}\cdot\text{TMEDA}]$ (**12**) and stannylidenide anion $[\text{L}^4\text{SnK}]$ (**13**) respectively. The first base-stabilized lead(I) dimer **15** was synthesized by oxidation of plumbylidenide anion **14** with SnCl_2 . The reduction of **15** with lithium afforded the aromatic plumbylidenide anion **14**. The reactivity of **12** towards $(\text{PPh}_3)_2\text{PdCl}_2$ which afforded the dimeric palladium(0) germylene complex $[2-(\text{CH}=\text{NAr})-6-(\text{CH}=\text{NAr})\text{C}_6\text{H}_3]_2[\text{GePd}(\text{PPh}_2)_2]_2$ (**18**) is also discussed.

Chapter 3 describes the reaction of $[L^3GeCl]$ (**5**) with Me_3SnOH and NaN_3 in THF to afford the $[[L^3GeOH(SnMe_3Cl)] \cdot SnMe_3Cl]$ (**17**) and $[L^3GeN_3]$ (**18**), respectively. Compound **18** underwent an uncatalysed 1,3-dipolar cycloaddition reaction with 1-adamantyl phosphalkyne to afford the $[L^3Ge\{N_3C(Ad)P\}]$ (**19**).

CHAPTER 1

Heteroleptic Germanium(II) and Tin(II) Chlorides Supported by Derived Anionic Ligands of 1,4-Diaza-2,3-dimethyl-1,3- butadiene *

Introduction

Enormous effort has been invested in the design of ligands with new electronic and steric features for improving the reactivities of metals. Various multidentate ancillary ligands with ketimine donors such as aminotroponimines, amidinates, guanidines, β -diketimines, bis(imino)phenyl have been developed (Chart 1.1).^[1] The cooperation of a metal ion and the ligands leads to an amazingly broad array of geometries and reactivities of the corresponding complexes.^[2] Another member of such family is 1,4-diaza-1,3-butadiene ligands (DABs).^[3] Due to their inherent tunable and flexible coordination modes, DABs are widely utilized not only for transition metals and f-block metals,^[4] but also for s-block and p-block main-group elements.^[5] The resulting complexes exhibit extraordinary electronic structures and catalytic activities.

Our interest in the DAB family of ligands was initiated by the reactivity of 1,4-diaza-2,3-dimethyl-1,3-butadiene **L** with lithium reagents to give new anionic ligands **L¹Li** and **L²Li** (Chart 1.2). **L¹Li** was prepared by the nucleophilic attack at one of the imine carbon

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atom of **L** with MeLi, whereas **L²Li** was afforded by the deprotonation of a methyl group at the imine carbon of **L** with LiNiPr₂.^[6] Different reactivity of **L** with lithium reagents is probably due to the basicity and steric effect of the latter, which determines the nucleophilic attack or the proton deprotonation. We anticipate that both lithiated species **L¹Li** and **L²Li** may have potential to be useful ligands for stabilizing main-group elements.

Chart 1.1. (a) Aminotroponimine; (b, c) amidinates; (d) guanidnates; (e) β -diketiminates; (f-h) bis(imino)phenyl ligands.

Chart 1.2. 1,4-diaza-1,3-butadiene (**L**) ligand and the lithiated imine/amide complexes **L¹Li** and **L²Li**.

We are interested in employing the derived anionic ligands **L¹** and **L²** to synthesize base-stabilized germanium(II) and tin(II) chlorides. It is because Ge(I) and Sn(I) complexes containing a functionalized substituent such as H, OH have been demonstrated that they

can be versatile building blocks for the synthesis of new low-valent germanium and tin derivatives and synthons for the activation of small molecules.^[7]

Herein, we report the synthesis and structures of organogermanium(II) and tin(II) chloride complexes $[L^1ECl]$ [$L^1 = ArN=C(Me)C(Me)_2-NAr$; $E = Ge$ (**1**), Sn (**2**), $[\{C(=CH)-NAr\}\{C(Me)=NAr\}]_2(GeCl)_2$ (**3**) and $[L^2SnCl]$ (**6**).

Results and Discussion

Scheme 1.1. Synthesis of **1** and **2**.

Synthesis of [L¹ECl] (E = Ge, Sn). The reaction of **L** with MeLi in Et₂O at 0°C, followed by treatment with GeCl₂·dioxane or SnCl₂, afforded [L¹ECl] (E = Ge (**1**), Sn (**2**), Scheme 1.1) respectively. Compounds **1** and **2** were isolated as highly air- and moisture-sensitive yellow crystalline solids. They are soluble in hydrocarbon solvents and have been characterized by NMR spectroscopy. The ¹H NMR spectra of **1** and **2** show two singlets (**1**: δ 0.78 and 1.38; **2**: δ 0.83 and 1.39 ppm) correspond to the non-equivalent *gem*-dimethyl groups and a singlet (**1**: δ 1.71; **2**: 1.80 ppm) attributable to the methyl group at the imine skeleton. For compound **1**, eight doublets at δ 0.88 - 1.55 ppm and four septets at δ 3.16 - 4.52 ppm for the *i*Pr groups of Ar substituents are observed. For compound **2**, five broad signals at δ 0.91 - 1.51 ppm and four broad signals at δ 2.97 - 4.57 ppm for the *i*Pr groups of the Ar substituents are observed. The ¹H NMR spectra of **1** and **2** also show one set of resonances due to the phenyl protons. Moreover, the ¹¹⁹Sn{¹H} NMR spectrum of **2** displays a singlet at δ -40 ppm, which lies between that of reported heteroleptic tin(II) halides supported by ketimine-containing ligands (δ -266 – 69.7 ppm) (Chart 1.3).^[2d, 8]

(a)

(b)

(c) R = 2,6-Me₂C₆H₃

(d) R = Ar

(e) R = SiMe₃(f) R = GePh₃

(g)

(h) R = Ar, R' = 4-*t*BuC₆H₄(i) R = *t*Bu, R' = Ph(j) R = *i*Pr, R' = N(SiMe₃)₂(k) R = Cy, R' = N(SiMe₃)₂(l) R = EDC, R' = N(SiMe₃)₂(m) R = *p*Tol, R' = N(SiMe₃)₂(n) R = *i*Pr, R' = *n*Bu(o) R = Cy, R' = *n*Bu(p) R = Ar, R' = *n*Bu(q) R = Ar, R' = *t*Bu

Chart 1.3. Examples of heteroleptic tin(II) halides supported by ketimine-containing ligands. ¹¹⁹Sn{¹H} NMR [ppm]: (a) δ -246.7; (b) δ -205.4; (c) δ -264; (d) δ -266; (e) δ -64.6; (f) δ -89.7; (g) δ -235.5; (h) δ 28.4; (i) δ 29.6; (j) δ -51.1; (k) δ -51.0; (l) δ -250.6; (m) δ -220.0; (n) δ 69.1; (o) δ 69.7; (p) δ -124.0; (q) δ 2.97.

Compounds **1** and **2** have been characterized by X-ray crystallography. The molecular structure of **1** (Figure 1.1) shows that the Ge atom adopts a distorted trigonal-pyramidal geometry (sum of bond angles: 275.95°), which is comparable with that of [2,6-(CH=NAr)₂C₆H₃GeCl] (**5**; 267.40°),^[2g] [2-(CH=NAr)-5,6-(OCH₂O)C₆H₃GeCl] (268.76°; Chart 1.4b),^[2g] [(Mamx)GeCl] (Mamx = 2,4-di-*tert*-butyl-6-(*N,N*-dimethylaminomethyl)phenyl, 270.26°; Chart 1.4c)^[9] and [{dpp-bian(*n*Bu)}GeCl] (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene, 277.20°; Chart 1.4d).^[10] The geometry at the Ge atom indicates that it is almost non-hybridized and possesses lone pair

electrons with high *s* character. The N1-Ge1 (1.8804(17) Å) bond is comparable with that in [Me₂Si(*Nt*Bu)(*Nt*BuH)GeCl] (1.894(3) Å) (Chart 1.4e)^[11] and [(Me₃Si)₂N]₂Ge] (1.873(5) and 1.878(5) Å).^[12] The Ge1-N2 bond (2.0634(18) Å) is comparable with the N-Ge dative bonds in *N*-donor-stabilized chlorogermynes such as [{C₅H₄N-2-C(SiMe₃)₂}GeCl] (2.082(4), 2.075(4) Å; Chart 1.4f)^[13] and [(Mamx)GeCl] (2.0936(13) Å).^[9] The Ge1-Cl1 (2.3397(6) Å) is comparable with that in bis(chlorogermyl) complex [ClGe(dipp-tip)GeCl] (dipp-tip = 1,2-tetrakis[(2,6-diisopropylphenyl)imino]pyracene, 2.278(2)Å; Chart 1.4g)^[14] and [{dpp-bian(*n*Bu)}GeCl] (2.3500(7) Å).^[10]

Figure 1.1. Molecular structure of **1** (ellipsoids set at 50% probability). Hydrogen atoms and the disorder dioxane molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1-Cl1 2.3397(6), Ge1-N1 1.8804(17), Ge1-N2 2.0634(18), C15-N1 1.457(3), C15-C16 1.512(3), C16-N2 1.290(3), C16-C17 1.487(4), C15-C14 1.558(4), C15-C13 1.538(3), N1-Ge1-N2 79.99(7), N1-Ge1-Cl1 102.04(6), N2-Ge1-Cl1 93.93(6), C15-N1-Ge1 119.83(13), C16-C15-N1 106.48(18), N2-C16-C15 116.7(2), C16-N2-Ge1 114.88(15).

Chart 1.4. (a) **5**; (b) [2-(CH=NAr)-5,6-(OCH₂O)C₆H₃GeCl]; (c) [(Mamx)GeCl]; (d) [{dpp-bian(*n*Bu)}GeCl]; (e) [Me₂Si(N*t*Bu)(N*t*BuH)GeCl]; (f) [{C₅H₄N-2-C(SiMe₃)₂}GeCl]; (g) [ClGe(dipp-tip)GeCl].

The molecular structure of **2** (Figure 1.2) shows that the Sn atom adopts a distorted trigonal-pyramidal geometry (sum of bond angles: 265.61°), which is comparable with [SnCl{(S)-box-Ph}] (266.55°, (S)-box-Ph = 1,1-bis[(4*S*)-4-phenyl-1,3-oxazolin-2-yl]ethane; Chart 1.3b).^[8h] The geometry of the Sn atom indicates that it is almost non-hybridized and possesses lone pair electrons with high *s* character. The Sn1-Cl1 (2.5011(5) Å) is longer than that in base-stabilized chlorostannylenes (2.440(5)-2.488(3) Å) (Chart 1.5),^[15] but is shorter than that in [2,6-(CH=N*t*Bu)₂C₆H₃SnCl] (**6**; 2.5624(5) Å).^[2h] The Sn1-N2 (2.0676(13) Å) bond is slightly shorter than that in [SnCl{(S)-box-Ph}] (2.134(3) Å),^[8h] [DIPY-SnCl] (DIPY = dipyrromethene, 2.1802(16) Å; Chart 1.3a)^[8b] and [C₆H₄-2-CH₂N(CH₃)₂-1-N(GePh₃)SnCl] (2.107(2) Å; Chart 1.3f).^[8d] The Sn1-N1 bond (2.2741(13) Å) is significantly longer than the Sn1-N2 bond, which indicates that the Sn1-N1 bond is a dative bond.

Figure 1.2. Molecular structure of **2** (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1-Cl1 2.5011(5), Sn1-N1 2.2741(13), Sn1-N2 2.0676(13), C13-N1 1.2897(19), C13-C15 1.523(2), C15-N2 1.456(2), C13-C14 1.488(2), C15-C16 1.537(2), C15-C17 1.555(2), N1-Sn1-N2 73.62(5), N1-Sn1-Cl1 89.68(3), N2-Sn1-Cl1 102.31(4), C13-N1-Sn1 116.32(10), C15-C13-N1 117.15(14), N2-C15-C13 108.35(12), C15-N2-Sn1 120.39(10).

Chart 1.5. Examples of base-stabilized chlorostannylenes. Sn-Cl bond lengths [Å]: (a) 2.488(3); (b) 2.446(5); (c) 2.4708(8); (d) 2.6286(3); (e) 2.8544(3); (f) 2.473(9).

Scheme 1.2. Synthesis of **3** - **4**.

Synthesis of $[\{C(=CH)-NAr\}\{C(Me)=NAr\}]_2(GeCl)_2$ (3**).** The reaction of L^2Li with $GeCl_2 \cdot dioxane$ in Et_2O at $0^\circ C$ afforded a mixture of $[\{C(=CH)-NAr\}\{C(Me)=NAr\}]_2(GeCl)_2$ (**3**), $[\{C(CH_2)-NAr\}\{C(Me)=NAr\}Ge]_2$ (**4**) and L^2H (**5**, Scheme 3),^[16] which was confirmed by NMR spectroscopy. Other by-products such as $[L^2_2Ge]$ cannot be observed. The reaction mixture was then filtered and the filtrate was concentrated to give a mixture of **3** and **4** as highly air- and moisture-sensitive yellow crystalline solids. The mother liquor was further concentrated to afford pure compound **3** as yellow crystals. However, an attempt to isolate pure compound **4** by recrystallization failed. Moreover, the reaction of L^2Li with $GeCl_2 \cdot dioxane$ in THF at -78 or $0^\circ C$ afforded compound **3** as major product, which was confirmed by NMR spectroscopy. Compounds **3** and **4** (Figures 1.3 and 1.4) have been analysed by X-ray crystallography. However, the mechanism for the formation of **3** and **4** is unknown as yet. We propose that the reaction may proceed through the formation of an intermediate $[L^2GeCl]$, which may then undergo

a ligand coupling reaction with L^2Li and $GeCl_2$.dioxane, followed by rearrangement to form **3** -**5**.

Compound **3** was isolated as a highly air- and moisture-sensitive yellow crystalline solid, which is soluble in hydrocarbon solvents. The 1H NMR spectrum shows two doublets at δ 1.17 and 1.25 ppm and one septet at δ 3.07 ppm corresponding to the *i*Pr group of the Ar substituents. It also shows a singlet at δ 1.79 ppm and a broad signal at δ 5.93 ppm corresponding to the methyl protons at the imine skeleton and methine protons, respectively. Moreover, there is a multiplet at δ 7.06-7.26 ppm for the phenyl protons. Furthermore, the 1H NMR spectrum acquired at -60 °C is same as that at room temperature.

With the NMR data of compound **3** on hand, the 1H NMR data of **4** in the mixture of **3** and **4** can be identified. Compound **4** shows four doublets at δ 1.12, 1.21, 1.24 and 1.25 ppm and two septets at δ 2.97 and 3.07 ppm attributable to the *i*Pr group of the Ar substituents. It also shows a singlet at δ 1.33 and 2.43 ppm corresponding to the methyl protons at the imine skeleton and methylene protons, respectively. Moreover, there is a multiplet at δ 7.07-7.25 ppm for the phenyl protons.

The molecular structure of **3** (Figure 1.3) shows that the Ge atoms adopt a distorted trigonal-pyramidal geometry (sum of angles: 273.24°) which is comparable with that of compound **1**. This indicates that the Ge atoms possess lone pair electrons with high s character. The N1-Ge1 (1.931(2) Å), Ge1-Cl1 (2.2924(9) Å), N2-Ge1 (2.019(2) Å) bonds are comparable to those in compound **1** (N1-Ge1: 1.8804(17); Ge1-Cl1: 2.3397(6); N2-Ge1: 2.0634(18) Å). The C14-C14A (1.414(6) Å), C13-C15 (1.467(4) Å) and C13-C14 (1.385(4) Å) bonds are shorter than typical C-C single bond (1.53 Å), but are longer than

typical C-C double bond (1.34 Å). The C15-N2 (1.308(4) Å) bond lies between typical C-N single bond (1.47 Å) and C-N double bond (1.27 Å). The results indicate that there is an appreciable electron delocalization in the ligand skeleton.

Figure 1.3. Molecular structure of **3** (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1-Cl1 2.2924(9), Ge1-N1 1.931(2), Ge1-N2 2.019(2), C13-N1 1.366(4), C13-C15 1.467(4), C15-N2 1.308(4), C15-C16 1.494(4), C13-C14 1.385(4), C14-C14A 1.414(6), Ge1A-Cl1A 2.2924(9), Ge1A-N1A 1.931(2), Ge1A-N2A 2.019(2), C13A-N1A 1.366(4), C13A-C15A 1.467(4), C15A-N2A 1.308(4), C15A-C16A 1.494(4), C13A-C14A 1.385(4), C14-C14A 1.414(6), N1-Ge1-N2 79.57(10), N1-Ge1-Cl1 97.91(8), N2-Ge1-Cl1 95.76(7), C13-N1-Ge1 117.83(19), C15-C13-N1 112.1(2), N2-C15-C13 114.7(3), C15-N2-Ge1 115.7(2), C13-C14-C14A 127.9(3), N1A-Ge1A-N2A 79.57(10), N1A-Ge1A-Cl1A 97.91(8), N2A-Ge1A-Cl1A 95.76(7), C13A-N1A-Ge1A 117.83(19), C15A-C13A-N1A 112.1(2), N2A-C15A-C13A 114.7(3), C15A-N2A-Ge1A 115.7(2), C13A-C14A-C14 127.9(3).

Figure 1.4. Molecular structure of **4** (ellipsoids set at 50% probability). Hydrogen atoms except H16A and H16B atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1-N1 1.859(6), Ge1-N2 1.872(6), C13-N1 1.395(9), C13-C15 1.367(10), C15-N2 1.396(9), C13-C14 1.509(10), C15-C16 1.492(10), C16-C16A 1.508(14), N1-Ge1-N2 83.4(3), C13-N1-Ge1 125.1(5), C15-C13-N1 113.6(7), N2-C15-C13 113.6(6), C15-N2-Ge1 114.5(5), C15-C16-C16A 112.3(8).

In the molecular structure of **4** (Figure 1.4), the bite angle N1-Ge1-N2 angle ($83.4(3)^\circ$) is comparable with that of the *N*-heterocyclic germylenes derived from 1,2-bis(arylimino)acenaphthenes ($85.0(2) - 85.2(1)^\circ$).^[17] Moreover, the Ge-N, N-C and C-C bonds in the metallacycle Ge1-N1-C13-C15-N2 are similar to those in the *N*-heterocyclic germylenes (Ge-N: average 1.886 Å, N-C: average 1.375 Å, C-C: average 1.388 Å).^[17] The C16-C16A bond (1.492(10) Å) is a C-C single bond.

Synthesis of [L²SnCl] (6**).** The reaction of **L** with Li*Ni*Pr₂ in Et₂O at 0°C, followed by treatment with SnCl₂, afforded [L²SnCl] (**6**, Scheme 1.2). Compound **6** was isolated as a highly air- and moisture-sensitive yellow crystalline solid, which is soluble in hydrocarbon solvents. The ¹H NMR spectrum displays one set of resonances for the *i*Pr substituents and two signals (δ 3.90 and 4.88 ppm) for vinylic protons. The ¹¹⁹Sn{¹H}

NMR resonance of **6** (δ -88 ppm) is comparable with that of **2**. Single crystals of **6** have been analyzed by X-ray crystallography, but the X-ray crystal structure shows serious disordering (Figure 1.5), in which the methyl group (C1/C1A) is disordered over two positions with an occupancy of 0.5. This results in averaging the bond lengths of the ligand and these data is improper for any meaningful discussion. Although there is a disorder, it is still clear to observe that the Sn atom is coordinated with two nitrogen atoms of the ligand and the chlorine atom, which adopts a distorted trigonal pyramidal geometry. An attempt to isolate single crystals without the disorder failed.

Figure 1.5. Molecular structure of **6** (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond length [$\text{\AA}$] and angles [$^\circ$]: Sn1-Cl1 2.4723(5), Sn1-N1 2.1851(10), Sn1-N1A 2.1851(10), C2-N1 1.3325(15), C2A-N1A 1.3325(15), C2-C2A 1.480(2), C2-C1A 1.368(12), C2A-C1B 1.368(12), N1-Sn1-N1A 73.72(5), N1-Sn1-Cl1 93.48(3), N1A-Sn1-Cl1 93.48(3), C2-N1-Sn1 117.27(7), C2A-C2-N1 115.36(6), N1A-C2A-C2 115.36(6), C2A-N1A-Sn1 117.27(7).

Conclusion

Heteroleptic germanium(II) and tin(II) chlorides supported by derived anionic ligands of 1,4-diaza-2,3-dimethyl-1,3-butadiene were synthesized by the reaction of **L** with lithium reagents and group 14 metal(II) chlorides. The X-ray crystal structures of **1 – 3** and **6** show that the germanium(II) or tin(II) atom is bonded to the bidentate ligand and chlorine atom, which adopts a distorted trigonal pyramidal geometry. The results indicate that the Ge and Sn atoms possess lone pair electrons with high *s* character. Attempts in synthesizing the Ge(I) and Sn(I) dimers supported by 1,4-diaza-2,3-dimethyl-1,3-butadiene ligand failed with mixture of unidentified products formed and cannot be isolated.

Experimental Section

All manipulations were carried out under an inert atmosphere of argon by using standard Schlenk techniques. Solvents were dried over and distilled over Na/K alloy prior to use. **L**¹ and **L**² were prepared as described in the literature.^[3] The ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to SiMe₄ for ¹H and ¹³C and SnMe₄ for ¹¹⁹Sn. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

[L¹GeCl] (1). MeLi (0.75 ml, 1.6 M in Et₂O, 1.2 mmol) was added dropwise to a stirring solution of **L** (0.41 g, 1.01 mmol) in Et₂O (10 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1h. The resulting yellow solution was then added dropwise to a solution of GeCl₂.dioxane (0.27 g, 1.17 mmol) in Et₂O (5 mL) at –78 °C. The resulting red suspension was warmed to room temperature and stirred for 15 h. After filtration and concentration of the filtrate, **1** was obtained as yellow crystals. Yield: 0.35 g (65 %). M.p. 184 °C. Elemental analysis (%) calcd for C₂₉H₄₃ClGeN₂: C 65.98, H 8.22, N 5.31. Found: C 65.64, H 12.65, N 5.13; ¹H NMR (395.9 MHz, C₆D₆, 25 °C): δ 0.78 (s, 3H, (CH₃)₂C-N), 0.89 (d, ³J_{H-H} = 6.8 Hz, 3H, CH(CH₃)₂), 1.10 (d, ³J_{H-H} = 7.2 Hz, 3H, CH(CH₃)₂), 1.16 (d, ³J_{H-H} = 6.8 Hz, 3H, CH(CH₃)₂), 1.20 (d, ³J_{H-H} = 6.8 Hz, 3H, CH(CH₃)₂), 1.23 (d, ³J_{H-H} = 6.8 Hz, 3H, CH(CH₃)₂), 1.38 (s, 3H, (CH₃)₂C-N), 1.43 (d, ³J_{H-H} = 7.2 Hz, 3H, CH(CH₃)₂), 1.44 (d, ³J_{H-H} = 6.8 Hz, 3H, CH(CH₃)₂), 1.54 (d, ³J_{H-H} = 6.81 Hz, 3H, CH(CH₃)₂), 1.71 (s, 3H, (CH₃)C=N), 3.16 (sept, ³J_{H-H} = 6.8 Hz, 1H, CH(CH₃)₂), 3.25 (sept, ³J_{H-H} = 6.8 Hz, 1H, CH(CH₃)₂), 3.40 (sept, ³J_{H-H} = 6.8 Hz, 1H, CH(CH₃)₂), 4.52 (sept, ³J_{H-H} = 6.8 Hz, 1H, CH(CH₃)₂), 7.00-7.31 ppm (m, 6H, aryl); ¹³C{¹H} NMR (99.6 MHz, C₆D₆, 25 °C): δ 17.95, 23.04, 23.30, 24.12, 24.24, 24.55, 24.67, 26.70, 28.19, 28.21, 28.34, 28.41, 29.46, 29.63, 29.76 (iPr, (CH₃)₂C-N, (CH₃)C=N),

75.15 ((CH₃)₂C-N), 123.61, 124.17, 124.90, 125.84, 126.74, 128.57, 137.00, 138.16, 140.90, 142.60, 150.37, 153.76 (Ar), 195.14 ppm (C=N).

[L¹SnCl] (2). MeLi (0.75 ml, 1.6 M in Et₂O, 1.2 mmol) was added dropwise to a stirring solution of **L** (0.41 g, 1.01 mmol) in Et₂O (10 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1h. The resulting yellow solution was then added dropwise to a solution of SnCl₂ (0.23 g, 1.21 mmol) in Et₂O (5 mL) at – 78 °C. The reaction mixture was warmed to room temperature and the resulting orange suspension was stirred for 15 h. After filtration and concentration of the filtrate **2** was obtained as yellow crystals. Yield: 0.36 g (6 3%). M.p. 157 °C (dec.). Elemental analysis (%) calcd for C₂₉H₄₃ClN₂Sn: C 60.68, H 7.56, N 4.88. Found: C 59.27, H 11.24, N 4.71. Attempts to obtain acceptable elemental analysis data for compound **2** failed as the sample have decomposed during sample preparation. ¹H NMR (395.9 MHz, C₆D₆, 25 °C): δ 0.83 (s, 3H, (CH₃)₂C-N), 0.91 (br, 3H, CH(CH₃)₂), 1.12 (br, 6H, CH(CH₃)₂), 1.24 (br, 6H, CH(CH₃)₂), 1.39 (s, 3H, (CH₃)₂C-N), 1.43 (br, 6H, CH(CH₃)₂), 1.51 (br, 3H, CH(CH₃)₂), 1.80 (s, 3H, CH₃C=N), 2.97 (br, 1H, CH(CH₃)₂), 3.34 (br, 1H, CH(CH₃)₂), 3.47 (br, 1H, CH(CH₃)₂), 4.56 (br, 1H, CH(CH₃)₂), 7.02-7.28 ppm (m, 6H, aryl); ¹³C{¹H} NMR (99.6 MHz, C₆D₆, 25 °C): δ 18.88, 22.95, 23.70, 24.01, 24.20, 24.55, 25.14, 26.51, 27.87, 28.00, 28.34, 28.63, 29.14, 29.53, 31.61 (*i*Pr, (CH₃)₂C-N, (CH₃)C=N), 75.32 ((CH₃)₂C-N), 123.42, 124.15, 124.77, 125.85, 125.85, 126.64, 138.92, 140.01, 141.35, 141.84, 149.86, 153.10 (Ar), 197.34 ppm (C=N); ¹¹⁹Sn{¹H} NMR (147.6 MHz, C₆D₆, 25 °C): δ -40 ppm.

[[C(=CH)-NAr]{C(Me)=NAr}]₂(GeCl)₂ (3) and [[C(CH₂)-NAr]{C(Me)=NAr}Ge]₂ (4).

LiNiPr₂ (0.6 ml, 2.0 M in THF/heptanes/ethylbenzene, 1.2 mmol) was added dropwise to a stirring solution of **L** (0.41 g, 1.01 mmol) in Et₂O (10 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 15 h. The resulting yellow solution was added dropwise to a stirring solution of GeCl₂.dioxane (0.27 g, 1.17 mmol) in Et₂O (5

mL) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was warmed to room temperature and the resulting dark green suspension was stirred for 15 h. Volatiles were removed in vacuum and the residue was extracted with toluene. After filtration and concentration of the filtrate, a mixture of **3** and **4** was obtained. The mother liquor was further concentrated to afford pure **3** as yellow crystals. Yield: 0.37 g (36 %). M.p. $162\text{ }^{\circ}\text{C}$. Elemental analysis (%) calcd for $\text{C}_{56}\text{H}_{76}\text{Cl}_2\text{Ge}_2\text{N}_4$: C 65.83, H 7.50, N 6.95. Found: C 65.48, H 7.14, N 6.82. ^1H NMR (395.9 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): 1.17 (d, $^3J_{\text{H-H}} = 6.8\text{ Hz}$, 24H, $\text{CH}(\text{CH}_3)_2$), 1.25 (d, $^3J_{\text{H-H}} = 6.8\text{ Hz}$, 24H, $\text{CH}(\text{CH}_3)_2$), 1.79 (s, 6H, $\text{CH}_3\text{C}=\text{N}$), 3.07 (sept, $^3J_{\text{H-H}} = 6.8\text{ Hz}$, 8H, $\text{CH}(\text{CH}_3)_2$), 5.93 (br, 2H, $-\text{CH}=\text{CH}-$), 7.06-7.26 ppm (m, 12H, Ar); $^{13}\text{C}\{^1\text{H}\}$ NMR (99.6 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ 14.07, 19.39, 23.23, 24.30, 25.32, 26.47, 28.27 (*i*Pr, $\text{CH}_3\text{C}=\text{N}$), 49.22 ($\text{C}=\text{C}-\text{N}$), 67.04 ($\text{C}=\text{C}-\text{N}$), 112.53, 123.49, 127.26, 128.73, 139.51, 145.71 (Ar), 172.25 ppm ($\text{C}=\text{N}$).

With the NMR data of compound **3** on hand, the NMR data of **4** in the mixture of **3** and **4** can be identified. **4**: ^1H NMR (395.9 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ 1.12 (d, $^3J_{\text{H-H}} = 6.77\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.21 (d, $^3J_{\text{H-H}} = 6.77\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.24 (d, $^3J_{\text{H-H}} = 6.33\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.25 (d, $^3J_{\text{H-H}} = 6.77\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.33 (s, 3H, $\text{CH}_3\text{C}=\text{N}$), 2.43 (s, 4H, $-\text{CH}_2-\text{CH}_2-$), 2.97 (sept, $^3J_{\text{H-H}} = 6.81\text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 3.07 (sept, $^3J_{\text{H-H}} = 6.81\text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 7.07-7.25 ppm (m, 12H, Ar); $^{13}\text{C}\{^1\text{H}\}$ NMR (99.6 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ 13.09, 22.66, 23.19, 26.36, 27.91, 28.26, 28.32, 28.43 (*i*Pr, $\text{CH}_3\text{C}=\text{N}$, $\text{NC}-\text{C}-\text{C}-\text{CN}$), 123.59 ($\text{N}=\text{CCH}_3$), 127.31, 128.42, 130.89, 139.28, 139.31, 145.75 (Ar).

[L²SnCl] (6). LiNiPr_2 (0.6 ml, 2.0 M in THF/heptanes/ethylbenzene, 1.2 mmol) was added dropwise to a stirring solution of **L** (0.41 g, 1.01 mmol) in Et_2O (10 mL) at $0\text{ }^{\circ}\text{C}$. The reaction mixture was warmed to room temperature and stirred for 15h. The resulting yellow solution was added dropwise to a stirring solution of SnCl_2 (0.23 g, 1.21 mmol) in Et_2O (5 mL) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was warmed to room temperature and the

resulting dark yellow suspension was stirred for 15 h. After filtration, the filtrate was concentrated to afford **6** as yellow crystals. Yield: 0.32 g (57 %). M.p. 167 °C (dec.). Elemental analysis (%) calcd for C₂₈H₃₉ClN₂Sn: C 60.24, H 6.99, N 5.02. Found: C 55.45, H 10.29, N 4.55. Attempts to obtain acceptable elemental analysis data for compound **6** failed as the sample have decomposed during sample preparation. ¹H NMR (395.9 MHz, THF-*d*₈, 25 °C): δ 1.18 (d, ³*J*_{H-H} = 6.7 Hz, 6H, CH(CH₃)₂) , 1.19 (d, ³*J*_{H-H} = 6.7 Hz, 6H, CH(CH₃)₂), 1.22 (d, ³*J*_{H-H} = 6.7 Hz, 6H, CH(CH₃)₂), 1.31 (d, ³*J*_{H-H} = 6.7 Hz, 6H, CH(CH₃)₂), 2.21 (s, 3H, CH₃C=N), 3.11 (br, 2H, CH(CH₃)₂), 3.46 (br, 2H, CH(CH₃)₂), 3.90 (s, 1H, (CH₂)CN), 4.88 (s, 1H, (CH₂)CN), 7.00-7.33 (m, 6H, Ar); ¹³C{¹H} NMR (99.6 MHz, C₆D₆, 25 °C): δ 18.41, 22.72, 23.18, 24.30, 25.38, 28.66, 28.99 (*i*Pr, CH₃C=N), 66.07 (CH₂=C-N), 97.58 (CH₂=C-N), 123.50, 126.64, 135.14, 138.57, 140.12, 156.05 (Ar), 179.47 (C=N). ¹¹⁹Sn{¹H} NMR (147.63 MHz, C₆D₆, 25°C): δ -88.0 ppm.

Crystal Structure Determinations of Compounds 1-4 and 6. X-ray data collection and structural refinement: The crystal data were collected using a Bruker APEX II diffractometer. The crystals were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least squares methods on *F*².^[16] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parents atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations.

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CHAPTER 2

Base-Stabilized Germylidenide, Stannylidenide and Plumbylidenide Anions[†]

Introduction

Stable heavier group 14 alkyne analogues of composition REER (R = bulky terphenyl or silyl ligand; E = Si, Ge, Sn, Pb) have attracted much attention in the past decades due to their unique structures and reactivities.^[1] X-ray crystallography showed that they have a *trans*-bent and planar geometry in which the R-E-E angle decreases from silicon to tin. Recent theoretical studies and UV/Vis spectroscopy showed that they adopt a multiply bonded structure **M** in solution (Chart 2.1).^[2] The reactivity of stable disilynes, digermynes and distannynes has been investigated extensively.^[1d, 3] They can undergo one-electron and two-electron reduction to give the radical anions [REER]^{•-} and the doubly reduced species [REER]²⁻, respectively.^[1i, 4] Comparison of their structural data with those of the heavier alkyne analogues can provide insight into the E-E bonding.^[2, 5] For example, an addition of two electrons resulted in the lengthening of Ge-Ge bond, while shortening the Sn-Sn bond. This is due to the former has LUMO with lone pair in character while the latter has LUMO with π bonding in character. In contrast, a

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diplumbyne is uncommon. Only $[\text{Ar}^*\text{PbPbAr}^*]$ ($\text{Ar}^* = \text{C}_6\text{H}_3-2,6-(\text{C}_6\text{H}_2-2,4,6-i\text{Pr}_3)_2$) was synthesized and structurally characterized by Power et al. in 2000 (Scheme 2.1).^[1e] X-ray crystallography showed that it is a singly strongly-bent bonded structure **S** with a long Pb-Pb single bond and a lone pair of electrons on each lead atom. However, theoretical studies and UV/Vis spectroscopy showed that $[\text{Ar}^*\text{PbPbAr}^*]$ has a multiply bonded structure **M** in solution.^[6] The singly bonded structure of $[\text{Ar}^*\text{PbPbAr}^*]$ in the solid state is ascribed to packing effects. Moreover, little is known about its reactivity^[7] and the reduction of $[\text{Ar}^*\text{PbPbAr}^*]$ is not yet reported.

Chart 2.1. Multiple bonded **M** and single bonded **S** structures

Scheme 2.1. Synthesis of the first example of diplumbyne.

Recently, a series of novel base-stabilized group 14 element(I) dimers $[R\ddot{E}-\ddot{E}R]$ ($E = Si, Ge, Sn, R =$ amidinate, guanidinate, β -diketimate, N-functionalized aryl etc.) was synthesized (Chart 2.2).^[8] They comprise a $\ddot{E}-\ddot{E}$ single bond and a lone pair of electrons on each E atom. Their structures resemble the singly bonded structure **S** (Chart 2.1). Thus, they are considered as base-stabilized heavier alkyne analogues. The reactivity of $[L\ddot{E}-\ddot{E}L]$ ($E = Si, Ge, Sn$) showed that they are powerful reagents for the activation of small molecules, unsaturated substrates etc.^[8j, 8k, 8o, 9] No examples of base-stabilized lead(I) dimer have yet been reported because of the synthetic difficulties in preparing such molecules. For example, Jones et al. reported that an attempt to isolate a β -diketimate or amidinate Pb^I dimer by the reduction of the corresponding lead(II) chloride or triflate with the magnesium(I) dimer failed, which led to the formation of homoleptic Pb^{II} complex $[HC(CtBuNMes)_2Pb:]$ ($Mes = 2,4,6$ -trimethylphenyl) or lead metal, respectively.^[8i, 8n] However, the lighter analogues were synthesized in very high yield by a similar method. It seems that a lead(I) dimer is unstable towards disproportionation. The fact that heavier alkyne analogues supported by bulky terphenyl and silyl ligands can be singly or doubly reduced prompted us to investigate the reduction of intramolecularly base-stabilized group 14 element(I) dimers.

Herein, we report (i) the syntheses of group 14 element(I) dimers stabilized by 2,6-diiminophenyl (**L'**) (Scheme 2.3) and (ii) their reduction to afford the respective group 14 element(I) anions.

Chart 2.2. Examples of base-stabilized group 14 element(I) dimers supported by (a, b) amidinates; (c) guanidinate; (d) substituted aryl; (e, f) β -diketiminates and (g) N-functionalized aryl ligands.

Results and Discussion

Scheme 2.2. Syntheses of **7-9**

Synthesis of [LEX]. The reaction of $[\text{L}^1\text{Br}]^{[10]}$ with *n*BuLi in THF at $-78\text{ }^\circ\text{C}$,^[11] followed by treatment with $\text{GeCl}_2\cdot\text{dioxane}$ or PbBr_2 , afforded $[\text{L}^3\text{GeCl}]$ (**7**) and $[\text{L}^3\text{PbBr}]$ (**9**) respectively (Scheme 2.2). $[\text{L}^4\text{SnCl}]$ (**8**) was synthesized similarly with the reaction of $[\text{L}^2\text{Br}]^{[10]}$ with *n*BuLi in THF at $-78\text{ }^\circ\text{C}$,^[11] followed by treatment with SnCl_2 (Scheme 2.2). Compound **7** was isolated as highly air and moisture-sensitive orange, and compounds **8** and **9** were isolated as highly air and moisture-sensitive yellow crystalline solids. They are soluble in hydrocarbon solvents and have been characterized by NMR spectroscopy. The ^1H NMR spectrum of **7** displays one set of signals due to the 2,6-diiminophenyl ligand. In the spectrum, there are two singlets at δ 8.06 and 8.08 ppm, which correspond to two non-equivalent $\text{HC}=\text{N}$ protons. The results indicate that compound **7** retains its solid-state structure in solution. The ^1H NMR spectrum of **8** displays a singlet at δ 1.29 ppm, a multiplet at δ 7.15–7.19 ppm, and a singlet at δ 8.10 ppm for the *t*Bu, Ph, and $\text{HC}=\text{N}$ protons, respectively. The results indicate that the imino substituents are equivalent in solution, although the X-ray crystal structure of **8** shows that the Sn–N bond lengths are slightly different (Sn(1)–N(1): 2.507(2) Å, Sn(1)–N(2): 2.597(2) Å, see below). The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum displays a singlet at δ 0.14 ppm,

which lies between that of the pincer ligand stabilized chlorostannylenes [2,6-(CH₂NMe₂)₂C₆H₃SnCl] (δ 155.6 ppm; Chart 1.5a)^[12] and [4-*t*Bu-2,6-{P(O*i*Pr)₂=O}₂C₆H₂}]SnCl (δ -99 ppm; Chart 1.5c).^[13] The ¹H and ¹³C NMR spectra of **9** show one set of signals owing to the 2,6-diiminophenyl ligand. No ²⁰⁷Pb NMR resonance could be observed because the quadrupolar ^{79/81}Br nuclei may broaden the signal. The result is in accord with reported problems in recording ²⁰⁷Pb NMR spectra of organolead(II) halides, such as [{Ar*PbBr}₂],^[14] [Ar*Pb-(NC₅H₅)Br],^[14] and [4-*t*Bu-2,6-{P(OEt)₂=O}₂C₆H₂PbCl] (Chart 2.3).^[15]

Chart 2.3. Examples of organolead(II) halides without ²⁰⁷Pb NMR spectra.

Compounds **7** - **9** have been characterized by X-ray crystallography. The molecular structures of **7** - **9** are shown in Figures 2.1-2.3 respectively. In the molecular structure of **7**, the NAr substituent at the C20 atom and the Ge-Cl moiety are disordered. The disordered substituents are omitted for clarity in Figure 2.1. The 2,6-diiminophenyl ligand is bidentate bonded to the Ge1 atom. The Ge atom adopts a distorted trigonal-pyramidal geometry. The sum of the bond angles at the Ge1 atoms (267.40°) is comparable with that of the three-coordinated chlorogermylene [(Mamx)GeCl] (270.25°, Chart 1.4c).^[16] The

geometry at the Ge1 atoms indicates that it is almost non hybridized and possesses lone pair electron with high s character. The Ge1–C19 [2.028(3) Å] and Ge1–N1 [2.247(3) Å] bonds are comparable with those in [{2,6-(CH₂NEt₂)₂C₆H₃}GeCl] [Ge–C, 1.941(11) Å; Ge–N, 2.337(11) Å, Chart 2.4a], which comprises an aryl ligand with two o-amino donors.^[17] The Ge1...N2 distance [2.62(1) Å] is significantly longer than the N–Ge dative bonds in N-donor-stabilized chlorogermynes such as [{C₅H₄N-2-C(SiMe₃)₂}GeCl] [2.082(4) and 2.075(4) Å, Chart 1.4f]^[18] and [(Mamx)GeCl] [2.0936(13) Å],^[16] but it is shorter than the sum of the van der Waals radii (ca. 3.55 Å). The results indicate that the interaction between the Ge1 and N2 atoms is weak.

Figure 2.1. Molecular structure of compound **7** (50% thermal ellipsoids). Hydrogen atoms, the disordered NAr substituent at the C20 atom, the disordered Ge1A and Cl1A atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–C19 2.028(3), Ge1–Cl1 2.3288(8), Ge1–N1 2.247(3), N1–C13 1.286(4), C13–C14 1.453(5), C14–C19 1.393(5), C18–C19 1.387(4), C18–C20 1.461(5), N2–C21 1.424(9), C19–Ge1–Cl1 100.61(8), C19–Ge1–N1 76.97(12), N1–Ge1–Cl1 89.82(7), Ge1–N1–C13 111.5(2), N1–C13–C14 118.2(3), C13–C14–C19 115.6(3), C14–C19–Ge1 116.0(2).

In the molecular structure of **8**, the 2,6-diiminophenyl ligand is tridentate bonded to the Sn1 atom, which adopts a seesaw geometry with the N atoms at the axial positions and

the C1 and Cl1 atoms at the equatorial positions (Figure 2.2). The Sn–C (2.177(2) Å) and Sn–N (2.507(2), 2.597(2) Å) bonds are comparable with those in the 2,6-diaminophenyltin(II) chloride [2,6-(CH₂NMe₂)₂C₆H₃SnCl] (Sn–C: 2.158(8) Å, Sn–N: 2.525(8), 2.602(8) Å, Chart 2.4b).^[12] The Sn1–Cl1 bond (2.5624(5) Å) is longer than that in the base-stabilized chlorostannylenes (2.440(5)–2.488(3) Å) (Chart 1.5).^[12-13, 19]

Chart 2.4. (a) [$\{C_5H_4N-2-C(SiMe_3)_2\}GeCl$]; (b) [2,6-(CH₂NMe₂)₂C₆H₃SnCl].

Figure 2.2. Molecular structure of **8** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–Sn1 2.177(2), Sn1–Cl1 2.5624(5), Sn1–N1 2.507(2), N1–C7 1.277(3), C6–C7 1.476(3), C1–C6 1.397(3), N2–C12 1.283(3), Sn1–N2 2.597(2), C1–Sn1–Cl1 90.99(6), N1–Sn1–Cl1 87.11(5), C1–Sn1–N1 71.53(8), C1–Sn1–N2 70.10(8), N2–Sn1–Cl1 90.79(5), N1–Sn1–N2 141.52(7), Sn1–N1–C7 111.88(16), N1–C7–C6 119.4(2), C6–C1–Sn1 119.66(16).

In the molecular structure of **9**, the 2,6-diiminophenyl ligand is also tridentate bonded to the lead atom, which adopts a seesaw geometry with the N atoms at the axial positions and the C1 and Br1 atoms at the equatorial positions (Figure 2.3). The C1-Pb1-Br1 ($95.0(4)^\circ$) and N-Pb-Br (average 88.2°) angles indicate little hybridization of the lead valence orbitals as well as the presence of a lone pair with high s character at the lead atom. The Pb-C ($2.289(19)$ Å) and Pb-Br bonds ($2.701(2)$ Å) are comparable with those in the pyridine-stabilized terphenyllead(II) bromide [Ar*Pb-(NC₅H₅)Br] (Pb-C $2.322(4)$, Pb-Br $2.7063(6)$ Å, Chart 2.3b).^[14] Furthermore, the Pb-N bonds ($2.637(16)$, $2.691(17)$ Å) are longer than the intermolecular Pb-N bond in [Ar*Pb(NC₅H₅)Br] ($2.502(4)$ Å).^[14]

Figure 2.3. Molecular structure of compound **9** (50% thermal ellipsoids). Disordered *i*Pr substituent and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pb1-C1 $2.289(19)$, Pb1-Br1 $2.701(2)$, Pb1-N1 $2.637(16)$, Pb1-N2 $2.691(17)$, N1-C7 $1.27(2)$, N2-C20 $1.25(3)$, C2-C20 $1.46(3)$, C6-C7 $1.48(3)$, C1-C6 $1.36(3)$, C1-C2 $1.38(3)$; C1-Pb1-Br1 $95.0(4)$, C1-Pb1-N1 $68.6(6)$, C1-Pb1-N2 $68.0(6)$, N1-Pb1-N2 $135.9(5)$, N1-Pb1-Br1 $88.1(4)$, N2-Pb1-Br1 $88.2(4)$.

Synthesis of [L³Ge–GeL³] and [L⁴Sn–SnL⁴]. The reaction of [L³GeCl] (**7**) with KC₈ in THF at room temperature afforded the Ge(I) dimer [L³Ge–GeL³] (**10**, Scheme 2.3). Similarly, the reaction of **8** with excess KC₈ (two equivalents) in Et₂O afforded the Sn(I)

dimer $[\text{L}^4\text{Sn}-\text{SnL}^4]$ (**11**, Scheme 2.3). Other examples of Ge(I) dimers and Sn(I) dimers stabilized by amidinate ligands and pincer ligands have been reported by several research groups (Chart 2.2).^[8a-c, 8i, 8j, 8o] Recently, the Ge^{I} radical $[\text{HC}\{\text{C}(\text{tBu})\text{NAr}\}_2\text{Ge}^\bullet]$ was synthesized by the reduction of the corresponding chlorogermylene with $\text{Na}(\text{C}_{10}\text{H}_8)$ or $[\text{HC}(\text{CMeNMes})_2\text{Mg}]_2$ in THF (Scheme 2.4).^[20] The results imply that Ge(I) and Sn(I) dimers are formed via the dimerization of Ge^{I} and Sn^{I} radical intermediates, respectively.

Scheme 2.3. Syntheses of **10** – **13**.

Scheme 2.4. Synthesis of Ge^{I} radical by the reduction of the corresponding chlorogermylene with $\text{Na}(\text{C}_{10}\text{H}_8)_2$ or $[\text{HC}(\text{CMeNMes})_2\text{Mg}]_2$.

Compound **10** and **11** were isolated as highly air- and moisture-sensitive purple and dark blue crystalline solid respectively. They are soluble in hydrocarbon solvents and have been characterized by NMR spectroscopy. The ^1H NMR spectrum of **10** at room temperature displays one doublet at δ 0.87 ppm and one broad singlet at δ 2.74 ppm for the *i*Pr substituents. The results are not consistent with the solid-state structure, suggesting that the imino substituents are fluxional in solution at room temperature. In this regard, the ^1H NMR spectrum of **10** was acquired at $-100\text{ }^\circ\text{C}$, whereupon a multiplet at δ 0.28– 1.40 ppm for the $\text{CH}(\text{CH}_3)_2$ protons and seven broad singlets at δ 2.04–3.74 ppm for the $\text{CH}(\text{CH}_3)_2$ protons were resolved. The IR spectrum of **10** also shows two N=C stretching modes of the non-equivalent imino substituents at ν 1587 and 1624 cm^{-1} . The ^1H NMR spectrum of **11** at room temperature displays two broad singlets at δ 0.61 and 1.64 ppm for the *t*Bu substituents. Moreover, the ^1H NMR spectrum at $60\text{ }^\circ\text{C}$ shows a broad signal at δ 1.15 ppm for the *t*Bu substituents. These imply that the imino substituents are fluxional in solution at room temperature and $60\text{ }^\circ\text{C}$. In this regard, the ^1H NMR spectrum of **11** was acquired at $-60\text{ }^\circ\text{C}$, whereupon two sharp singlets at δ 0.55 and 1.63 ppm for the *t*Bu protons were resolved. The results indicate that compound **11** retains its solid-state structure at $-60\text{ }^\circ\text{C}$ in solution. The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum displays a singlet with satellites due to coupling to the ^{117}Sn nucleus at δ 79 ppm ($J_{^{117}\text{Sn}-^{119}\text{Sn}} = 4156\text{ Hz}$). The signal shows a downfield shift compared with that of **8** (δ 0.14 ppm). Similarly, Jones et al. reported that the ^{119}Sn NMR resonance of the base-stabilized Sn(I) dimer $[\text{HC}\{\text{C}(\textit{t}\text{Bu})\text{N}(\text{Mes})\}_2\text{Sn:}]_2$ (δ 502.1 ppm; Chart 2.2f) shows a downfield shift compared with that of the corresponding chlorostannylene (δ -235.5 ppm).^[8n]

The UV/Vis spectrum of **10** in toluene shows three absorption bands at 438, 586, and 702 nm in the visible-light region, which shows a bathochromic shift compared with that of **11**

in THF with two absorption bands at 461 and 657 nm. The shifts are comparable with that observed in the electronic spectra of the amidinate-stabilized group 14 element(I) dimers $[\{RC(NAr)_2\}\ddot{E}]_2$ [$R = C_6H_4-4-tBu$; $E = Si$ (629 nm), Ge (502 nm), Sn (388 nm)].^[8i] Moreover, these are opposite to the electronic spectra of multiple-bonded heavier group 14 alkyne analogues, in which there is a bathochromic shift upon descending the group (lowest energy transition: $\pi \rightarrow \pi^*$).^[10] These imply that the Ge–Ge bond in **10** and Sn–Sn bond in **11** have little π character.

Figure 2.4. Molecular structure of compound **10** (50% thermal ellipsoids). Hydrogen atoms and *iPr* substituents are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–Ge2 2.5059(5), Ge2–C1 1.990(3), Ge1–C33 1.967(3), C1–C6 1.413(5), C33–C38 1.418(5), C6–C7 1.438(4), C38–C39 1.440(5), C7–N1 1.305(4), C39–N3 1.300(4), Ge2–N1 2.036(3), Ge1–N3 1.986(3), N3–Ge1–C33 83.21(13), N1–Ge2–C1 81.92(12), N3–Ge1–Ge2 102.31(8), C1–Ge2–Ge1 89.10(9), C33–Ge1–Ge2 116.11(10), N1–Ge2–Ge1 112.82(8), Ge1–C33–C38 110.4(3), Ge2–C1–C6 112.0(2), C33–C38–C39 114.9(3), C1–C6–C7 114.6(3), C38–C39–N3 116.7(3), C6–C7–N1 117.8(3), C39–N3–Ge1 113.4(2), C7–N1–Ge2 112.6(2).

Compound **10** and **11** have been characterized by X-ray crystallography. Their molecular structures are shown in Figure 2.4 and 2.5. In the molecular structure of **10**, it is comprised of *gauche*-bent structures similar to the amidinate-stabilized Ge(I) dimer $[\text{PhC}(\text{N}t\text{Bu})_2\text{Ge}]_2$ (Chart 2.2b).^[8c] In contrast, its structure is different from the more sterically hindered Ge(I) dimer $[t\text{BuC}(\text{NAr})_2\text{Ge}]_2$ (Chart 2.2a),^[8a] which shows a *trans*-bent structure. The Ge atoms in **10** adopt a distorted trigonal-pyramidal geometry, which indicates that there is a lone pair of electrons on each Ge atom. The Ge–Ge bond [2.5059(5) Å] is comparable with that in $[\text{PhC}(\text{N}t\text{Bu})_2\text{Ge}]_2$ [2.569(5) Å] and $[t\text{BuC}(\text{NAr})_2\text{Ge}]_2$ [2.6380(8) Å].^[8a, 8c] The results imply that the Ge–Ge bond does not have any multiple bond character. The Ge–C and Ge–N bonds in compound **10** are slightly shorter than those in **7**.

Chart 2.5. Examples of base-stabilized Sn(I) dimers. Sn–Sn bond length [Å]: (a) 3.0685(9); (b) 2.8981(9); (c) 2.9712(12); (d) 3.0685(9); (e) 3.0486(6).

In the molecular structure of **11**, the 2,6-diiminophenyl ligand is tridentate bonded to the Sn1 and Sn2 atoms, which adopts a seesaw geometry with the N atoms at the axial positions and the C atoms at the equatorial positions. The structure is different from that of $[2,6-(\text{CMe}=\text{NAr})_2\text{C}_6\text{H}_3\text{Sn:}]_2$ supported by a comparable ligand, in which two ligands coordinate to the Sn atoms in different bonding modes.^[8j] Compound **11** comprises a *gauche*-bent structure (C-Sn-Sn-C : 91.34°), which is similar to other base-stabilized Sn(I) dimer such as $[\text{HC}\{\text{C}(t\text{Bu})\text{N}(\text{Mes})\}_2\text{Sn:}]_2$,^[8n] $[2,6-(\text{CMe}=\text{NAr})_2\text{C}_6\text{H}_3\text{Sn:}]_2$,^[8j] and $[2,6-(\text{CH}_2\text{NMe}_2)_2\text{C}_6\text{H}_3\text{Sn:}]_2$,^[8b] whereas a *trans*-bent structure can be found in $[(4-t\text{BuC}_6\text{H}_4)\text{C}(\text{NAr})_2\text{Sn:}]_2$ ^[8i] and $[4-t\text{Bu}-2,6-\{\text{P}(\text{OiPr})_2=\text{O}\}_2\text{C}_6\text{H}_2\text{Sn:}]_2$.^[8o] The Sn1–Sn2 bond ($2.9491(4)$ Å) is comparable with that in the base-stabilized Sn(I) dimers ($2.8981(9)$ – $3.0685(9)$ Å) (Chart 2.5).^[8b, 8i, 8j, 8n, 8o] This indicates that the Sn–Sn bond is a single bond. The Sn–N bonds ($2.482(4)$ – $2.636(4)$ Å) are comparable with those in divalent organotin compounds containing intramolecular coordination of neutral N donors (Chart 2.6).^[21]

Chart 2.6. Examples of divalent organotin compounds containing intramolecular coordination of neutral N donors. Sn–N bond lengths [Å]: (a) 2.516(3) and 2.660(3); (b) 2.564(4); (c) 2.593(4) and 2.608(4); (d) 2.449(7), 2.384(6) and 2.420(6).

Figure 2.5. Molecular structure of **11** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn1–Sn2 2.9491(4), Sn1–N1 2.482(4), Sn1–N2 2.636(4), Sn1–C1 2.148(4), C1–C6 1.413(6), C6–C7 1.454(6), N1–C7 1.294(6), Sn2–N3 2.439(4), Sn2–N4 2.616(4), Sn2–C17 2.138(5), C17–C18 1.406(6), C18–C28 1.475(6), C28–N4 1.280(6), N1–Sn1–C1 72.31(14), N1–Sn1–Sn2 98.74(9), N1–Sn1–N2 141.96(11), C1–Sn1–Sn2 101.26(12), C1–Sn1–N2 69.66(13), N2–Sn1–Sn2 88.38(8), N3–Sn2–C17 73.01(15), N3–Sn2–Sn1 99.48(9), N3–Sn2–N4 142.92(11), C17–Sn2–Sn1 101.99(11), C17–Sn2–N4 69.90(14), N4–Sn2–Sn1 87.77(8).

Synthesis of $[L^3GeK \cdot TMEDA]$ and $[L^4SnK \cdot THF]$. The reaction of the Ge(I) dimer **10** with 2 equiv of KC_8 in Et_2O , followed by the addition of excess tetramethylethylenediamine (TMEDA), results in cleavage of the Ge^I-Ge^I bond to afford the germylidenide anion $[L^3GeK \cdot TMEDA]$ (**12**, Scheme 2.3).^[22] Similarly, the reaction of **11** with two equivalents of KC_8 in THF afforded $[L^4SnK \cdot THF]$ (**13**, Scheme 2.3). The results are in contrast with the reduction of the heavier alkyne analogue $[Ar'EEAr']$ with potassium, by which the doubly reduced species $K_2[Ar'EEAr']$ was formed.^[11] Moreover, the reduction of the amidinate-stabilized Ge(I) dimer $[tBuC(NAr)_2Ge]_2$ leads to decomposition to give elemental germanium and $[tBuC-(NAr)_2K]$.^[8a]

Chart 2.7. Germalidenes **I**, **II** and lithium stannylidenide **III**

Power et al. showed that the radical anions $[\text{REER}]^{\bullet-}$ and the doubly reduced species $[\text{REER}]^{2-}$ ($\text{E} = \text{Ge}, \text{Sn}$; $\text{R} = \text{terphenyl}$ substituent) were synthesized by the reaction of the corresponding heavier chlorocarbene analogues $[\text{RECl}]$ with excess alkali metal.^[23] In this regard, the reaction of compound **7** and **8** with 2 equiv of KC_8 in ethereal solvents afforded compounds **12** and **13** respectively. The reactions appear to proceed through the formation of compounds **10** and **11**, which then react with two molecules of KC_8 to form the respective compounds **10** and **11**. The crystallographic data also suggests that the negative charges at the Ge and Sn atoms are stabilized by electron delocalization in the ECCCCN ($\text{E}=\text{Ge}, \text{Sn}$) five-membered ring. Recently, research groups of Driess and Jones reported the synthesis of the N-heterocyclic germalidenide and stannylidenide complexes **I**, **II** and **III** by the reaction of $[\text{HC}\{\text{C}(\text{R})\text{N}(\text{Ar})\}\text{ECl}]$ ($\text{E}=\text{Ge}, \text{Sn}$; $\text{R} = \text{Me}, t\text{Bu}$) with 2 equiv of alkali metal (Chart 2.7).^[24] It is worth noting that the mechanisms for the formation of **I**, **II** and **III** are suggested to proceed through several reductive processes and ring contraction, which is different from that for **12** and **13**.

Compound **12** and **13** were isolated as a highly air- and moisture sensitive green crystalline solids. Compound **12** is stable in solution and the solid state at room temperature in an inert atmosphere. The ^1H NMR spectrum of **12** displays one doublet at δ 1.18 ppm and one septet at δ 3.23 ppm for the *i*Pr substituents. The results indicate that

compound **12** has C_{2v} symmetry in solution and the imino substituents may be equivalently coordinated to the Ge atom. The ^1H NMR signal for the $\text{HC}=\text{N}$ proton (δ 8.15 ppm) shows a downfield shift compared with that of **7**, suggesting that the negative charge at the Ge atom is stabilized by electron delocalization in the GeCCCN five-membered ring. The electronic delocalization is also supported by the bond lengths of the GeCCCN five-membered ring (see below).

Compound **13** is stable in ethereal solvents and the solid state. However, it decomposes in C_6D_6 , which was confirmed by NMR spectroscopy. Thus, the spectroscopic analyses of **13** can be performed only in $\text{THF-}d_8$. The ^1H NMR spectra of **13** at room temperature and $-60\text{ }^\circ\text{C}$ display one singlet at δ 1.54 ppm for the *t*Bu substituents and δ 8.40 ppm for the $\text{HC}=\text{N}$ protons. The result is not consistent with the solid-state structure. Compound **13** may have a C_{2v} symmetry in solution with the ligand tridentate bonded and the potassium atom η^1 -coordinated to the tin atom. The $^{119}\text{Sn}\{^1\text{H}\}$ NMR signal of **13** (δ 310 ppm) shows a significant downfield shift compared with that of **8** and **11**, which indicates that the negative charge at the Sn atom is stabilized by an electron delocalization in the SnCCCN five-membered ring. Similarly, Jones et al. reported that the ^{119}Sn NMR resonance of **III** (δ 524.2 ppm) shows a downfield shift compared with that of $[\text{HC}\{\text{C}(t\text{Bu})\text{N}(\text{Ar})\}_2\text{SnCl}]$ (δ -252.0 ppm).^[24b] Moreover, the electron delocalization in **13** is also supported by the bond lengths of the SnCCCN five-membered ring (see below).

Compounds **12** and **13** have been characterized by X-ray crystallography. Compound **12** has a polymeric structure by the interaction of the K1 atoms with the C4 atoms of the adjacent germylidenide molecules (Figure 2.6b). In the monomeric unit of compound **12** (Figure 2.6a), the K1 atom is η^1 -coordinated with the Ge1 atom of the GeCCCN ring, which is different from **I** and **II** comprising a η^5 -coordinated alkali-metal center.^[24] The K1 atom is also coordinated with the N2–4 atoms of the imino substituent and TMEDA

(a)

(b)

Figure 2.6. Molecular structure of compound **12** (20% thermal ellipsoids): (a) perspective view of the molecule and (b) its polymeric form. Hydrogen atoms (Figures 2.6a, b) and *i*Pr substituents (Figure 2.6b) are omitted for clarity. Selected bond lengths (Å) and angles (deg): K1-N2 3.179(3), Ge1-C1 1.909(4), Ge1-K1 3.3560(9), Ge1-N1 1.925(3), N1-C7 1.361(4), C6-C7 1.396(5), C1-C6 1.450(5), C1-C2 1.423(5), C2-C20 1.460(5), N2-C20 1.281(4), C1-Ge1-K1 126.84(11), C1-Ge1-N1 83.43(13), K1-Ge1-N1 148.44(9), Ge1-N1-C7 115.5(2), N1-C7-C6 114.5(3), C7-C6-C1 114.0(3), C6-C1-Ge1 112.6(2), Ge1-C1-C2 130.2(3), C1-C2-C20 121.4(3), C2-C20-N2 124.2(3), C20-N2-K1 160.8(2), N2-K1-Ge1 55.45(6).

(average K–N bond length: 2.961 Å). The coordination sphere on the K1 atom is further supplemented by an interaction with the *ipso*-C atom of a Ar substituent [K1...C21, 3.314(4) Å]. The GeCCCN five-membered ring in **12** is planar, whereas those in **7** and **10** are puckered. The Ge1–K1 bond [3.3560(9) Å] is comparable with the tris-(trimethylgermyl)germanide complex [(Me₃Ge)₃GeK(18-crown-6)] [3.4213(11) Å]^[25] and the germylidenide complex **I** [3.449(1) and 3.573(1) Å].^[24a] In addition, the Ge1–N1 [1.925(3) Å], N1–C7 [1.361(4) Å], C6–C7 [1.396(5) Å], C1–C6 [1.450(5) Å], and Ge1–C1 [1.909(4) Å] bond lengths suggest that there is an appreciable electron delocalization in the GeCCCN five-membered ring compared with those in compounds **7** and **I** [Ge–N, 1.944(2) Å; N–C, 1.382(3) Å; C–C, 1.371(3) and 1.411(3) Å; Ge–C, 1.887(2) Å].^[24a]

In the monomeric unit of compound **13** (Figure 2.7a), the K1 atom is η^5 -coordinated to the SnCCCN ring. The K1 atom is also coordinated with a THF molecule. The coordination sphere on the K1 atom is further supplemented by an interaction with the SnCCCN ring of another stannylidenide anion (Figure 2.7b). Moreover, the SnCCCN five-membered ring is planar. The Sn1–K1 (3.6144(8) Å) is comparable with that in the stannylpotassium [K{Sn-(CH₂*t*Bu)₃}(η^6 -C₆H₅Me)₃] (3.548(3) Å).^[26] In addition, comparing the Sn1–N1 (2.268(3) Å), N1–C7 (1.350(6) Å), C2–C7 (1.412(4) Å), C1–C2 (1.448(6) Å), and Sn1–C1 (2.114(4) Å) bond lengths with those in compounds **8** and **III**, it is suggested that there is an appreciable electron delocalization in the SnCCCN five-membered ring.

(a)

(b)

Figure 2.7. Molecular structure of **13** (20% thermal ellipsoids): (a) perspective view of the molecule; (b) its polymeric form. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn1-K1 3.6144(8), K1-N1 3.108(4), K1-C7 2.964(5), K1-C2 2.976(4), K1-C1 3.185(4), Sn1-N1 2.268(3), N1-C7 1.350(6), C7-C2 1.412(4), C2-C1 1.448(6), Sn1-C1 2.114(4), C12-N2 1.274(5), N1-Sn1-C1 75.28(12), Sn1-C1-C2 116.4(2), C1-C2-C7 116.5(4), C2-C7-N1 117.2(4).

Synthesis of $[\text{L}^3\text{Pb-PbL}^3]$ and $[\text{Li}(\text{THF})_4][\text{L}^3\text{Pb}]$. An attempt to isolate the 2,6-diiminophenyllead(I) dimer $[\text{L}^3\text{Pb-PbL}^3]$ (**15**) by the reduction of **7** with alkali metals or the magnesium(I) dimer^[27] failed. The reaction of **7** with one equivalent of Li in THF at -40°C afforded a mixture of 2,6-diiminophenyllithium $(\text{L}^3\text{Li})_2$ (major product), lead(I) dimer $[\text{L}^3\text{Pb-PbL}^3]$, homoleptic plumbylene $[\text{L}^3_2\text{Pb}]$,^[28] and unidentified products, which was confirmed by NMR spectroscopy. Only $(\text{L}^3\text{Li})_2$ can be isolated from the mixture by recrystallization (Figure 2.8). Similarly, the reaction of **9** with 0.5 equivalent of $[\text{HC}(\text{CMeNMe})_2\text{Mg}]_2$ in THF at -40°C afforded $[\text{L}^3_2\text{Pb}]$ and $[\text{HC}(\text{CMeNMe})_2\text{MgBr}]$, which was confirmed by NMR spectroscopy. The results are consistent with the reduction of amidinate- or β -diketiminate lead(II) halides.^[8i, 8n] In contrast, the reaction of **9** with excess Li in THF at -40°C afforded the plumbylidenide anion $[\text{Li}(\text{THF})_4][\text{L}^3\text{Pb}]$ (**14**, Scheme 2.5), in which the negative charge is aromatically delocalized in the PbCCCN five-membered ring. Compound **14** is the first aromatic low-valent lead analogue of an indenyl anion. The results indicate that $2p$ orbitals of C/N atoms and a $6p$ orbital of a low valent Pb atom can sufficiently overlap to form an aromatic compound. In contrast, a similar tetravalent lead analogue of a cyclopentadienyl anion, which is the lithiomesitylplumbole $[\text{C}_4\text{Ph}_4\text{Pb}(\text{Mes})\text{Li}]$ (Chart 2.8a),^[29] does not show any aromatic character. Until now, only one tetravalent lead compound, which is the dianionic plumbole $[\text{Li}(\text{DME})_3][(\text{DME})\text{Li}(\eta^5\text{-PbC}_4\text{Ph}_4)]$ (Chart 2.8b), shows considerable aromaticity.^[29]

Chart 2.8. (a) Lithiomesitylplumbole $[\text{C}_4\text{Ph}_4\text{Pb}(\text{Mes})\text{Li}]$ and (b) dianionic plumbole $[\text{Li}(\text{DME})_3][(\text{DME})\text{Li}(\eta^5\text{-PbC}_4\text{Ph}_4)]$.

Scheme 2.5. Syntheses of **14** and **15**.

Figure 2.8. Molecular structure of $[L^3Li]$ (50% thermal ellipsoids): H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C1-Li1 2.312(3), C1-Li2 2.288(3), C33-Li1 2.247(3), C33-Li2 2.279(3), N1-Li1 2.023(3), N4-Li1 2.045(2), N2-Li2 2.027(3), N3-Li2 2.031(3), C1-C6 1.4221(19), C6-C7 1.4649(19), C7-N1 1.2802(17); Li1-C1-Li2 62.94(9), Li1-C33-Li2 64.06(9), C1-Li1-C33 116.64(11), C1-Li2-C33 116.33(11).

Compound **14** was isolated as a light-sensitive dark-red crystalline solid. It is stable in ether solvents and the solid state. It decomposes in toluene and C₆D₆ to form LLi and lead metal, which was confirmed by NMR spectroscopy. Thus, the spectroscopic analyses of **14** can only be performed in THF-*d*₈. The ¹H NMR spectrum at room temperature shows a doublet and septet at δ 1.12 and 3.35 ppm for the *i*Pr substituents. It also displays signals for phenyl protons at δ 6.37–7.04 ppm. It is noteworthy that the signal for HCNAr (δ 7.92 ppm) shows an upfield shift compared with that of **9** (δ 9.15 ppm) and falls in the aromatic proton region. Moreover, the ¹H NMR spectrum of **14** was also acquired at -60°C, whereupon two sharp doublets (δ 1.05, 1.10 ppm) and two septets (δ 3.12, 3.24 ppm) for the non-equivalent *i*Pr protons were resolved. The results indicate that compound **14** retains its solid-state structure at -60°C in solution, and the imino substituents are fluxional in solution at room temperature. Moreover, the ²⁰⁷Pb{¹H} NMR signal (δ 3415 ppm) at room temperature shows a significant downfield shift compared with that of the 2,6-diiminophenyllead(I) dimer [L³Pb-PbL³] (**15**, δ 1684 ppm). The results indicate that the negative charge at the Pb atom is stabilized by an aromatic delocalization in the PbCCCN five-membered ring. It is also supported by DFT calculations of **14**^{•-} (Appendix B, Figure S1, M06-2x/LanL08(d) level), which reveal pronounced aromaticity of the PbCCCN ring, indicated by the negative nucleus independent chemical shift value^[30] (NICS(1)= -6.33 ppm). Furthermore, the NICS(1) value of the PbCCCN ring is comparable with that of the dianionic plumbole [Li(DME)₃][(DME)Li(*η*⁵-PbC₄Ph₄)] (NICS(1)= -6.28 ppm).^[29]

Figure 2.9. Molecular structure of compound **14** (50% thermal ellipsoids). Disordered THF and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pb1-N1 2.425(5), Pb1-N2 2.899(5), N1-C7 1.347(10), C6-C7 1.380(10), C1-C6 1.444(9), Pb1-C1 2.180(5), N2-C20 1.293(11), C20-C2 1.456(10); C1-Pb1-N1 73.2(2), Pb1-N1-C7 111.3(4), C1-C6-C7 118.8(7), C6-C7-N1 120.1(7), Pb1-C1-C6 116.6(5).

X-ray crystallography showed that compound **14** is monomeric (Figure 2.9). The 2,6-diiminophenyl ligand is bidentate bonded to the lead atom. The PbCCCN ring is planar and the sum of the internal bond angles is 540.0°. The Li1 atom is coordinated with four THF molecules. The Pb1-Li1 distance (8.041(8) Å) is longer than the sum of van der Waals radii, which suggests that there is no interaction between these atoms. Comparing the bonding in the PbCCCN five-membered ring (Pb1-N1 2.425(5) Å, N1-C7 1.347(10) Å, C6-C7 1.380(10) Å, C1-C6 1.444(9) Å, Pb1-C1 2.180(5) Å) with those in compound **9** (Pb-N average 2.664 Å, N1-C7 and N2-C20 average 1.26 Å, C6-C7 and C2-C20 average 1.47 Å, C1-C2 and C1-C6 average 1.37 Å, Pb-C 2.289(19) Å), it is suggested that there is an aromatic delocalization in the PbCCCN five-membered ring. Moreover, the Pb1-N1

bond is still longer than reported Pb^{II}-N_{amide} single bonds (2.07(5)–2.35(5) Å) (Chart 2.9).^[31]

Chart 2.9. Examples of Pb(II) complexes with Pb-N single bonds. Pb-N bond lengths [Å]: (a) 2.07(5) and 2.35(5); (b) 2.155(10) and 2.330(7); (c) 2.350(5) and 2.268(5).

Recently, Sekiguchi et al. reported that a stannylsodium intermediate [*t*Bu₂MeSi]₃SnNa underwent an oxidation with SnCl₂·dioxane to form a stable stannyl radical.^[32] It is anticipated that a lead(I) radical or its dimeric derivative can be prepared by a similar strategy. The reaction of two equivalents of **14** with SnCl₂ in THF at -78°C afforded the 2,6-diiminophenyllead(I) dimer [L³Pb-PbL³] (**15**). The ¹H and ¹³C NMR spectra of **15** show one set of signals for the 2,6-diiminophenyl ligand. The ²⁰⁷Pb NMR signal of **15** (δ 1684 ppm) shows an upfield shift compared with that of **14**. Compound **15** was isolated as a light-sensitive dark-green crystalline solid. It is stable in hydrocarbon solvents and the solid state. The UV/Vis spectrum of **15** in THF shows three absorption bands at 396, 473, and 526 nm in the visible light region, which shows a hypsochromic shift compared with that of the lighter congeners **10** (438, 586 and 702 nm) and **11** (425, 457 and 561 nm).^[8b,e] The shift is comparable with that observed in the electronic spectra of the amidinate-stabilized group 14 element(I) dimers [{R¹C(NAr)₂}E]₂ [R¹ = C₆H₄-4-*t*Bu; E = Si (629 nm), Ge (502 nm), Sn (388 nm)].^[8i] Moreover, these are opposite to the electronic spectra of multiple-bonded heavier group 14 alkyne analogues, in which there is a

bathochromic shift upon descending the group.^[10] The results imply that the Pb-Pb bond in **15** has little π character in solution, which is different from $[\text{Ar}^*\text{PbPbAr}^*]$ comprising a multiply bonded structure **M** in solution.

Figure 2.10. Molecular structure of compound **15** (50% thermal ellipsoids). Disordered Ar substituent and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pb1-Pb2 3.1283(6), Pb1-N1 2.613(10), Pb1-N2 2.706(9), Pb2-N3 2.715(9), Pb2-N4 2.650(8), Pb1-C1 2.287(11), Pb2-C33 2.240(11), N1-C3 1.276(14), N2-C8 1.287(14), C2-C3 1.455(17), C7-C8 1.463(16), C1-C2 1.423(16), C1-C7 1.400(16); C1-Pb1-Pb2 111.3(3), C1-Pb1-N1 69.5(4), C1-Pb1-N2 68.6(4), N1-Pb1-Pb2 81.2(2), N2-Pb1-Pb2 119.42(19), C33-Pb2-Pb1 105.7(3), C33-Pb2-N3 68.5(3), C33-Pb2-N4 68.7(3).

The molecular structure of **15** showed that the 2,6-diiminophenyl ligand is tridentate bonded to the lead atoms, which adopt a seesaw geometry with the N atoms at the axial positions and the C atoms at the equatorial positions (Figure 2.10). The C-Pb-Pb angles (average 108.5°) indicate that there is a lone pair of electrons at the lead atoms. Moreover, compound **15** has a *gauche*-bent structure (C-Pb-Pb-C 102.2°), which is different from $[\text{Ar}^*\text{PbPbAr}^*]$ comprising a *trans*-bent structure. The Pb-Pb bond (3.1283(6) Å) is comparable with that in $[\text{Ar}^*\text{PbPbAr}^*]$ (3.1881(1) Å), which indicates that the Pb-Pb

bond is a single bond. The C_{imine}-N bonds (average 1.270 Å) are shorter and the Pb-N (average 2.671 Å) and Pb-C (average 2.264 Å) bonds are longer compared with those of **14**, which indicate that there is no electronic delocalization in the PbCCCN rings. Moreover, the bond lengths of the PbCCCN rings are comparable with those in **9**. It is concluded that compound **15** has a singly bonded structure **S** in both solution and the solid state.

To compare with the reactivity of multiply bonded heavier group 14 alkyne analogues, the reduction of compound **15** with two equivalents of lithium in THF was performed, which quantitatively afforded compound **14**. It is in contrast to the reduction of stable disilynes, digermynes, and distannynes to give the radical anions [REER]^{•-} or the doubly reduced species [REER]²⁻. Moreover, the results imply that the reaction of **9** with excess Li in THF proceeds through the formation of a lead(I) radical intermediate, which then reacts with lithium to form **15**.

Scheme 2.6. Synthesis of compound **18**.

Synthesis of [2-(CH=NAr)-6-(CH-NAr)C₆H₃]₂[GePd(PPh₂)₂]₂. The reaction of [L³GeK.TMEDA] (**12**) with (PPh₃)₂PdCl₂ in THF at room temperature afforded the dimeric palladium(0) germylene complex [2-(CH=NAr)-6-(CH-NAr)C₆H₃]₂[GePd(PPh₂)₂]₂ (**18**) and the by-product is the Ge(I) dimer (**10**) (Scheme 2.6). It is suggested that compound **18** was obtained via radical mechanism (Scheme 2.7).

Upon a salt elimination, the Ge(I) intermediate and $[\text{Pd}(\text{PPh}_3)_2]$ are formed. The Ge(I) intermediate then coordinates to $[\text{Pd}(\text{PPh}_3)_2]$ to form intermediate **16** or dimerize to form Ge(I) dimer (**8**). **16** undergoes an intramolecular rearrangement between the Ge(I) center and the C=N bond to form intermediate **17**, which dimerizes to form compound **18**.

Scheme 2.7. Proposed mechanism for the formation of compound **18**.

Compound **18** was isolated as a highly air- and moisture-sensitive orange crystalline solid. It is soluble in hydrocarbon solvents and has been characterized by NMR spectroscopy. The ^1H NMR spectrum of **18** displays four doublets and one multiplet due to the overlapping of two doublets at δ 0.0047 -1.09 ppm for the $\text{CH}(\text{CH}_3)_2$ of the *i*Pr substituent and two septets at δ 2.43, 4.27 and one broad signal at δ 2.72 ppm for the $\text{CH}(\text{CH}_3)_2$ of

the *i*Pr substituent. A doublet at δ 5.69 ppm corresponds to the two methine protons with a coupling constant of $^3J_{\text{HH}} = 6.49$ Hz. $^{31}\text{P}\{^1\text{H}\}$ NMR shows two doublets at 29 and 31 ppm ($^3J_{\text{PP}} = 47.68$ Hz) indicates the two P atoms coordinated to each Pd are in a slightly different chemical environment. The ^1H NMR spectrum of the mother liquor shows the presence of Ge(I) dimer (**10**).

Figure 2.11. Molecular structure of compound **18** (50% thermal ellipsoids). Hydrogen atoms are omitted and only ipso carbons of the phenyl rings are shown for clarity. Selected bond lengths [Å] and angles [°]: Ge1-Pd1 2.3008(10), Ge2-Pd2 2.3027(11), Ge1-N1 1.829(6), Ge2-N3 1.848(7), Ge1-C37 1.962(8), Ge2-C87 1.952(8), C56-N1 1.439(10), C69-N3 1.496(10), C56-C69 1.580(12), N1-Ge1-C37 86.2(3), N3-Ge2-C87 86.5(3), N1-Ge1-Pd1 133.0(2), N3-Ge2-Pd2 135.9(2), C37-Ge1-Pd1 140.3(2), C87-Ge2-Pd2 137.2(2), P2-Pd1-Ge1 116.17(7), Ge1-Pd1-P1 127.55(6), P2-Pd1-P1 116.28(8), P4-Pd2-Ge2 127.28(7), Ge2-Pd2-P3 118.4(4), P4-Pd2-P3 113.9(4).

Compound **18** has been characterized by X-ray crystallography. The molecular structure of **18** is shown in Figure 2.11. The Ge atoms adopt a distorted trigonal planar geometry

[avg. C-Ge-Pd: 139°; avg. N-Ge-Pd: 134°; avg. C-Ge-N: 86°]. The C-N [C56-N1: 1.439(10) Å, C69-N3 1.496(10) Å] bonds and C69-C56 [1.580(12) Å] bond are comparable to typical C-N single bond (avg 1.48 Å) and C-C single bond (avg 1.53 Å) respectively. The Ge-Pd [Ge1-Pd1: 2.3008(10) Å, Ge2-Pd2: 2.3027(11) Å] bonds are comparable to that in the previously reported Pd(0)-germylene complexes [2.3281(4) – 2.337(2) Å]^[33] (Chart 2.10a-c) but are longer than that in the bis(organogermeryl)Pd(II) complex [2.427(2) and 2.404(2) Å] (Chart 2.10d).^[34] The result indicates a greater π back-bonding from Pd to Ge. The Pd atoms also adopt a distorted trigonal planar geometry [avg. Ge-Pd-P: 122°; avg. P-Pd-P: 115°]. Compound **16** displays an almost orthogonal arrangement P-Pd-P plane versus the C-Ge-N plane with an average dihedral angle of 94° (P-Pd-Ge-N and P-Pd-Ge-C).

Chart 2.10. Pd(0)-germylene complexes (a-c) and bis(organogermeryl)Pd(II) complex (d). Ge-Pd bond length [Å]: (a) 2.3281(4); (b) 2.330(5); (c) 2.337(2); (d) 2.427(2) and 2.404(2).

Conclusion

In conclusion, the $[\text{L}^3\text{GeK}\cdot\text{TMEDA}]$ (**12**) and $[\text{L}^4\text{SnK}\cdot\text{THF}]$ (**13**) can be synthesized by the reduction of $[\text{L}^3\text{Ge}-\text{GeL}^3]$ (**10**) and $[\text{L}^4\text{Sn}-\text{SnL}^4]$ (**11**). The crystallographic and spectroscopic data show that the negative charges at the Ge and Sn atoms in compounds **12** and **13** are stabilized by electron delocalization in the germanium and tin heterocycles, respectively. Furthermore, the first base-stabilized lead(I) dimer **15** was synthesized by oxidation of plumbylidenide anion **14** with SnCl_2 . X-ray crystallography and NMR spectroscopy showed conclusively that compound **15** has a singly bonded structure **S** in both solution and the solid state. The reduction of **15** with lithium afforded the aromatic plumbylidenide anion **14**, which is in contrast to the outcome by the reduction of multiply bonded heavier Group 14 alkyne analogues.

Experimental Section

General Procedure. All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. Solvents were dried over and distilled over Na/K alloy prior to use. L³Br was prepared as described in the literatures.^[10] The ¹H, ¹³C, ¹¹⁹Sn, ²⁰⁷Pb NMR and ⁷Li spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to SiMe₄ for ¹H and ¹³C, SnMe₄ for ¹¹⁹Sn, Pb(NO₂)₂ for ²⁰⁷Pb and LiCl for ⁷Li. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in seal glass tubes and were not corrected.

[L³GeCl] (7). *n*BuLi (2.0 M in cyclohexane, 3.0 ml, 6.00 mmol) was added dropwise to a THF solution (50 mL) of L³Br (2.66 g, 5.00 mmol) at – 78°C and the reaction mixture was stirred for 1 h. It was warmed to –40°C and stirred for another 2 h. A THF solution (10 ml) of GeCl₂.dioxane (1.27 g, 5.50 mmol) was then added to the reaction mixture at – 78 °C. The resulting red solution was warmed to room temperature gradually and was stirred for 12 h. Solvent was removed under vacuum and the residue was extracted with toluene. LiCl was then filtered off and the red filtrate was concentrated to afford **7** as orange crystals. Yield: 2.24 g (80 %). Mp: 245 °C. Elemental analysis (%) calcd for C₃₂H₃₉ClGeN₂: C, 68.64; H, 7.03; N, 5.01. Found: C, 68.31; H, 6.91; N, 4.85. ¹H NMR (395.9 MHz, C₆D₆, 25 °C): δ = 1.14-1.26 (m of overlapping d, *J*_{H-H}= 6.4 Hz, 24H, CH(CH₃)₂), 3.37 (br s, 4H, CH(CH₃)₂), 7.00-7.05 (m, 2H, Ph), 7.14-7.18 (m, 7H, Ph), 8.06 (s, 1H, CH=N), 8.08 ppm (s, 1H, CH=N). ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 25 °C): δ = 24.44 (CH(CH₃)₂), 24.56 (CH(CH₃)₂), 24.99 (CH(CH₃)₂), 25.16 (CH(CH₃)₂), 28.63 (CH(CH₃)₂), 28.69 (CH(CH₃)₂), 123.96, 126.61, 128.93, 132.29 (*Ph*-Ge), 140.41, 140.56, 145.06, 145.24 165.48, 165.59 (N-*Ar*), 171.69, 171.93 ppm (C=N-*Ar*). UV-Vis (toluene):

$\lambda_{\text{max}}(\epsilon) = 218$ (15538), 245 (18501), 336 (1786), 407 nm (932 dm³ mol⁻¹cm⁻¹). IR (Nujol, cm⁻¹): 2955s, 2924s, 2853s, 1628w, 1609w, 1551w, 1458m, 1377m, 1364w, 1323w, 1260w, 1175w, 1167w, 1096w, 1049w, 799m, 750w, 721w.

[L⁴SnCl] (8). BuⁿLi (2.0 M in cyclohexane, 3.0 mL, 6.00 mmol) was added dropwise to a THF solution (50 mL) of L⁴Br (1.62 g, 5.00 mmol) at – 78 °C. The resulting red solution was stirred for 3 h. A THF solution (10 mL) of SnCl₂ (1.04 g, 5.49 mmol) was then added to the reaction mixture at – 78 °C. The resulting orange solution was warmed to room temperature gradually and was stirred for 12 h. Solvent was removed under vacuum and the residue was extracted with CH₂Cl₂. LiCl was then filtered off and the orange filtrate was concentrated to afford **8** as yellow crystals. Yield: 1.49 g (75 %). M.p. 231 °C. Elemental analysis (%) calcd for C₁₆H₂₃ClN₂Sn: C, 48.32; H, 5.83; N, 7.05. Found: C, 47.89; H, 5.61; N, 6.94. ¹H NMR (395.9 MHz, C₆D₆, 25°C): δ = 1.29 (s, 18H, C(CH₃)₃), 7.15-7.19 (m, 3H, Ph), 8.10 (s, 2H, CH=N). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25°C): δ = 30.65 (C(CH₃)₃), 59.18 (C(CH₃)₃), 131.40, 143.48, 160.36, 160.65 (Ph), 175.12 ppm (C=N-C). ¹¹⁹Sn{¹H} NMR (149.12 MHz, C₆D₆, 25°C): δ = 0.14 ppm.

[L³PbBr] (9). *n*BuLi (2.0 M in cyclohexane, 1.10 mL, 2.20 mmol) was added dropwise to a THF solution (20 mL) of L³Br (1.06 g, 2.00 mmol) at – 78 °C and the reaction mixture was stirred for 1 h. It was warmed to – 40 °C and stirred for another 2 h. The mixture was then added to a THF solution (5 mL) of PbBr₂ (0.81 g, 2.21 mmol) at – 78 °C. The resulting solution was warmed to – 40 °C gradually and stirred for 12 h. Volatiles were removed under vacuum, and the residue was extracted with Et₂O. LiBr was then filtered off and the orange filtrate was concentrated to afford **9** as yellow crystals. Yield: 0.71 g (48 %); M.p. 220 °C; ¹H NMR (395.9 MHz, THF-*d*₈, 25 °C): δ 1.17 (br s, 24H, CH(CH₃)₂), 3.23 (br s, 4H, CH(CH₃)₂), 7.00–7.20 (m, 6H, Ph), 7.69 (t, ³J_{HH} = 7.2 Hz, 1H,

Ph-Pb), 8.20 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2H, Ph-Pb), 9.15 ppm (s, 2H, CH=N); $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, THF- d_8 , 25 °C): δ 25.94 (CH(CH₃)₂), 29.00 (CH(CH₃)₂), 124.24, 126.41, 128.48, 136.99, 140.53, 148.32 (Ph), 150.47 (C-Pb), 175.53 ppm (C=NAr); elemental analysis calcd (%) for C₃₂H₃₉BrN₂Pb: C 52.02, H 5.32, N 3.79, found: C 51.78, H 5.16, N 3.47.

[L³Ge—GeL³] (10). THF (20 mL) was added to a mixture of **7** (1.12 g, 2.00 mmol) and KC₈ (0.28 g, 2.07 mmol) at room temperature. The resulting blue mixture was stirred for 1 day. The insoluble precipitate was then filtered off and volatiles were removed under vacuum. The residue was extracted with hexane and then filtered. The blue filtrate was concentrated to afford **10** as purple crystals. Yield: 0.56 g (53 %). Mp: 250 °C. Elemental analysis (%) calcd for C₆₄H₇₈Ge₂N₄: C, 73.25; H, 7.44; N, 5.34. Found: C, 73.11; H, 7.25; N, 5.21. ^1H NMR (399.5 MHz, THF- d_8 , 25 °C): δ = 0.87 (br d, 48H, CH(CH₃)₂), 2.74 (br s, 8H, CH(CH₃)₂), 6.93 (br s, 2H, Ph), 7.00 – 7.12 (m, 13H, Ph), 7.75 – 7.77 (br m, 3H, Ph), 8.03 ppm (br s, 4H, CH=N). ^1H NMR (399.5 MHz, THF- d_8 , – 100 °C): δ = 0.28 – 1.40 (m, 48H, CH(CH₃)₂), 2.04 (br s, 1H, CH(CH₃)₂), 2.14 (br s, 2H, CH(CH₃)₂), 2.56 (br s, 1H, CH(CH₃)₂), 2.78 (br s, 1H, CH(CH₃)₂), 3.05 (br s, 1H, CH(CH₃)₂), 3.20 (br s, 1H, CH(CH₃)₂), 3.74 (br s, 1H, CH(CH₃)₂), 6.52–7.37 (m, 15H, Ph), 7.51 (s, 1H, CH=N), 7.53 (s, 1H, CH=N), 8.03 – 8.14 (m, 2H, Ph), 8.39 (s, 1H, Ph), 8.61 (s, 1H, CH=N), 8.70 ppm (s, 1H, CH=N). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C₆D₆, 25 °C): δ = 24.78 (br s, CH(CH₃)₂), 28.47 (CH(CH₃)₂), 123.43, 124.55, 125.88, 138.48, (Ph-Ge), 140.60 (br, N-Ar), 146.96 (br, N-Ar), 161.25 (br, N-Ar), 179.19 ppm (br, C=NAr). UV-Vis (toluene): $\lambda_{\text{max}}(\epsilon) = 284$ (12453), 438 (1373), 586 (1693), 702 nm (6516 dm³ mol^{–1}cm^{–1}). IR (Nujol, cm^{–1}): 2955s, 2924s, 2853s, 1624m, 1587w, 1549w, 1489w, 1460m, 1381m, 1360w, 1337w, 1304m, 1260w, 1211w, 1175w, 1159w, 1090w, 1057w, 1020w, 995w, 924w, 887w, 880w, 799w, 758w, 716w.

[L⁴Sn—SnL⁴] (11). Et₂O (20 mL) was added to a mixture of **8** (0.80 g, 2.00 mmol) and KC₈ (0.54 g, 4.00 mmol) at room temperature. The resulting blue mixture was stirred for 15h. The insoluble precipitate was then filtered off and the filtrate was concentrated to afford **11** as dark blue crystals. Yield: 0.084 g (12 %). M.p. 250 °C. Elemental analysis (%) calcd for C₃₂H₄₆N₄Sn₂: C, 53.05; H, 6.40; N, 7.74. Found: C, 52.62; H, 6.10; N, 7.62. ¹H NMR (395.9 MHz, THF-*d*₈, 25°C): δ = 0.61 (br s, 18H, C(CH₃)₃), 1.64 (br s, 18H, C(CH₃)₃), 7.17 (m, 2H, Ph), 7.59 (br s, 4H, Ph), 8.41 (br s, 2H, CH=N), 8.85 (br s, 2H, CH=N). ¹H NMR (395.9 MHz, THF-*d*₈, – 60°C): δ = 0.55 (s, 18H, C(CH₃)₃), 1.63 (s, 18H, C(CH₃)₃), 7.21 (m, 2H, Ph), 7.52 (d, ³J_{HH} = 7.28 Hz, 2H, Ph), 7.67 (d, ³J_{HH} = 7.24 Hz, 2H, Ph), 8.47 (s, 2H, CH=N), 8.92 (s, 2H, CH=N). ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈, 25°C): δ = 28.49 (C(CH₃)₃), 29.59 (C(CH₃)₃), 120.88, 128.15, 147.86, 156.93 (Ph), 184.09 ppm (C=N-C). ¹¹⁹Sn{¹H} NMR (149.12 MHz, THF-*d*₈, 25°C): δ = 79 ppm. UV–vis (THF): λ_{max} (ε) 248 (3473), 253 (4003), 259 (3789), 264 (3282), 293 (1504), 314 (1393), 461 (494), 657 nm (1044 dm³ mol^{–1} cm^{–1}).

[L³GeK.TMEDA] (12). *Method A:* Et₂O (20 mL) was added to a mixture of **10** (0.54 g, 0.52 mmol) and KC₈ (0.14 g, 1.03 mmol) at room temperature. The resulting green mixture was stirred for 1 day. The insoluble precipitate was then filtered off and TMEDA (0.90 ml, 6.04 mmol) was added at 0 °C. The resulting green solution was stirred at room temperature for 3 h. The solution was filtered and concentrated to afford **12** as green crystals. Yield: 0.53 g (76 %).

Method B: Et₂O (20 mL) was added to a mixture of **7** (1.12 g, 2.00 mmol) and KC₈ (0.56 g, 4.15 mmol) at room temperature. The resulting green mixture was stirred for 1 day. The insoluble precipitate was then filtered off and TMEDA (0.90 ml, 6.04 mmol) was

added at 0°C. The resulting green solution was stirred at room temperature for 3 h. The solution was filtered and concentrated to afford **12** as green crystals. Yield: 0.76 g (56 %).

Mp: 155 °C. Elemental analysis (%) calcd for C₃₈H₅₅GeKN₄: C, 67.14; H, 8.16; N, 8.25. Found: C, 66.21; H, 7.13; N, 7.51. Attempts to obtain acceptable elemental analysis data for compound **12** failed due to its extreme air sensitivity. ¹H NMR (399.5 MHz, C₆D₆, 25 °C): δ = 1.18 (d, ³J_{H-H} = 6.9 Hz, 24H, CH(CH₃)₂), 1.87 (s, 12H, NCH₃), 2.00 (s, 4H, NCH₂), 3.23 (sept, ³J_{H-H} = 6.9 Hz, 4H, CH(CH₃)₂), 6.85 (t, ³J_{H-H} = 7.3 Hz, 1H, Ph), 7.09 – 7.18 (m, 6H, Ph), 7.36 (d, ³J_{H-H} = 7.3 Hz, 2H, Ph), 8.15 (s, 2H, CH=N). ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 25 °C): δ = 25.27 (CH(CH₃)₂) 28.05 (CH(CH₃)₂), 45.45 (NCH₃), 57.59 (NCH₂), 118.01, 123.30, 125.20, 128.88 (*Ph*-Ge), 137.27, 141.87, 149.37, 149.96 (NAr), 167.43 ppm (C=NAr). UV-Vis (THF): $\lambda_{\text{max}}(\epsilon)$ = 224 (6987), 236 (6218), 241 (6092), 246 (6059), 252 (5950), 258 (5875), 267 (6000), 278 (6107), 292 (6168), 395 (2170), 433 (2020), 703 nm (739 dm³ mol⁻¹cm⁻¹). IR (Nujol cm⁻¹): 2955s, 2922s, 2853s, 1601m, 1584w, 1547w, 1504w, 1462m, 1433m, 1414w, 1391w, 1377w, 1358w, 1335w, 1315m, 1290w, 1258w, 1190w, 1175w, 1155w, 1136w, 1098w, 1080w, 1034w, 1011w, 962w, 949w, 932w, 845w, 802w, 789w, 779w, 756w, 682w.

[[L⁴SnK(THF)] (13). *Method A.* THF (20 mL) was added to a mixture of **8** (0.80 g, 2.00 mmol) and KC₈ (0.54 g, 4.00 mmol) at room temperature. The resulting green mixture was stirred for 15 h. The insoluble precipitate was then filtered off and the filtrate was concentrated to afford **13** as dark green crystals. Yield: 0.20 g (22 %).

Method B. THF (20 mL) was added to a mixture of **11** (0.084 g, 0.12 mmol) and KC₈ (0.033 g, 0.24 mmol) at room temperature. The resulting green mixture was stirred for 15 h. The insoluble precipitate was then filtered off and the filtrate was concentrated to afford **13** as dark green crystals Yield: 0.037 g (34 %).

M.p. 200 °C. Elemental analysis (%) calcd for C₂₀H₃₁KN₂OSn: C, 50.73; H, 6.60; N, 5.92. Found: C, 43.35; H, 8.08; N, 4.66. Attempts to obtain acceptable elemental analysis data for compound **13** failed due to its extreme air sensitivity. ¹H NMR (395.9 MHz, THF-*d*₈, 25 °C): δ = 1.54 (s, 18H, C(CH₃)₃), 1.76 (m, 4H, THF), 3.60 (m, 4H, THF), 6.46 (t, ³J_{HH} = 7.2 Hz, 1H, Ph), 6.92 (d, ³J_{HH} = 7.28 Hz, 2H, Ph), 8.40 (s, 2H, CH=N); ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈, 25 °C): δ = 26.56 (THF), 33.80 (C(CH₃)₃), 57.55 (C(CH₃)₃), 68.40 (THF), 116.33, 125.82, 141.64, 145.12 (Ph), 185.53 ppm (C=N-C). ¹¹⁹Sn{¹H} NMR (149.1 MHz, THF-*d*₈, 25 °C): δ = 310 ppm. UV-vis (THF): λ_{max} (ε) 244 (4208), 247 (4826), 252 (4257), 258 (3361), 266 (3080), 273 (3135), 460 (74), 657 nm (160 dm³ mol⁻¹ cm⁻¹).

[Li(THF)₄][L³Pb] (14). *Method A:* THF (20 mL) was added to a mixture of **9** (0.74 g, 1.00 mmol) and Li (0.020 g, 2.90 mmol) at - 78 °C. The resulting dark red mixture was stirred for 2h at - 40 °C. The insoluble precipitate was then filtered off and the filtrate was concentrated to afford **14** as dark red crystals. Yield: 0.12 g (13 %).

Method B: THF (10 mL) was added to a mixture of **15** (0.660 g, 0.50 mmol) and Li (0.007 g, 1.00 mmol) at - 78 °C. The resulting dark red mixture was stirred for 2 h at - 40 °C. The insoluble precipitate was then filtered off and the filtrate was concentrated to afford **14** quantitatively.

M.p. 178 °C (dec.). Elemental analysis calcd (%) for C₄₈H₇₁LiN₂O₄Pb: C 60.37, H 7.44, N 2.93. Found: C 60.13, H 7.15, N 2.86. ¹H NMR (395.9 MHz, THF-*d*₈, 25 °C): δ = 1.12 (d, 24H, ³J_{HH} = 6.73 Hz, CH(CH₃)₂), 1.78 (m, 16H, THF), 3.35 (sept, ³J_{HH} = 6.7 Hz, 4H, CH(CH₃)₂), 3.62 (m, 16H, THF), 6.37 (t, ³J_{HH} = 6.7 Hz, 1H, Ph-Pb), 6.81–6.88 (m, 4H, Ph), 7.04 (m, 4H, Ph), 7.92 ppm (s, 2H, CH=N); ¹H NMR (395.9 MHz, THF-*d*₈, - 60 °C): δ = 1.05 (d, 12H, ³J_{HH} = 6.3 Hz, CH(CH₃)₂), 1.10 (d, ³J_{HH} = 6.3 Hz, 12H, CH(CH₃)₂),

1.70 (m, 16H, THF), 3.12 (sept, $^3J_{\text{HH}} = 6.3$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 3.24 (sept, $^3J_{\text{HH}} = 6.3$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 3.54 (m, 16H, THF), 6.35 (t, $^3J_{\text{HH}} = 6.8$ Hz, 1H, Ph-Pb), 6.86 – 6.89 (m, 4H, Ph), 7.03 (m, 4H, Ph), 7.97 ppm (br s, 2H, $\text{CH}=\text{N}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $\text{THF}-d_8$, 25 °C): $\delta = 24.34$ ($\text{CH}(\text{CH}_3)_2$), 26.58 (THF), 28.12 ($\text{CH}(\text{CH}_3)_2$), 68.42 (THF), 113.76, 122.57, 122.83, 123.63, 135.63, 142.28, 144.22 (Ph), 154.24 (C-Pb), 161.87 ppm ($\text{CH}=\text{N}$); $^7\text{Li}\{^1\text{H}\}$ NMR (155.27 MHz, $\text{THF}-d_8$, 25 °C): $\delta = 4.85$ ppm; $^{207}\text{Pb}\{^1\text{H}\}$ NMR (82.6 MHz, $\text{THF}-d_8$, 25 °C): $\delta = 3415$ ppm; UV-vis (THF): λ_{max} (ϵ) 370 (1825), 471 (1695), 589 (665), 734 nm ($565 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

[L³Pb-PbL³] (15). A THF solution (5 mL) of SnCl_2 (0.057g, 0.30 mmol) was added dropwise to a THF solution (10 mL) of **14** (0.58 g, 0.60 mmol) at – 78 °C. The reaction mixture was then stirred for 1 h. Volatiles were removed under vacuum, and the residue was extracted with hexane. The insoluble precipitate was then filtered off and the dark green filtrate was concentrated to afford **15** as dark green crystals. Yield: 0.048 g (12 %). M.p. 110 °C (dec.). Elemental analysis calcd (%) for $\text{C}_{64}\text{H}_{78}\text{N}_4\text{Pb}_2$: C 58.33, H 5.97, N 4.25. Found: C 58.18, H 5.63, N 4.10. ^1H NMR (399.5 MHz, C_6D_6 , 25 °C): δ 0.83 – 1.07 (m, 48H, $\text{CH}(\text{CH}_3)_2$), 2.91 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 3.26 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 6.90 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2H, Ph), 7.08-7.10 (m, 14H, Ph), 7.60 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2H, Ph), 7.65 (br s, 1H, $\text{CH}=\text{N}$), 8.42 (br s, 1H, $\text{CH}=\text{N}$), 8.79 ppm (s, 2H, $\text{CH}=\text{N}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , 25 °C): δ 24.83 ($\text{CH}(\text{CH}_3)_2$), 29.04 ($\text{CH}(\text{CH}_3)_2$), 123.27, 124.70, 125.05, 125.70, 134.01, 135.96, 139.18, 148.23, 148.29, 148.88 (Ph), 149.75 (C-Pb), 150.64 ppm (C=NAr); $^{207}\text{Pb}\{^1\text{H}\}$ NMR (83.6 MHz, C_6D_6 , 25 °C): δ 1684 ppm; UV-vis (THF): λ_{max} (ϵ) 396 (4968), 473 (2442), 526 nm ($3263 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

[2-(CH=NAr)-6-(CH-NAr) C_6H_3] $[\text{GePd}(\text{PPh}_2)_2]_2$ (18). A THF solution (10 mL) of **12** (0.68 g, 1.00 mmol) was added to a THF solution (5 mL) of $(\text{PPh}_3)_2\text{PdCl}_2$ at – 78°C. The

resulting dark green solution was stirred at room temperature for 15 h. Solvent was removed under vacuum and the residue was extracted with Et₂O/hexane (1:1). The insoluble precipitate was then filtered off and the filtrate was concentrated to afford **18** as orange crystals. Yield: 0.0682 g (11 %). Mp: 168 °C (dec.). Elemental analysis (%) calcd for C₁₃₆H₁₃₈Ge₂N₄P₄Pd₂: C, 70.69; H, 6.02; N, 2.42. Found: C, 68.40; H, 8.54; N, 2.96. Attempts to obtain acceptable elemental analysis data for compound **18** failed as the sample have decomposed during sample preparation. ¹H NMR (399.5 MHz, THF-*d*₈, 25 °C): δ = 0.0047 (d, 6H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 0.57 (d, 6H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 0.75 (m of overlapping d, 18H, CH(CH₃)₂), 0.87 (d, 12H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 1.08 (d, 6H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 2.43 (sept, 2H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 2.72 (br, 4H, CH(CH₃)₂), 4.27 (sept, 2H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 5.35 (d, 2H, ³J_{HH} = 4.1 Hz, CH(Ph)(NAr)), 6.64–7.70 (m, 74H, Ph), 7.91 (d, 2H, ³J_{HH} = 7.8 Hz, Ph), 8.13 (d, 2H, ³J_{HH} = 7.8 Hz, Ph), 9.50 ppm (s, 2H, CH=N). ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 25 °C): δ = 23.00, 23.19, 23.24, 23.39, 23.43, 24.91 (CH(CH₃)₂), 27.10, 27.38, 28.50, 28.69, 29.00 (CH(CH₃)₂), 79.16 (C(NAr)), 123.17, 123.86, 124.67, 124.78, 125.61, 131.49, 132.35, 132.44, 134.16, 134.25, 134.33, 136.77, 137.68, 137.92, 138.04, 138.27, 141.01, 143.13, 146.04, 146.39, 146.79, 149.74, 150.96 (Ph), 161.58 ppm (s, C=NAr). ³¹P{¹H} NMR (161.7 MHz, THF-*d*₈, 25°C): δ = 31 (³J_{PP} = 47.68 Hz), 29 ppm (³J_{PP} = 47.68 Hz).

Crystal Structure Determinations of Compounds 7-15, 18 and L³Li. X-ray data collection and structural refinement: The crystal data were collected using a Bruker APEX II diffractometer. The crystals were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least squares methods on F^2 .^[35] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in

their respective parents atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations.

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CHAPTER 3

Base-stabilized Germanium(II) Hydroxide, Azide and Triazaphospole[‡]

Introduction

The chemistry of low-valent germanium complexes has attracted much attention due to their carbene like properties.^[1] In the past decades, the concepts of thermodynamic and/or kinetic stabilization have been applied successfully in the isolation of a large number of stable germylenes.^[2] In particular, germylenes containing a functionalized substituent such as H, OH, Cl, have drawn much attention as they were utilized as versatile ligands, as building blocks for the synthesis of new low-valent germanium derivatives and as synthons for the activation of small molecules.^[3] For example, a) the formation of a potassium germylidenide by the reduction of RGeCl [R = HC(CMeNAr)₂],^[4] b) the formation of an unsymmetric Ge(I) complex RGe–GeR' (R' = HC{C(Me)NAr}{C(CH₂)NAr}) by the salt elimination of RGeCl,^[5] c) small molecules (N₂O, CO₂, Me₃SiN₃ etc) activation by RGeH,^[3c,6] and d) the formation of heterobimetallic complexes [RGe(μ-O)M(THF)Cp₂] (M = Yb, Y) upon the reaction of RGeOH with Cp₃M have been reported (Scheme 3.1).^[7] The aforementioned examples illustrate the fruitful research area of functionalized germylenes, and it is not surprising that there is still intensive research activity focused on developing new ligands

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(amidinate, aminotroponimate, guanidinate, pyrrolylaldiminato etc) (Chart 3.1) for the preparation of new functionalized germylenes and for their reactivity studies.^[8]

Scheme 3.1. Examples of the reactivities of functionalized germylenes.

Chart 3.1. Examples of functionalized germylenes supported by (a, b) amidinate; (c) guanidinate; (d) pyridyl-1-azaallyl and (e) aminotroponimate ligands.

In the previous chapter, 2,6-diiminophenylgermanium(II) chloride (**7**) and its reduction to form the Ge(I) dimer (**10**) and germylidenide anion (**12**) were discussed. In continuation of our research using 2,6-diiminophenyl ligand, we are interested in isolating other functionalized germylenes, which comprise hydroxide and azide substitutes. Moreover, azides can undergo an uncatalysed 1,3-dipolar cycloaddition with phosphalkynes to give 1,2,3,4-triazaphospholes with stereospecificity and approximate quantitative yield,^[9] which fulfil all of the requirements of “click” chemistry (Scheme 3.2).^[9b,c] We are interested in exploring the uncatalysed 1,3-dipolar cycloaddition of a germanium(II) azide with phosphalkyne and understanding the effect of the low-valent germanium atom in the reaction.

Scheme 3.2. 1,3 dipolar cycloaddition reaction between azide and phosphalkyne.

Herein, we report the synthesis of the 2,6-diiminophenylgermanium(II) hydroxide $[\text{L}^1\text{GeOH}(\text{SnMe}_3\text{Cl})]\cdot\text{SnMe}_3\text{Cl}$ (**19**) which is stabilized by Me_3SnCl . We also describe the synthesis of the 2,6-diiminophenylgermanium(II) azide (**20**) and its reaction with 1-adamantyl phosphalkyne. To the best of our knowledge, no reactivity of a germanium(II) azide has been reported.

Results and Discussion

Scheme 3.3. Syntheses of compounds **19** – **21**.

Synthesis of $[\text{L}^3\text{GeOH}(\text{SnMe}_3\text{Cl})]\cdot\text{SnMe}_3\text{Cl}$. Compound **7** was treated with Me_3SnOH in THF at room temperature to afford $[\text{L}^3\text{GeOH}(\text{SnMe}_3\text{Cl})]$ (**19**, Scheme 3.3). An attempt to separate **19** and SnMe_3Cl by recrystallization or vacuum evacuation failed. They were cocrystallized in Et_2O to form **19**· SnMe_3Cl (Figure 3.1) as an air- and moisture-sensitive colorless crystalline solid in 42.6% yield. When one equivalent of Me_3SnCl was added to the reaction mixture, compound **19**· SnMe_3Cl can be isolated in a higher yield (63.8%). Besides compound **19**, only three examples of organogermanium(II) hydroxide **A** - **C** have been reported by research groups of Roesky and Driess, and Couret, respectively (Chart 3.2).^[3b,10] They were prepared by reacting their parent germylenes toward water.

There is a possibility of water, even in stoichiometric amount, decomposing the compound **7**. Hence a milder reactant, Me_3SnOH was used as the hydroxide source.

Chart 3.2. β -diketiminate germanium (II) hydroxides **A**, **B** and 2,6-bis((diethylamino)methyl)phenyl germanium (II) hydroxide **C**.

Compound **19**· SnMe_3Cl is soluble in hydrocarbon solvents and was characterized by NMR spectroscopy. The ^1H NMR spectrum of **19**· SnMe_3Cl in C_6D_6 displays one set of signals due to the 2,6-diiminophenyl ligand. There are two singlets at δ 8.06 and 8.08 ppm, which correspond to two nonequivalent $\text{HC}=\text{N}$ protons. A singlet at δ 1.56 ppm corresponds to the hydroxide proton, which is comparable to that in **A** (δ =1.56 ppm) and **B** (δ =1.60 ppm). There is only one signal at δ 0.23 ppm for the methyl protons of SnMe_3Cl in the ^1H NMR spectrum and one signal at δ 161 ppm in the $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum, which corresponds to SnMe_3Cl . The ^1H NMR spectrum acquired at -60°C is same as that at room temperature, but the signal for the SnMe_3Cl is broadened in the ^1H NMR spectrum performed at -95°C . The results are inconsistent with the X-ray crystal structure, which indicate that SnMe_3Cl moieties undergo a rapid interchange in solution. The IR spectrum of **19**· SnMe_3Cl shows an absorption at $\nu = 3443\text{ cm}^{-1}$ which can be attributed to the O-H stretching frequency. This value shows a bathochromic shift compared with that of **A** (3571 cm^{-1}) and **B** (3643 cm^{-1}) because the O-H moiety in compound **19**· SnMe_3Cl forms a donor acceptor interaction with SnMe_3Cl .

The molecular structure of **19**•SnMe₃Cl is illustrated in Figure 3.1. The disorder in the *i*Pr is omitted for clarity. The germanium atom adopts a distorted trigonal pyramidal geometry (sum of bond angles: 250.18°), by coordinating with the C(1) and N(1) atoms of the 2,6-diiminophenyl ligand and the O(1) atom of the hydroxide substituent. This indicates the presence of a lone pair with high *s*-character at the germanium atom. The Ge(1)-O(1) bond (1.906(7) Å) is slightly longer as compared to that in **A** (1.828(1) Å) and **B** (1.823(2) Å). A longer Ge-O bond length could be due to the intermolecular O(1)→Sn(1) interaction with the SnMe₃Cl moiety. The O(1)-Sn(1) bond (2.272(8) Å) is slightly shorter than that in [2,6-(CH₂O*t*Bu)₂C₆H₃Sn(Ph₂)OH•Sn(*n*Bu)₃Cl] (2.342(4) Å, Chart 3.3).^[11] The Ge1⋯N2 distance [2.493(11) Å] is longer than Ge1-N1 bond [2.325(10) Å] but it is shorter than the sum of the van der Waals radii (ca. 3.55 Å). The results indicate that there is weak interaction between the Ge1 and N2 atoms.

Chart 3.3. [2,6-(CH₂O*t*Bu)₂C₆H₃Sn(Ph₂)OH•Sn(*n*Bu)₃Cl] (O→Sn bond length: 2.342(4) Å).

Synthesis of [L³GeN₃]. Compound **7** was treated with NaN₃ in THF at room temperature, which quantitatively afforded [L³GeN₃] (**20**) as an air- and moisture-sensitive yellow solid. However, X-ray quality crystals of **20** cannot be obtained. Other examples of base-stabilized germanium(II) azides have been reported by other research groups (Chart 3.4).^{6c,12}

Figure 3.1. Molecular structure of **19**·SnMe₃Cl with thermal ellipsoids at the 50% probability level. Hydrogen atoms except the H(1) atom are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-Ge(1) 2.010(12), Ge(1)-O(1) 1.906(7), Ge(1)-N(1) 2.325(10), N(1)-C(7) 1.282(14), C(6)-C(7) 1.450(16), C(1)-C(6) 1.364(16), N(2)-C(20) 1.268(15), Ge(1)···N(2) 2.493(11), O(1)-Sn(1) 2.272(8), C(1)-Ge(1)-O(1) 101.7(4), N(1)-Ge(1)-O(1) 91.8(3), C(1)-Ge(1)-N(1) 75.1(4), N(1)-C(7)-C(6) 116.4(11), C(6)-C(1)-Ge(1) 118.1(9).

Compound **20** is soluble in hydrocarbon solvents and was characterized by NMR spectroscopy. The ¹H NMR spectrum of **20** in C₆D₆ displays one set of signals due to the 2,6-diiminophenyl ligand. In the spectrum, there are one doublet at δ 1.18 ppm and one broad singlet at δ 3.26 ppm for the *i*Pr substituents. The ¹H NMR spectrum was acquired at -60 °C, whereupon 4 doublets at δ 1.12 – 1.28 ppm for the CH(CH₃)₂ protons and two broad signals at δ 2.99 and δ 3.19 ppm for the CH(CH₃)₂ protons were resolved. The results indicate that the imino substituents are fluxional in solution at room temperature. The IR spectrum of **20** shows a strong absorption at ν = 2064 cm⁻¹ which can be attributed to the N₃ asymmetric stretching frequency. This value is comparable with that of [(*n*Pr)₂ATI]GeN₃ (2048 cm⁻¹, ATI = aminotroponimate, Chart 4.3f)^[12] and

$[(\text{Mes})_2\text{DAP}]\text{GeN}_3$ (2062 cm^{-1} , $((\text{Mes})_2\text{DAP} = 2,4\text{-dimethyl-}N\text{-}N'\text{-bis}(2,4,6\text{-trimethylphenyl})\text{-}1,5\text{-diazapentadienyl}$, Chart 3.4c).^[13]

Chart 3.4. Examples of base-stabilized germanium(II) azides.

Synthesis of $[\text{L}^3\text{Ge}\{\text{N}_3\text{C}(\text{Ad})\text{P}\}]$. Compound **20** was treated with 1-adamantyl phosphaaalkyne in toluene at room temperature for 5 hours to quantitatively afford $[\text{L}^3\text{Ge}\{\text{N}_3\text{C}(\text{Ad})\text{P}\}]$ (**21**). Volatiles of the reaction mixture were removed by vacuum and the crude product was analyzed by NMR spectroscopy. The ^1H and ^{31}P NMR spectra show the presence of **21** and unreacted **20** (0.75 % w.r.t. **21**). No by-products, which are due to the [1+2] cycloaddition of the low-valent germanium atom with phosphaaalkyne, were observed.^[14] The results are quite similar to the reaction of β -diketminate germanium(II) hydride with tert-butylphosphaaalkyne, in which the lone pair of electrons

on the low-valent germanium atom does not undergo a [1+2] cycloaddition with the phosphaaalkyne, instead the $\text{Ge}^{\text{II}}\text{-H}$ bond inserts into the $\text{C}\equiv\text{P}$ bond to form $[\text{RGe}\{\text{C}(\text{tBu})=\text{PH}\}]$ (Scheme 3.4).^[6d] Besides AdCP, we attempted to react compound **20** with PhCN, but no reaction was observed.

Scheme 3.4. Reaction between β -diketminate germanium(II) hydride with tert-butylphosphaaalkyne.

Compound **21** was isolated as an air- and moisture-sensitive orange crystalline solid from the reaction mixture by crystallization in toluene. It is soluble in hydrocarbon solvents and is characterized by NMR spectroscopy. The ^1H NMR spectrum of **21** in $\text{THF-}d_8$ at room temperature displays a broad signal at δ 0.89 - 1.22 ppm for the *i*Pr substituents. The results are inconsistent with the solid-state structure. In this regard, the ^1H NMR spectrum was acquired at $-60\text{ }^\circ\text{C}$, whereupon four doublets at δ 0.58-1.24 ppm for the $\text{CH}(\text{CH}_3)_2$ protons and two septets at δ 1.69 and 3.00 ppm were observed for the $\text{CH}(\text{CH}_3)_2$ protons. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a singlet at δ 181.4 ppm which is comparable to the previously reported 1,2,3,4-triazaphospholes (161.8 – 183.2 ppm).^[15]

Chart 3.5. Some examples of 1,2,3,4-triazaphospholes. ³¹P{¹H} NMR [ppm]: (a) δ 174.4; (b) δ 182.5; (c) δ 178.4; (d) δ 177.7; (e) δ 161.8; (f) δ 183.2; (g) δ 173.2; (h) δ 177.0; (i) δ 172.4.

Compound **21** is also characterized by X-ray crystallography (Figure 3.2). The germanium atom is bonded to the bidentate 2,6-diiminophenyl ligand and the 1,2,3,4-triazaphosphole ring, which adopts a distorted trigonal pyramidal geometry (sum of bond angles: 243.51°). This indicates the presence of a lone pair with high *s*-character at the germanium atom. The Ge1...N5 distance [2.465(3) Å] is longer than Ge1-N4 bond [2.370(3) Å] but it is shorter than the sum of the van der Waals radii (ca. 3.55 Å). The results indicate that there is weak interaction between the Ge1 and N4 atoms. The Ge(1)-N(1) bond (1.971(3) Å) is comparable with typical Ge-N single bonds (1.854 - 1.925 Å).^[16] The bond lengths [N(1)-N(2) 1.344(4) Å, N(2)-N(3) 1.317(4) Å, N(3)-C(33) 1.372(5) Å, N(1)-P(1) 1.675(3) Å and P(1)-C(33) 1.724(4) Å] of the 1,2,3,4-triazaphosphole ring are comparable with the 1,2,3,4-triazaphosphole-containing tripodal ligand (Chart 3.5g-l),^[15c] which indicate the presence of an aromatic delocalization.

Figure 3.2. Molecular structure of **21** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-Ge(1) 2.000(4), Ge(1)-N(1) 1.971(3), Ge(1)-N(4) 2.370(3), N(4)-C(7) 1.280(4), C(6)-C(7) 1.462(5), C(1)-C(6) 1.394(5), N(5)-C(20) 1.276(5), Ge(1)···N(5) 2.465(3), N(1)-N(2) 1.344(4), N(2)-N(3) 1.317(4), N(1)-P(1) 1.675(3), P(1)-C(33) 1.724(4), N(3)-C(33) 1.372(5), C(1)-Ge(1)-N(1) 94.33(13), N(4)-Ge(1)-N(1) 88.93(10), C(1)-Ge(1)-N(4) 75.61(12), Ge(1)-N(4)-C(7) 109.1(2), N(4)-C(7)-C(6) 118.9(3), C(6)-C(1)-Ge(1) 119.3(3), Ge(1)-N(1)-N(2) 116.8(2), N(1)-N(2)-N(3) 111.8(3), N(2)-N(3)-C(33) 113.1(3), N(1)-P(1)-C(33) 87.71(16).

Conclusion

In conclusion, the 2,6-diiminophenylgermanium(II) hydroxide **19** and azide **20** were synthesized by the reaction of the corresponding germanium(II) chloride with SnMe_3OH and NaN_3 . The uncatalysed 1,3-dipolar cycloaddition reaction of **20** with 1-adamantyl phosphalkyne fulfils all of the requirements of “click” chemistry.

Experimental Section

All manipulations were carried out under an inert atmosphere of argon by using standard Schlenk techniques. Solvents were dried over and distilled over Na/K alloy prior to use. The ^1H , ^{13}C , ^{31}P and ^{119}Sn NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to SiMe_4 for ^1H and ^{13}C , 85% H_3PO_4 for ^{31}P and SnMe_4 for ^{119}Sn . Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Infrared data were recorded on a Shimadzu IR Prestige-21 spectrometer. Melting points were measured in sealed glass tubes and were not corrected.

[[$\text{L}^3\text{GeOH}(\text{SnMe}_3\text{Cl})$] $\cdot\text{SnMe}_3\text{Cl}$] (19** $\cdot\text{SnMe}_3\text{Cl}$).** A THF solution (10 mL) of **7** (0.28 g, 0.50 mmol) was added to a THF solution (10 mL) of Me_3SnOH (0.11 g, 0.60 mmol) and Me_3SnCl (0.12g, 0.60 mmol) at room temperature. The resulting red solution was stirred for 2 h. Solvent was removed under vacuum. The resulting residue was extracted with Et_2O and filtered. The filtrate was concentrated to afford **19** $\cdot\text{SnMe}_3\text{Cl}$ as colorless crystals. Yield: 0.30 g (64 %). M.p. 215 °C. Elemental analysis (%) calcd for $\text{C}_{38}\text{H}_{58}\text{Cl}_2\text{GeN}_2\text{OSn}_2$: C, 48.56; H, 6.22; N, 2.98. Found: C, 50.65; H, 8.45; N, 3.44. Attempts to obtain acceptable elemental analysis data for compound **19** $\cdot\text{SnMe}_3\text{Cl}$ failed as the sample have decomposed during sample preparation. ^1H NMR (399.5 MHz, C_6D_6 , 25 °C): δ = 0.23 (s, 18H, $\text{Sn}(\text{CH}_3)_3\text{Cl}$), 1.11-1.31 (m of overlapping d, 24H, $\text{CH}(\text{CH}_3)_2$), 1.56 (s, 1H, OH) 3.37 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 7.02-7.29 (m, 9H, Ph), 8.06 (s, 1H, $\text{CH}=\text{N}$), 8.08 (s, 1H, $\text{CH}=\text{N}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , 25 °C): δ = 1.37 ($\text{Sn}(\text{CH}_3)_3\text{Cl}$), 23.51, 23.76, 23.98, 24.11, 24.25, 24.44, 24.56, 24.98 ($\text{CH}(\text{CH}_3)_2$), 28.11, 28.33, 28.63, 28.71 ($\text{CH}(\text{CH}_3)_2$), 123.10 - 123.90 (m), 126.57, 126.61, 128.95, 132.24, 140.39, 140.53, 145.06, 145.24 (Ph), 165.48, 165.58, ($\text{C}=\text{NAr}$). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.0 MHz, C_6D_6 , 25 °C): δ = 161 ppm. IR (Nujol, cm^{-1}): 3443br, 2953s, 2920s, 2851s, 1624m, 1611m, 1585w, 1551m, 1462s,

1454s, 1379s, 1323m, 1254w, 1175m, 1165m, 1098m, 1049s, 933m, 849m, 793s, 750s, 721m.

[L³GeN₃] (20). A THF solution (10 mL) of **5** (0.28 g, 0.5 mmol) was added to a THF solution (10 mL) of NaN₃ (0.039 g, 0.6 mmol) at room temperature. The resulting orange suspension was stirred for 15 h. NaCl was then filtered off and solvent was removed under vacuum. The resulting orange residue was extracted with toluene and filtered. Solvent was removed under vacuum to quantitatively afford **20** as yellow solid. M.p. 220 °C. Elemental analysis (%) calcd for C₃₂H₃₉GeN₅: C, 67.85; H, 6.94; N, 12.37. Found: C, 66.07; H, 9.44; N, 10.53. Attempts to obtain acceptable elemental analysis data for compound **20** failed as the sample have decomposed during sample preparation. ¹H NMR (399.5 MHz, C₆D₆, 25 °C): δ = 1.18 (d, 24H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 3.26 (br, 4H, CH(CH₃)₂), 7.01-7.05 (m, 1H, Ph), 7.12-7.18 (m, 8H, Ph), 8.04 (s, 2H, CH=N). ¹H NMR (399.5 MHz, THF-*d*₈, -60°C): δ = 1.12 (d, 6H, ³J_{HH} = 6.3 Hz, CH(CH₃)₂), 1.16 (d, 6H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 1.20 (d, 6H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 1.28 (d, 6H, ³J_{HH} = 6.3 Hz, CH(CH₃)₂), 2.99 (br, 2H, CH(CH₃)₂), 3.19 (br, 2H, CH(CH₃)₂), 7.11-7.24 (m, 6H, Ph), 7.71 (t, 1H, ³J_{HH} = 7.7 Hz, Ph), 8.04 (d, 2H, ³J_{HH} = 7.7 Hz, Ph), 8.75 (s, 2H, CH=N). ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 25 °C): δ = 24.16 (CH(CH₃)₂), 28.65 (CH(CH₃)₂), 123.86, 126.70, 129.17, 132.32, 140.2, 141.01, 145.21 (Ph), 165.96 ppm (C=NAr). IR (Nujol, cm⁻¹): 2957s, 2922s, 2853s, 2064s, 1612m, 1549w, 1458s, 1377w, 1364w, 1323w, 1271w, 1260w, 1171w, 1098w, 1047m, 1022w, 793m, 752w.

[L³Ge{N₃C(Ad)P}] (21). A toluene solution (5 mL) of 1-adamantyl phosphalkyne (0.09 g, 0.5 mmol) was added dropwise to a toluene solution (5 mL) of **20** (0.28 g, 0.5 mmol) at room temperature. The resulting orange solution was stirred for 5 h and filtered. Solvent was removed under vacuum to quantitatively afford **21** as yellow solid. Compound **21** was re-extracted with toluene and filtered. The filtrate was concentrated to afford **21** as

yellow crystals. The filtrate was concentrated to afford **21** as yellow crystals. Yield: 0.15 g (40 %). M.p. 190 °C. Elemental analysis (%) calcd for C₄₃H₅₄GeN₅P: C, 69.35; H, 7.31; N, 9.41. Found: C, 69.50; H, 9.04; N, 9.15. ¹H NMR (399.5 MHz, THF-*d*₈, 25 °C): δ = 0.79-1.22 (br, 28H, *i*Pr), 1.77 (s, 6H, Ad), 2.01 (s, 9H, Ad), 7.09 (m, 6H, Ph), 7.74 (t, 1H, ³*J*_{HH} = 7.75 Hz, Ph), 8.06 (d, 2H, ³*J*_{HH} = 7.79 Hz, Ph), 8.60 (s, 2H, CH=N). ¹H NMR (395.9 MHz, THF-*d*₈, -60 °C): δ = 0.58 (d, 6H, ³*J*_{HH} = 6.4 Hz, CH(CH₃)₂), 0.85 (d, 6H, ³*J*_{HH} = 6.3 Hz, CH(CH₃)₂), 1.13 (d, 6H, ³*J*_{HH} = 6.3 Hz, CH(CH₃)₂), 1.24 (d, 6H, ³*J*_{HH} = 6.3 Hz, CH(CH₃)₂), 1.69 (septet, 2H, ³*J*_{HH} = 6.3 Hz, CH(CH₃)₂), 1.74 (s, 6H, Ad), 1.98 (s, 9H, Ad), 3.00 (septet, 2H, ³*J*_{HH} = 6.3 Hz, CH(CH₃)₂), 7.03-7.21 (m, 6H, Ph), 7.79 (t, 1H, ³*J*_{HH} = 7.2 Hz, Ph), 8.13 (d, 2H, ³*J*_{HH} = 7.2 Hz, Ph), 8.77 (s, 2H, CH=N). ¹³C{¹H} NMR (100.46 MHz, C₆D₆, 25 °C): δ = 24.08 (Ad), 25.15 (CH(CH₃)₂), 28.45 (CH(CH₃)₂), 29.36 (CH(CH₃)₂), 37.21 (CH(CH₃)₂), 37.43 (d, ²*J*_{P-C} = 14 Hz, Ad), 45.29 (d, ³*J*_{P-C} = 6.7 Hz, Ad), 123.75, 126.60, 129.07, 132.72, 140.23, 141.19, 145.32, 166.14 (Ph), 167.25 (d, ⁴*J*_{P-C} = 9.6 Hz, C=NAr), 197.99 ppm (d, *J*_{P-C}, 60.4 Hz, P=C). ³¹P{¹H} NMR (161.73 MHz, THF-*d*₈, 25 °C): δ = 181.4 ppm.

Crystal Structure Determinations of Compounds 19 and 21. X-ray data collection and structural refinement: The crystal data were collected using a Bruker APEX II diffractometer. The crystals were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least squares methods on *F*².^[16] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parents atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations.

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Appendix A: Crystallographic Data

Table 1. Crystallographic Data of Compounds 1-4 and 6.

Table 2. Crystallographic Data of Compounds 7-11.

Table 3. Crystallographic Data of Compounds 12-15 and 18.

Table 4. Crystallographic Data of Compounds L^3Li , 19 and 21.

Table 1. Crystallographic Data of Compounds 1-4 and 6.

	1	2	3	4	6
formula	C ₂₉ H ₄₃ ClGeN ₂ O _{0.33}	C ₂₉ H ₄₃ ClN ₂ Sn	C ₇₀ H ₉₂ Cl ₂ Ge ₂ N ₄	C ₅₆ H ₇₈ Ge ₂ N ₄	C ₂₈ H ₃₉ ClN ₂ Sn
formula weight	541.03	573.79	1205.56	952.40	557.75
color	Yellow	Yellow	Yellow	Yellow	Yellow
crystal system	Trigonal	Monoclinic	Triclinic	Monoclinic	Orthorhombic
space group	<i>R</i> -3	<i>P</i> 2(1)/c	<i>P</i> -1	<i>P</i> 2(1)/n	<i>Pnma</i>
<i>a</i> / Å	26.6462(6)	17.8671(2)	11.6097(4)	13.121(3)	11.9540(4)
<i>b</i> / Å	26.6462(6)	10.6751(2)	11.6803(4)	11.775(3)	21.6098(7)
<i>c</i> / Å	21.6114(6)	16.9547(3)	13.1414(5)	17.909(4)	10.4850(3)
α / deg	90	90	90.528(2)	90	90
β / deg	90	118.0080(10)	101.511(2)	103.455(7)	90
γ / deg	120	90	110.985(2)	90	90
<i>V</i> / Å ³	13288.7(6)	2855.08(8)	1624.02(10)	2690.9(10)	2708.52(15)
<i>Z</i>	18	4	1	2	4
<i>d</i> _{calcd} / mg cm ⁻³	1.217	1.335	1.233	1.175	1.368
μ / mm ⁻¹	1.148	1.007	1.050	1.154	1.059
<i>F</i> (000)	5160	1192	638	1012	1152
crystal size / mm ³	0.36 x 0.26 x 0.20	0.40 x 0.32 x 0.24	0.10 x 0.08 x 0.06	0.10 x 0.02 x 0.01	0.40 x 0.30 x 0.26
Index ranges	-37 ≤ <i>h</i> ≤ 26	-30 ≤ <i>h</i> ≤ 22	-15 ≤ <i>h</i> ≤ 14	-16 ≤ <i>h</i> ≤ 11	-19 ≤ <i>h</i> ≤ 18
	-37 ≤ <i>k</i> ≤ 38	-17 ≤ <i>k</i> ≤ 18	-15 ≤ <i>k</i> ≤ 15	-14 ≤ <i>k</i> ≤ 14	-34 ≤ <i>k</i> ≤ 34
	-25 ≤ <i>l</i> ≤ 30	-26 ≤ <i>l</i> ≤ 28	0 ≤ <i>l</i> ≤ 17	-22 ≤ <i>l</i> ≤ 22	-16 ≤ <i>l</i> ≤ 16
no. of rflns collected	52998	56625	7758	25280	55489
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0457, 0.1312	0.0345, 0.0814	0.0424, 0.1031	0.0749, 0.1631	0.0250, 0.0679
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0788, 0.1543	0.0583, 0.0991	0.0644, 0.1223	0.2149, 0.2530	0.0346, 0.0833
no. of data/restraints/params	9025 / 12 / 321	14648 / 0 / 309	7758 / 0 / 362	5520 / 108 / 289	6124 / 32 / 162
goodness-of-fit on <i>F</i> ²	1.020	1.093	1.094	0.956	1.203
largest diff. peak and hole/ eÅ ⁻³	1.076 and -0.834	1.218 and -1.249	0.559 and -0.806	0.874 and -0.908	0.579 and -0.897

Table 2. Crystallographic Data of Compounds 7-11.

	7	8	9	10	11
formula	C ₃₂ H ₃₉ ClGeN ₂	C ₁₆ H ₂ ClN ₂ Sn	C ₃₂ H ₃₉ BrN ₂ Pb	C ₆₄ H ₇₈ Ge ₂ N ₄	C ₃₂ H ₄₆ N ₄ Sn ₂
formula weight	559.69	397.50	738.75	1048.48	724.11
color	Orange	Yellow	Yellow	Purple	Dark blue
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
space group	<i>P2(1)/c</i>	<i>P2(1)/n</i>	<i>P2(1)/n</i>	<i>P2(1)/c</i>	<i>Pbca</i>
<i>a</i> / Å	9.0808(2)	8.8447(2)	8.9984(8)	13.8962(6)	18.2275(5)
<i>b</i> / Å	26.5379(5)	16.2398(4)	27.360(2)	20.0041(9)	17.1965(5)
<i>c</i> / Å	14.0952(2)	12.1115(3)	12.5394(11)	23.8699(10)	20.7428(7)
α / deg	90	90	90	90	90
β / deg	118.9330(10)	97.2410(10)	101.985(5)	120.555(3)	90
γ / deg	90	90	90	90	90
<i>V</i> / Å ³	2972.78(10)	1725.78(7)	3019.8(5)	5714.0(4)	6501.8(3)
<i>Z</i>	4	4	4	4	8
<i>d</i> _{calcd} / mg cm ⁻³	1.251	1.530	1.625	1.219	1.479
μ / mm ⁻¹	1.142	1.628	6.932	1.094	1.562
<i>F</i> (000)	1176	800	1448	2216	2928
crystal size / mm ³	0.20 x 0.20 x 0.06	0.40 x 0.30 x 0.30	0.40 x 0.24 x 0.04	0.16 x 0.08 x 0.06	0.22 x 0.18 x 0.06
Index ranges	-12 ≤ <i>h</i> ≤ 12	-16 ≤ <i>h</i> ≤ 16	-12 ≤ <i>h</i> ≤ 12	17 ≤ <i>h</i> ≤ 17	-23 ≤ <i>h</i> ≤ 23
	-37 ≤ <i>k</i> ≤ 37	-29 ≤ <i>k</i> ≤ 29	0 ≤ <i>k</i> ≤ 39	-25 ≤ <i>k</i> ≤ 25	-22 ≤ <i>k</i> ≤ 17
	-20 ≤ <i>l</i> ≤ 20	-22 ≤ <i>l</i> ≤ 22	0 ≤ <i>l</i> ≤ 18	-29 ≤ <i>l</i> ≤ 29	-27 ≤ <i>l</i> ≤ 27
no. of rflns collected	73916	30357	8956	79103	41107
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0572, 0.1605	0.0492, 0.1471	0.1257, 0.3350	0.0440, 0.1032	0.0368, 0.0949
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0952, 0.1840	0.0642, 0.1564	0.1981, 0.3636	0.0835, 0.1309	0.0710, 0.1353
no. of data/restraints/params	9068 / 380 / 474	11217 / 0 / 187	8956 / 587 / 364	11671 / 38 / 668	7740 / 0 / 355
goodness-of-fit on <i>F</i> ²	1.087	1.036	1.062	1.031	1.057
largest diff. peak and hole/ eÅ ⁻³	1.651 and -0.926	5.863 and -1.227	5.195 and -6.305	0.499 and -0.594	0.989 and -1.115

Table 3. Crystallographic Data of Compounds 12-15 and 18.

	12	13	14	15	18
formula	C ₃₈ H ₅₅ GeKN ₄	C ₂₀ H ₃₁ KN ₂ OSn	C ₄₈ H ₇₁ LiN ₂ O ₄ Pb	C ₆₄ H ₇₈ N ₄ Pb ₂	C ₁₃₆ H ₁₃₈ Ge ₂ N ₄ P ₄ Pd ₂
formula weight	679.55	473.26	954.20	1317.68	2540.7
color	Green	Dark green	Dark red	Dark green	Orange
crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
space group	<i>P2(1)/c</i>	<i>P2(1)2(1)2(1)</i>	<i>P2(1)2(1)2(1)</i>	<i>P2(1)/c</i>	<i>P</i> -1
<i>a</i> / Å	12.0702(6)	10.2822(5)	10.2966(4)	23.8435(9)	15.149(2)
<i>b</i> / Å	19.1886(10)	11.0911(5)	21.1306(8)	13.6384(6)	22.051(3)
<i>c</i> / Å	16.1095(7)	20.2384(12)	21.3587(7)	18.8299(7)	22.566(3)
α / deg	90	90	90	90	68.646(7)
β / deg	95.285(3)	90	90	109.728(2)	73.154(7)
γ / deg	90	90	90	90	74.223(7)
<i>V</i> / Å ³	3715.3(3)	2308.0(2)	4647.1(3)	5763.8(4)	6601.3(15)
<i>Z</i>	4	4	4	4	2
<i>d</i> _{calcd} / mg cm ⁻³	1.215	1.362	1.364	1.518	1.278
μ / mm ⁻¹	0.967	1.297	3.673	5.875	0.820
<i>F</i> (000)	1448	968	1960	2616	2646
crystal size / mm ³	0.40 x 0.20 x 0.12	0.40 x 0.20 x 0.20	0.40 x 0.26 x 0.24	0.20 x 0.10 x 0.06	0.240 x 0.300 x 0.400
Index ranges	-18 ≤ <i>h</i> ≤ 17	-16 ≤ <i>h</i> ≤ 17	-14 ≤ <i>h</i> ≤ 12	0 ≤ <i>h</i> ≤ 28	-18 ≤ <i>h</i> ≤ 18
	0 ≤ <i>k</i> ≤ 28	-18 ≤ <i>k</i> ≤ 17	-30 ≤ <i>k</i> ≤ 30	-16 ≤ <i>k</i> ≤ 0,	-27 ≤ <i>k</i> ≤ 27
	0 ≤ <i>l</i> ≤ 23	-24 ≤ <i>l</i> ≤ 34	-30 ≤ <i>l</i> ≤ 27	-22 ≤ <i>l</i> ≤ 21	-27 ≤ <i>l</i> ≤ 27
no. of rflns collected	12818	25101	51308	10478	92696
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0749, 0.1558	0.0515, 0.1055	0.0539, 0.0735	0.0562, 0.1508	0.0829, 0.2120
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1812, 0.1866	0.0826, 0.1336	0.1001, 0.0839	0.0883, 0.1795	0.1853, 0.2876
no. of data/restraints/params	12818 / 0 / 409	11182 / 205 / 278	14284 / 505 / 606	10478 / 1068 / 760	24715 / 1204 / 1746
goodness-of-fit on <i>F</i> ²	0.916	1.010	1.014	1.140	1.053
largest diff. peak and hole/ eÅ ⁻³	0.622 and -0.798	1.041 and -1.717	3.188 and -2.529	1.343 and -2.774	2.073 and -1.760

Table 4. Crystallographic Data of Compounds L³Li, 19 and 21.

	L³Li	19	21
formula	C ₆₄ H ₇₈ Li ₂ N ₄	C ₃₈ H ₅₈ Cl ₂ GeN ₂ OSn ₂	C ₄₃ H ₅₄ GeN ₅ P
formula weight	917.18	939.73	744.47
color	Yellow	Colorless	Yellow
crystal system	Triclinic	Monoclinic	Monoclinic
space group	<i>P</i> -1	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> / Å	13.5342(3)	10.3032(6)	12.8309(5)
<i>b</i> / Å	13.7408(3)	19.4736(16)	20.8700(9)
<i>c</i> / Å	17.4203(4)	21.6635(17)	14.7922(6)
α / deg	98.8310(10)	90	90
β / deg	104.7100(10)	77.597(5)	98.060(2)
γ / deg	109.7820(10)	90	90
<i>V</i> / Å ³	2844.68(11)	4245.1(5)	3921.9(3)
<i>Z</i>	2	4	4
<i>d</i> _{calcd} / mg cm ⁻³	1.071	1.470	1.261
μ / mm ⁻¹	0.061	2.026	0.858
<i>F</i> (000)	992	1896	1576
crystal size / mm ³	0.40 x 0.40 x 0.20	0.08 x 0.02 x 0.02	0.40 x 0.40 x 0.20
Index ranges	-19 ≤ <i>h</i> ≤ 19	-13 ≤ <i>h</i> ≤ 13	-15 ≤ <i>h</i> ≤ 15
	-18 ≤ <i>k</i> ≤ 19	-22 ≤ <i>k</i> ≤ 25	0 ≤ <i>k</i> ≤ 25
	-22 ≤ <i>l</i> ≤ 24	-25 ≤ <i>l</i> ≤ 28	0 ≤ <i>l</i> ≤ 17
no. of rflns collected	51405	53188	7193
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0578, 0.1398	0.0774, 0.1638	0.0626, 0.1671
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1057, 0.1662	0.2626, 0.2538	0.0843, 0.1789
no. of data/restraints/params	17369 / 0 / 647	10517 / 76 / 459	7193 / 402 / 541
goodness-of-fit on <i>F</i> ²	1.030	0.928	1.093
largest diff. peak and hole/ eÅ ⁻³	0.393 and -0.362	1.203 and -1.539	3.005 and -0.424

Appendix B: DFT Calculation of **14**⁺

1. Theoretical studies of compound **14**⁺

Compound **14**⁺ (Figure S1) was investigated using DFT^[1] M06-2X^[2] method with the LanL08(d) basis set. All calculations were carried out using the Gaussian 09 packages.^[3] The optimized geometry of **14**⁺ is in good agreement with the X-ray crystallographic data of **14**.

2. **Figure S1.** Compound **14**⁺ at the M06-2X/LANL08d level

Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pb1-N1 2.319, N1-C7 1.338, C6-C7 1.409, C1-C6 1.442, Pb1-C1 2.163, N2-C20 1.282, C20-C2 1.455; C1-Pb1-N1 73.9, Pb1-N1-C7 114.6, N1-C7-C6 117.9, C1-C6-C7 117.4, Pb1-C1-C6 116.2.

3. The optimized geometry of compound **14**⁺

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-0.035331	-0.000741	1.624380
C	-1.266087	-0.000909	2.334839
C	-1.328140	-0.001513	3.720634
H	-2.294834	-0.001654	4.220331
C	-0.139914	-0.001930	4.484669

H	-0.188007	-0.002381	5.568581
C	1.078843	-0.001747	3.838516
H	1.998498	-0.002049	4.421981
C	1.162629	-0.001174	2.427287
C	2.396742	-0.000945	1.748364
H	3.349491	-0.001234	2.280597
C	3.607977	-0.000311	-0.270869
C	4.214702	-1.222866	-0.623983
C	3.589784	-2.548752	-0.230813
H	2.665227	-2.327300	0.306564
C	3.221185	-3.379306	-1.463772
H	2.545985	-2.820716	-2.115428
H	2.717685	-4.303956	-1.166325
H	4.109028	-3.651779	-2.044037
C	4.510152	-3.339407	0.705015
H	5.445087	-3.616308	0.206636
H	4.022003	-4.261460	1.034312
H	4.762591	-2.752246	1.590974
C	5.410513	-1.199775	-1.341888
H	5.880914	-2.137605	-1.625421
C	6.010314	-0.000018	-1.702858
H	6.938368	0.000099	-2.265754
C	5.411143	1.199591	-1.340337
H	5.881963	2.137534	-1.622787
C	4.215278	1.222375	-0.622517
C	3.591134	2.548067	-0.227437
H	2.666228	2.326408	0.309257
C	3.223563	3.380918	-1.459160
H	4.111772	3.653514	-2.038802
H	2.720853	4.305559	-1.160347
H	2.547993	2.823992	-2.111855
C	4.511735	3.336544	0.709999
H	5.447051	3.613547	0.212398
H	4.763434	2.747792	1.595115
H	4.024154	4.258433	1.040594
C	-2.520167	-0.000500	1.597872
H	-3.453110	-0.000514	2.179233
C	-3.794233	0.000619	-0.342736
C	-4.387572	-1.224043	-0.704385
C	-3.701994	-2.531377	-0.350968
H	-2.633970	-2.315951	-0.252626
C	-4.199572	-3.061465	0.999410
H	-4.023689	-2.339148	1.798727
H	-3.684343	-3.989302	1.264139
H	-5.274698	-3.265764	0.957630
C	-3.864217	-3.602369	-1.431349
H	-4.893833	-3.967229	-1.494986
H	-3.230302	-4.462357	-1.199984
H	-3.575667	-3.222686	-2.413885
C	-5.612026	-1.199415	-1.370299
H	-6.089411	-2.133686	-1.648529
C	-6.230056	0.002242	-1.694291
H	-7.182831	0.002902	-2.213557
C	-5.610129	1.203084	-1.370771
H	-6.086165	2.137971	-1.649233
C	-4.385591	1.226086	-0.704990
C	-3.698001	2.532424	-0.351845

H	-2.630189	2.315468	-0.254397
C	-3.859632	3.603880	-1.431851
H	-3.572584	3.223985	-2.414749
H	-3.224213	4.462865	-1.200901
H	-4.888763	3.970288	-1.494457
C	-4.193735	3.062938	0.999040
H	-5.268616	3.268714	0.958162
H	-3.677017	3.990031	1.263468
H	-4.018164	2.340302	1.798131
N	2.374174	-0.000433	0.410937
N	-2.549144	-0.000034	0.315724
Pb	0.250501	-0.000025	-0.519791

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