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Coordination Chemistry Reviews 251 (2007) 2253–2265

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Review

Reactions of some organogermanium(II) chlorides

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Received 20 September 2006; accepted 20 December 2006

Contents

Abstract

The synthesis of organogermanium(II) chloride RGeCl has played an important role in the development of heavier group 14 metal chemistry. This review covers the reactions of some organogermanium(II) chlorides which are starting precursors in the synthesis of novel germanium derivatives such as terminal germanium(II) hydrides, bisgermavinylidene, 1,3-digermacyclobutane, digermylene, metal-germyne, germanium chalcogenocarboxylic acid and other heterogermanium(II) compounds. The supporting ligands used in these organogermanium(II) complexes are mainly bulky and/or bear electron donating substituents which are essential in coordinating to the gemanium(II) center for stabilization.

Keywords: Germanium; Chloride; Germavinylidene; Digermylene; Metal-germyne

1. Introduction

The chemistry of organogermanium(II) chloride RGeCl (R = alkyl, aryl, amido groups) has attracted much attention in the past decades, because it can act as a precursor in the synthesis of some organogermanium derivatives. These organogermanium(II) chlorides also play an important role as the precursor or intermediate during the synthesis of novel compounds such as bigermylene, bisgermavinylidene and 1,3-digermayclobutane. The synthesis of monomeric organogermanium chloride experienced some difficulties; as this type of compound can readily re-distribute to homoleptic germylene and germanium(II) dichloride. By incorporating bulky ligands and/or electron-donating substituents at the germanium(II) centre, monomeric organogermanium chlorides have been synthesized by a metathesis reaction. This paper reviews the use of organogermanium(II) chlorides in the synthesis of some interesting compounds reported in the past decade.

2. Reactions of pyridyl-1-azaallylgermanium(II) chloride

Using alkali metal 1-azaallyl complexes as ligand transfer reagents, pyridyl-1-azaallyl germanium(II) chloride (PAA)GeCl (**1**) (PAA = N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)) has been synthesized [1]. Species **1** can behave as (i) a Lewis base, (ii) a Lewis acid, (iii) a reactive species undergoing oxidative addition reac-

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doi:10.1016/j.ccr.2006.12.012

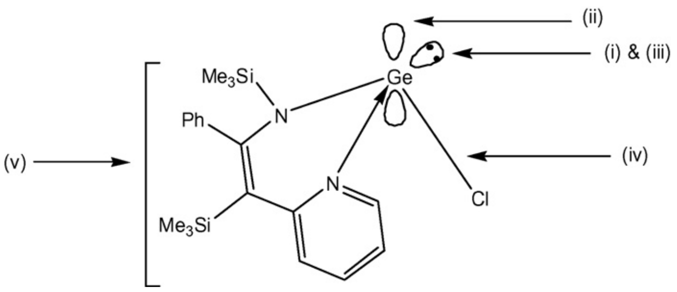


Fig. 1. The reactive centers in (PAA)GeCl (**1**).

tion, (iv) a reactive species undergoing nucleophilic substitution reaction and (v) a ligand transfer reagent. The reactive centers in **1** are depicted in Fig. 1.

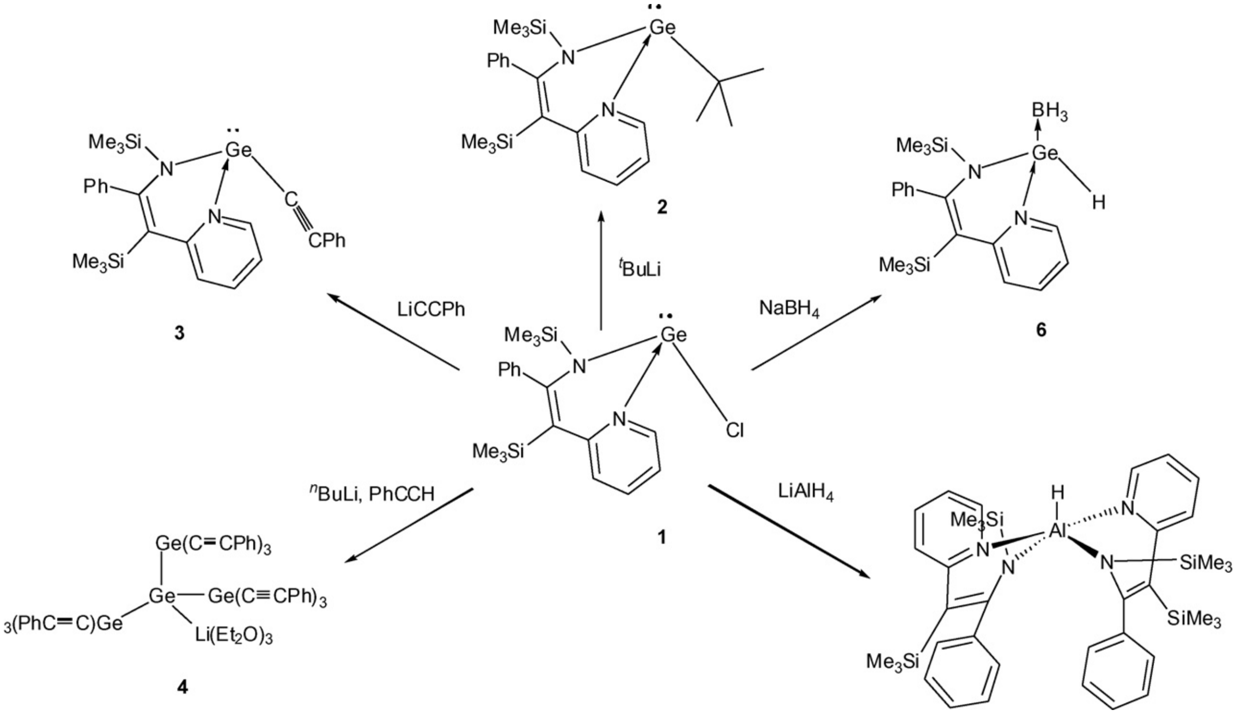
The reaction of **1** with Li^{t}Bu or LiC≡CPh afforded the substituted compounds (PAA)GeR (R = ^{t}Bu (**2**) or C≡CPh (**3**)), respectively [2] (Scheme 1). However, a 'one-pot' reaction of **1** together with PhC≡CH and ^{n}BuLi gave $\{(PhC{\equiv}C)_3Ge\}_3GeLi(Et_2O)_3$ (**4**) instead of **3** [2] (Scheme 1). A hypothetical mechanism for the formation of **4** has been proposed (Scheme 2) [2]. Thus intermediate **3** underwent a ligand transfer reaction to give **A**. Subsequent addition reaction of **A** with LiC≡CPh formed $[LiGe\{C{\equiv}CPh\}_3]$ (**B**) as the intermediate. The lithium germinate **B** then reacted as a transfer reagent with **1** to form **C**, which underwent substitution and addition to afford **4**. Treatment of **1** with $LiAlH_4$ gave Al $(PAA)_2H$ (**5**) [2] (Scheme 1). Thus **1** undergoes a ligand transfer reaction with $LiAlH_4$. In contrast, the reaction of **1** with excess $NaBH_4$ afforded germanium(II) hydride–borane adduct Ge $(BH_3)(PAA)H$ (**6**) [2] (Scheme 1).

The reaction of **1** with MI (M = Cu and Au) afforded novel $[Ge(CuI)(PAA)C1]_4$ (**7**) and Ge(AuI)(PAA)Cl (**8**), respectively [2] (Scheme 3). X-ray structure analysis showed that the former is tetrameric while the latter is monomeric in the solid state, thereby demonstrating the Lewis base behavior of **1**. Oxidative-addition reaction of **1** with elemental chalcogens (S, Se) gave thermally stable germanethione Ge(S)(PAA)Cl (**9**) and germaneselone Ge(Se)(PAA)Cl (**10**) [3] (Scheme 3). Similarly β-diketiminato germathioacid chloride and germaselenaacid chloride were prepared by Barrau and co-workers [5] and Roesky and co-workers [4] in the same manner.

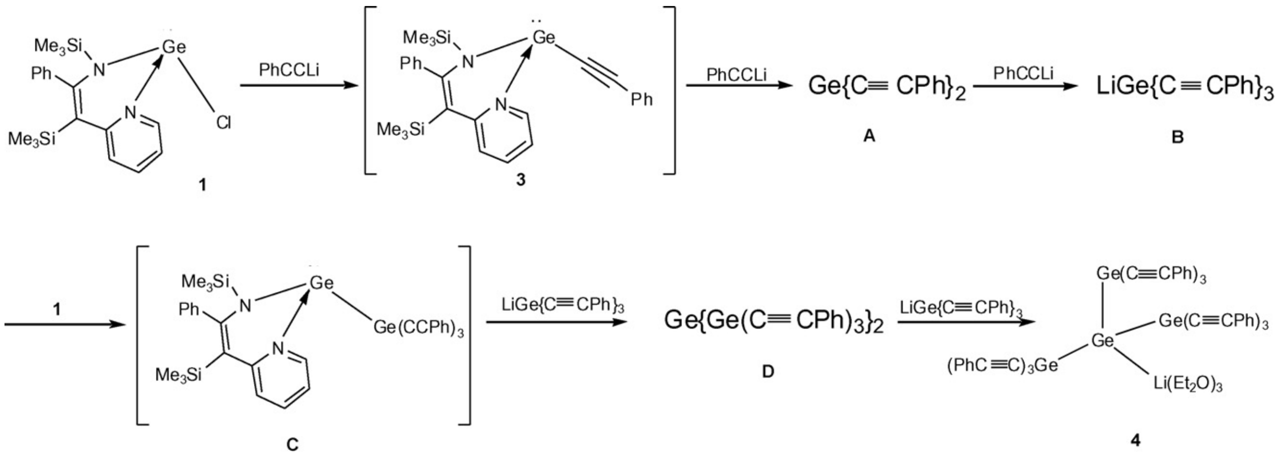
3. Reactions of β-diketiminato germanium(II) chloride

β-Diketiminato germanium(II) chloride $(R_2DAP)GeCl$ ($[R_2DAP] = \{N(R)C(Me)\}_2CH$ and R = aryl substituents) was studied by Roesky and Barrau. Some reactions were reviewed by Kühl in 2004 [6]. Dias and co-workers published a report on β-diketiminato germanium(II) complexes comparing their properties to those of the respective aminotroponimate complexes [7]. Here, we review some of the reactivities reported in the past few years.

The reaction of $(R_2DAP)GeCl$ (R = 2,6-$^iPr_2C_6H_3$ (**11a**), 2,6-$Me_2C_6H_3$ (**11b**)) with $NaBH_4$ gave the same result as the reaction of (PAA)GeCl with $NaBH_4$, a four-coordinate germanium(II) hydride–borane adduct $(R_2DAP)Ge(H)(BH_3)$ (R = 2,6-$^iPr_2C_6H_3$ (**12a**), 2,6-$Me_2C_6H_3$ (**12b**)) was obtained [8] (Scheme 4). This reaction was also carried out by Dias and Wang in the reaction of (ATI)GeCl with $NaBPh_4$ as the borane source [18]. Similar results were observed when $(R_2DAP)GeCl$ and (PAA)GeCl was treated with $LiAlH_4$; both of them gave ligand transfer products aluminium hydride, $[(R)_2DAP]A1H_2$ and $A1(PAA)_2H$, respectively. However, the thermally stable but air-sensitive monomeric and terminal ger-



Scheme 1. The reactivity of (PAA)GeCl (**1**).

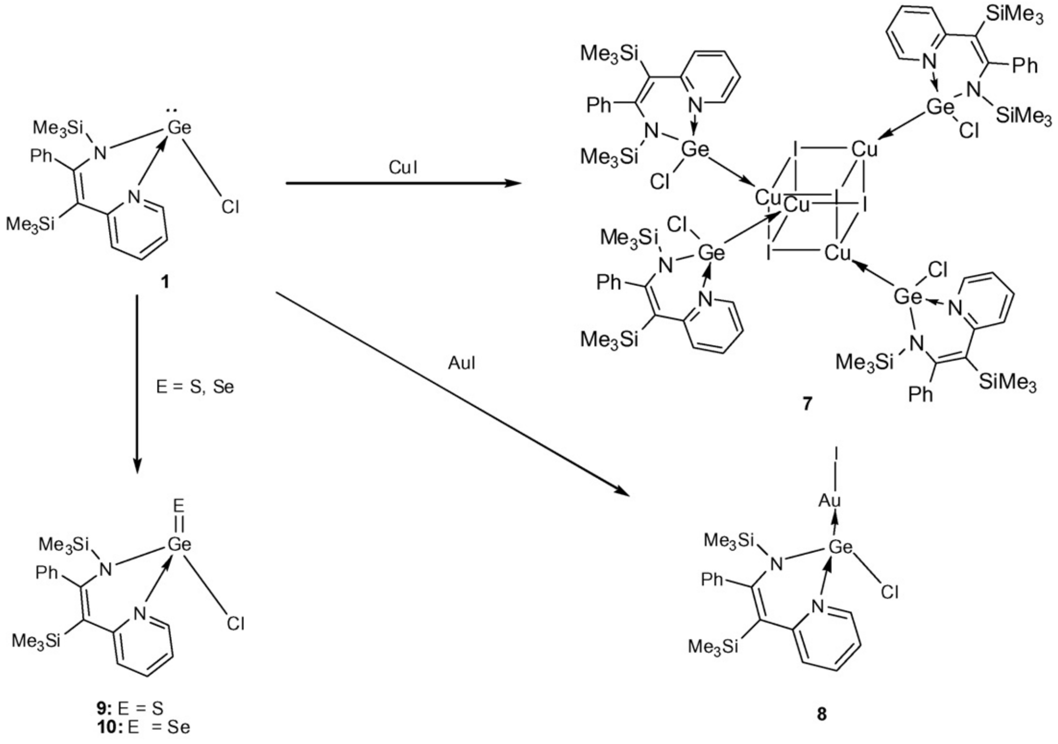


Scheme 2. The formation of $\{(PhC\equiv C)_3Ge\}_3GeLi(Et_2O)_3$ (**4**).

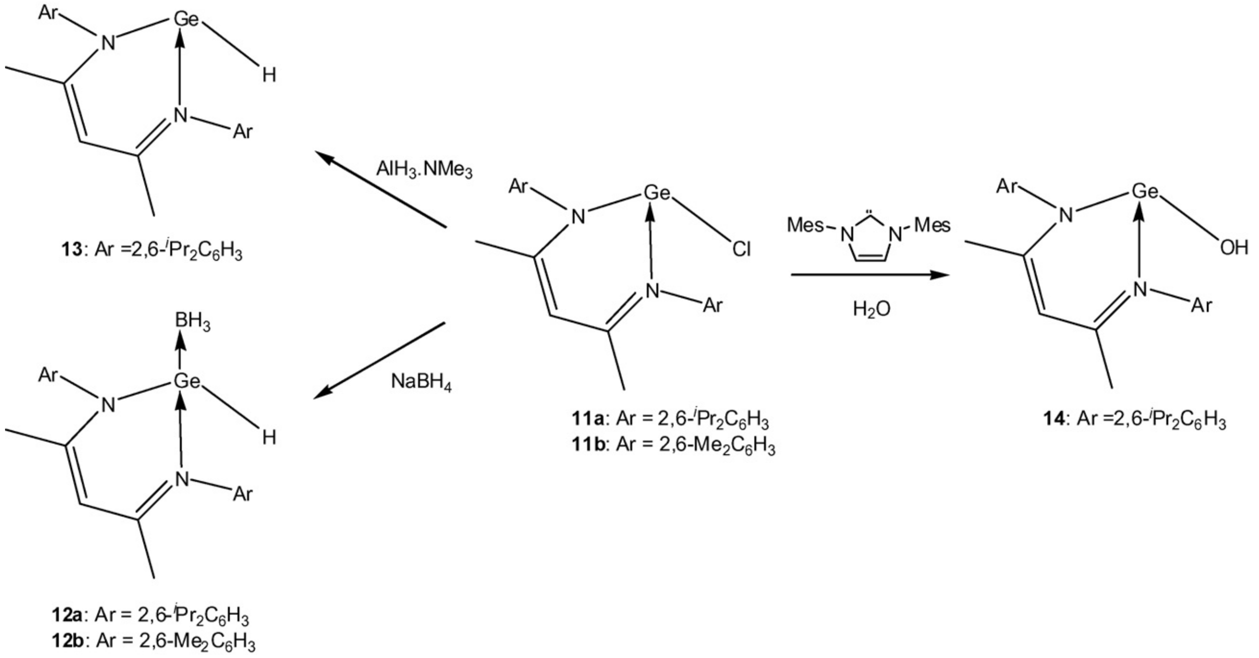
manium(II) hydride compound $[(2,6\text{-}^iPr_2C_6H_3)_2DAP]GeH$ (**13**) can be synthesized when $AlH_3{\cdot}NMe_3$ was used to react with **11a** [9] (Scheme 4). The synthesis of germanium(II) hydroxide has also been reported. Hydrolysis of **11a** with a slight excess of water and one equivalent of l,3-dimesitylimidazol-2-ylidene (mesityl = $2,4,6\text{-}Me_3C_6H_2$) led to the formation of $[2,6\text{-}^iPr_2C_6H_3)_2DAP]GeOH$ (**14**) [10] (Scheme 4). The IR spectrum of the compound showed a strong absorption around 3571 cm^{-1}, which is consistent with the theoretical calculations of 3675 and 3755 cm^{-1} for ν(OH).

Roesky and co-workers investigated the reactivity of **14**. The first germanium chalcogenocarboxylic acid $[(2,6\text{-}^iPr_2C_6H_3)_2DAP]Ge(E)OH$ (E = S (**15**), Se (**16**)) was obtained by reacting **14** with elemental chalcogens [11,12] (Scheme 5). An X-ray structure analysis showed that the Ge–E bond contains double bond character.

Moreover, reaction of **14** with an equivalent amount of Cp_2MMe_2 (Cp = $\eta^5\text{-}C_5H_5$, M = Zr, Hf) gave a discrete new μ-oxo heterobimetallic oxide $[(2,6\text{-}^iPr_2C_6H_3)_2DAP]\text{-}GeOM(Me)Cp_2$ (M = Zr (**17**), Hf (**18**)) [13] (Scheme 5). Compound **14** can either react at the OH functionality with a transition metal or acts as a base. The basic property of **14** can be shown in the reaction of **14** with $Fe_2(CO)_9$ and $CpMn(CO)_2(THF)$ to give $[(2,6\text{-}^iPr_2C_6H_3)_2DAP]Ge(OH)Fe(CO)_4$ (**19**) and $[(2,6\text{-}^iPr_2C_6H_3)_2DAP]Ge(OH)Mn(Cp)(CO)_2$ (**20**), respectively. [14] (Scheme 5).

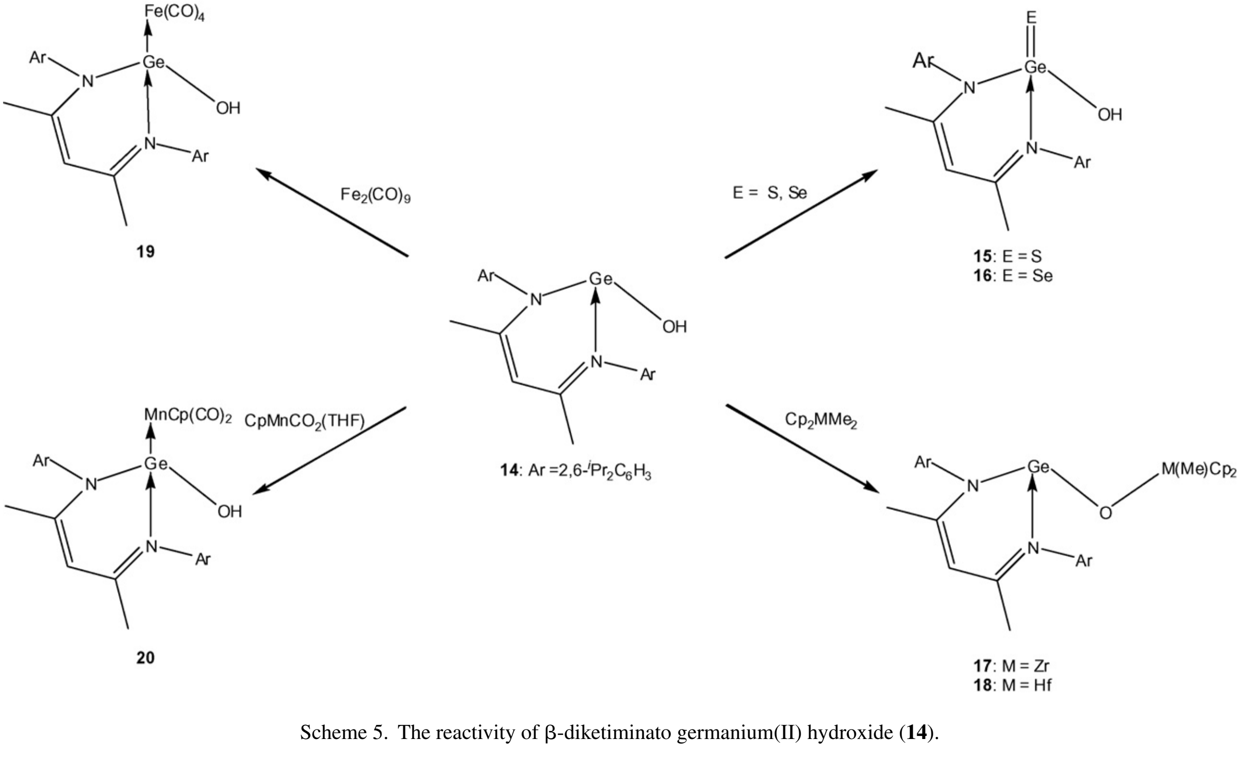


Scheme 3. The reactivity of (PAA)GeCl (**1**).

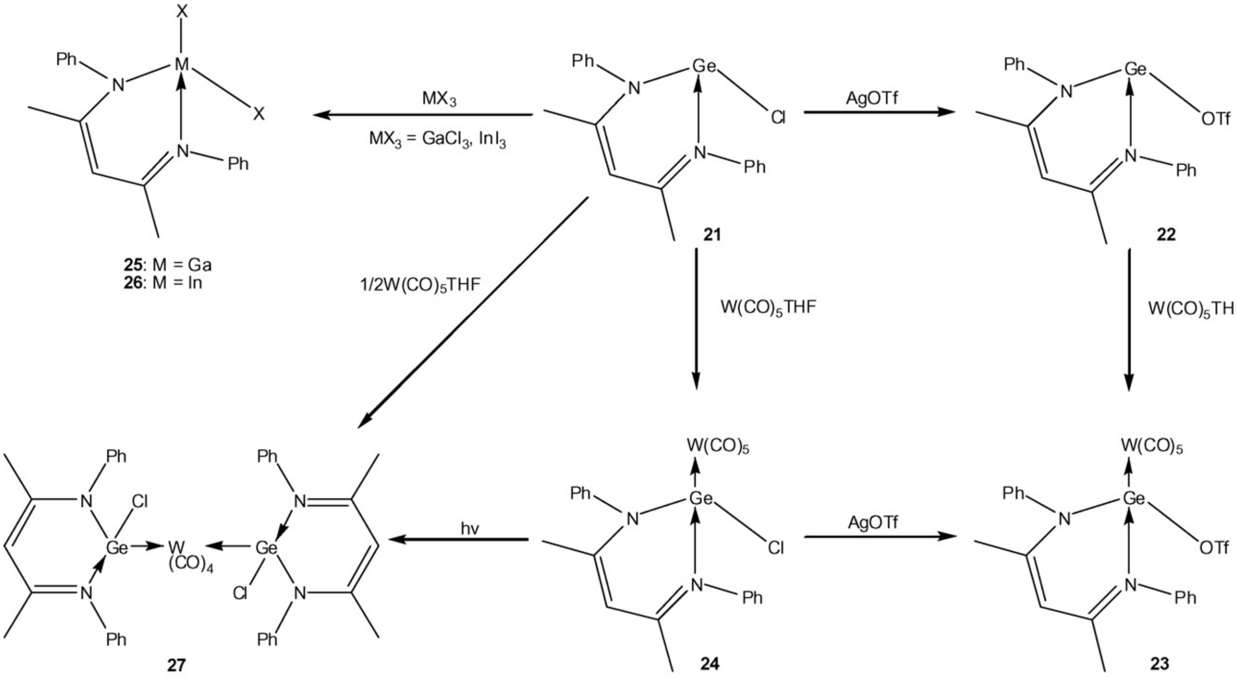


Scheme 4. The reactivity of aryl substituted β-diketiminato germanium(II) chloride (**11**).

Using the β-diketiminato ligand, Barrau and co-workers investigated the possibility of isolating cationic germanium(II)–transition metal complexes [15,16] (Scheme 6). Though the novel cationic germanium(II) compound $[\{(^i\mathrm{Pr})_2\mathrm{ATI}\}]\mathrm{Ge}[\mathrm{CpZrCl_2}(\mu\text{-Cl})_3\mathrm{ZrCl_2Cp}]$ (**29**) was prepared by Dias and co-workers [18], no studies have dealt with cationic germanium(II)–transition metal complexes. The attempted synthesis of cationic germanium(II)–tungsten complex was unsuccessful when $[(\mathrm{Ph})_2\mathrm{DAP}]\mathrm{GeOTf}$ (**22**) was reacted with $\mathrm{W(CO)_5(THF)}$. Instead, a triflate-substituted germanium(II)–tungsten complex $[(\mathrm{Ph})_2\mathrm{DAP}](\mathrm{OTf})\mathrm{GeW(CO)_5}$ (**23**) was obtained where the triflate group is weakly bound to the germanium(II) center (Scheme 6). Further attempts in abstracting the chloride ions of $[(\mathrm{Ph})_2\mathrm{DAP}]\mathrm{GeCl}$ (**21**) were unsuccessful. However, ligand transfer reactions were observed when **21** reacted with $\mathrm{GaCl_3}$ and $\mathrm{InCl_3}$ to give $[(\mathrm{Ph})_2\mathrm{DAP}]\mathrm{GaCl_2}$ (**25**) and $[(\mathrm{Ph})_2\mathrm{DAP}]\mathrm{InI_2}$ (**26**), respectively. Irradiation of two equivalents of **21** with $\mathrm{W(CO)_6}$ in



Scheme 5. The reactivity of β-diketiminato germanium(II) hydroxide (**14**).



Scheme 6. The reactivity of phenyl substituted β-diketiminato germanium(II) chloride (**21**).

THF afforded the first digermanium(II)–tungsten complex $[\{(Ph)_2DAP\}GeCl]_2W(CO)_4$ (**27**) (Scheme 6), but the X-ray structure determination of the dicationic species was not successful.

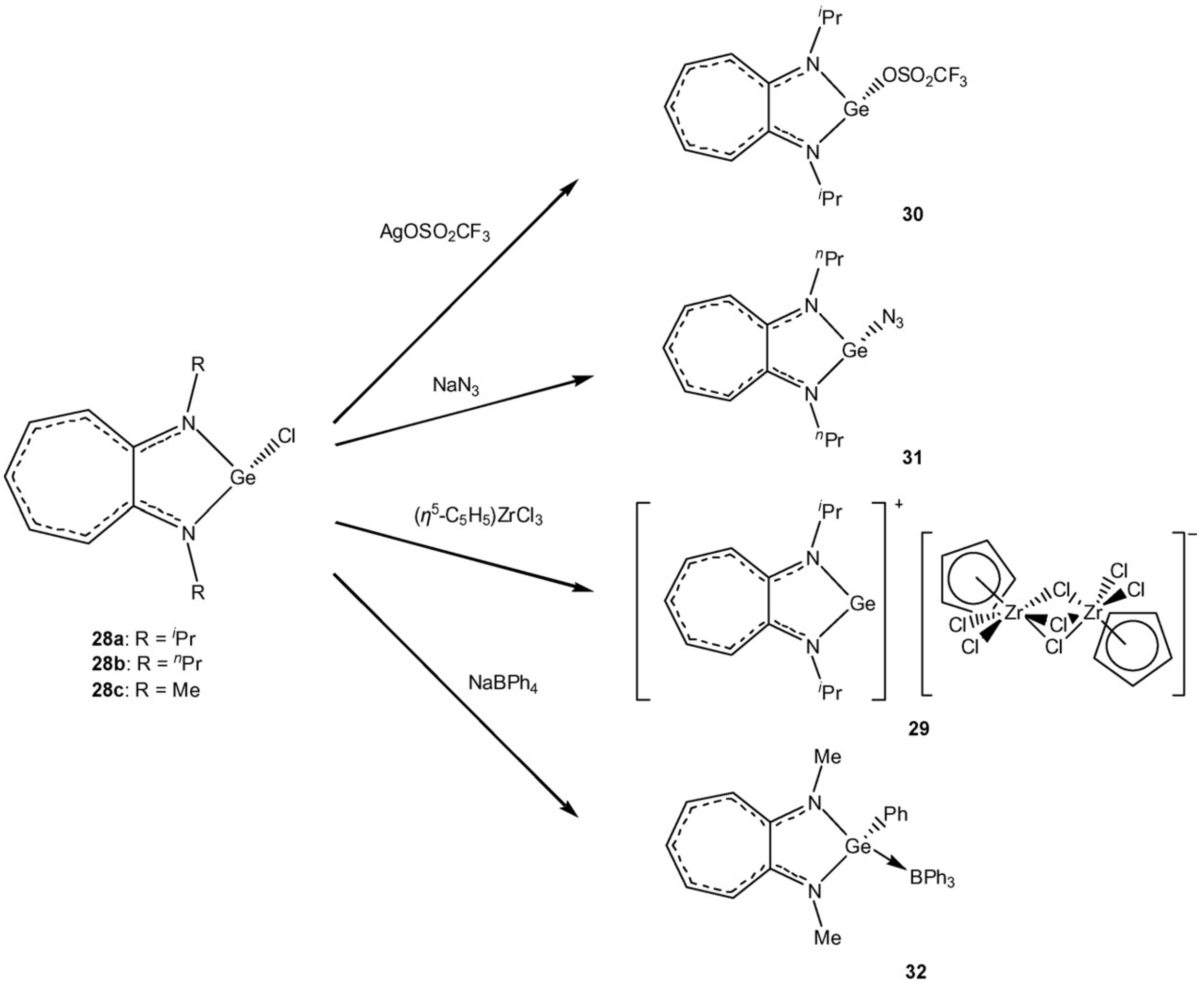
4. Reactions of aminotroponiminato germanium(II) chloride

Aminotroponimate ligand (ATI) is very useful in the synthesis of low valent group 14 compounds due to its bulkiness and amino functionality. A review covering the synthesis and structures of Group 14 metal complexes derived from this ligand has been published recently [17]. $(R_2ATI)GeCl$ (where $R = {}^{i}Pr$ (**28a**), ${}^{n}Pr$ (**28b**), Me (**28c**) and ATI = aminotroponiminate) can be prepared by the reaction of $GeCl_2$(dioxane) and $(R_2ATI)Li$ in 1:1 ratio [17,18]. Dias and co-workers also reported the synthesis of a novel cationic germanium(II) compound $[\{({}^{i}Pr)_2ATI\}]Ge[CpZrCl_2(\mu\text{-}Cl)_3ZrCl_2Cp]$ (**29**) [18]. Treatment of **28a** with 2 equivalents of $CpZrCl_3$ in CH_2Cl_2 at room temperature gave yellow crystals of **29** (Scheme 7) which has been structurally characterized. $CpZrCl_3$ serves as a chloride abstracting agent in the reaction. The synthesis and structural characterization of organogermanium(II) derivatives, $[({}^{i}Pr)_2ATI]GeOSO_2CF_3$ (**30**) [18], $[({}^{i}Pr)_2ATI]GeN_3$ (**31a**) [19] have also been reported. Compound **30** was synthesized by a metathesis reaction of **28a** with $AgOSO_2CF_3$ to yield yellow crystals, while **31** was obtained from the reaction of **28a** and NaN_3. These reactions were also observed by Barrau and co-workers through reaction of β-diketiminato chlorogermylene with $AgOSO_2CF_3$or NaN_3 [5]. Attempts to generate cationic germanium(II) species by treating **28c** with $NaBPh_4$ were unsuccessful, but a novel phenyl group transferred product with a Ge–B bond was isolated. Treatment of **28c** with $NaBPh_4$ in CH_2Cl_2 at room temperature yielded reddish-orange crystals of $[(Me)_2ATI]GePh{\cdot}BPh_3$ (**32**) [18], which suggested that a phenyl group had transferred from $[BPh_4]^-$. The reactivities of $(R_2ATI)GeCl$ (**28**) are summarized in Scheme 7.

Compounds containing a Ge → Ag interaction are rare. Dias and Wang reported the synthesis of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag \leftarrow GeCl[(Me)_2ATI]$ (**33**) [20], $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag \leftarrow Ge(OSO_2CF_3)[(Me)_2ATI]$ (**34**) [20] and $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]Ag \leftarrow Ge(N_3)[({}^{n}Pr)_2ATI]$ (**35**) [21]. Similar gold–germylene and copper–germylene adducts were synthesized by Leung et al. [2] in the reactions of (PAA)GeCl with AuI and CuI, respectively. Treatment of **28c** with $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ in CH_2Cl_2 at room temperature gave a 1:1 adduct of **33**. The reaction of **33** with $AgOSO_2CF_3$ gave crystals of **34** under the same conditions; with both featuring a silver–germanium bond interaction. Similarly, **35** was obtained from the reaction of $[({}^{n}Pr)_2ATI]GeN_3$ (**31b**) with $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ in CH_2Cl_2 at room temperature (Scheme 8).

5. Reactions of terphenyl germanium(II) chloride

Using the very bulky terphenyl ligand, Power and co-workers synthesized Ar′GeCl ($Ar' = \{C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}{}^{i}Pr_3)_2\}$ (**36a**) [22] and $(Ar^*GeCl)_2$ ($Ar^* = \{C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}Me_3)_2\}$ (**36b**) in which the organic ligands are monodentate and purely σ-bonded [23]. Neither **36a** nor **36b** contain a donor base to stabilize the germanium(II) center. It is suggested that the terphenyl ligand stabilized the germanium(II) compounds by purely a kinetic stabilization. Compound **36a** is monomeric while **36b** is dimeric featuring a Ge–Ge bond. These



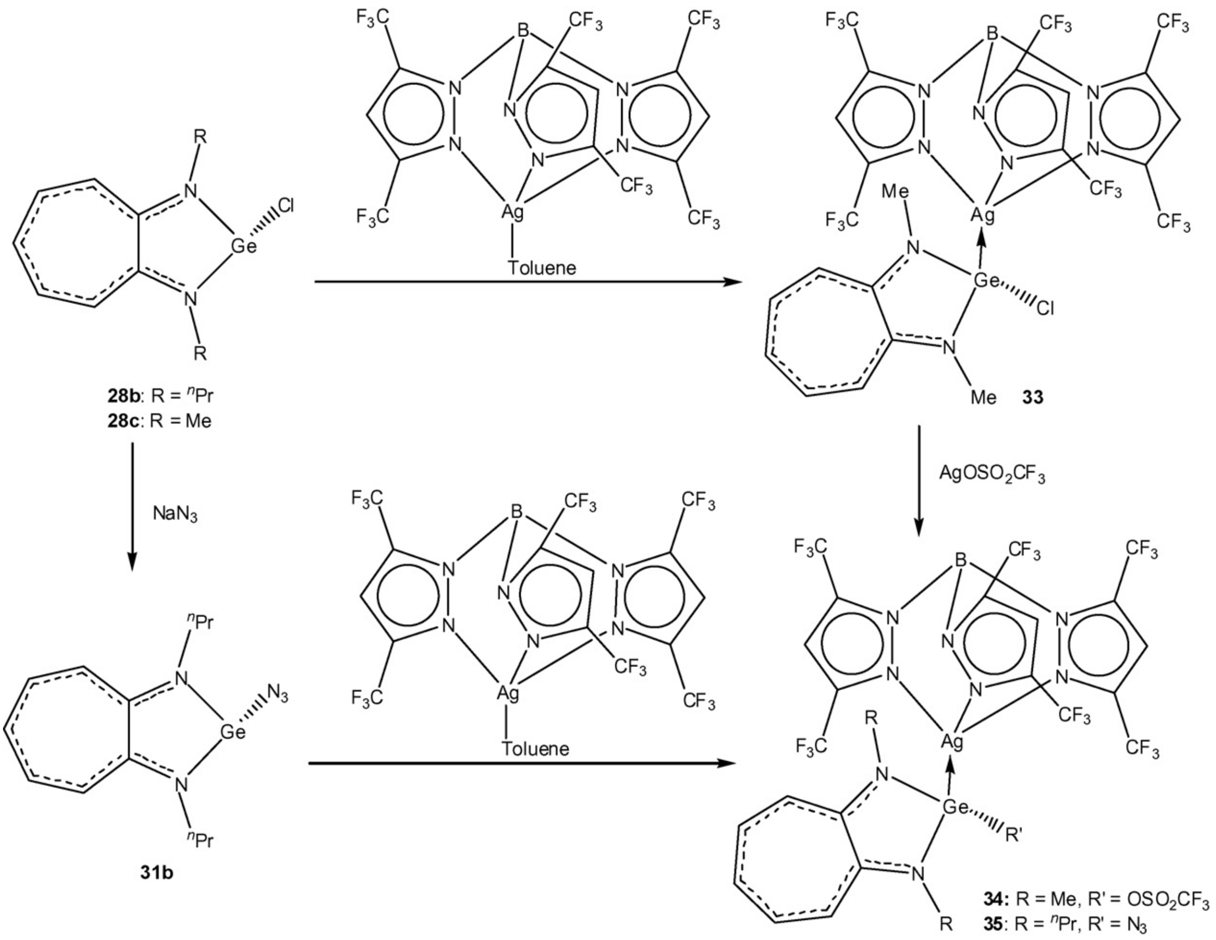
Scheme 7. The reactivity of (R_2ATI)GeCl (**28**).

organogermanium(II) chlorides act as useful halide precursors in synthesizing terphenyl germanium(II) derivatives (Scheme 9). The reduction of terphenyl germanium(II) chlorides to form digermylene will not be discussed here as relevant results have been reviewed by Power [24].

Reaction of **36a** with MeMgBr or LiPh afforded Ar′GeR (R = Me (**37**) or Ph (**38**)) [25]. These compounds exist as dimers featuring a Ge–Ge bond. The first stable germylgermylene Ar*GeGe^{t}Bu$_3$ (**39**) was obtained by reaction of **36b** with LiGe^{t}Bu$_3$ [26]. Furthermore, the synthesis of a novel molybdenum germylyne complex Cp(CO)$_2$Mo≡GeAr* (**40**) was successful by reacting **36b** with Na[MoCp(CO)$_3$] at room temperature [27]. The first examples of heteroleptic germylenes containing transition metal complex substituents [{Cp(CO)$_3$M}GeAr′] (M = Cr (**41**), W(**42**)) by the same synthetic routes [28] were also reported. However, under refluxing conditions, **41** and **42** were converted into transition metal germylynes Cp(CO)$_2$M≡GeAr′ (M = Cr (**43**), W (**44**)) with the elimination of carbon monoxide [27]. Moreover, the synthesis and stabilization of stable germanium(II) amide have been reported by taking advantage of the very bulky terphenyl ligands. Compounds **36a** and Ar″GeCl (**36c**) (Ar″ = {C$_6$H$_3$-2,6-(C$_6$H$_2$-2,6-^{i}Pr$_2$)$_2$} when treated with excess liquid NH$_3$ afforded dimeric (Ar′GeNH$_2$)$_2$ (**45a**) and (Ar″GeNH$_2$)$_2$ (**45b**), respectively [29].

6. Reactions of 2,6-bis((diethylamino)methyl)phenyl germanium(II) chloride

Recently, Couret and co-workers reported the synthesis of two new functionalized germylenes ArGeNR$_2$ (R = SiMe$_3$ (**47**) or ^{i}Pr (**48**)) from chlorogermylene ArGeCl (**46**) (AR = 2,6-bis((diethylamino)methyl)phenyl) [30,31]. The nitrogen donor functionality of 2,6-bis((diethylamino)methyl)phenyl ligand enables the synthesis of a series of heteroleptic germylenes. The heteroleptic aminogermylene (**47**) was prepared by metathesis reaction of **46** with lithium bis(trimethylsilyl) amide in Et$_2$O in 1:1 ratio at −78 °C. Similarly, β-diketiminato aminogermylene has been prepared by Barrau and co-workers [5]. The aminogermylene (**48**) was prepared in a similar manner. Hydrolysis of the tungsten-germanium complex ArN(SiMe$_3$)$_2$GeW(CO)$_5$ (**49**) gave ArOHGeW(CO)$_5$ (**50**). It is the first stable heteroleptic hydroxygermylene stabilized as



Scheme 8. The reactivity of $(R_2ATI)GeCl$ (**28**) towards a silver complex.

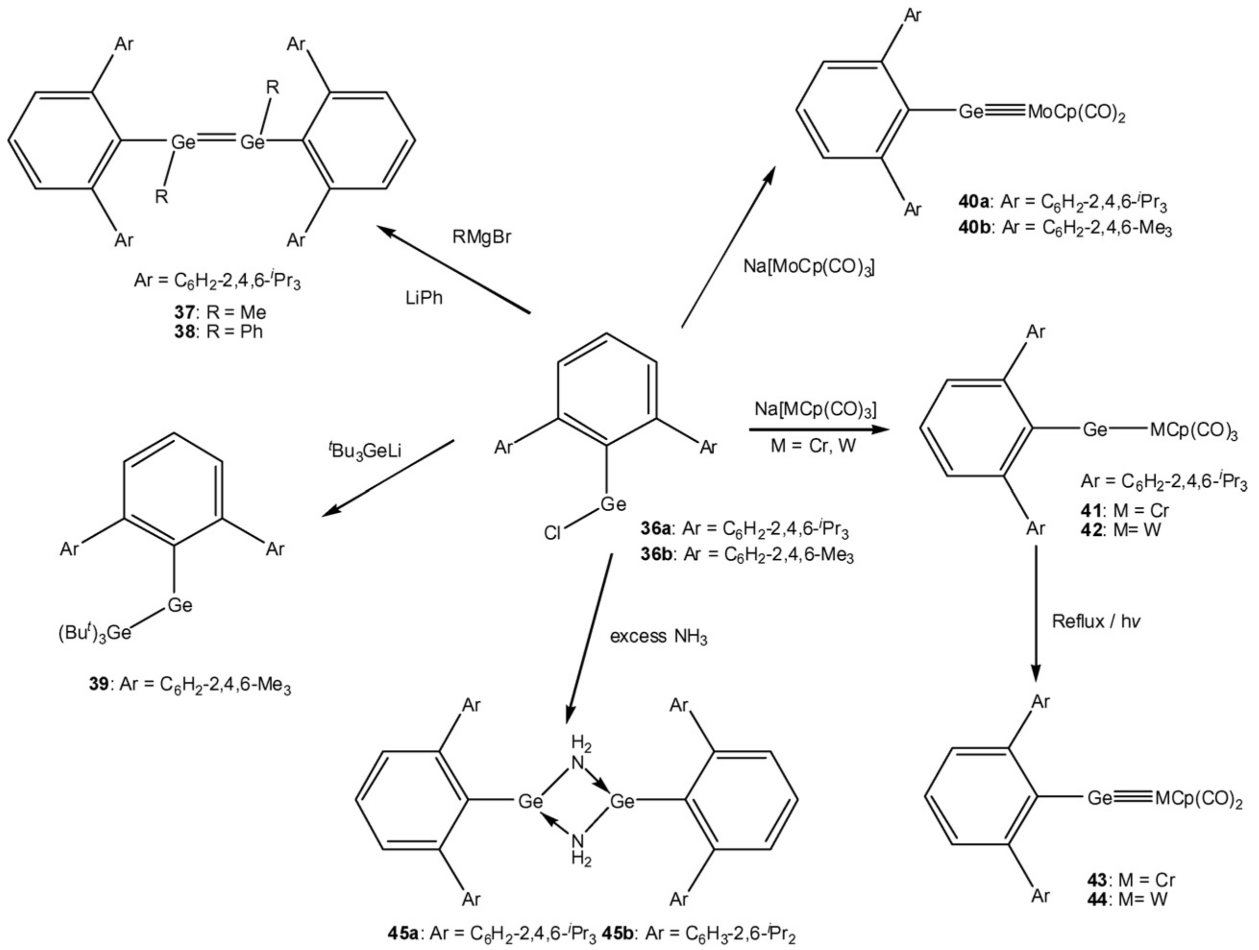
a pentacarbonyltungsten complex to be isolated and structurally characterized (Scheme 10). Hydrolysis of **47** gave only oligomeric germoxanes $(ArGeO)_n$. These results suggested the importance of stabilization of the ArGeOH as a transition metal complex. Roesky and co-workers reported the synthesis of the first monomeric β-diketiminato hydroxygermylene by hydrolysis of the corresponding chlorogermylene. The 2,6-bis((diethylamino)-methyl)phenyl groups are suitable for the synthesis of the stable diazogermylene $ArGeC(N_2)SiMe_3$ (**51**) which is a potential precursor for the synthesis of germa-alkyne [32]. Couret and co-workers have studied the diazogermylene by photolysis to provide evidence for the possible existence of germa-alkyne [32].

7. Reactions of methylamino-methyl-*m*-xylylgermanium(II) chloride

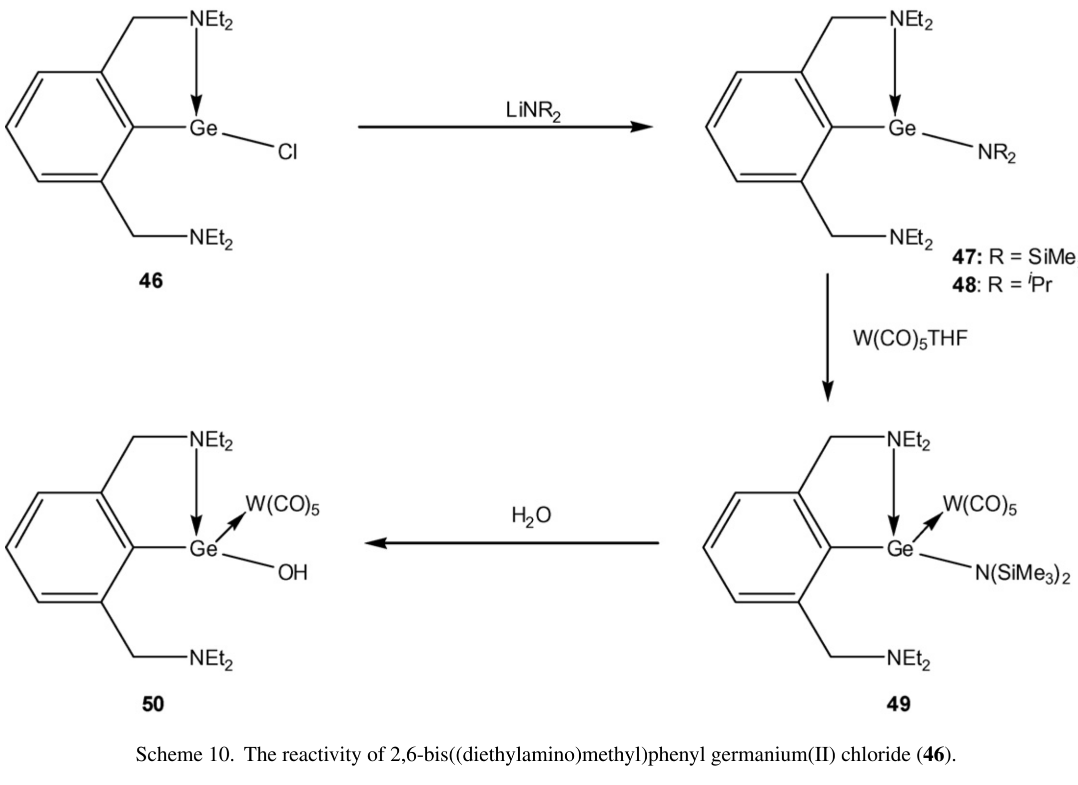
Jutzi et al. reported the synthesis of (Mamx)GeCl (**52**) (Mamx = methylamino-methyl-*m*-xylyl) and performed a series of substitution reactions with this precursor [33] (Scheme 11). The synthesis of alkoxy-substituted germanium(II) compounds has been reported. Treatment of (Mamx)GeCl with an excess of the corresponding potassium alkoxide (1:4) in the presence of 15-crown-5 afforded (Mamx)GeOR (R = ^{t}Bu (**53**), ^{i}Pr (**54**), Et (**55**), Me (**56**)). The reaction of **52** with Li(C≡CPh) and Na(C≡CH) gave ethynyl-substituted species (Mamx)Ge(C≡CPh) (**57**) and (Mamx)Ge(C≡CH) (**58**), respectively. The Mamx ligand is capable of stabilizing germanium(II) species containing non-bulky alkyl ligands, leading to the formation of (Mamx)GeR (R = ^{t}Bu (**59**), ^{n}Bu (**60**), Me (**61**)). The germyl cations $[MamxGe(Me)(R)]^+$ (R = ^{t}Bu (**62**), ^{n}Bu (**63**), Me (**64**)) can be obtained when (Mamx)GeR reacts with MeI. Mamx ligand can be used in the synthesis of variety of germylenes by stabilization in coordinating the amino side chain.

8. Reactions of bis(iminophosphorano)methanide germanium(II) chloride

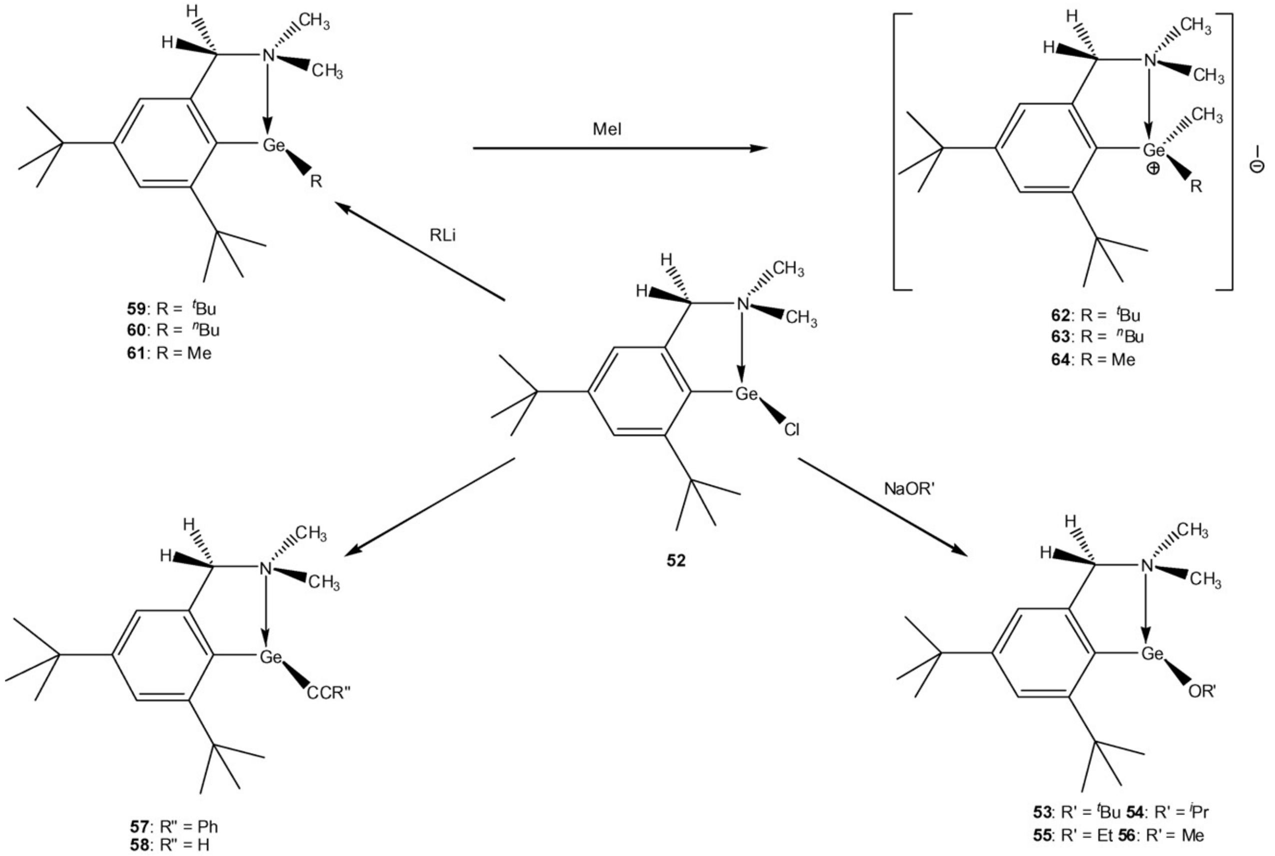
Bis(iminophosphorano)methanide germanium(II) chloride $[HC(PPh_2{=}NSiMe_3)_2GeCl]$ (**66**) can be prepared by the reaction of $[CH(Ph_2P{=}NSiMe_3)_2Li(THF)]$ (**65**) with $GeCl_2$ (dioxane) in 1:1 ratio. However, the reaction of two equivalents of **65** with $GeCl_2$ (dioxane) for 2 days afforded stable bisgermavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge \rightarrow Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**67**) [34,35] (Scheme 12). When the reaction was stopped after 1 day, compound **66** was isolated. Therefore, **66** is an intermediate compound during the formation of **67**. The organogermanium(II) chloride formed *in situ* could be further



Scheme 9. The reactivity of terphenyl germanium(II) chloride (**36**).



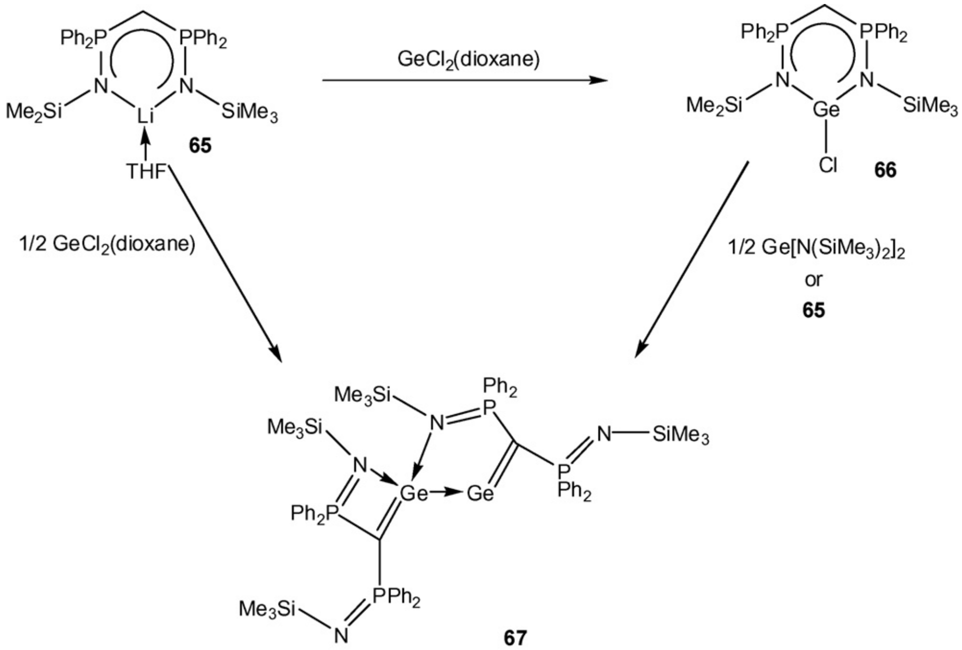
Scheme 10. The reactivity of 2,6-bis((diethylamino)methyl)phenyl germanium(II) chloride (**46**).



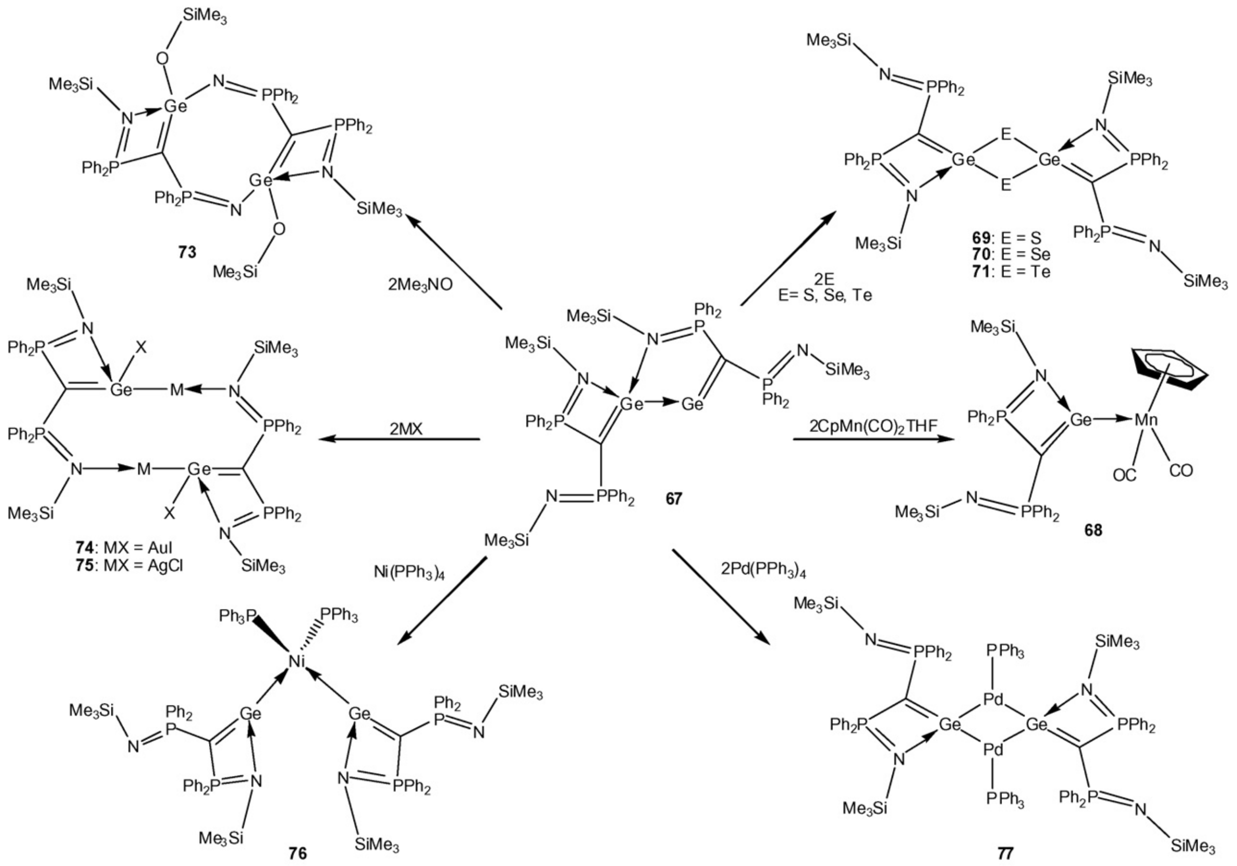
Scheme 11. The reactivity of methylamino-methyl-*m*-xylyl germanium(II) chloride (**52**).

dehydrochlorinated by **65** to form bisgermavinylidene, if the reaction mixture was kept for a further 24 h. It is suggested that the lithiated complex acts both as a ligand transfer reagent and as a base for dehydrochlorination.

Bisgermavinylidene can also be prepared stepwisely by the reaction of [Ge{N(SiMe$_3$)$_2$}$_2$] or **65** with **66** [35] (Scheme 12). X-ray results showed that the bisgermavinylidne (**67**) consists of two germavinylidene moieties bonded together in a

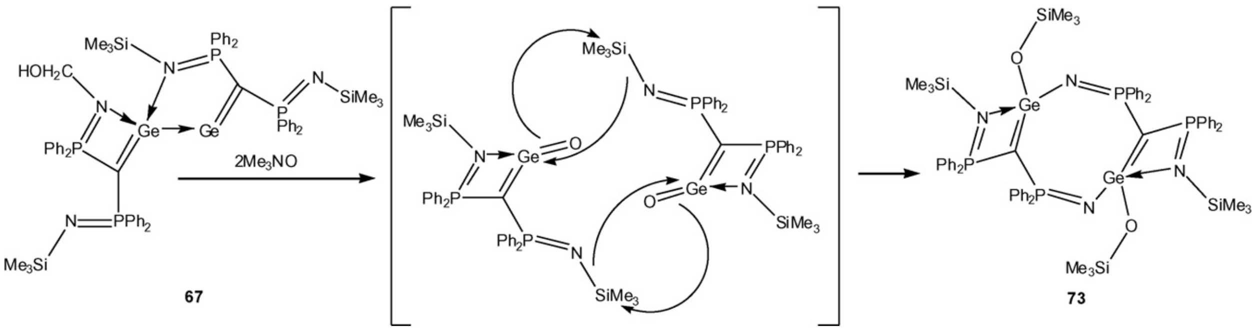


Scheme 12. Synthesis of bis(iminophosphorano)methanide germanium(II) chloride (**66**) and bisgermavinylidene (**67**).

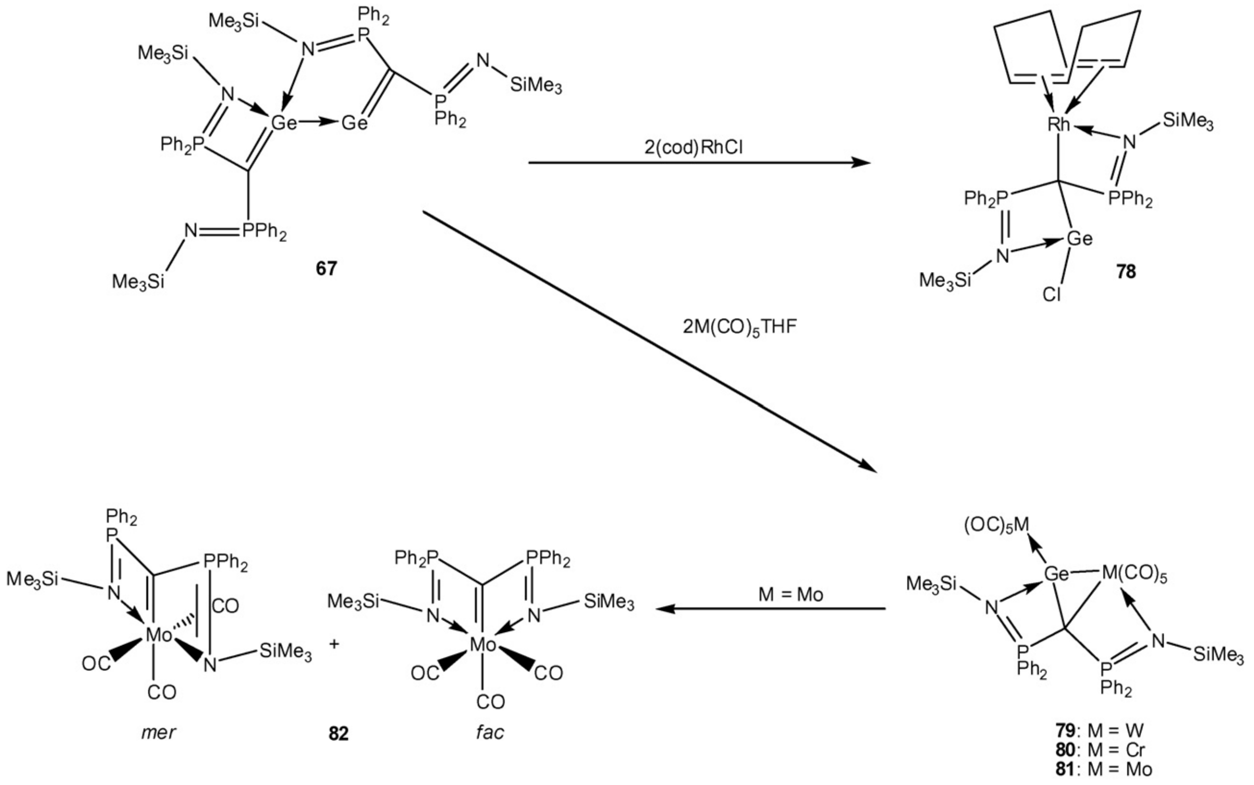


Scheme 13. The reactivity of bisgermavinylidene (**67**).

"head-to-head" manner with the two germanium centres in different environments. The Ge–Ge bonding is described as a donor-acceptor interaction and the C-Ge distance of 1.907 Å is consistent with a double bond character. The chemistry of bisgermavinylidene has been studied further. The reaction of bisgermavinylidene with two equivalents of CpMn(CO)$_2$(THF) afforded [(Me$_3$SiN=PPh$_2$)$_2$C=Ge → Mn(CO)$_2$Cp] (**68**) [36] (Scheme 13). Thus monomeric germavinylidene might exist in the solution state and act as a two-electron ligand. Apart from the Lewis base behavior of bisgermavinylidene, oxidative reaction of bisgermavinylidene with elemental chalcogens has led to the formation of chalcogen-bridged dimers of germaketene analogues [(Me$_3$SiN=PPh$_2$)$_2$C=Ge(μ-E)]$_2$ (E = S (**69**), Se (**70**), Te (**71**)) [35] (Scheme 13). The terminal germaketene moieties ⟩C=Ge=E cannot be isolated as they readily dimerized. However, a similar reaction of bisgermavinylidene with two equivalents of Me$_3$NO did not give the expected [(Me$_3$SiN=PPh$_2$)$_2$C=Ge(μ-O)]$_2$ (**72**), but instead [(μ-N=Ph$_2$P)(Me$_3$SiN=Ph$_2$P)C=Ge(OSiMe$_3$)]$_2$ (**73**) was formed [35] (Scheme 13). It is proposed that an intermediate with a ⟩C=Ge=O moiety underwent an insertion of the GeO unit into the N–SiMe$_3$ bond of the imino group (Scheme 14). Treatment of bisgermavinylidene with two equivalents of AgCl or AuI gave [(Me$_3$SiN=PPh$_2$)$_2$C=GeAgCl]$_2$ (**74**) and [(Me$_3$SiN=PPh$_2$)$_2$C=GeAuI]$_2$ (**75**), respectively [37] (Scheme 13). X-ray structures showed that the formation resulted from the insertion of germavinylidene moieties into the M–X bond. The synthesis of unprecedented group 10



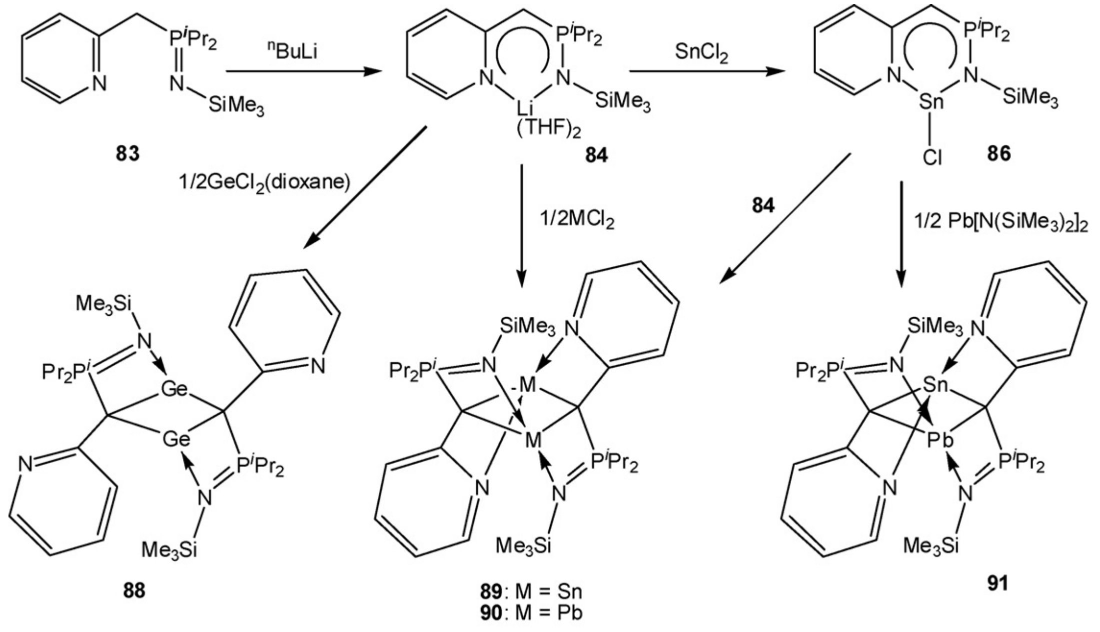
Scheme 14. The formation of [(μ-N=Ph$_2$P)(Me$_3$SiN=Ph$_2$P)C=Ge(OSiMe$_3$)]$_2$ (**73**).



Scheme 15. The reactivity of bisgermavinylidene (**67**).

metal-germavinylidene complexes has been reported [37] (Scheme 13). Reaction of bisgermavinylidene with $Ni(PPh_3)_4$ afforded $[\{(Me_3SiN{=}PPh_2)_2C{=}Ge\}_2Ni(PPh_3)_2]$ (**76**). Similar reaction of bisgermavinylidene with stoichiometric amounts of $Pd(PPh_3)_4$ gave the binuclear 14-electron Pd(0) complex $[\{(Me_3SiN{=}PPh_2)_2C{=}Ge\text{-}\mu^2\}Pd(PPh_3)]_2$ (**77**) with two bridging germavinylidene ligands. Similar to the synthesis of manganese germavinylidene complex, these results can show that germavinylidene also acts a two electron donor ligand. Moreover, treatment of bisgermavinylidene with $Cl_2Pd(PPh_3)_2$ afforded $Pd(PPh_3)_2$, showing that germavinylidene acts as a reducing agent.

Addition reaction of bisgermavinylidene can be shown when bisgermavinylidene reacted with two equiva-



Scheme 16. Synthesis of 1,3-dimetallacyclobutanes.

lents of (cod)RhCl (cod = 1,5-cyclooctadiene) to give $[(Me_3SiN{=}PPh_2)_2\{(cod)Rh\}CGeCl]$ (**78**) [36] (Scheme 15). The (cod)RhCl underwent a 1,2-addition with germavinylidene in solution as Ge=C bond inserted into the Rh-Cl bond. The nucleophilic character of the C=Ge bond of germavinylidene can also be demonstrated by synthesizing a series of group 6 metallacyclopropanes [38] (Scheme 15). Treatment of bisgermavinylidene with stoichiometric amounts of $M(CO)_5(THF)$ for 2 days afforded the metallacyclopropanes $[(Me_3SiN{=}PPh_2)_2CGeM(CO)_3(M(CO)_5)]$ (M = W (**79**), Cr (**80**), Mo (**81**)). X-ray results showed that the $M(CO)_5$ moiety generated by UV light added across the C=Ge bond of the germavinylidene moiety with concomitant displacement of two CO molecules and formed the three-membered C-Ge-M ring. It also showed that the germanium atom of the metallacyclopropane coordinated to another $M(CO)_5$ fragment. Interestingly, reaction of bisgermavinylidene with $Mo(CO)_5(THF)$ for three days gave a novel molybdenum carbene complex $[(CO)_3Mo\{C(Ph_2P{=}NSiMe_3)_2\}]$ (**82**). The X-ray result showed that it is a 'pincer' type carbene complex with two imino nitrogen atoms which displaced two CO ligands coordinated to molybdenum. Thus bisgermavinylidene plays a role as a carbene ligand transfer reagent in the synthesis of molybdenum carbene complex.

9. The reactions of iminophosphorano(2-pyridyl)methanide germanium(II) chloride

1,3-Digermacyclobutane $1,3\text{-}[Ge\{C(^iPr_2P{=}NSiMe_3)(2\text{-}Py)]_2$ (**88**) can be synthesized by the reaction of 2 equivalents of $(^iPr_2P{=}NSiMe_3)(2\text{-}Py)CHLi(THF)_2$ (**84**) with $GeCl_2$(dioxane). The $[Ge\{CH^iPr_2P{=}NSiMe_3)(2\text{-}Py)\}Cl]$ (**85**) is an intermediate. Similar reactions with $SnCl_2$ and $PbCl_2$ afforded 1,3-distannacyclobutane $1,3\text{-}[Sn\{C(^iPr_2P{=}NSiMe_3)(2\text{-}Py)]_2$ (**89**) and 1,3-diplumbacyclobutane $1,3\text{-}[Pb\{C(^iPr_2P{=}NSiMe_3)(2\text{-}Py)]_2$ (**90**), respectively [39,40] (Scheme 16). Reaction of equimolar of 84 with $SnCl_2$ gave iminophosphorano(2-pyridyl)methanide tin(II) chloride $[Sn\{CH(^iPr_2P{=}N\text{-}SiMe_3)(2\text{-}Py)\}Cl]$ (**86**) [39,40] (Scheme 16). Further reaction of **86** with the lithiated complex yielded **89** [39,40] (Scheme 16). The reactions proceed through the iminophosphorano(2-pyridyl)methanide metal(II) chloride similar to **86**, followed by further abstraction of the methine proton of $[M\{CH(^iPr_2P{=}NSiMe_3)(2\text{-}Py)\}Cl]$ (M = Ge (**85**), Sn (**86**) or Pb (**87**)) by the lithiated complex to form the unstable metallavinylidene ":$M{=}C(^iPr_2P{=}NSiMe_3)(2\text{-}Py)$". This intermediate then undergoes a "head-to-tail" cycloaddition to form 1,3-dimetallacyclobutanes. The lithium complex acts both as the ligand transfer reagent and strong base for dehydrochlorination. As compared to the synthesis of bisgermavinylidene, stabilization of ⟩C=Ge: bonding was successful by using the more bulky bis(iminophosphorano)methane ligand instead of forming 1,3-digermacyclobutane, though it is dimeric.

Treatment of two equivalents of iminophosphorano(2-pyridyl)methanide tin(II) chloride complex **86** with $Pb[N(SiMe_3)_2]_2$ afforded the mixed-metal 1,3-stannaplumbacyclobutane $[1\text{-}Sn\{C(^iPr_2P{=}NSiMe_3)(2\text{-}Py)\}\text{-}3\text{-}Pb\{C(^iPr_2P{=}NSiMe_3)(2\text{-}Py)\}]$ (**91**) [39,40] (Scheme 16). The mixed-metallacyclobutane could be a "head-to-tail" cycloaddition product from the stannavinylidene ":$Sn{=}C(^iPr_2P{=}NSiMe_3)(2\text{-}Py)$" and plumbavinylidene ":$Pb{=}C(^iPr_2P{=}NSiMe_3)(2\text{-}Py)$".

10. Conclusion

Organogermanium(II) chlorides are very versatile precursors in the synthesis of organogermanium derivatives due to their carbene character and chloride functionality. Some novel germanium(II) compounds derived from organogermanium(II) chlorides were successfully synthesized. Further investigation of the reactivities of organogermanium chloride may lead to the synthesis of more novel germanium compounds.

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