Modern Techniques in Synthesis of Organometallic Compounds of Germanium

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Additional information is available at the end of the chapter

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Abstract

Germanium is one of the most significant semiconductors to be used for electronic devices due to small bandgap and high intrinsic mobility of holes and electrons. Germanium has received a large attention due to its extraordinary reactivity and properties. It is commonly used in fluorescent lamps and as catalyst as well to produce various types of plastic. Germanium nanomaterials have broad range of applications from photovoltaic devices to phase-change memory materials. Germanium forms complexes by reacting with numerous elements such as carbon, oxygen, nitrogen, hydrogen, and phosphorous as a part of several organic compounds. Germanium coordinates with these elements by single, double, and triple linkages. Interestingly, all such reactions occur at ambient temperature usually in tetrahydrofuran under vacuum. Germanium may also react directly with primary and secondary nitrogen in the presence of a suitable base, whereas with tertiary nitrogen, it may react directly even in the absence of a base. Nevertheless, this chapter describes the modern techniques in synthesis of organometallic compounds of germanium.

Keywords: germylene, organometallic germanium, germanium coordination

1. Introduction

Organometallic compounds may be defined as *the compounds having at least one metal-carbon bond in a molecule*. This bond may be covalent in nature as in tetraethyl lead, $Pb(C_2H_5)_4$; pi-dative as in chromocene, $Cr(\eta^5\text{-}C_5H_5)_2$; ionic as in potassium cyclopentadienyl, $K^+(C_5H_5)^-$; and more interestingly, coordinate covalent as in silver(I)-*N*-heterocyclic carbene, $Ag(NHC)_2$ (**Figure 1**). However, the mentioned definition is not limited to metal-carbon bond only; there are several other examples where metal-nitrogen, metal-boron, metal-hydrogen, metal-oxygen,

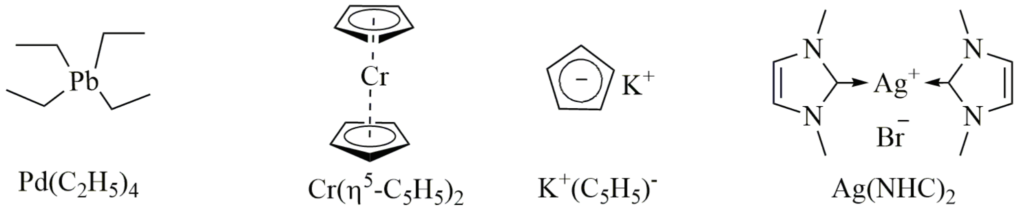


Figure 1. Different types of organometallic compounds having metal-carbon bonds.

metal-sulfur, etc. bonds are also included in organometallic chemistry. Nevertheless, their bonding way is uniquely different than in coordination compounds, which makes them organometallic compounds instead of coordination compounds. For instance, just keep in mind that metal-carbon bond-containing compounds are organometallic in nature.

The current chapter describes organometallic compounds of germanium. Germanium was exposed by Clemens Winkler in 1886, and its initial wide application was in the formation of point-contact Schottky diodes for radar response during WWII. Germanium is a conventional electronic material. The history of element germanium is at the closely same era as the story of transition from physics of dirt to beginning of recent semiconductor physics. The revelation of point-contact transistor of germanium by J. Bardeen and W. Brattain on Christmas Eve 1947 was followed by the discovery of germanium junction transistor by W. Shockley that represents the establishment of semiconductor age. The years succeeding the findings of germanium did not show any main scientific conclusion and technological applications for this expensive, brittle, rare, and metal-like element. F.W. Aston found three reasonably stable isotopes, namely, ^{70}Ge, ^{72}Ge, and ^{74}Ge in 1923. In the 1930s, germanium was supposed to be a bad conducting metal [1].

Germanium is one of the most significant semiconductors used for electronics due to small bandgap and high intrinsic mobility of holes and electrons. Germanium oxides are hygroscopic and water soluble. GeO_2 is thermally unstable and it is transformed into volatile germanium monoxide (GeO) [2]. Germanium compounds have great importance due to their distinctive applications in electronic field. Geranium films also gained attention due to their use in phase-change random access memory (PRAM) devices. They have fascinating great deal of interest due to high endurance, nonvolatility, and higher programming speed. GST ($Ge_2Sb_2Te_5$) mainly is a well-liked phase-change substance for phase-change random access memory devices [3]. Group 14 elements have extensive variety of application from photovoltaic devices to PRAM material [4].

Group 14 elements usually have wide significance because of their unusual properties. In recent times, surprising application of alkoxy germylenes has been described. Alkoxy germylene has been used as precursors of nanomaterials. Hypermetallyl germylenes may be appropriate for the preparation of nanomaterial alloys because hypermetallyl germylenes contain good leaving substituent and a low coordinate atom of group 14. Hypergermyl ligands demonstrate limitations of steric shielding for stabilization of low coordinate species [5].

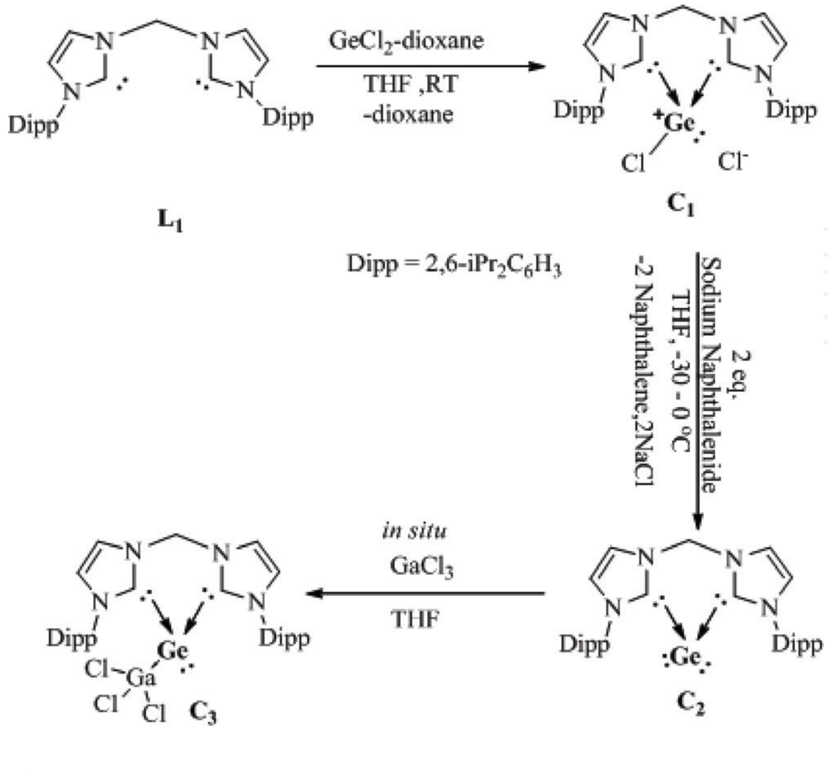
In earlier period, germylene compounds were used for transition metals as ligands due to their potential. Germylenes have been paying interest in organic chemistry. Germylenes are highly reactive derivatives and can be stabilized by sterically challenging substituent [6].

Germanium monocations may demonstrate both nucleophilic and electrophilic properties. Aminotroponiminate GeII monocation was synthesized by elimination of chloride from particular chlorogermylene using (η^5-C_5H_5) $ZrCl_3$ as a halide scavenger [7]. Germanium monocations may demonstrate both nucleophilic and electrophilic properties. Aminotroponiminate GeII monocation was synthesized by elimination of chloride from particular chlorogermylene using (η^5-C_5H_5) $ZrCl_3$ as a halide scavenger [7].

2. Germanium complexes involving bonding through carbon (C)

C1 (cholorogermyliumylidene) was obtained by reacting 1 equivalent of **L1** (a free bis-NHC) with $GeCl_2$-dioxane in dry tetrahydrofuran (THF) at room temperature under an inert atmosphere (**Scheme 1**). The reaction mixture was stirred overnight to isolate **C1** as white precipitates. Single crystals of **C1** were grown by slow evaporation at 4°C in acetonitrile. NHC-Ge bond was confirmed by ^{13}C NMR by obtaining a chemical shift at δ166.3 ppm. **C1** was further reacted with a dark green solution of sodium naphthalene in THF very carefully. According to the reported procedure, 1 equivalent of naphthalene was stirred in THF overnight with 1 equivalent of sodium metal to obtain sodium naphthalenide. A suspension of half equivalent of **C2** in THF (at −30°C) was added to the sodium naphthalenide solution at −30°C, and the mixture was stirred to bring the reaction mixture temperature up to 0°C in about 3 h.

The volatilities were removed under vacuum, and the residue was washed with cold THF during filtration. Single dark red-colored crystals, suitable for X-ray crystallography, of **C2** were obtained by a concentrated solution of C_2 in THF at −20°C (cooling method). The formation

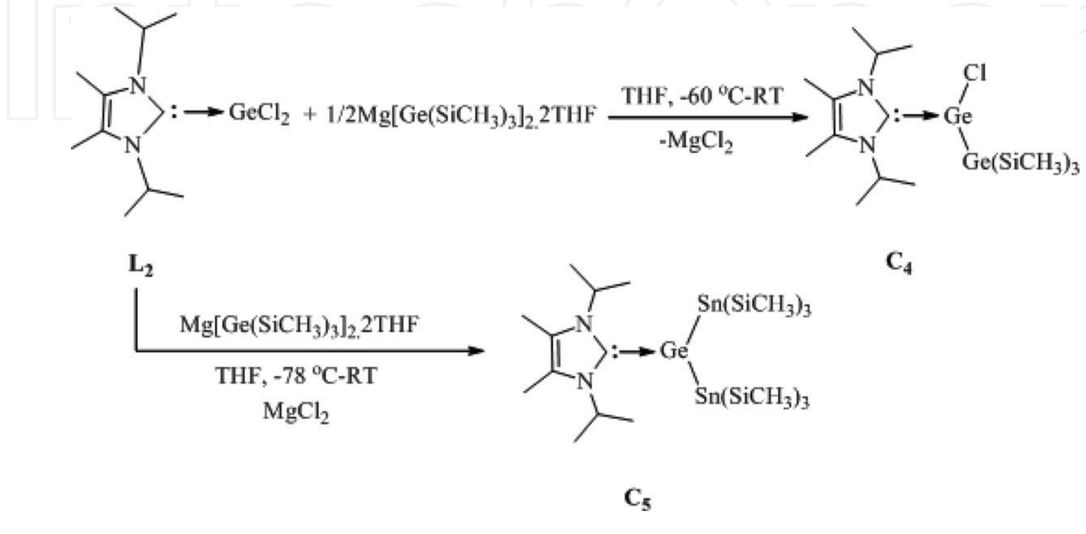


Scheme 1. Synthesis of Ge compounds involving bonding through carbon.

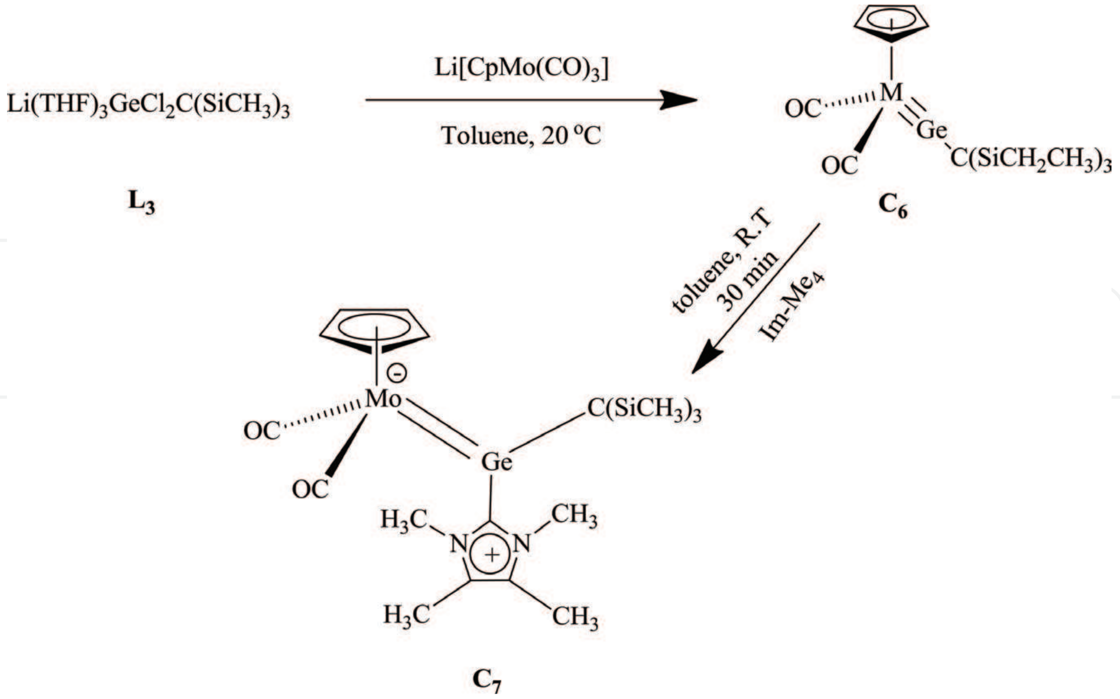
of NHC-Ge bond was confirmed by ^{13}C NMR where the respective chemical shift appeared at δ 196.1 ppm, which is interestingly much downfield compared to **C1** [8]. Compound **C3** can be prepared through *in situ* path, adding 1 equivalent of $GaCl_3$ in a solution of **C2** in THF at room temperature and stirring the reaction mixture for about 2 h. The volatilities are removed under vacuum, and the product can be extracted by THF. The single crystals of **C3** suitable for X-ray crystallography were obtained by cooling a concentrated solution of it in acetonitrile to 4°C. The ^{13}C NMR showed chemical shift of NHC-Ge at δ 174.16 ppm. This upfield movement of chemical shift might be because of electron drift from gallium toward NHC.

Synthesis of another NHC-Ge adduct **C4** was achieved by adding a dropwise solution of 1 equivalent of **L2** (NHC-$GeCl_2$) in 1 equivalent of $Mg[Ge(SiCH_3)_3]_2$.2THF in THF at −60°C (**Scheme 2**). The solution was then stirred at room temperature for 2 days to obtain the required product as precipitates. At the end, volatile components were removed under reduced pressure to obtain red residue, washed with pentane, and orange red product was isolated in 45% yield. ^{13}C NMR indicated the formation of NHC-Ge bond by showing a chemical shift at δ 173.9 ppm for the bonded carbene carbon [5]. The synthesis of derivative **C5** from **L2** can be achieved by adding a THF solution of 1 equivalent of $Mg[Sn(SiCH_3)_3]_2$.2THF into a THF solution of **L2** at −78°C, and the mixture is slowly warmed to room temperature in 12 h with consistent stirring. The solvent and other volatilities were removed from the reaction mixture under vacuum, and the residue was extracted with pentane, which was filtered and the filtrate was evaporated to obtain **C5** as orange red powder. Single crystals of orange color were obtained by slow evaporation of saturated solution of **C5** in pentane at −24°C. ^{13}C NMR indicated the NHC-Ge chemical shift at δ 175.5 ppm, whereas 119Sn NMR indicated the chemical shift for bonded tin at δ −589.7 ppm [5].

C6 was formed by dissolving **L3** to a solution of $GeCl_2$ at 0°C. After stirring the reaction mixture at 0°C for 15 min, the cooling bath was removed and mixture was kept stirred continuously at room temperature for 1 h. Yellow solid was obtained after removing all solvent in vacuum. The mixture (yellow solid) was treated with precooled toluene at 0°C with the addition of $Li[CpMo(CO)_3]$ and again stirred continuously for next 2.5 h (**Scheme 3**). The mixture was warmed at room temperature and solution color changed from yellow to brown



Scheme 2. Synthesis of NHC-stabilized hypermetallyl germylene.



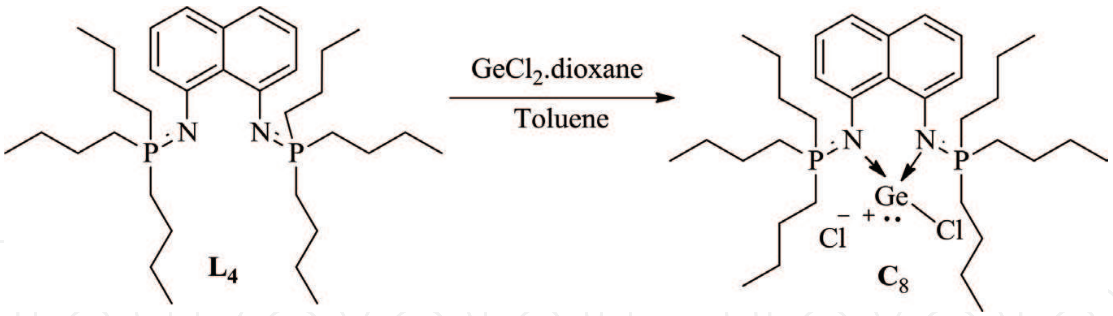
Scheme 3. Synthesis of [$Cp(CO)_2Mo{\cdot}GeC(SiCH_3)_3$] complex, **C7**.

and then red. The product was obtained with hexane and the extract was stored at −30°C for 16 h. At −30°C, mother liquor was removed by filtration of mixture. At room temperature, precipitate was dried in vacuum for 1 h. End product was extracted as orange red crystalline material in 73% yield. Melting point of the extracted product was 85°C. Production of **C7** was achieved when an Im-Me_4 (tetramethyl imidazolium salt) solution was added slowly in **C6** at room temperature. The solution color changed from red orange to red brown during addition of Im-Me_4. Solution was stirred continuously for 30 min. All volatiles were removed under vacuum, and the residue was dissolved in toluene-hexane mixture for the purpose of extracting the required material. The extract was concentrated and few drops of n-hexane were added on it, and then it was cooled to −60°C and stored for 16 h at the same temperature to isolate the red-brown crystals of **C7** from mother liquor in 69% yield [9].

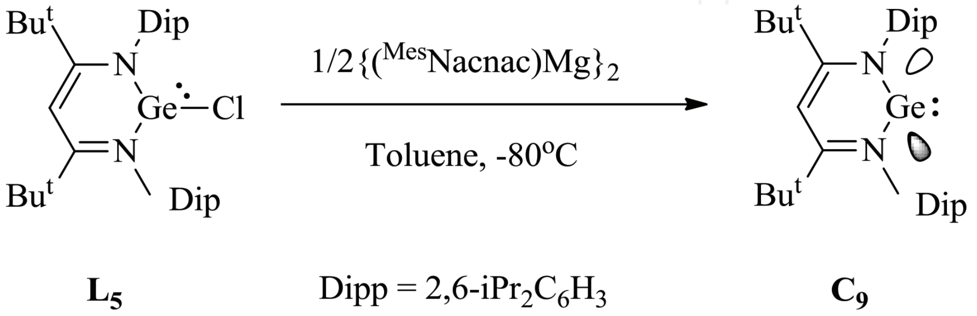
3. Germanium complexes involving bonding through nitrogen (N)

C8 (chlorogermyliumylidene) was formed by reacting **L4** (1,8-bis (tributylphosphazenyl)-naphthalene) with $GeCl_2$-dioxane in 60% isolated yield (**Scheme 4**). The addition of $GeCl_2$-dioxane into a solution of **L8** in toluene at ambient temperature generates white precipitates of the desired ionic species, which can be filtered from the reaction medium [8, 10].

C9 [(ButNacnac)Ge:] was obtained by mixing **L5** solution in toluene with [(^{Mes}Nacnac)Mg]$_2$ in toluene at −80°C for 5 min (**Scheme 5**). The mixture was then warmed slowly for 6 h at 0°C, and during this period of time, the mixture turned deep red colored. The residue was extracted into cold hexane at 0°C, and volatiles were removed in vacuum. The product was stored at −30°C overnight. At the end, purple-red crystals were formed in 38% isolated yield [11].



Scheme 4. Synthesis of β-diketiminate germanium complex.

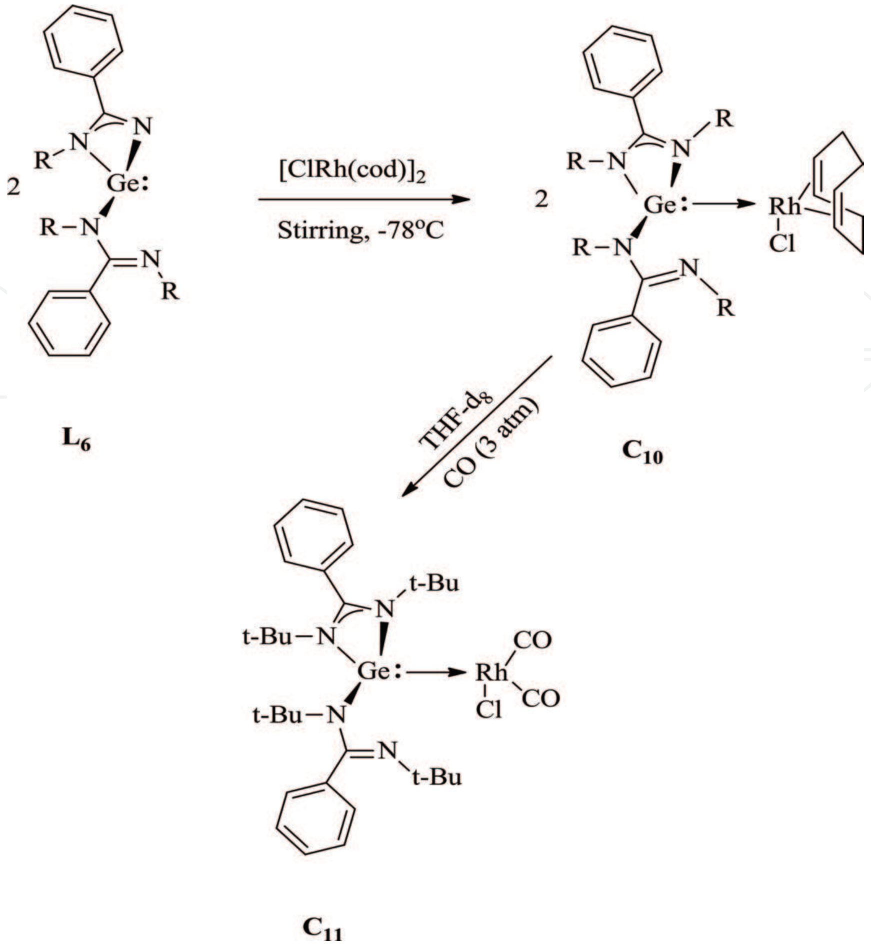


Scheme 5. Synthesis of [(ButNacnac)Ge:] complex.

C10 was formed when a colored solution of **L6** in diethyl ether was added into $[RhCl(cod)]_2$ solution in diethylether at −78°C (**Scheme 6**). The solution was placed at room temperature for 45 min. Then, the solution was stirred continuously for another 45 min. After filtration, the solvent was concentrated under reduced pressure. Yellow crystals were obtained in 49% isolated yield. Melting point of the product was 91°C. Reaction was occurred in dry and oxygen-free atmosphere of argon by using glove box techniques. Synthesis of **C11** was carried out in NMR tube. A solution of **C10** in deuterated tetrahydrofuran was contacted with carbon monoxide atmosphere at −80°C. The ligand exchange reaction was completed in less than 10 min as per monitoring by ^{1}H NMR [12].

C12.$[BF_4]$ was formed by reacting amino(imino)germylene in toluene with $BF_3{\cdot}OEt_2$ at −78°C (**Scheme 7**). The reaction mixture was stirred for 12 h, and during this course of time, it was allowed to slowly warm to the room temperature. Evaporation of solvent and washing residual material with diethyl ether provided the required compound as a yellow powder, which in turn provided compound as colorless crystals suitable for X-ray diffraction on recrystallization by THF. **C12** was formed via the intermediate fluorogermylene dimer $[FGeNIPr]_2$ as suggested by DFT calculations. The boron tetrafluoride played the role of fluorination reagent as well as fluoride abstraction agent. Multinuclear NMR spectroscopy was used to confirm the formulation of **C12** $[BF_4]$. The researchers found a highly disordered germanium-bonded fluorine atom by single crystal X-ray structure analysis, which possesses 50% site occupancy factor at each of the two germanium atoms [7].

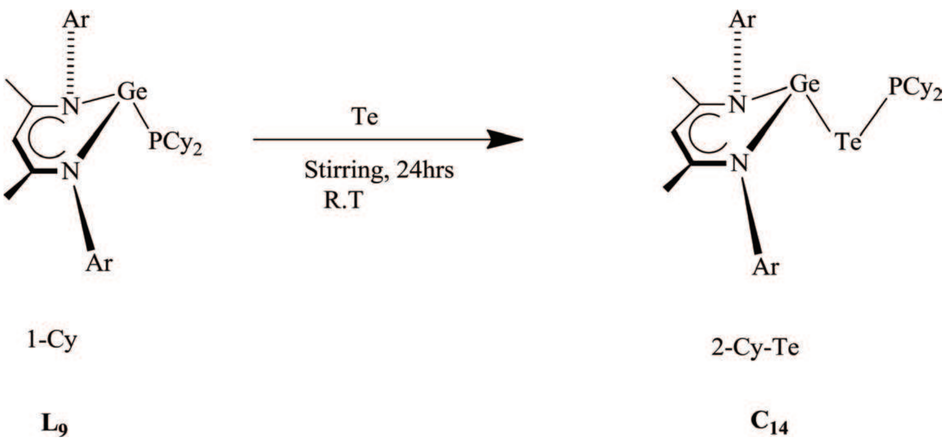
C13 was formed when a dark green solution of **L13** was added to a suspension of selenium powder in THF at 0°C (**Scheme 8**). Reaction can occur in the absence of light. A yellow solution was formed when mixture was stirred continuously at room temperature for 2 days. The residue was extracted with toluene and hexane, and volatiles were removed under vacuum.

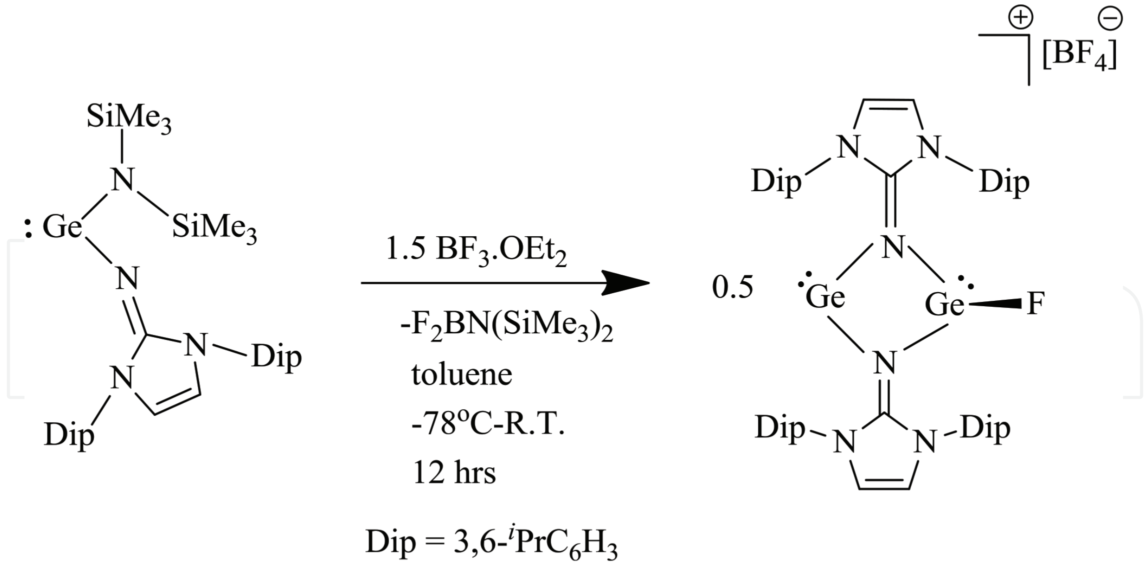


Scheme 6. Synthesis of the germylenedicarbonylrhodium(I) complex, **C11**.

The resulting product was separated as yellow crystals in 67.5% isolated yield. Melting point of the resulting product was 206.5°C [13].

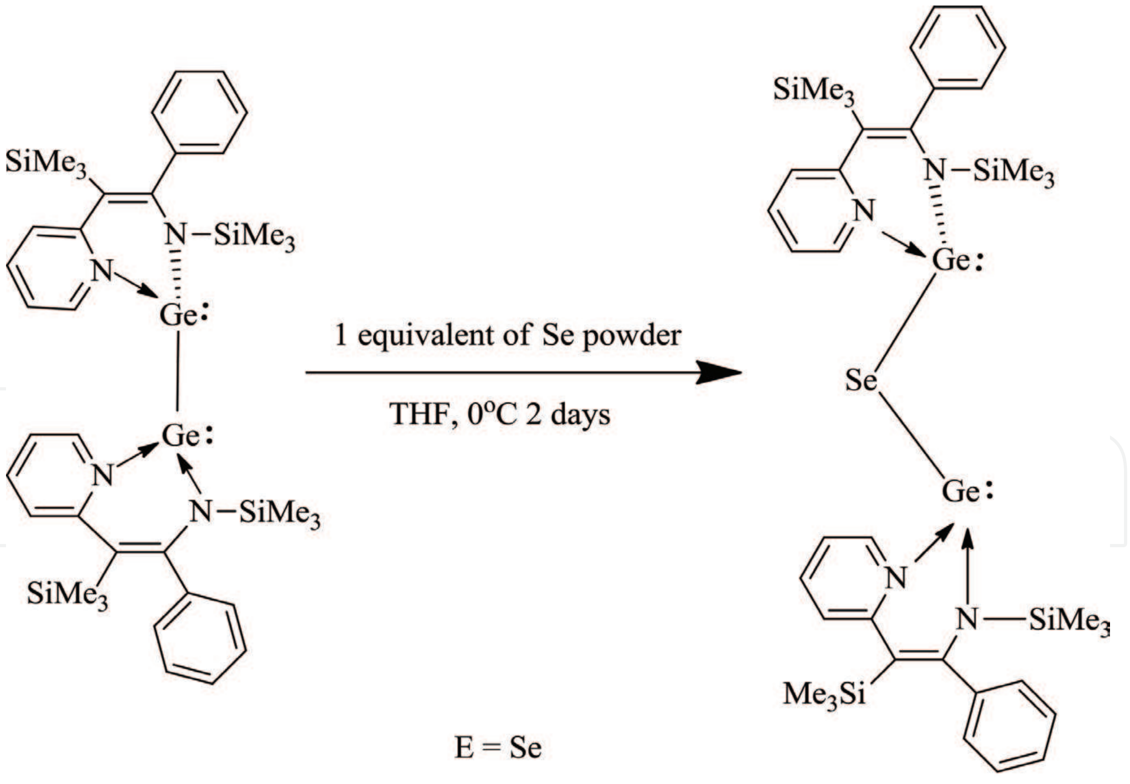
C14 was formed when slurry of tellurium suspended in toluene was added dropwise in 1-Cy solution (**Scheme 9**). Mixture was continuously stirred at ambient temperature for 24 h, meanwhile mixture color changed from purple to red. After filtration, the reaction mixture was concentrated under vacuum. Mixture was stored for 24 h at −27°C to obtain red crystals of the product [4].





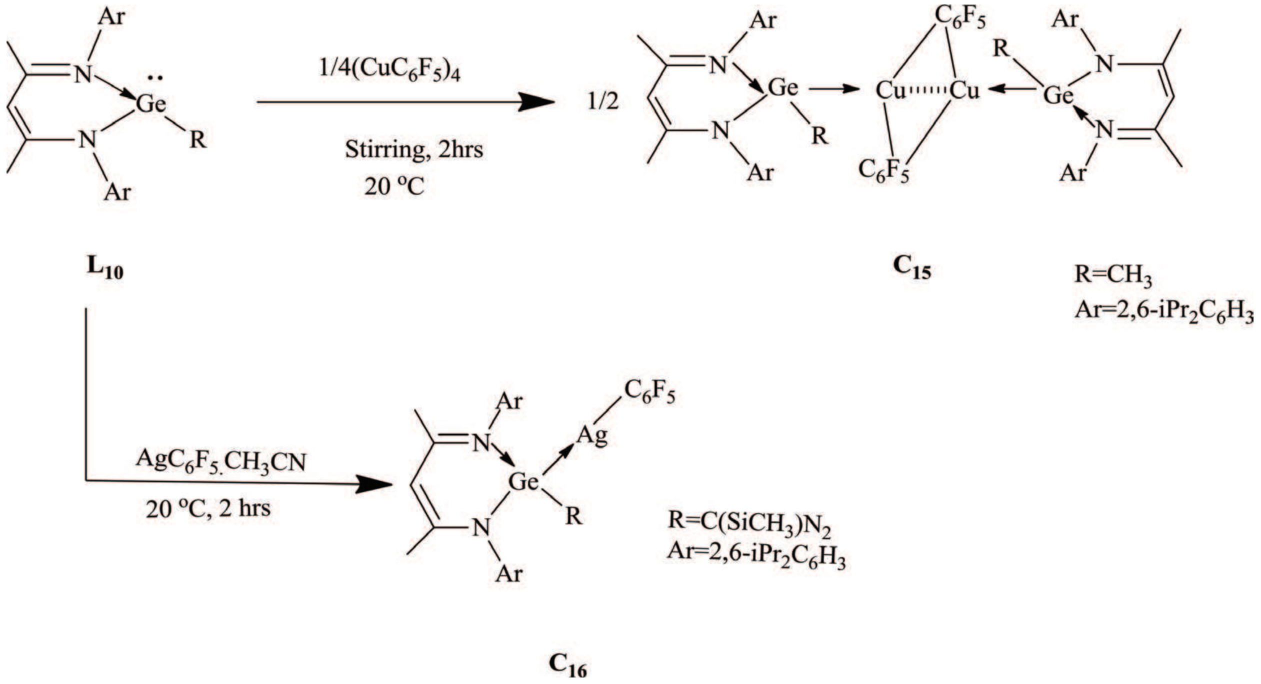
$\mathbf{L_7}$ $\mathbf{C_{12}}$

Scheme 7. Synthesis of germyliumylidene salt **C12**.[BF_4].



$\mathbf{L_8}$ $\mathbf{C_{13}}$

Scheme 8. Synthesis of bis(germylene)selenide.

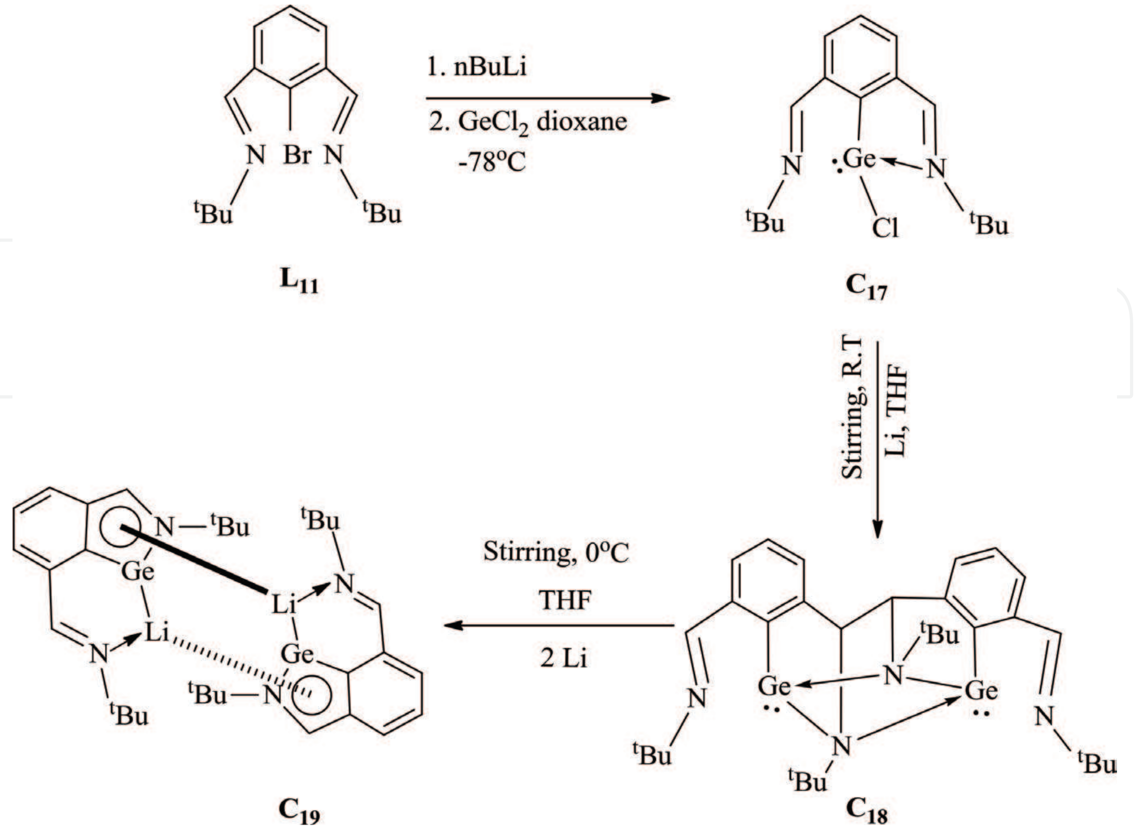


Scheme 9. β-Diketiminate germylene-supported pentafluorophenylcopper(I) and -silver(I) complexes.

4. Germanium complexes involving bonding through carbon and nitrogen (C, N)

C15 was formed when a solution of $(CuC_6F_5)_4$ in toluene was added to a solution of **L10** in toluene using a glove box with a consistent stirring. A quick color change was observed from orange red to light yellow. The mixture was further stirred continuously for next 2 h. After filtration, the filtrate was kept unattended at −20°C. After 5 days, crystals grew and the mixture was filtered and light yellow crystals of **C15** were obtained in 81% isolated yield. The X-ray crystallography showed that complex carries two toluene molecules packed during crystal growth. Melting point of the crystal was 206°C [14]. One more product was formed by mixing **L10** with $AgC_6F_5{\cdot}CH_3CN$ in a brown vial in the presence of toluene. For half an hour, the mixture was stirred and toluene was continuously added until all solids dissolved. After filtration, the filtrate was overlayered with n-hexane and placed unattended at −20°C for 2 days. After 48 h, light yellow crystals of **C16** were collected by filtration in 71% isolated yield. Melting point of the crystals was 156°C [14].

C17 was synthesized by mixing n-butyl lithium dropwise to a solution of **L11** in THF at −78°C (**Scheme 10**). After 3 h stirring of mixture, $GeCl_2{\cdot}$dioxane was added to reaction mixture at −78°C. The resulting product was reddish brown. The reddish brown solution was warmed gradually at room temperature and stirred overnight. The residue was extracted with dichloromethane, and solvent was removed under vacuum. Lithium chloride was filtered off, and the filtrate was concentrated. Orange crystals of **C17** were obtained in 47% isolated yield.

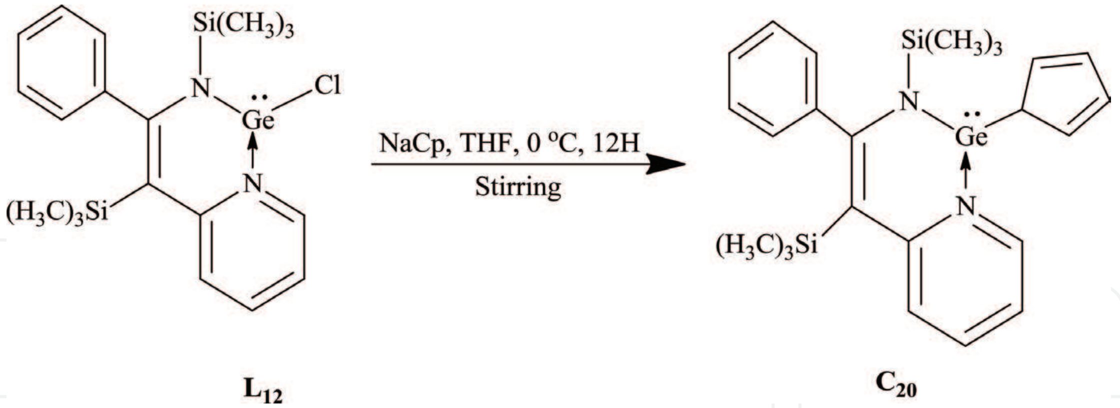


Scheme 10. Preparation of a germylidenide anion from the C■C bond activation of a bis(germylene).

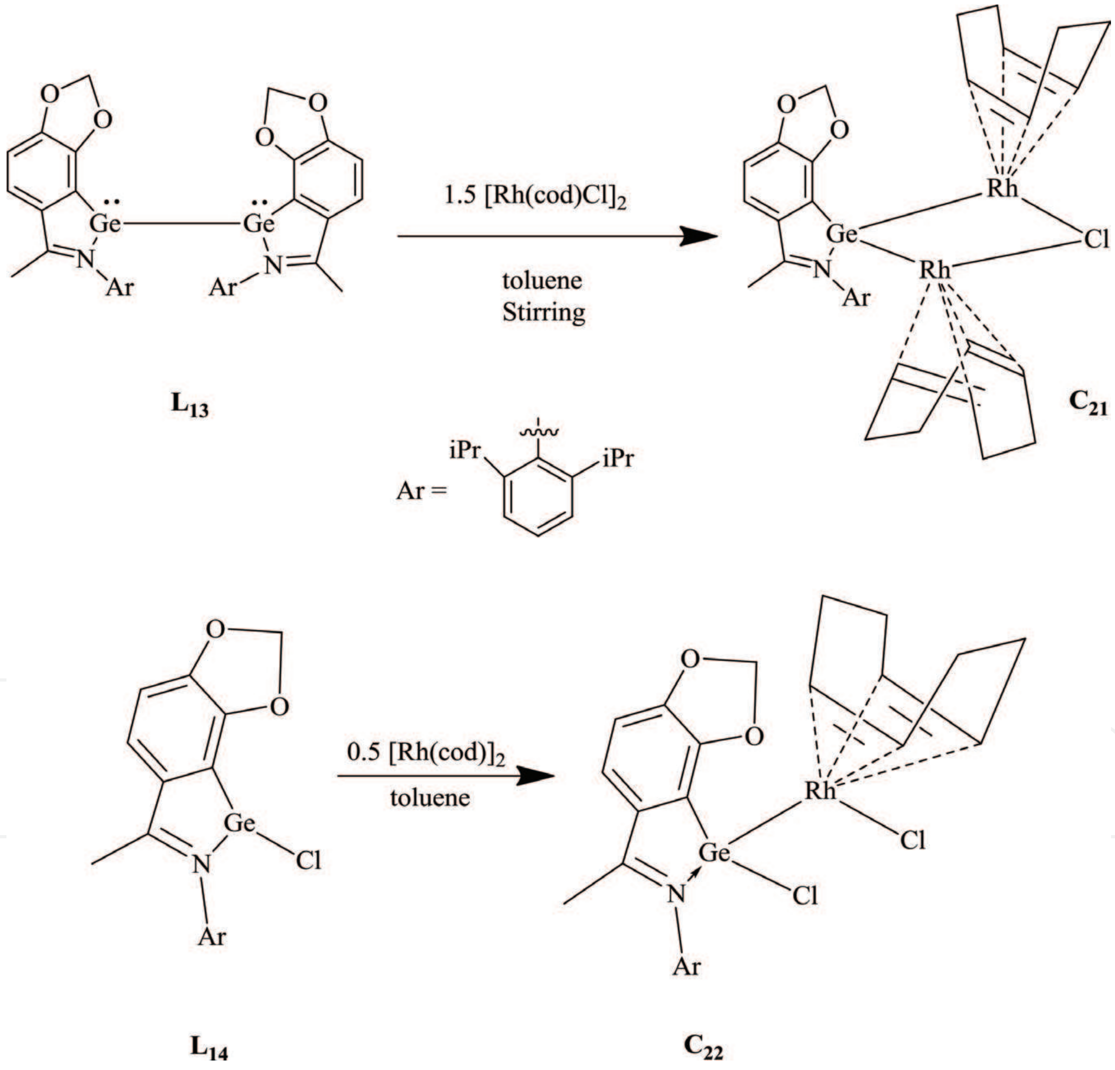
Melting point of the product was 163°C [15]. **C18** was formed when THF was added to a mixture of **C17** and Li metal at 0°C. The resulting mixture was warmed at room temperature and stirred for 15 h. The dark green residue was extracted with diethyl ether, and lithium chloride was filtered off. The resulting green solution was stirred at room temperature for 2 h. After filtration, the solution was concentrated affording dark green crystals of **C18** in 49% isolated yield. Melting point of the product was 218°C [15]. **C18** was further used to synthesize **C19** by adding THF into **C18** mixture and Li granules at 0°C. Dark green solution was formed when resulting red mixture was warmed at room temperature and stirred continuously for 15 h. The end product was obtained after removing the solvent under vacuum [15].

C20 was formed when in a solution of **L12** in THF was added sodium cyclopentadienyl in THF dropwise at 0°C (**Scheme 11**). Yellowish orange solution was obtained, which was warmed at room temperature with continuous stirring for 12 h. The mixture was extracted with diethyl ether, and volatiles were removed under reduced pressure. At the last, yellow crystals were extracted in 74% isolated yield. Melting point of the product was 128°C [16].

C21 was prepared by adding dropwise a solution of $[RhCl(cod)_2Cl]_2$ in THF in a stirred solution of **L13** in THF at room temperature (**Scheme 12**). The mixture was filtered after 16 h stirring. Dark purple crystals were obtained by concentrating the mixture. Melting point of the end product was 194°C [17]. **C22** was prepared by adding $[RhCl(cod)]_2$ solution dropwise in a stirred solution of **L22** in toluene at room temperature. After 16 h stirring, the reaction mixture was filtered and then concentrated. At the end, the resulting product was obtained as an orange-colored transparent crystalline solid in 85.7% yield. Melting point of the end product was 225°C [17].

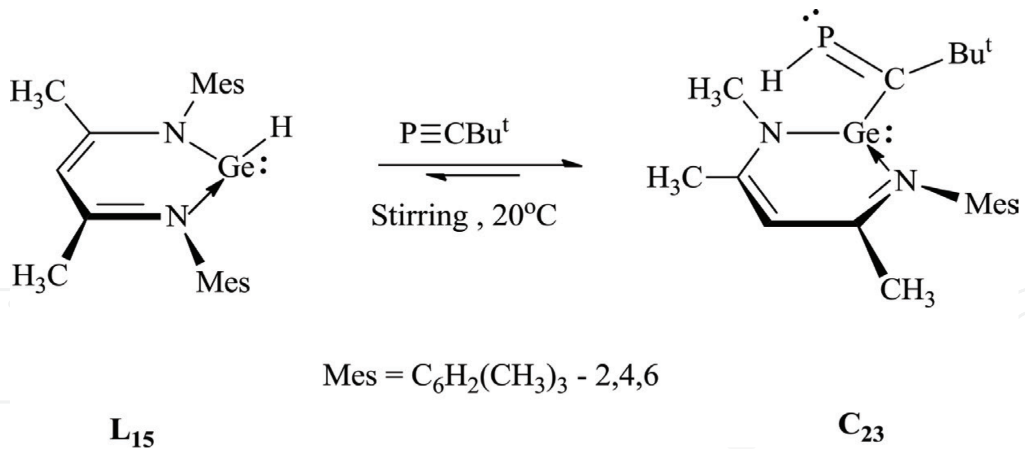


Scheme 11. Metallogermylenes, Cp-substituted germylene.



Scheme 12. Synthesis of germanium(I) dimer.

C23 was formed by reacting **L15** with $P \equiv CBu^t$ at 20°C in toluene (**Scheme 13**). The reaction mixture was warmed at 35°C and stirred continuously for 15 h. During stirring, the color of reaction mixture was changed into deep red. The residue was extracted by using hexane. All

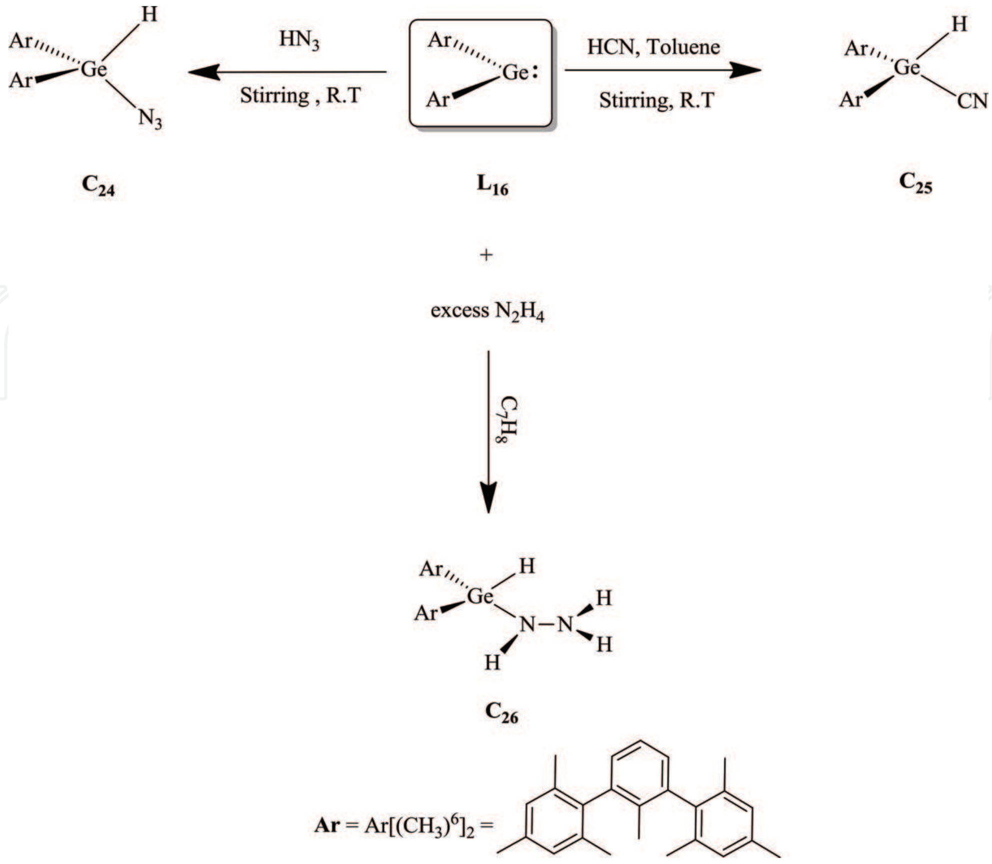


Scheme 13. Synthesis of *N*-heterocyclic germanium(II) hydride.

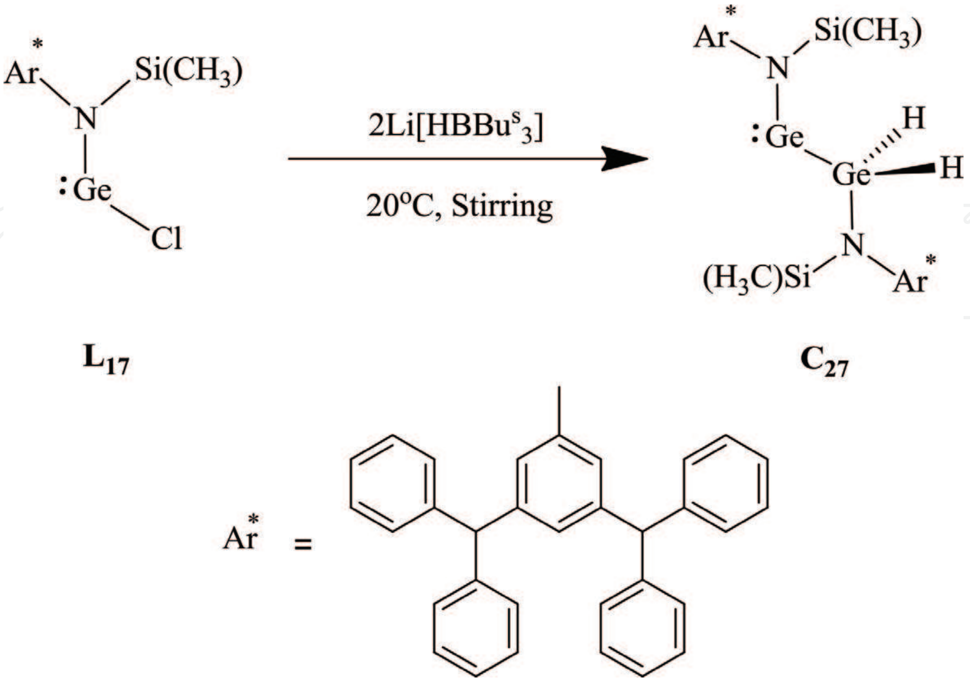
volatiles were removed in vacuum. After filtration, the filtrate was stored at 30°C overnight. The end product was obtained as dark red crystals in 67% isolated yield. Melting point of the end product was 142°C [18].

5. Germanium complexes involving bonding through nitrogen and hydrogen (N, H)

Three products were prepared from **L16** (diarylgermylene) by addition of different compounds such as hydrazoic acid, hydrogen cyanide, and anhydrous hydrazine in presence of toluene at room temperature (**Scheme 14**). First, an ethereal solution of hydrazoic acid was formed when methanol was added into $[(CH_3)_3Si]N_3$ solution in diethyl ether. After stirring of solution for 5 min, this colorless solution was added to a stirred solution of **L16** at room temperature. Purple solution became colorless when reaction mixture was stirred continuously overnight. The resulting product (white solid) was washed with pentane and mixed with small amount of hot hexane. Then, the solution was slowly cooled to 6°C and temperature was sustained overnight. **C24** was obtained as colorless blocks in 79% isolated yield [19]. These colorless blocks were suitable for single X-ray diffraction. Melting point of the end product was 177–183°C. Second, hydrogen cyanide was prepared by adding methanolic solution of $(CH_3Si)CN$ in diethyl ether. Colorless solution was stirred for 30 min. After stirring, it was added to stirred $Ge(Ar^{Me6})_2$ solution in toluene at room temperature. The purple solution became colorless when solution was stirred continuously overnight. **C25** was obtained as white solid product, which was washed with small amount of pentane, and all volatile materials were removed under reduced pressure. Third, **C26** was formed when stoichiometric amount of anhydrous hydrazine was added to a stirred solution of **L16** in toluene. The mixture was stirred continuously overnight, and deep purple color changed to colorless during stirring. The resulting microcrystalline white solid was washed by using small amount of hexane and dried under reduced pressure. The microcrystalline solid was stored at 20°C for 1 week after dissolving the solid in toluene. The colorless end product was obtained in 86% isolated yield [20].



Scheme 14. Synthesis of germylene complexes from diaryl germylene complexes.

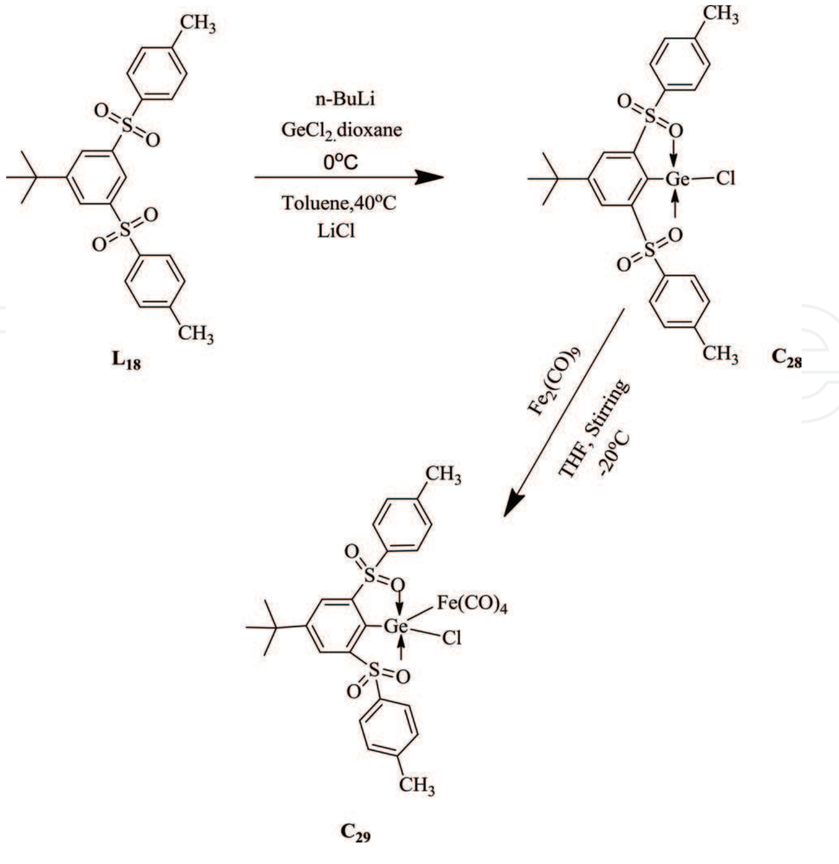


Scheme 15. Synthesis of digermylene complexes with a Ge▬Ge single bond.

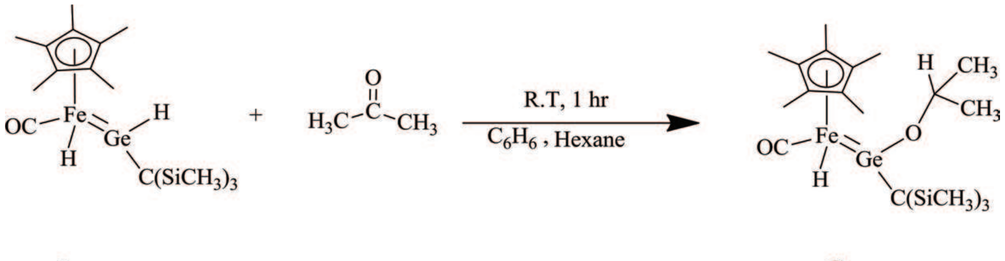
C27 was formed when a solution of **L17** in toluene left in Youngs Schlenk flask at 20°C under 1 atmospheric pressure of highly pure H_2 (**Scheme 15**). The reaction mixture was stirred continuously for 30 min. All volatiles were removed under vacuum. Pale orange solid was obtained as end product. By recrystallization, solid single crystals of complex were obtained from minimum volume of diethyl ether, which remained suitable for X-ray crystallography. Melting point of the end product was 190–194°C [21].

6. Germanium complexes involving bonding through carbon and oxygen (C, O)

C28 was formed when n-butyl lithium was added slowly to a solution of **L18** (bis-sulfone) in toluene at 40°C (**Scheme 16**). The solution color changed into deep red, and this solution was further stirred continuously for 20 min at 40°C. Then, the reaction mixture was added over a suspension of $GeCl_2$-dioxane in toluene at 0°C. The reaction mixture was heated to room temperature and stirred for 18 h. After stirring, all volatiles were removed and the residue was washed with CH_2Cl_2. White solid was obtained in 58% isolated yield. Melting point of the white solid was 260°C. Colorless crystals of **C28** were obtained by slow diffusion of pentane in CH_2Cl_2. **C29** was formed by adding a solution of $Fe_2(CO)_9$ into germylene solution in THF at −20°C. Then, the mixture was warmed slowly at room temperature and stirred for 24 h. All volatiles were evaporated. The product was extracted with diethyl ether. Colorless product was obtained at room temperature for X-ray crystallographic analysis [22].



Scheme 16. Synthesis of bis-sulfonyl O,C,O-chelated germylenes.



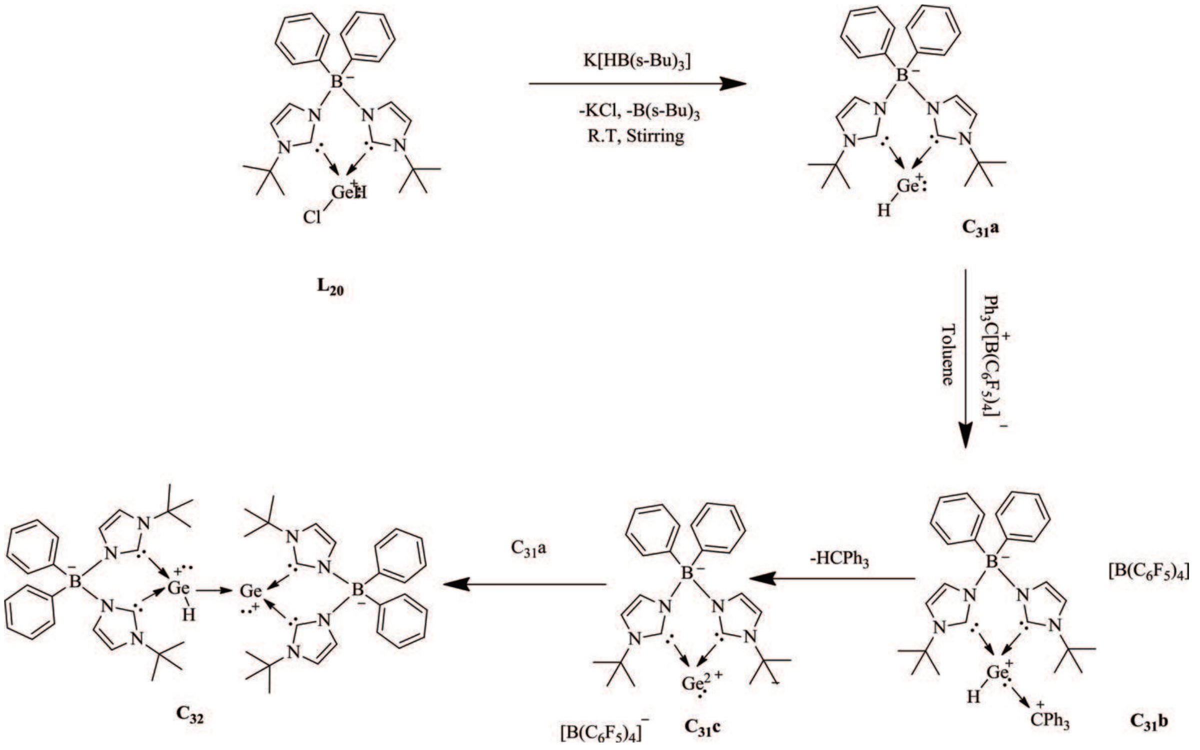
L_{19} **C_{30}**

Scheme 17. Synthesis of iron germylene complex having Fe-H and Ge-H bonds.

C30 was formed when a solution of **L19** in hexane was dissolved into acetone (**Scheme 17**). The reaction mixture was stirred continuously at room temperature for 1 h. All volatiles were removed under vacuum. The end product was obtained as a greasy solid. Pure red crystals were obtained by recrystallization of the greasy solid in hexane at 30°C in 42% isolated yield [23].

7. Germanium complexes involving bonding through carbon and hydrogen (C, H)

A red solution of **L20** was added into K[HB(s-Bu)$_3$] in THF at room temperature and stirred continuously (**Scheme 18**). The color of reaction mixture changed immediately into yellow. After 1 h, all volatiles were removed under vacuum. B(s-Bu)$_3$, the by-product, was removed away with n-pentane. Colorless crystals of **C31a** were obtained in THF solutions at −20°C in 91% isolated yield. Melting point of the end product was 270°C. [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and toluene



Scheme 18. Synthesis of germyliumylidene hydride [:GeH]$^+$ stabilized by a bis(NHC) borate ligand.

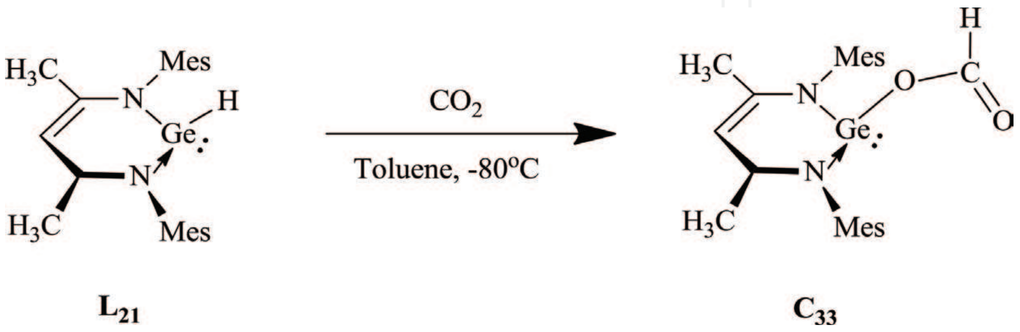
were added into **C31a** at room temperature and the mixture was stirred. Two phases were formed immediately when the mixture was stirred continuously. After 3 h, ^{1}H NMR indicated the formation of **C32** and $HCPh_3$ (a by-product). The formation of the by-product was indicated by a singlet at $\delta = 5.58$ ppm for $HCPh_3$. All volatiles were removed under vacuum. Ph_3CH, a by-product, was removed by using n-pentane. The residue was dissolved in acetonitrile, and **C32** was first crystallized in the form of yellowish rods at 4°C in 57% isolated yield. When the solution was further concentrated, the yellowish product changed into orange rods and was collected in 25% isolated yield. Melting point of the end product was 201°C [24].

8. Germanium complexes involving bonding through nitrogen and oxygen (N, O)

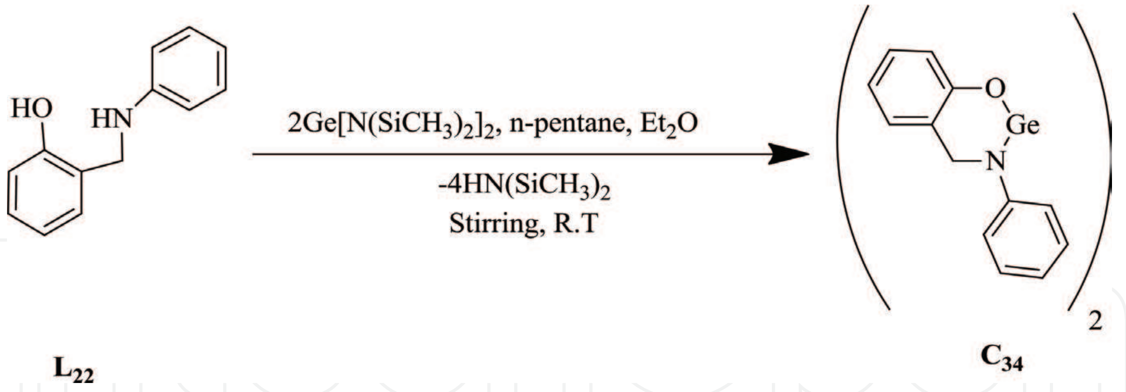
C33 was prepared by mixing a solution of **L21** in toluene at −80°C and was placed under an atmosphere of dry CO_2 gas (**Scheme 19**). The orange red reaction mixture was allowed to heat toward ambient temperature with consistent stirring. At about −30°C, the reaction mixture turned colorless. However, it was allowed to heat till room temperature. The resulting reaction mixture was concentrated toward saturation using rotary evaporator. The saturated solution was layered with n-hexane. Colorless crystals of **C34** were obtained in 75% isolated yield. Melting point of the product was 175–178°C [18].

C34 was formed by dissolving diethyl ether and $Ge[N(SiCH_3)_2]_2$ in **L22** (**Scheme 20**). In reaction mixture, n-pentane was added slowly. Then, mixture was stirred at ambient temperature for 5 min. After filtration of reaction mixture, a solid material was obtained and was dried in vacuum to obtain colorless crystalline solid. The product was recrystallized to obtain colorless crystals of **C34** in 85% isolated yield [25].

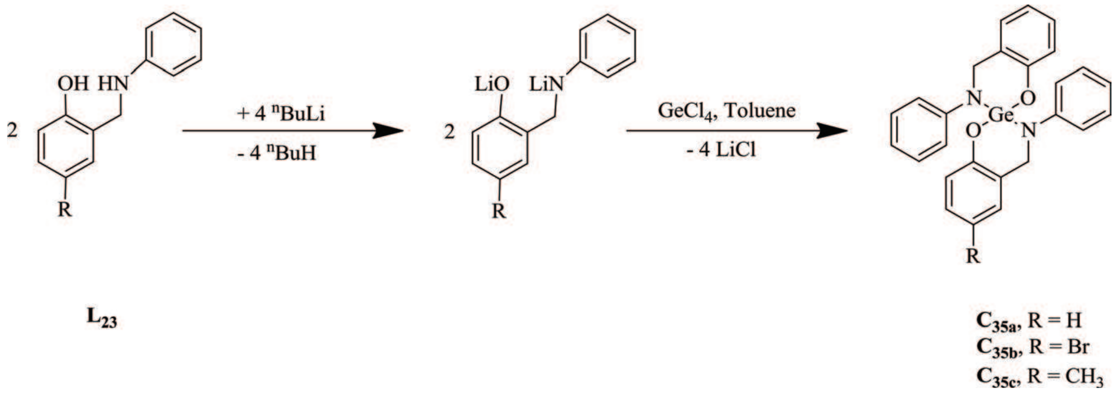
Spirocyclic compounds (**C35a**–**C35c**) were synthesized by adding n-butyl lithium in n-hexane into a solution of 2-(phenylaminomethyl)phenol in diethyl ether (**Scheme 21**). The reaction mixture was stirred at ambient temperature for 2 h. After filtration, the reaction mixture was washed with n-pentane and was then dried under low pressure. The solid was dispersed in toluene and $GeCl_4$ was added dropwise with the help of syringe. Then, the solution was stirred at ambient temperature for 16 h. The solution was filtered using celite 545 and was



Scheme 19. Synthesis of *N*-heterocyclic germanium(II) hydride.



Scheme 20. Synthesis of amido alkoxide of germanium.



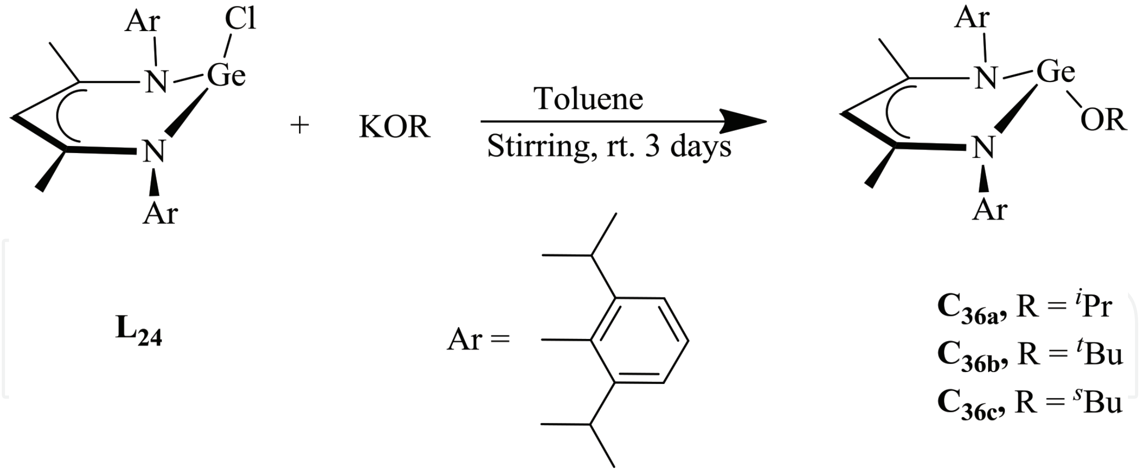
Scheme 21. Synthesis of spirocyclic compounds of germanium bonded through “N” and “O”.

concentrated in vacuum and hence finally gave solids, which were crystallized from an appropriate solvent. The end product was obtained in 82% isolated yield. For single X-ray diffraction, colorless crystal was grown from n-hexane at 18°C [25].

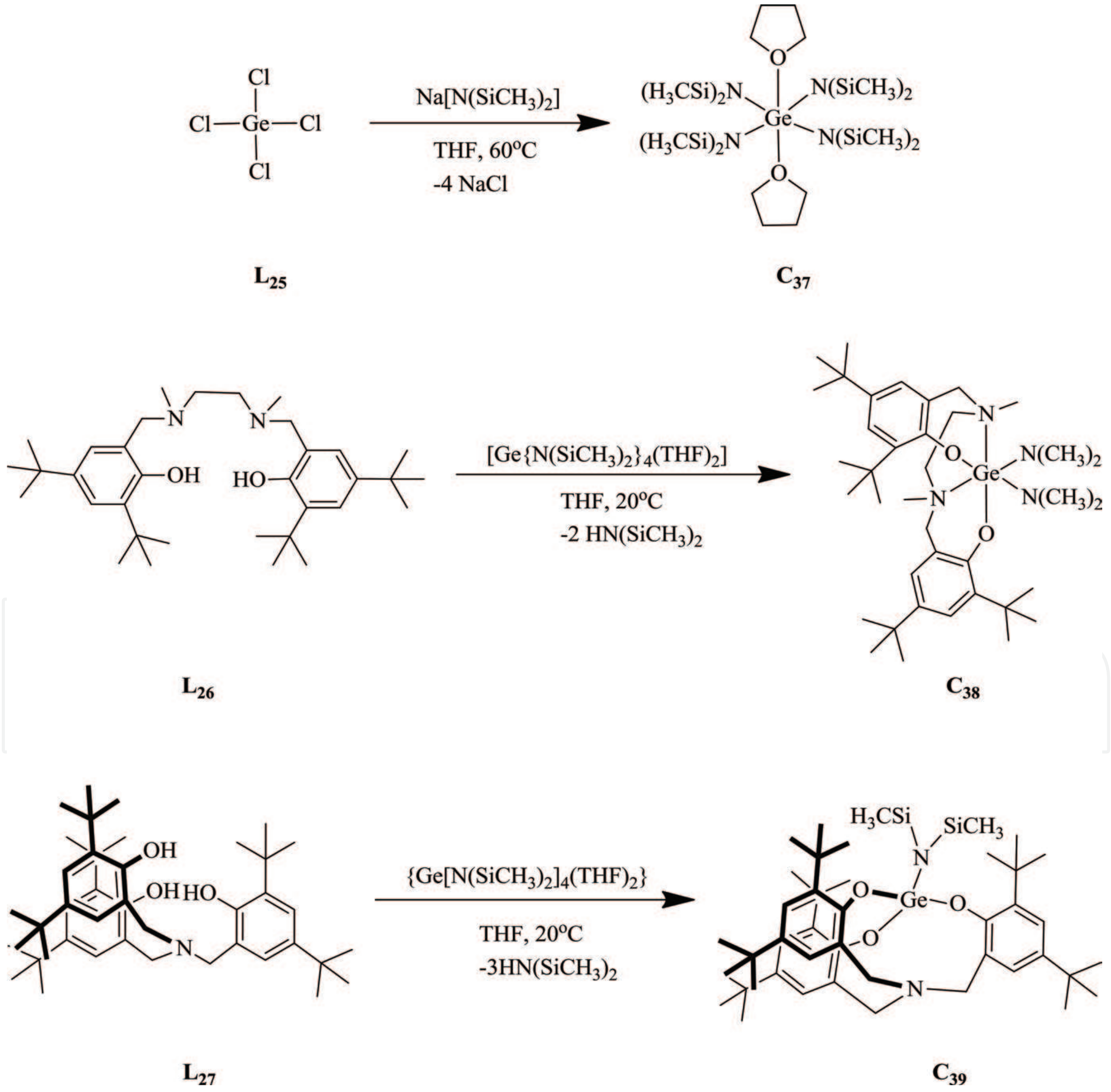
C36a–C36c were formed when a suspension of KOR (R = ^{i}Pr, ^{t}Bu, ^{s}Bu) was added into $GeCl_4$·dioxane solution in THF at ambient temperature (**Scheme 22**). The reaction mixture was stirred for 3 days at ambient temperature. All volatiles were removed using rotary evaporator. The orange crude product was extracted with toluene, and the solution was filtered through celite 545. The filtered material was evaporated to obtain a solid. Recrystallization of this solid was carried out by n-hexane through an overnight period at −27°C. The end product was obtained as orange crystals in 76% isolated yield [26].

C37 was formed when solution of sodium bis(trimethylsilyl)amide and $GeCl_4$ in THF was stirred and refluxed for 96 h (**Scheme 23**). All volatiles were removed under low pressure. The residue was extracted three times by pentane. The pentane solution was concentrated and was kept in glove box at −40°C overnight. The white solid was washed with cold n-pentane, and the product was dried in vacuum. The end product was obtained as white powder in 65% isolated yield [27].

Synthesis of **C38** was carried out when a solution of **L26** and $Ge[N(SiCH_3)_2]_4$.(THF) was mixed and stirred for 10 min at room temperature. After removing solvent from reaction mixture, the



Scheme 22. Synthesis of germanium alkoxide complexes.

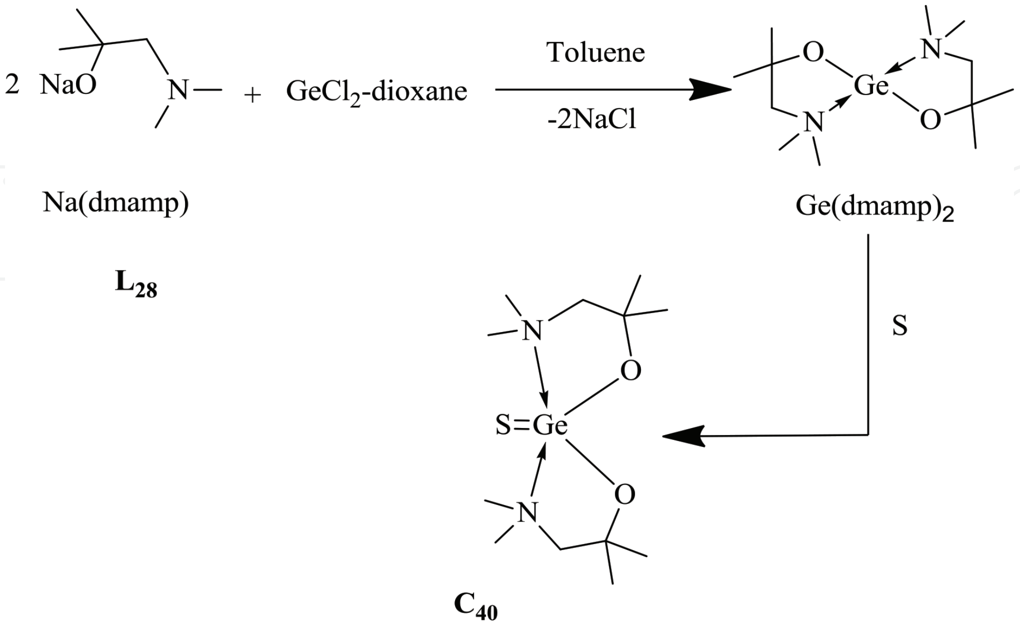


Scheme 23. Synthesis of germanium complexes involving bonding through "N" and "O".

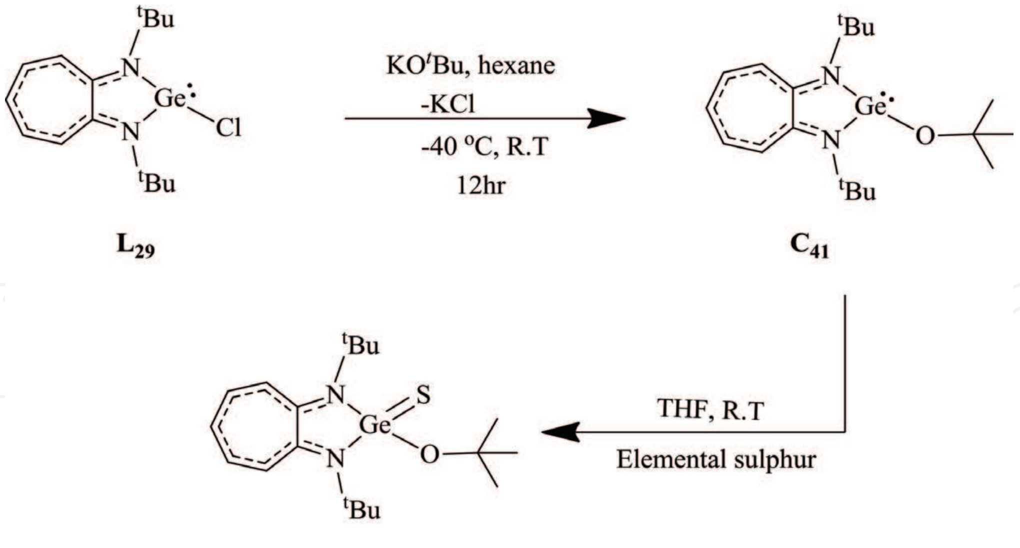
solid residue was dissolved in n-pentane. Then, n-pentane solution was kept in a glove box at −40°C overnight. A white crystalline solid was extracted out from solution and was washed with clean and cold n-pentane. The extracted product was dried in vacuum. The end product was obtained as white powder in 90% isolated yield [27]. Similarly, **C39** was formed when **L27** was added to a stirred solution of $\mathrm{Ge[N(SiCH_3)_2]_4.(THF)_2}$ in toluene at room temperature. The reaction mixture was stirred for 10 min at room temperature. All volatiles were removed under vacuum. The extracted residue was washed several times by n-pentane and was dried under vacuum. The end product was obtained as white powder in 85% isolated yield [27].

C40 was synthesized in two steps (**Scheme 24**). Firstly, $\mathrm{GeCl_2}$·dioxane was added slowly into a solution of Na(dmamp), where dmamp = 1-dimethylamino-2-methyl-2-propanolate, in THF. The reaction mixture was stirred continuously at room temperature overnight. The reaction mixture was filtered to remove sodium chloride salt as by-product. After filtration, the filtrate was concentrated in vacuum to obtain $\mathrm{Ge(dmamp)_2}$ as crude product. The end product was obtained as colorless liquid by distillation in 81% isolated yield. Sulfur powder was then added slowly into a solution of $\mathrm{Ge(dmamp)_2}$ in toluene. The reaction mixture was stirred at room temperature overnight. **C40** was obtained as a white solid after removing all the volatiles from the reaction mixture. Recrystallization of the crude product from an ethereal solution of it gave the pure product as colorless crystals in 82% [28].

C41 $[(^t\mathrm{Bu})_2\mathrm{ATI}]\mathrm{GeO}^t\mathrm{Bu}$ was formed by adding **L29** solution in hexane into $\mathrm{KO}^t\mathrm{Bu}$ at −40°C (**Scheme 25**). The reaction mixture was stirred at room temperature for 12 h. After filtration, hexane was removed and **C41** was obtained as red solid in 97% isolated yield. Melting point of the end product was 78°C. **C42** was formed when elemental sulfur was added into **L28** solution in THF at room temperature. The reaction mixture was stirred at room temperature for 2 h. All volatiles were removed under reduced pressure. The residue was washed with n-hexane and was dried to get the product as yellow solid in 98% isolated yield. Single



Scheme 24. Synthesis of germanium complex containing Ge═S double bond.

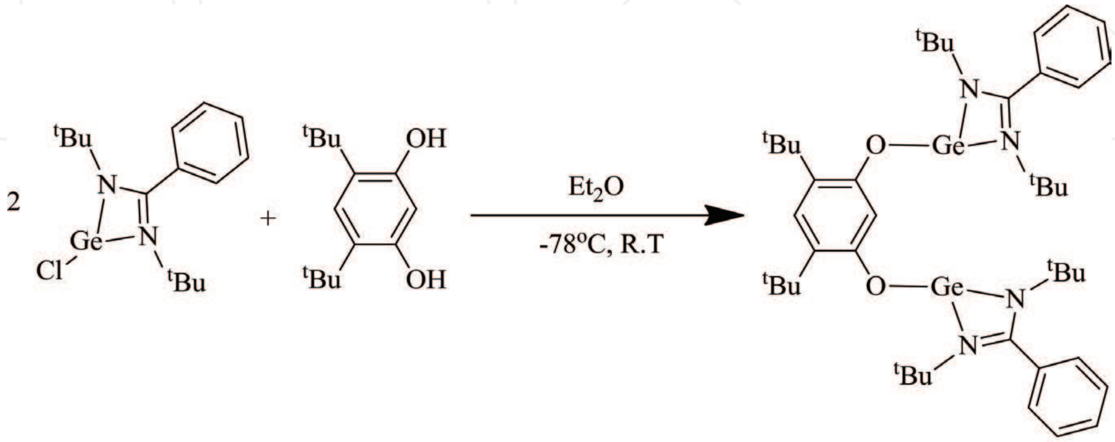


L_{29} C_{41} C_{42}

Scheme 25. Synthesis of aminotroponiminatogermylenealkoxide complexes.

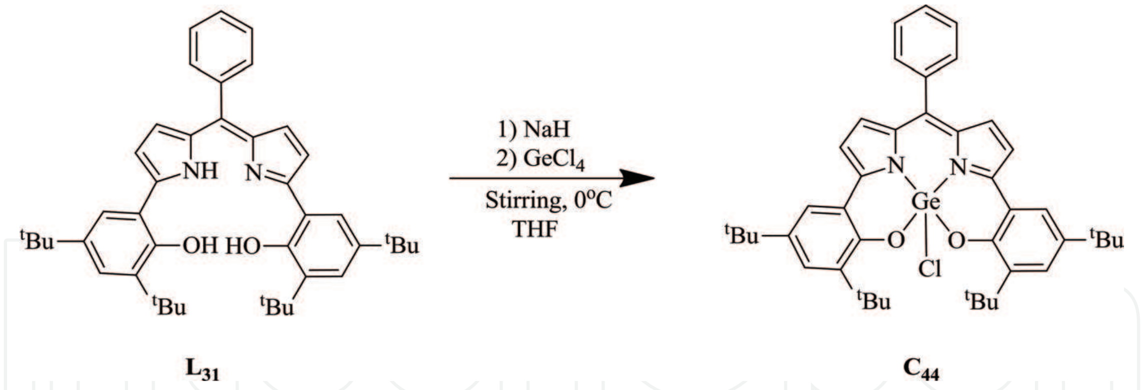
crystals of **C42** were obtained by the slow evaporation of solvent from its chloroform solution. Crystals of **C42** were remained suitable for X-ray crystallographic studies. Melting point of the end product was 178°C [29].

n-BuLi was added into a cold solution of 4,6-di-ter-butylresorcinol of dry diethyl ether at −30°C (**Scheme 26**). After mixing, immediately a milky solid suspension was observed. Cooling bath was removed and reaction material was again stirred for 3 h at ambient temperature. The reaction mixture was then cooled and N,N-di-tert-butylchloro(phenylamidinate)-germanium(II) was added dropwise in the reaction mixture. After complete addition, the reaction mixture was maintained at ambient temperature overnight. All volatile solvents were removed in vacuum. **C43** was extracted with the addition of hot hexane in reaction mixture *via* cannula filtration. The reaction mixture was concentrated and cooled at −3°C, which led



L_{30} C_{43}

Scheme 26. Synthesis of $GeC_{aromatic}Ge$-type pincer for further coordination with iridium.



Scheme 27. Synthesis of salophene-like germanium complex.

to the crystallization of product overnight. Product was dried in vacuum for 2 h. The end product was obtained as yellowish crystalline product in 83% isolated yield [30].

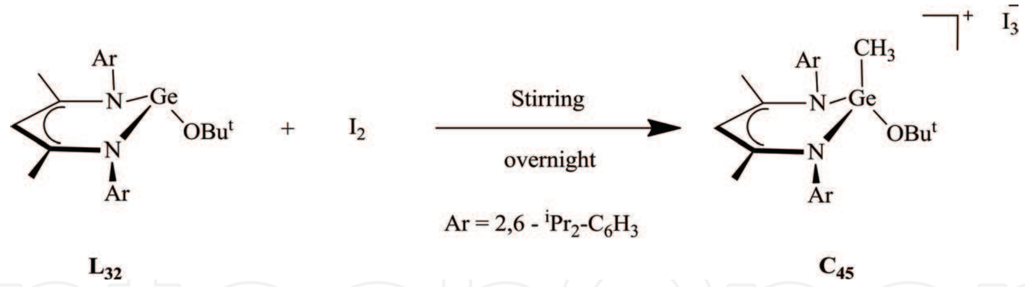
C44 was synthesized by mixing NaH and $GeCl_4$ with **L31** (**Scheme 27**). The solution was stirred for 1 h at ambient temperature. After filtration, the filtrate was placed in Schlenk tube and the tube was taken outside the glove box. $GeCl_4$ was added dropwise in the reaction mixture at 0°C. After stirring of solution for 25 min at same temperature, the reaction mixture was warmed at room temperature for another 1 h and was concentrated under reduced pressure. The residue was filtered through syringe filter in a glove box by using Et_2O. The resulting residue was redissolved in pentane and was concentrated to remove uncoordinated THF. The end product was obtained as green solid in 98% isolated yield [31].

9. Three linkages

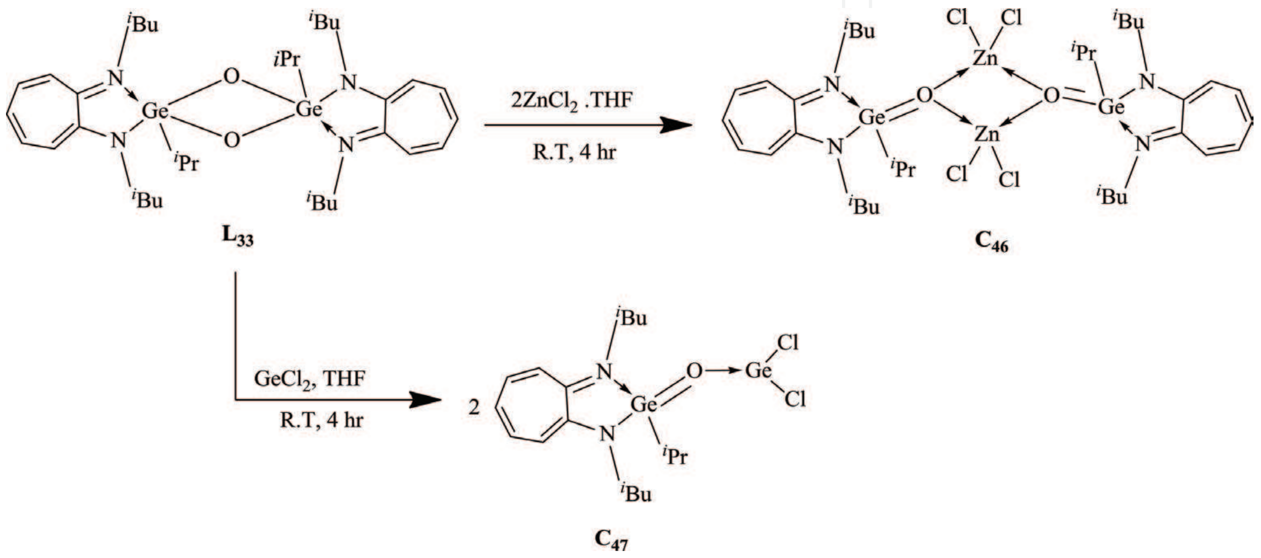
9.1. Germanium complexes involving bonding through carbon, nitrogen, and oxygen (C, N, O)

C45 was synthesized when iodine was added to a solution of **L32** (**Scheme 28**). Pale yellow precipitates were formed when the reaction mixture was stirred for a period of 12 h. Then, precipitates were washed several times with n-pentane and the end product was obtained as a dark orange powder in 92% isolated yield. Dark red crystals were produced by storing the saturated solution of **C45** in THF/C_6H_5F mixture at −27°C for 7 days [26].

C46 was formed by mixing **L33** with $ZnCl_2$ in THF (**Scheme 29**). The reaction mixture was stirred for 4 h at ambient temperature. All volatiles were removed using rotary evaporator. Yellow solid product was washed with toluene and was dried in vacuum. Single crystals of **C46** were grown from its hot acetonitrile solution for X-ray diffraction studies. The end product was obtained as yellow solid in 94% isolated yield. Melting point of the end product was 152°C [32]. **C47** was synthesized when a solution of **L34** was transferred into $GeCl_2$ solution in THF at room temperature, and the reaction mixture was stirred for 4 h. All volatiles were removed using rotary evaporator. The yellow solid was washed with n-hexane and was



Scheme 28. Synthesis of germanium alkoxide complex.



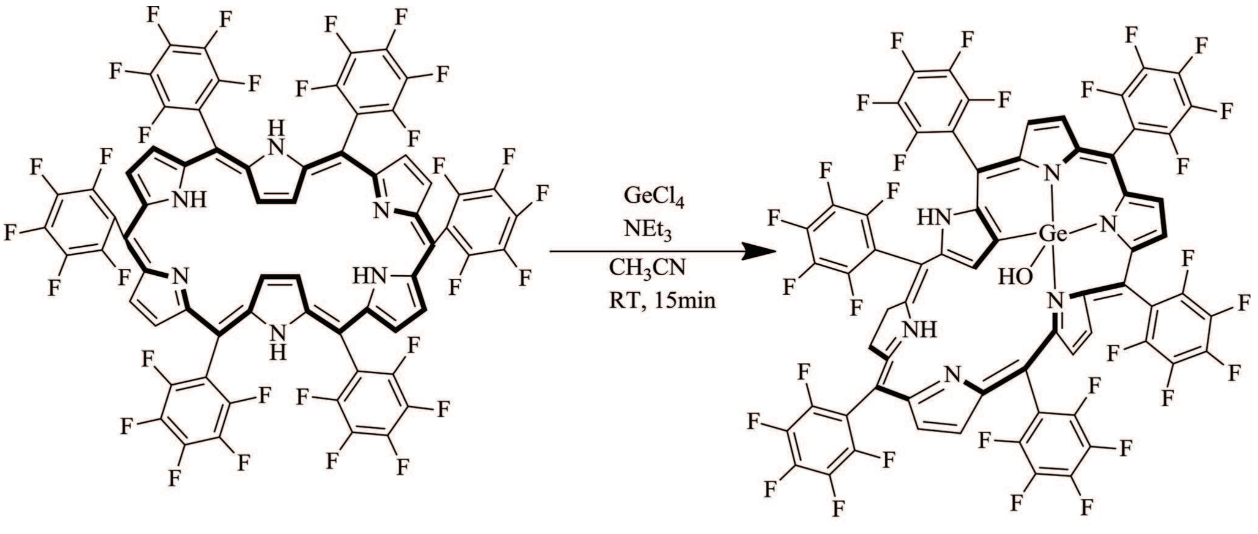
Scheme 29. Synthesis of germanone from a germanium-μ-oxo dimer.

dried in vacuum to obtain pure sample of **C47** as yellow solid. Single crystals of complex were grown from its solution in THF and hexane at −40°C, which remained suitable for X-ray diffraction studies. The end product was obtained as yellow solid in 94% isolated yield. Melting point of the end product was 110°C [32].

L34 in CH_3CN was placed in a round bottom flask under an inert atmosphere using argon gas (**Scheme 30**). Triethyleneamine (NEt_3) and $GeCl_4$ were added in the reaction medium. The reaction mixture was then stirred at room temperature for 15 min and passed through a short pad of silica gel column (C-200, CH_2Cl_2). Separation through silica gel column (C-300, n-hexane: CH_2Cl_2 = 2:1) gave **C48** as a second fraction. All volatiles were removed. The end product was obtained as dark brown solid in 76% isolated yield [33].

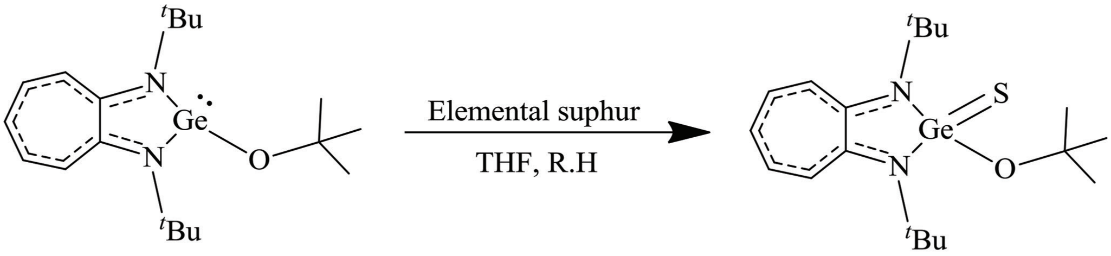
9.2. Germanium complexes involving bonding through nitrogen, oxygen, and sulfur/selenium (N, O, S/Se)

C49 was formed when elemental sulfur was added into a solution of **L35** in THF at room temperature (**Scheme 31**). The reaction mixture was stirred at room temperature for 2 h. All volatiles were removed using rotary evaporator. The residue was washed with n-hexane and dried to obtain product as yellow solid. Single crystals of complex were obtained



L$_{34}$ **C$_{48}$**

Scheme 30. Synthesis of aromatic [28]hexaphyrin germanium(IV) complex.



L$_{36}$ **C$_{49}$**

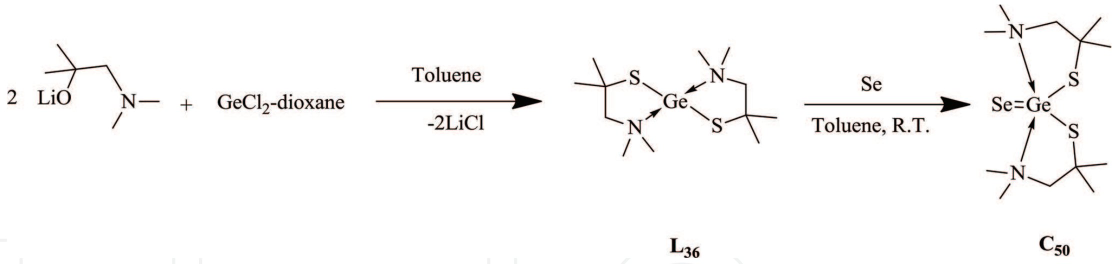
Scheme 31. Synthesis of sulfur-bonded germaester complex.

by evaporation method. According to this method, a slow evaporation of solvent from its saturated solution in chloroform was managed to obtain crystals suitable for X-ray diffraction study. The end product was obtained as yellow solid in 98% isolated yield. Melting point of the end product was 178°C [29].

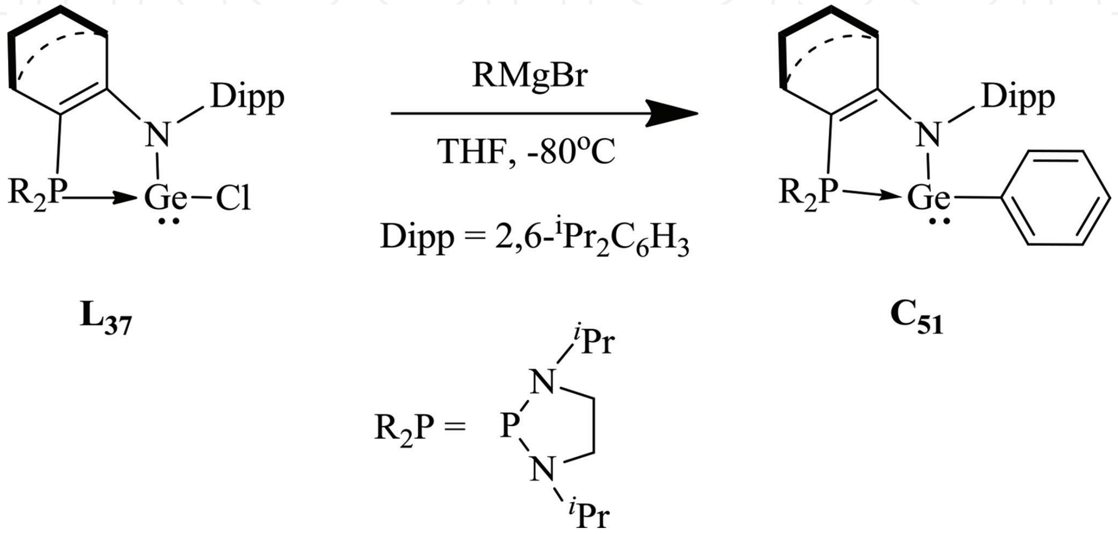
C50 was obtained when selenium powder was added slowly into a Ge(dmampS)$_2$ solution in toluene (**Scheme 32**). The reaction mixture was stirred at room temperature overnight. All volatiles were removed from reaction mixture under vacuum. The product was obtained as yellow solid. The pure product was synthesized by recrystallization of yellow solid from an ether solution. At the end, yellow crystals were obtained in 89% isolated yield [28].

9.3. Germanium complexes involving bonding through nitrogen, phosphorus, carbon (N, P, C)

C51 was synthesized by adding **L37** solution in THF slowly into phenyl lithium at −80°C (**Scheme 33**). The reaction mixture was warmed slowly at room temperature and stirred continuously for 2 h. All volatiles were removed in vacuum. The product was extracted twice with n-pentane. The major diastereomer as **C51** was obtained in pure form from a concentrated



Scheme 32. Synthesis of selenium-bonded germaester complex.

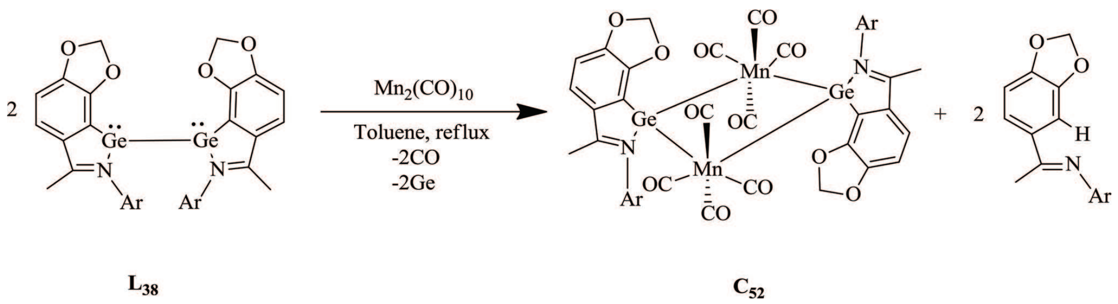


Scheme 33. Synthesis of phosphine-stabilized germylene complex.

solution of n-pentane at −30°C. At the end, pale yellow crystals were obtained in 45% isolated yield. Melting point of the end product was 25°C [6].

9.4. Germanium complexes involving bonding through nitrogen, carbon, manganese (N, C, Mn)

C52 was formed when a solution of **L38** was added dropwise to a stirred suspension of $Mn_2(CO)_{10}$ in toluene at room temperature (**Scheme 34**). The reaction mixture was refluxed overnight. After filtration, the filtrate was concentrated. The end product was obtained as dark red crystals in 46.3% isolated yield. Melting point of the end product was 261°C [17].



Scheme 34. Synthesis of germanium(I) dimer stabilized by dimanganese decarbonyl.

10. Miscellaneous

10.1. Germanium complexes involving bonding through oxygen

C53 was formed when N-methoxypropanamide was added dropwise to a stirring diethyl ether solution of **L39** (**Scheme 35**). After reaction mixture was placed overnight at room temperature, volatiles were removed in vacuum and crude product was distilled at 10^{-1} torr to afford pure complex. The resulting pure complex was obtained as a colorless liquid at 120°C in 33% isolated yield [3].

10.2. Germanium complexes involving bonding through phosphorus (P)

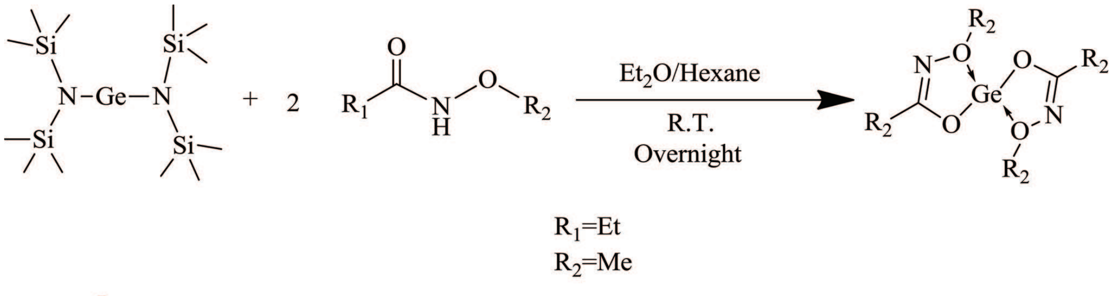
L40 was dissolved in THF and n-butyl lithium was added into reaction mixture through a syringe (**Scheme 36**). The resulting white suspension was stirred for 30 min at room temperature. $GeCl_2$ was added as a solid, and dark yellow solution was formed. The dark yellow solution was stirred for 3 h at room temperature. All volatiles were removed under vacuum. n-Pentane was added in residue, which was then filtered to remove LiCl. n-Pentane solution was concentrated and cooled at 25°C. The end product was obtained as yellow rod-like crystals in 6% isolated yield. Melting point of the end product was 110–112°C [34].

10.3. Germanium complexes involving bonding through carbon and sulfur (C, S)

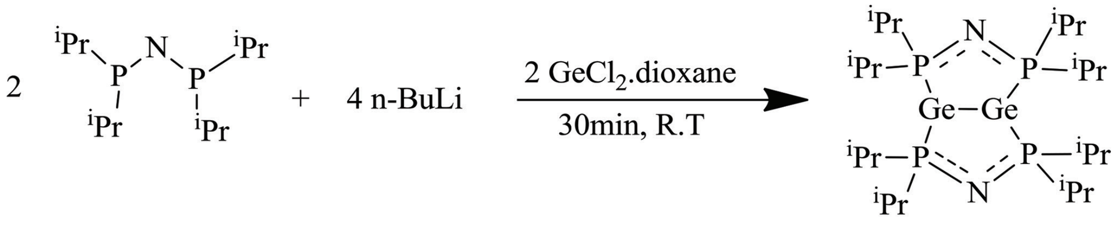
C55 was synthesized when superhydride was added into the solution of naphthol in THF (**Scheme 37**). The reaction mixture was stirred continuously for 30 min. $(CH_3)_2GeCl_2$ was added and the reaction mixture was stirred overnight. All volatiles were removed under vacuum. The product was dissolved in DCM and filtered through celite. The product was washed with hexane. The end product was obtained as cream crystalline solid in 25% isolated yield. Melting point of the end product was 79–80°C [35].

10.4. Germanium complexes involving bonding through nitrogen and boron (N, B)

C56 was formed by adding **L42** solution into a solution of $B(C_6F_5)_3$ in Et_2O at 0°C (**Scheme 38**). The resultant yellow reaction mixture was warmed at room temperature and stirred for 24 h. All volatiles were removed under vacuum and were extracted with toluene. The end product was obtained as yellow crystals in 60% isolated yield. Melting point of the end product was 157°C [16].

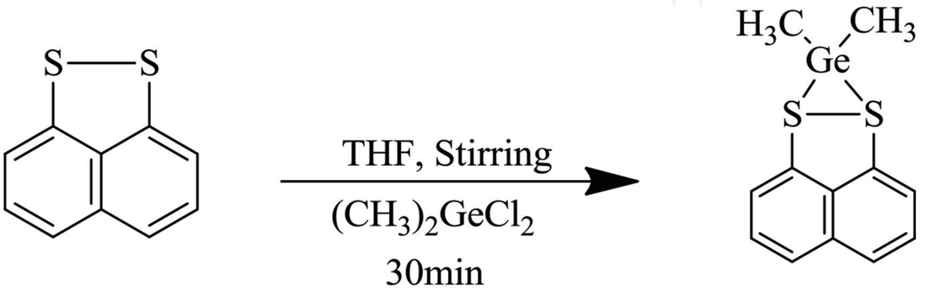


Scheme 35. Synthesis of *N*-alkoxy carboxylamide-stabilized germanium(II) complexes.



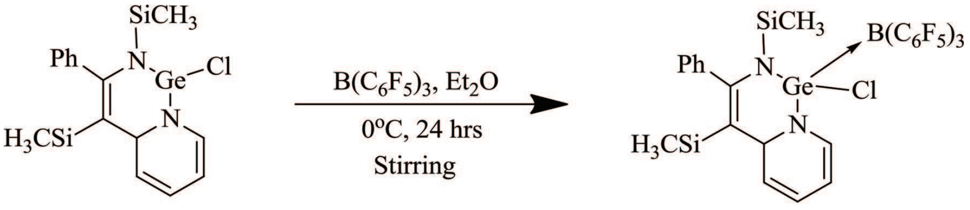
L_{40} **C_{54}**

Scheme 36. Synthesis of bicyclic low-valent germanium complex bridged by bis(diisopropylphosphino)amine.



L_{41} **C_{55}**

Scheme 37. Complexation of aromatic dichalcogen ligands to germanium.



L_{42} **C_{56}**

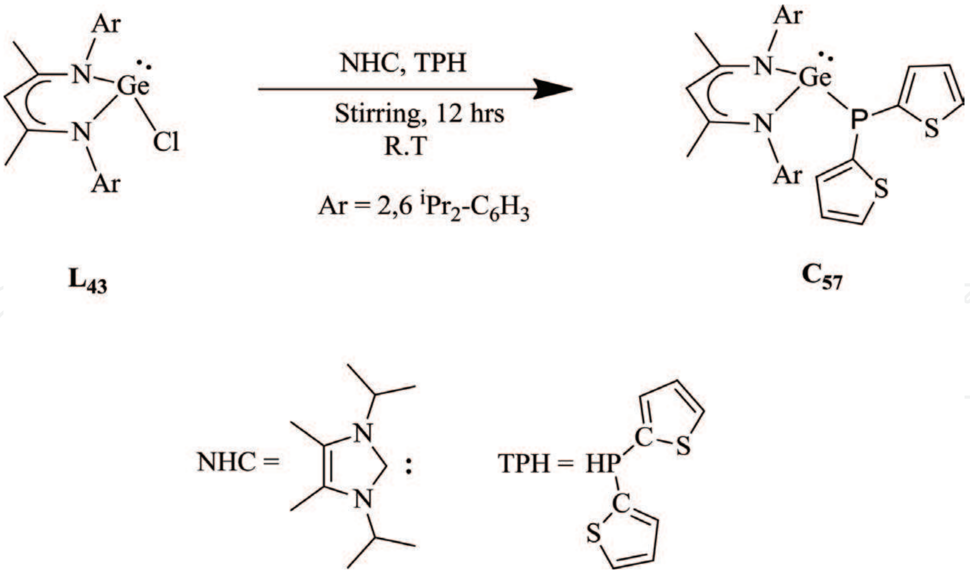
Scheme 38. Synthesis of boron-substituted metallogermylenes.

10.5. Germanium complexes involving bonding through nitrogen and phosphorous (N, P)

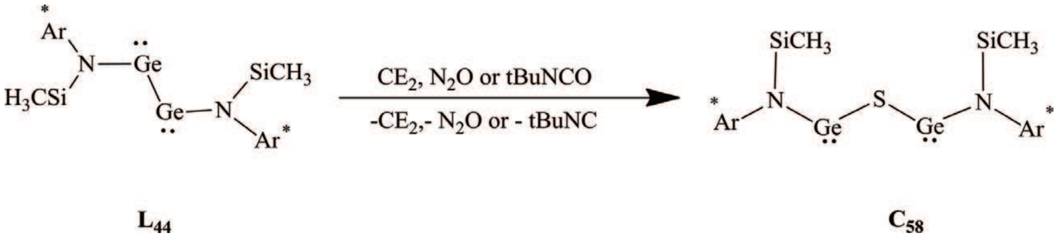
C57 was formed when a suspension of TPH was added to a mixture of LGeCl (**L43**) in presence of free NHC in Et_2O at −18°C (**Scheme 39**). After stirring for 12 h, all volatiles were removed using rotary evaporator to get an oily paste. n-hexane was layered on this paste. The n-hexane-layered oily paste was stored at room temperature for 1 week. The end product was obtained as dark red crystals in 38% isolated yield. Melting point of the end product was 198°C [36].

10.6. Germanium complexes involving bonding through nitrogen and sulfur (N, S)

C58 was formed when CS_2 was added in **L44** solution in toluene at −70°C (**Scheme 40**). The reaction mixture was warmed at room temperature and was further stirred for 18 h. All



Scheme 39. Synthesis of β-diketiminate germanium(II) complex.

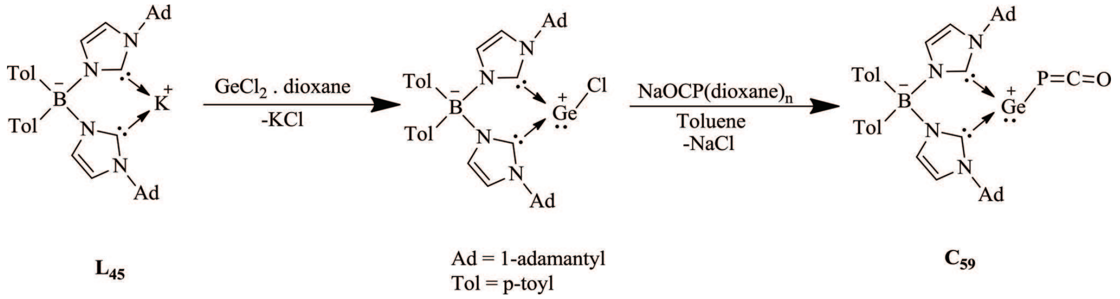


Scheme 40. Synthesis of digermyne with a Ge-Ge single-bonded compounds.

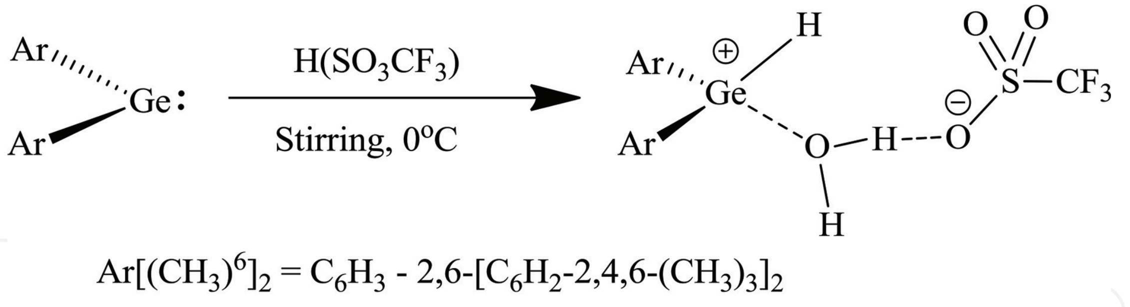
volatiles were removed under vacuum. Pure pale yellow crystals of **C58** were obtained in 93% isolated yield by recrystallization of compound using diethyl ether. Melting point of the end product was 146–150°C [37].

10.7. Germanium complexes involving bonding through phosphorus and carbon (P, C)

C59 was synthesized by mixing **L45** and NaOCP·dioxane in toluene at room temperature (**Scheme 41**). The solution was stirred for 2 h. At that time, the reaction flask was wrapped



Scheme 41. Synthesis of the bis-NHC chlorogermyliumylidene borate.



$Ar[(CH_3)^6]_2 = C_6H_3$ - 2,6-$[C_6H_2$-2,4,6-$(CH_3)_3]_2$

L_{47} C_{60}

Scheme 42. Synthesis of functionalized germanium complex.

with aluminum foil to protect day light. The precipitate of NaCl was separated from reaction mixture through centrifugation. All volatiles were removed under reduced pressure. Then, the residue was washed with n-hexane and extracted with diethyl ether. The end product was crystallized as yellow rods in 67% isolated yield. Melting point of the end product was 190°C [38].

10.8. Germanium complexes involving bonding through oxygen and hydrogen (O, H)

C60 was formed when HSO_3CF_3 was added to a stirred solution of **L46** in toluene at 0°C (**Scheme 42**). The color of reaction mixture changed immediately into pale yellow. The reaction mixture was further stirred for 2 h, and volume of solution is reduced under vacuum. After addition of n-hexane in flask, the reaction mixture was cooled slowly. The reaction mixture was placed unattended at −20°C overnight. The end product was obtained as colorless blocks in 83% isolated yield [19].

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References

[1] Haller E. Germanium: From its discovery to SiGe devices. Materials Science in Semiconductor Processing. 2006;**9**(4-5):408-422

[2] Svarnas P, Botzakaki M, Skoulatakis G, Kennou S, Ladas S, Tsamis C, et al. Controllable growth of stable germanium dioxide ultra-thin layer by means of capacitively driven radio frequency discharge. Thin Solid Films. 2016;**599**:49-53

[3] George SM, Nam JH, Lee GY, Han JH, Park BK, Kim CG, et al. N-alkoxy carboxamide stabilized tin (II) and germanium (II) complexes for thin-film applications. European Journal of Inorganic Chemistry. 2016;**2016**(36):5539-5546

[4] Harris LM, Tam EC, Cummins SJ, Coles MP, Fulton JR. The reactivity of germanium phosphanides with chalcogens. Inorganic Chemistry. 2017;**56**(5):3087-3094

[5] Katir N, Matioszek D, Ladeira S, Escudié J, Castel A. Stable N-heterocyclic carbene complexes of hypermetallyl germanium (II) and tin (II) compounds. Angewandte Chemie International Edition. 2011;**50**(23):5352-5355

[6] García JM, Ocando-Mavárez E, Kato T, Coll DS, Briceño A, Saffon-Merceron N, et al. Synthesis and characterization of rhodium complexes with phosphine-stabilized germylenes. Inorganic Chemistry. 2012;**51**(15):8187-8193

[7] Ochiai T, Szilvási T, Franz D, Irran E, Inoue S. Isolation and structure of germylene-germyliumylidenes stabilized by N-heterocyclic imines. Angewandte Chemie. 2016; **128**(38):11791-11796

[8] Yao S, Xiong Y, Driess M. A new area in main-group chemistry: Zerovalent monoatomic silicon compounds and their analogues. Accounts of Chemical Research. 2017; **50**(8):2026-2037

[9] Filippou AC, Stumpf KW, Chernov O, Schnakenburg G. Metal activation of a germylenoid, a new approach to metal–germanium triple bonds: Synthesis and reactions of the germylidyne complexes [Cp (CO) 2M Ge–C (SiMe3) 3](M= Mo, W). Organometallics. 2012;**31**(2):748-755

[10] Xiong Y, Yao S, Inoue S, Berkefeld A, Driess M. Taming the germyliumylidene [ClGe:]+ and germathionium [ClGe=S]+ ions by donor-acceptor stabilization using 1,8-bis (tributylphosphazenyl)naphthalene. Chemical Communications. 2012;**48**(100):12198-12200. DOI: 10.1039/C2CC36926E

[11] Woodul WD, Carter E, Müller R, Richards AF, Stasch A, Kaupp M, et al. A neutral, monomeric germanium (I) radical. Journal of the American Chemical Society. 2011;**133**(26): 10074-10077

[12] Matioszek D, Saffon N, Sotiropoulos J-M, Miqueu K, Castel A, Escudié J. Bis (amidinato) germylenerhodium complexes: Synthesis, structure, and density functional theory calculations. Inorganic Chemistry. 2012;**51**(21):11716-11721

[13] Leung W-P, Chan Y-C, So C-W, Mak TC. Reactivity study of a pyridyl-1-azaallylgermanium (I) dimer: Synthesis of heavier ether and Ester analogues of germanium. Inorganic Chemistry. 2016;**55**(7):3553-3557

[14] Zhao N, Zhang J, Yang Y, Zhu H, Li Y, Fu G. β-diketiminate germylene-supported pentafluorophenylcopper(I) and -silver(I) complexes $[LGe(Me)(CuC_6F_5)_n]_2$ (n = 1, 2), $LGe[C(SiMe_3)N_2]AgC_6F_5$, and $\{LGe[C(SiMe_3)N_2](AgC_6F_5)_2\}_2$ (L = HC[C(Me)N-2,6-*i* $Pr_2C_6H_3]_2$): Synthesis and structural characterization. Inorganic Chemistry. 2012;**51**(16): 8710-8718

[15] Seow C, Xi H-W, Li Y, So C-W. Synthesis of a germylidenide anion from the C–C bond activation of a bis (germylene). Organometallics. 2016;**35**(8):1060-1063

[16] Leung W-P, Chiu W-K, Mak TC. Synthesis and structural characterization of metallogermylenes, Cp-substituted germylene, and a germanium (II)-borane adduct from pyridyl-1-azaallyl germanium (II) chloride. Organometallics. 2012;**31**(19):6966-6971

[17] Ismail MLB, Liu F-Q, Yim W-L, Ganguly R, Li Y, So C-W. Reactivity of a base-stabilized germanium (I) dimer toward group 9 metal (I) chloride and dimanganese decacarbonyl. Inorganic Chemistry. 2017;**56**(9):5402-5410

[18] Choong SL, Woodul WD, Schenk C, Stasch A, Richards AF, Jones C. Synthesis, characterization, and reactivity of an N-heterocyclic germanium (II) hydride: Reversible hydrogermylation of a phosphaalkyne. Organometallics. 2011;**30**(20):5543-5550

[19] Brown ZD, Erickson JD, Fettinger JC, Power PP. Facile, high-yield functionalization of germanium and tin by oxidative insertion of tetrelenes into the E–H bonds of inorganic acids (E = C, N, O, F): Arene elimination versus oxidative addition and formation of a germanium cation–water complex. Organometallics. 2013;**32**(2):617-622. DOI: 10.1021/om301121x

[20] Brown ZD, Guo J-D, Nagase S, Power PP. Experimental and computational study of auxiliary molecular effects on the mechanism of the addition of hydrazines to a low-valent germanium complex. Organometallics. 2012;**31**(9):3768-3772

[21] Li J, Schenk C, Goedecke C, Frenking G, Jones C. A digermyne with a Ge–Ge single bond that activates dihydrogen in the solid state. Journal of the American Chemical Society. 2011;**133**(46):18622-18625

[22] Deak N, Petrar PM, Mallet-Ladeira S, Silaghi-Dumitrescu L, Nemeş G, Madec D. Bis-sulfonyl O, C, O-chelated metallylenes (Ge, Sn) as adjustable ligands for iron and tungsten complexes. Chemistry—A European Journal. 2016;**22**(4):1349-1354

[23] Dhungana TP, Hashimoto H, Tobita H. An iron germylene complex having Fe-H and Ge-H bonds: Synthesis, structure and reactivity. Dalton Transactions. 2017;**46**:8167-8179

[24] Xiong Y, Szilvási T, Yao S, Tan G, Driess M. Synthesis and unexpected reactivity of germyliumylidene hydride [: GeH]+ stabilized by a bis (N-heterocyclic carbene) borate ligand. Journal of the American Chemical Society. 2014;**136**(32):11300-11303

[25] Dannenberg F, Thiele G, Dornsiepen E, Dehnen S, Mehring M. Synthesis, structure and thermolysis of oxazagermines and oxazasilines. New Journal of Chemistry. 2017; **41**:4990-4997

[26] Ferro L, Hitchcock PB, Coles MP, Fulton JR. Reactivity of divalent germanium alkoxide complexes is in sharp contrast to the heavier tin and lead analogues. Inorganic Chemistry. 2012;**51**(3):1544-1551

[27] Guo J, Haquette P, Martin J, Salim K, Thomas CM. Replacing tin in lactide polymerization: Design of highly active germanium-based catalysts. Angewandte Chemie International Edition. 2013;**52**(51):13584-13587

[28] Kim H-S, Jung EA, Han SH, Han JH, Park BK, Kim CG, et al. Germanium compounds containing Ge=E double bonds (E= S, Se, Te) as single-source precursors for germanium chalcogenide materials. Inorganic Chemistry. 2017;**56**(7):4084-4092

[29] Siwatch RK, Nagendran S. Germaester complexes with a Ge (E) O t-Bu moiety (E= S or Se). Organometallics. 2012;**31**(8):3389-3394

[30] Brück A, Gallego D, Wang W, Irran E, Driess M, Hartwig JF. Pushing the σ-donor strength in iridium pincer complexes: Bis (silylene) and Bis (germylene) ligands are stronger donors than Bis (phosphorus (III)) ligands. Angewandte Chemie International Edition. 2012;**51**(46):11478-11482

[31] Nakano K, Kobayashi K, Nozaki K. Tetravalent metal complexes as a new family of catalysts for copolymerization of epoxides with carbon dioxide. Journal of the American Chemical Society. 2011;**133**(28):10720-10723

[32] Sinhababu S, Yadav D, Karwasara S, Sharma MK, Mukherjee G, Rajaraman G, et al. The preparation of complexes of germanone from a germanium μ-Oxo dimer. Angewandte Chemie International Edition. 2016;**55**(27):7742-7746

[33] Izawa M, Kim T, Si I, Tanaka T, Mori T, Kim D, et al. Möbius aromatic [28] hexaphyrin germanium (IV) and tin (IV) complexes: Efficient formation of triplet excited states. Angewandte Chemie International Edition. 2017;**56**(14):3982-3986

[34] Miller CJ, Chadha U, Ulibarri-Sanchez JR, Dickie DA, Kemp RA. Structure and Lewis-base reactivity of bicyclic low-valent germanium and tin complexes bridged by bis (diisopropylphosphino) amine. Polyhedron. 2016;**114**:351-359

[35] Meigh CB, Nejman PS, Slawin AM, Woollins JD. Complexation of aromatic dichalcogen ligands to germanium. Inorganica Chimica Acta. 2017;**456**:120-127

[36] Yang Y, Zhao N, Wu Y, Zhu H, Roesky HW. Synthesis and characterization of β-diketiminate germanium (II) compounds. Inorganic Chemistry. 2012;**51**(4):2425-2431

[37] Li J, Hermann M, Frenking G, Jones C. The facile reduction of carbon dioxide to carbon monoxide with an amido-digermyne. Angewandte Chemie International Edition. 2012;**51**(34):8611-8614

[38] Xiong Y, Yao S, Szilvási T, Ballestero-Martínez E, Grützmacher H, Driess M. Unexpected photodegradation of a phosphaketenyl-substituted germyliumylidene borate complex. Angewandte Chemie International Edition. 2017;**56**(15):4333-4336