From Germacarbonyl Compounds' Perspective: Glad to be Formed and Stable in the Real World[†]

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Germacarbonyl compounds are the germanium analogs of carbonyl compounds, and they require an inert atmosphere for stability. Making these compounds survive the ambient conditions was not feasible given the lability of the Ge=E bonds (E = O, S, Se, Te). However, the first examples of germacarbonyl compounds synthesized under ambient conditions by taking advantage of dipyrromethene ligand stabilization are detailed here; the isolated compounds are germanones **3**-**4**, germacarboxylic acids **6**-**7**, germaesters **9**-**10**, and germaamides **12**-**13** with Ge=E bonds (E = S, Se). The germaamides **12**-**13** can react under atmospheric conditions with copper(I) halides offering air and water stable monomeric **14**-**15** and dimeric **16**-**19** copper(I) complexes (halide = Cl, Br, I). Apart from just binding, selectivity was also observed; thiogermaamide **12** and selenogermaamide **13** bind CuCl and CuBr, respectively, when treated with a mixture of copper(I) halides.

Introduction

Inspired by the variety and usefulness of carbonyl compounds, such as aldehydes, ketones, amides, esters, carboxylic acids, acid halides, and acid anhydrides in organic chemistry, the synthesis of their heavier analogs constitutes an essential aspect of the modern main group chemistry.[1-9] Thermodynamic and kinetic stabilizations are essential for isolating these compounds in a stable form; however, this stability is only under an inert atmosphere.[1-9] Examples of heavy ketones are shown in (Chart 1).[10-17] Silanone **i** and germanones **ii-iii** [LL'M=O] were isolated through the reaction of the corresponding NHC-silylene and germylene adducts [LL'M] with N_2O, respectively (Chart 1) (L = [CH{(C=CH$_2$)(CMe)(NAr)$_2$}], L' = [{(Me)CN(R)}$_2$C]; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; M = Si; R = Me (**i**); M = Ge; R = Me (**ii**), ^{i}Pr (**iii**)).[10-11] The reaction of pentacoordinate silane [C$_{11}$H$_8$N(Me$_2$)SiH$_2$Ph] with elemental sulfur and selenium resulted in silanethione and silaneselenone [(C$_{11}$H$_8$N(Me$_2$)Si(E)Ph); E = S (**iv**) and Se (**v**)] (Chart 1).[12] The desulfurization and deselenation of tetrathiogermolane and tetraselenogermolane ([Tbt(Tip)Ge(E)$_4$]; E = S and Se), gave germanethione and germaneselenone [Tbt(Tip)Ge=E; E = S (**vi**) and

Se (**vii**)], respectively (Chart 1).[13-14] Germatellurones ([Tbt(R)Ge(Te)]; R = Tip (**viii**), Dis (**ix**)) were synthesized by the oxidation of the corresponding kinetically stabilized germylenes ([Tbt(R)Ge]; R = Tip and Dis) with elemental tellurium (Chart 1).[15] The desulfurization of the tetrathiostannolanes [Tbt(Ditp)Sn(S)$_4$] by PPh$_3$ afforded stannanethione ([Tbt(Ditp)Sn=S]) (**x**).[16] Stannaneselenone and stannanetellurone ([L$_2$Sn=E]; E = Se (**xi**), E = Te (**xii**)) were isolated through the reaction of alkyl stannylene [L$_2$Sn] with elemental selenium and tellurium (L = CH(SiMe$_3$)C$_9$H$_6$N-8) (Chart 1).[17] These seminal works have spurred interest in heavy carbonyl compounds; the current literature has a variety of them synthesized and studied.[18-69] However, there is no example of a heavy carbonyl compound that is stable in air and water to the best of our knowledge. With an object to develop the air and water stable low-valent main group chemistry, we were looking at the possibility of making air and water stable heavy carbonyl compounds. Overcoming various challenges, we successfully isolated air and water stable germacarbonyl compounds with Ge=E bonds (E = S, Se). Consequently, the synthesis of the first examples of air and water stable germanones (DPMGe(E)Ph; E = S (**3**), Se (**4**)), germacarboxylic
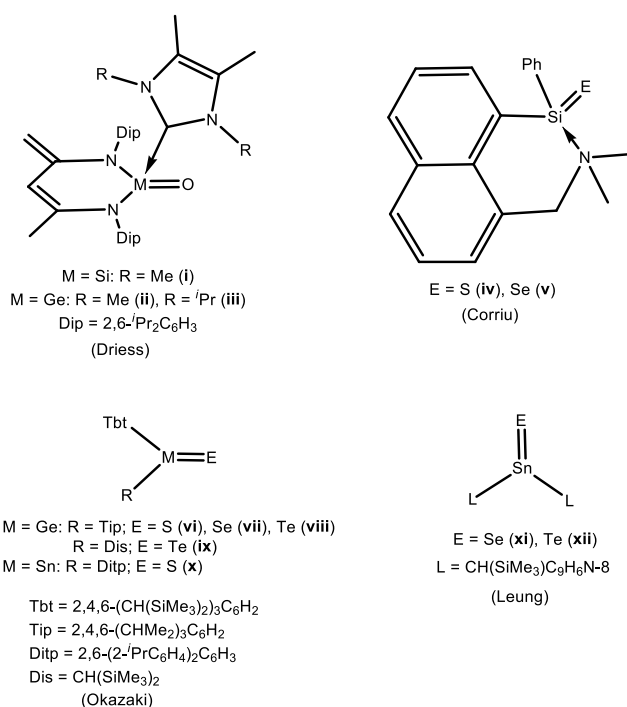
M = Si: R = Me (**i**)
M = Ge: R = Me (**ii**), R = ^{i}Pr (**iii**)
Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$
(Driess)

E = S (**iv**), Se (**v**)
(Corriu)

M = Ge: R = Tip; E = S (**vi**), Se (**vii**), Te (**viii**)
R = Dis; E = Te (**ix**)
M = Sn: R = Ditp; E = S (**x**)

E = Se (**xi**), Te (**xii**)
L = CH(SiMe$_3$)C$_9$H$_6$N-8
(Leung)

Tbt = 2,4,6-(CH(SiMe$_3$)$_2$)$_3$C$_6$H$_2$
Tip = 2,4,6-(CHMe$_2$)$_3$C$_6$H$_2$
Ditp = 2,6-(2-^{i}PrC$_6$H$_4$)$_2$C$_6$H$_3$
Dis = CH(SiMe$_3$)$_2$
(Okazaki)

Chart 1. Examples of heavy ketones

acids (DPMGe(E)OH; E = S (**6**), Se (**7**)), germaesters (DPMGe(E)OEt; E = S (**9**), Se (**10**)), and germaamides (DPMGe(E)N(TMS)$_2$; E = S (**12**), Se (**13**)) are reported (DPM = dipyrrinate). Further described are the reactions of compounds **12** and **13** with copper(I) halides (X = Cl, Br, I) to afford germaamide stabilized copper(I) complexes (DPMGe(E)N(TMS)$_2$→CuCl) (E = S (**14**), Se (**15**)) and [(DPMGe(E)(N(TMS)$_2$)→CuX]$_2$ (E = S; X = Br (**16**), I (**17**) and E = Se; X = Br (**18**), I (**19**)) that are air and water stable. All the reactions offering these copper complexes were conducted under ambient conditions using non-dried solvents. Intriguing is the discovery of selectivity involved in the reactions of compounds **12** and **13** with a mixture of copper(I) halides (X = Cl, Br, I); the former and latter binds only with CuCl and CuBr, respectively.

Synthesis and Spectra:

With the knowledge of dipyrrinate stabilized monochlorogermylenes being air and water stable,[70, 71] we studied the utility of DPMGeCl (**1**) to afford air and water stable germaacid chlorides. The reactions of compound **1** were carried out with elemental sulphur and selenium in toluene for 12 h at room temperature; the result was no reaction between the reagents and even excessive amounts of chalcogens offering no help. When the reactions between compound **1** and excess of chalcogens were carried out at high temperature (60 °C) for 12 h, desired germaacyl chlorides were formed along with an unidentified side product. However, efforts to separate this product were not fruitful until now. In light of this, it was envisaged that replacing the chlorine of compound **1** with other functional groups may bring in clean reactions between germylenes and chalcogens. Phenyl germylene DPMGePh (**2**) was synthesized in 95% yield as air and water stable solid (vide infra) through the reaction of germylene **1** with phenyl lithium at -20 °C in toluene for 12 h. As the handling of phenyl lithium requires an inert atmosphere, phenyl germylene **2** was synthesized under a nitrogen atmosphere using a dried solvent. As anticipated, the reactions of compound **2** under ambient conditions with stoichiometric amounts of elemental sulphur and selenium occurred smoothly in toluene at room temperature for 1 h to afford germanethione DPMGe(S)Ph (**3**) and germaneselenone DPMGe(Se)Ph (**4**) in 95% and 93% yields (Scheme 1). THF and DCM as solvents instead of toluene did not offer germanones **3** and **4** cleanly. Attempts to isolate germatellurone through the reaction between phenyl germylene **2** and elemental tellurium did not succeed. Similarly, the reactions of compound **2** with nitrous oxide, *N*-(methyl)morpholine-*N*-oxide, and pyridine *N*-oxide also failed to offer germanone with Ge=O bond.
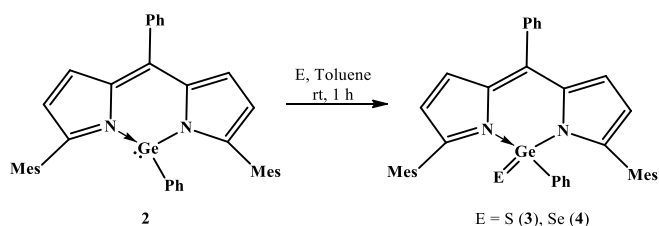

Scheme 1. Synthesis of germanones **3**-**4**

The synthesis of thio- and selenogermaaldehydes was tried; this requires a germylene hydride precursor. The reaction of monochlorogermylene **1** with various hydride sources, such as NaBH$_4$, LiAlH$_4$, K-selectride, and NaH, did not result in the anticipated germylene hydride. The reactions of germylene hydroxide DPMGeOH[70] (**5**) with elemental sulphur and selenium powder at room temperature in toluene were checked to isolate germacarboxylic acids. These reactions offered thiogermacarboxylic acid DPMGe(S)OH (**6**) and selenogermacarboxylic acid DPMGe(Se)OH (**7**) in 95% and 96% yields after 20 min (Scheme 2). Similarly, under the same reaction conditions, thiogermaester DPMGe(S)OEt (**9**) and selenogermaester DPMGe(Se)OEt (**10**) were also synthesized from germylene ethoxide DPMGeOEt[70] (**8**) in 97% and 96% yields (Scheme 2).
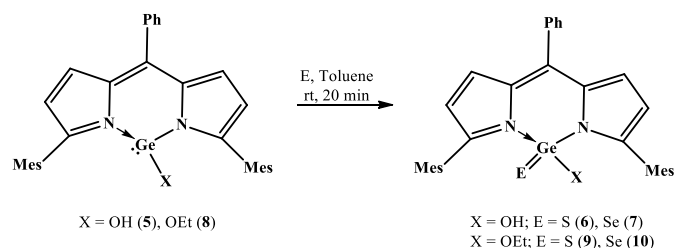
Scheme 2. Synthesis of germacarboxylic acids **6**-**7**, and germaesters **9**-**10**

Finally, the synthesis of germaamides was tried; the required aminogermylene **11** was obtained in 97% yield through the reaction of monochlorogermylene **1** with LiN(TMS)$_2$ at -20 °C for 12 h in toluene. The reactions of aminogermylene **11** with excess amounts of elemental sulphur and selenium in toluene at 60 °C for 12 h resulted in thiogermaamide DPMGe(S)N(TMS)$_2$ (**12**) and selenogermaamide DPMGe(Se)N(TMS)$_2$ (**13**) in 95% and 94% yields (Scheme 3). The steric crowding due to the bulky N(TMS)$_2$ group of germylene **11** may justify the high-temperature requirement to form germaamides **12** and **13**.
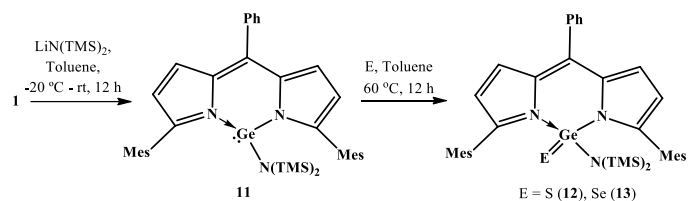
Scheme 3. Synthesis of germaamine **11** and germaamides **12**-**13**

Compounds **3**-**4**, **6**-**7**, **9**-**10**, and **12**-**13** are the first examples of air and water stable heavy carbonyl compounds (Table 1); this stability reveals the ability of bulky DPM ligands to protect the polar Ge=E bonds (E = S, Se). The air and water stability of these germacarbonyl compounds were monitored by ^{1}H NMR spectroscopy (see Figures S7-8, S11-12, S16, S19-20, S24-25, S28-29, S38-39, and S43-44). The air stability was checked for up to 10 days and found that all the compounds were stable. Concerning the water stability, the germacarbonyl compounds **3**, **4**, **9**, **10**, **12**, and **13** are stable in water for 2, 4, 3, 5, 2, and 5 days, respectively (Table 1). The germacarboxylic acids displayed poor water stability; the

selenogermacarboxylic acid **7** is stable for 6 h, while the thiogermacarboxylic acid **6** is not stable and produces DPMH (2%) just after 10 min of water addition. Among germanones, germaesters, and germaamides, germaesters **9-10** and germaamides **12-13** show more water stability than germanones **3-4**. This stability may be attributed to the electron-donating OEt and $N(TMS)_2$ moieties of germaesters **9-10** and germaamides **12-13**, enhancing electron density on the germanium centers and reducing the polarity of the formal Ge=E bonds, respectively (Table 1). Moreover, selenogermacarbonyl compounds displayed better stability than the corresponding thiogermacarbonyl compounds, perhaps due to the stronger Ge=Se bond in selenogermacarbonyl compounds than the Ge=S bond in thiogermacarbonyl compounds (Table 1).[51,54,56-57]

Table 1. Air and water stability of germacarbonyl compounds with Ge=E bonds (E = S/Se)

Compound	Air Stability[a] (Days)	Water Stability[b] (Day(s))
DPMGe(S)Ph (**3**)	10	2
DPMGe(Se)Ph (**4**)	10	4
DPMGe(S)OH (**6**)	10	Not Stable
DPMGe(Se)OH (**7**)	10	0.25
DPMGe(S)OEt (**9**)	10	3
DPMGe(Se)OEt (**10**)	10	5
DPMGe(S)N(TMS)$_2$ (**12**)	10	2
DPMGe(Se)N(TMS)$_2$ (**13**)	10	5

[a]Air stability was checked for up to 10 d only; therefore, they may be stable for a considerable period beyond this 10 d. For example, our experience with compound **13** reveals that it did not *start to* decompose even after one month of storage under ambient conditions. [b]Formation of 1-2% of DPMH was seen after the specified period of water stability.

The successful isolation of air and water stable germacarbonyl compounds prompted us to examine their reactivity at ambient conditions. Considering the presence of σ-donor chalcogen atoms (S, Se) in the germacarbonyl compounds **3-4**, **6-7**, **9-10**, and **12-13**, we started to scrutinize their ability to stabilize transition metal complexes.[46,52-53,73-74] The reactions of compounds **3-4**, **6-7**, and **9-10** with excess amounts of copper(I) halides Cu(I)X at room temperature for 1 h did not result in the desired complexes; the reactants remained unreacted (X = Cl, I). However, the reaction of thiogermaamide DPMGe(S)N(TMS)$_2$ (**12**) with an equimolar amount of Cu(I)Cl at room temperature in toluene for 30 min resulted in monomeric thiogermaamide stabilized copper(I) chloride complex [DPMGe(S)N(TMS)$_2$→CuCl] (**14**) in 89% yield (Scheme 4). In contrast, its reactions with other copper(I) halides (Cu(I)Br and Cu(I)I) in toluene at room temperature for 30 min resulted in dimeric thiogermaamide stabilized copper(I) complexes

[DPMGe(S)N(TMS)$_2$→CuX]$_2$ with Cu$_2$X$_2$ core in 94% and 90% yields, respectively (X = Br (**16**), I (**17**)) (Scheme 4). Similarly, equimolar reactions of selenogermaamide DPMGe(Se)N(TMS)$_2$ (**13**) with Cu(I)Cl and Cu(I)X (X = Br, I) in toluene for 30 min at room temperature afforded monomeric and dimeric selenogermaamide stabilized copper(I) halides complexes [DPMGe(Se)N(TMS)$_2$→CuCl] (**15**; yield 95%) and [DPMGe(Se)N(TMS)$_2$→CuX]$_2$, (X = Br (**18**; yield 92%), I (**19**; yield 94%)), respectively (Scheme 4). The thiogermaamide and selenogermaamide stabilized monomeric (**14**, **15**) and dimeric copper complexes (**16-17**, **18-19**) represent the first examples of germacarbonyl compound stabilized copper(I) halide complexes.
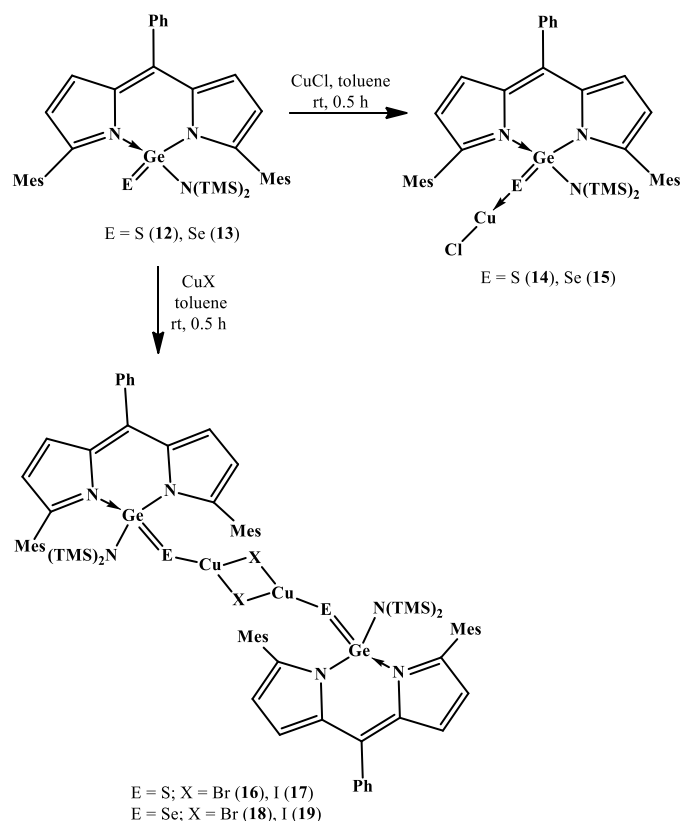
Scheme 4. Synthesis of germaamide stabilized monomeric and dimeric copper(I) complexes **14-19**

Germaamides, apart from reacting independently with CuX (X = Cl, Br, I), showed a novel aspect of selective binding towards a particular copper halide when a mixture of copper halides is present (see SI for details). The reaction of thiogermaamide **12** with an equimolar mixture of CuX (X = Cl, Br, I) in toluene for 15 min at room temperature gave exclusively compound **14** by reacting with CuCl only (see Scheme S1). In contrast, selenogermaamide **13** under the same reaction conditions reacted selectively with CuBr and gave compound **18** (see Scheme S2). Even when thiogermaamide **12** was reacted with a mixture CuX containing one equiv of copper chloride and an excess of copper bromide and copper iodide (three equivalents each), it reacted only with copper chloride affording copper chloride complex **14** (see Scheme S3). The same was the result for selenogermaamide **13**; its reaction with a mixture of CuX

salts containing copper chloride, copper bromide, and copper iodide in a ratio of 3:1:3, gave selectively copper bromide complex **18** (see Scheme S4). Further, germaamides **12** and **13** did not react with AgX (X = Cl, Br, I) and AuX (Cl, I).

Interestingly, compounds **14**-**19** are the first examples of germacarbonyl compound stabilized transition metal complexes that are air and water stable. This feat was achievable due to the favorable steric protection and electronic stabilization offered by the bulky dipyrrinate ligand to the Ge=E→Cu moieties in these complexes. Akin to the methodology followed with germacarbonyl compounds, the stability of these copper(I) complexes were studied using ^{1}H NMR spectroscopy (see Figures S49-50, S54-55, 60-61, 65-66, S70-71, and S76-77). The complexes were stable in the air up to the monitored period of 10 days. Regarding the water stability, thiogermaamide stabilized copper(I) complexes **14**, **16**, and **17** were stable for 3 h, 1 day, and 3 days, respectively. It is explicit from the data that ongoing from chloride to iodide, the water stability increases. The same trend is seen for the selenogermaamide stabilized copper(I) complexes **15**, **18**, and **19**; they were stable for 3 h, 12 h, and 2 days, respectively (Table 2). An interesting trend for the dimeric copper complexes is that thiogermaamide stabilized compounds display better stability than the selenogermaamide stabilized compounds.

Table 2. Air and water stability of germaamide stabilized copper(I) complexes **14**-**19**

Compound	Air Stability[a] (Days)	Water Stability[b] (Day(s))
[(DPMGe(S)N(TMS)$_2$→CuCl] (**14**)	10	0.125
[(DPMGe(S)N(TMS)$_2$→CuBr]$_2$ (**16**)	10	1
[(DPMGe(S)N(TMS)$_2$→CuI]$_2$ (**17**)	10	3
[(DPMGe(Se)N(TMS)$_2$→CuCl] (**15**)	10	0.125
[(DPMGe(Se)N(TMS)$_2$→CuBr]$_2$ (**18**)	10	0.50
[(DPMGe(Se)N(TMS)$_2$→CuI]$_2$ (**19**)	10	2

[a]Air stability was checked for up to 10 d only; therefore, they may be stable for a considerable period beyond this 10 d. For example, our experience with compound **16** reveals that it did not start to decompose even after one month of storage under ambient conditions. [b]Formation of 1-2% of DPMH was seen after the specified period of water stability.

The germanones **3**-**4**, germacarboxylic acids **6**-**7**, germaesters **9**-**10**, and germaamides **12**-**13** are freely soluble in toluene, tetrahydrofuran, dichloromethane, and chloroform. The germaamide stabilized copper(I) complexes **14**-**19** have limited solubility in tetrahydrofuran and toluene. The thiogermaamide

stabilized copper(I) complexes **14**, **16**, and **17** are also soluble in dichloromethane; however, their selenium analogs **15**, **18**, and **19** are only partially soluble. The newly synthesized compounds **2**-**4**, **6**-**7**, and **9**-**19** were characterized in the solution state through multinuclear NMR spectroscopic techniques (^{1}H, ^{13}C, ^{29}Si, ^{77}Se). In the ^{1}H NMR spectra of germanones **3**-**4**, germacarboxylic acids **6**-**7**, germaesters **9**-**10**, and germaamides **12**-**13**, all the resonances are slightly downfield shifted compared to their germylene precursors **1**, **5**, **8**, and **11**, respectively (see the SI for details). This shift is due to the germanium atoms' formal oxidation state increase from +2 (in compounds **1**, **5**, **8**, and **11**) to +4 (in compounds **3**-**4**, **6**-**7**, **9**-**10**, and **12**-**13**) owing to their attachment to electronegative sulphur/selenium atoms.

Almost all the resonances of thio- and selenogermaamide stabilized copper(I) complexes **14**, **16**, **17** and **15**, **18**, **19** showed further downfield shifts to those of thiogermaamide **12** and selenogermaamide **13**, respectively (see the SI for details). This effect is due to the donation of lone pair of electrons from sulphur/selenium atom of the Ge=E bond to the copper atom (E = S/Se). In the ^{13}C NMR spectra of compounds **2**-**4**, **6**-**7**, and **9**-**19**, the expected number of signals (ranging from 13 to 21 depending on the group attached to the germanium atom) were seen. In the ^{29}Si NMR spectra of compounds **11**-**19**, except germylene **11** that gave two resonances at -3 and 2 ppm, all the other compounds showed a signal

Table 3. ^{77}Se NMR spectroscopic data of germaselenocarbonyl compounds containing Ge=Se bonds.

Compound	^{77}Se Resonance, δ in ppm	Reference
[Tbt(Tip)Ge(Se)] (**vii**)	940.6	14
[(^{t}Bu)$_2$ATIGe(Se)Ph] (**xiii**)	-216.97	53
[{HC(CMe)(N(2,6-^{i}Pr$_2$C$_6$H$_3$))$_2$}Ge(Se)OH] (**xiv**)	-439.8	60
[(R)$_2$ATIGe(Se)O^{t}Bu] (R = ^{t}Bu (**xv**), ^{i}Bu (**xvi**)	-77.76 (**xv**), -285.10 (**xvi**)	57
[(R)$_2$ATIGe(Se)N(TMS)$_2$] (R = ^{t}Bu (**xvii**), ^{i}Bu (**xviii**))	-36.76 (**xvii**), -183.31 (**xviii**)	48
[DPMGe(Se)Ph] (**4**)	-386	This work
[DPMGe(Se)OH] (**7**)	-340	This work
[DPMGe(Se)OEt] (**10**)	-379	This work
[DPMGe(Se)N(TMS)$_2$] (**13**)	-178	This work
[(DPMGe(Se)(N(TMS)$_2$)→CuCl] (**15**)	-237	This work
[(DPMGe(Se)(N(TMS)$_2$)→CuBr]$_2$(**18**)	-228	This work
[(DPMGe(Se)(N(TMS)$_2$)→CuI]$_2$ (**19**)	-235	This work

close to -22 ppm; this data confirms the presence of trimethylsilyl group. In the ^{77}Se NMR spectroscopic studies of selenogermanone **4**, selenocarboxylic acid **7**, and selenoester **10**, the resonances for the selenium atoms were seen at -386 ppm, -340 ppm, and -379 ppm, respectively. For the selenogermaamide **13**, a signal was observed at -178 ppm; its copper(I) complexes **15**, **18**, and **19** showed upfield shifted resonances at -237, -228, and -235 ppm, respectively (see the SI for details). As the selenium resonances of these compounds are in between the resonances of $(H_3Ge)_2Se$ (-612 ppm) with a Ge-Se single bond[73] and [Tbt(Tip)Ge(Se)] (**vii**) (940.6 ppm)[14] having an electronically unperturbed Ge=Se double bond, the Ge=Se bonds in them should be polarized with partial positive and negative charges on the germanium and selenium atoms, respectively (Table 3). Despite such polarization, it is interesting to see them as air and water stable compounds, which should be attributed to the kinetic and thermodynamic stabilizations bestowed by the bulky DPM ligands.

X-ray Crystal Structures of Compounds 2-4, 9, 11-14, 16-17, and 19.

Molecular structures of germylenes (**2** and **11**), germacarbonyl compounds (**3**, **4**, **9**, **12**, and **13**), and metal complexes (**14**, **16**, **17**, and **19**) were confirmed by single-crystal X-ray diffraction analysis. Compounds **2**, **17**, and **19** crystallized in the monoclinic space group $P2_1/c$, while compounds **3**, **4**, **9**, and **11** crystallized in the monoclinic space group $P2_1/n$. Compounds **12-14** and **16** crystallized in the triclinic space group P-1. The germanium atom of the germylenes **2** and **11** is tricoordinate with two nitrogen atoms of the DPM ligands and one X atom of the functional group (X = C **2**, N **11**). In compounds **3**, **4**, **9**, **12-14**, **16**, **17**, and **19**, the germanium atom(s) has(have) distorted tetrahedral geometry with two DPM ligand nitrogens, one double-bonded sulphur/selenium, and one X atom of the functional group (X = C (**3-4**), O (**9**), and N (**12-14**, **16**, **17**, and **19**)) (see Figures S82-S92). The average length of Ge–N$_{ligand}$ bonds in compounds **3**
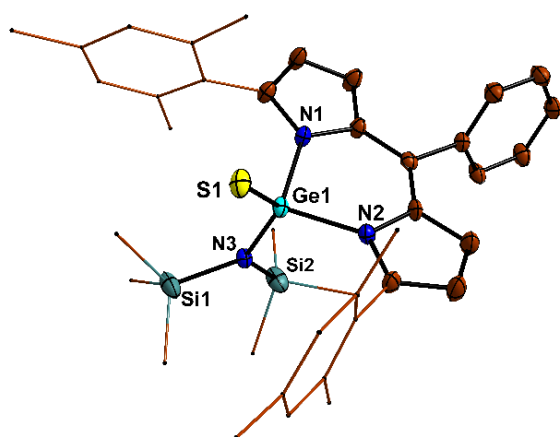

Figure 1. Molecular structure of thiogermaamide **12** with thermal ellipsoids at the 40% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–S(1) 2.062(1), Ge(1)–N(1) 1.951(4), Ge(1)–N(2) 1.953(3), Ge(1)–N(3) 1.843(3); N(3)–Ge(1)–N(1) 105.91(2), N(3)–Ge(1)–N(2) 107.46(2), N(1)–Ge(1)–N(2) 92.75(2). Data collection temperature: 100 K.

(1.945 Å), **4** (1.944 Å), **12** (1.952 Å), and **13** (1.952 Å) are shorter than those in their precursors **2** (2.009 Å) and **11** (2.033 Å). Similarly, the Ge-X bond in compounds **3** (1.928(6) Å; X = C_{Ph}), **4** (1.933(2) Å; X = C_{Ph}), **12** (1.843(3) Å; X = $N_{N(TMS)_2}$), and **13** (1.837(7) Å; X = $N_{N(TMS)_2}$) is also shorter compared to that in compounds **2** (2.001(2) Å; X = C_{Ph}) and **11** (1.924(2) Å; X = $N_{N(TMS)_2}$). These effects are due to the higher
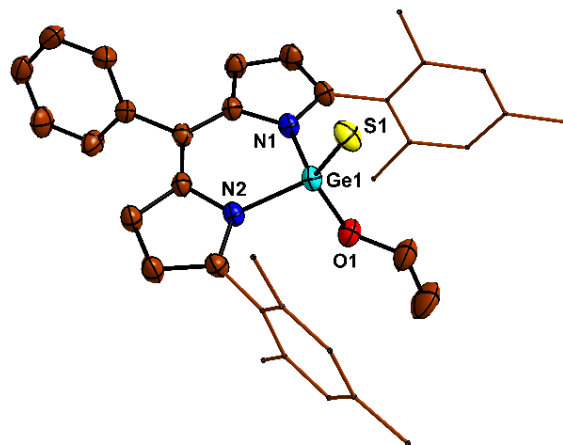

Figure 2. Molecular structure of thiogermaester **9** with thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–S(1) 2.058(5), Ge(1)–O(1) 1.751(2), Ge(1)–N(1) 1.914(2), Ge(1)–N(2) 1.915(2); O(1)–Ge(1)–N(1) 102.74(6), O1(1)–Ge(1)–N(2) 100.60(7) N(1)–Ge(1)–N(2) 93.05(6). Data collection temperature: 273 K.

electrophilicity of the germanium atom in compounds **3**, **4**, and **12-13** than that in germylenes **2** and **11**; the electrophilicity is increased by the electronegative chalcogen atom doubly bonded to germanium. The Ge=S bond in thiogermanone **3** (2.052(2) Å), thiogermaester **9** (2.058(5) Å), and thiogermaamide **12** (2.062(1) Å) are shorter than that in aminotroponimine ligand stabilized thiogermanone LGe(S)Ph (**xix**) (2.102(7) Å),[53] thiogermaester LGe(S)O^{t}Bu (**xvi**) (2.080(2) Å),[57] and thiogermaamide LGe(S)N(SiMe$_3$)$_2$ (**xviii**) (2.083(1) Å), respectively[48] (L = (^{i}Bu)$_2$ATI; ATI = aminotroponimine). Further, the Ge=S bond of compound **3** is much shorter than the Ge-S single bond (2.239(1) Å)[67] in compound [{(TMS)$_2$C(2-py)}{(TMS)C(2-py)}]GeS(TMS), and is slightly longer than the unperturbed Ge=S bond (2.049(3) Å) in the kinetically stabilized thiogermanone Tbt(Tip)Ge=S (**vi**).[13] These comparisons may indicate that the polarization in the Ge=S bond of compound **3** is in between that of compounds **vi** and **xix**. A similar trend was seen for the selenium analogs **4** and **13**. The Ge=Se bond of compounds **4** (2.195(3) Å) and **13** (2.194(1) Å) is shorter than that in ATI ligand stabilized selenogermanone (**xiii**) (2.235(2) Å)[53] and selenogermaamide (**xvii**) (2.222(1) Å),[48] respectively. The Ge=Se bond of compound **4** is much shorter than the Ge-Se single bond (2.433(1) Å) in compound [Tbt(Mes)GeSe]$_2$ and marginally longer than the Ge=Se bond 2.180 Å in kinetically stabilized selenogermanone [Tbt(Tip)Ge=Se] (**vii**).[14]

Due to the coordination of the sulfur atom of Ge=S bond with Lewis acid (CuCl/CuBr/CuI), the Ge=S bond of thiogermaamide stabilized metal complexes **14** (2.132(7) Å), **16** (2.101(7) Å), and **17** (2.103(8) Å)

is elongated compared to that in thiogermaamide **12** (2.062(1) Å) (see Figures S87 and S89-91). A similar trend is seen in the selenogermaamide stabilized copper complex **19**; its Ge=Se bond (2.234(6) Å) is longer than that of compound **13** (2.194(1) Å) (see Figures S88 and S92). In compound **14**, the copper atom is dicoordinate with a sulphur and chlorine atom; it has a linear geometry apparent from the S-Cu-Cl bond angle of 178.04° (see
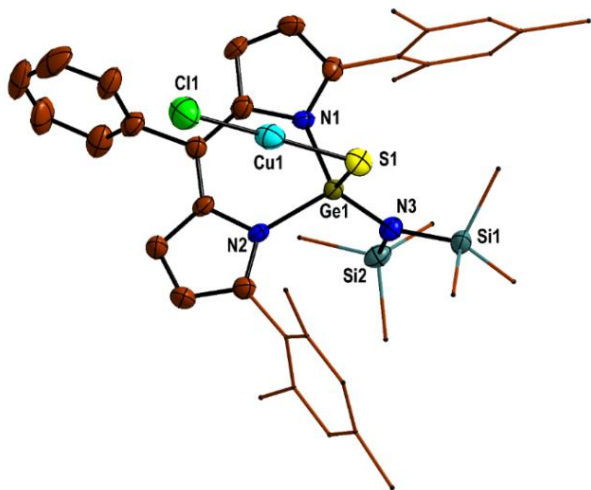
Figure S89). The Cu-Cl bond in compound **14** (2.087(2) Å) is marginally shorter than that in thiosilaamide stabilized dicoordinate copper(I) chloride complex (2.095 Å).[46] The complexes **16**, **17**, and **19** have a planar dimeric Cu_2X_2 (X = Br, I) core; the copper atoms are tricoordinate with the sum of bond angles around them, equalling 360°. The average Cu-I bond lengths in compounds **17** (2.604 Å) and **19** (2.599 Å) is comparable to that in germylene stabilized dimeric copper iodide complex {μ-Cu_2I_2}[(BDI)GeO^{t}Bu]$_2$ (2.608 Å).[75] The Cu…Cu distance in compounds **16** (2.725(5) Å), **17** (2.699(8) Å), and **19** (2.581(8) Å) is less than the sum of the Van der Waals radii of two copper atoms (2.80 Å) and indicates the presence of cuprophilic interaction (see Figures S90-92).

Conclusions

The first examples of germacarbonyl compounds **3**-**4**, **6**-**7**, **9**-**10**, and **12**-**13** that are stable under ambient conditions were synthesized and structurally characterized. Though germanones, germacarboxylic acids, and germaesters did not bind with copper(I) halides, germaamides did react at ambient conditions providing copper(I) complexes (**14**-**19**) that are also stable outside inert atmospheres. The air and water stabilities of these germacarbonyl compounds and copper(I) complexes were studied using ^{1}H NMR spectroscopy; the stability of these compounds is due to the precise thermodynamic and kinetic stabilizations provided by bulky dipyrromethene ligand. Uniquely, selective binding of thiogermaamide **12** and selenogermaamide **13** towards Cu(I)Cl and Cu(I)Br was noticed when they were reacted with a mixture of Cu(I)X salts, respectively (X = Cl, Br, I).

Figure 3. Molecular structure of thiogermaamide stabilized copper(I) chloride complex **14** with thermal ellipsoids at the 40% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–S(1) 2.132(7), Ge(1)–N(1) 1.934(1), Ge(1)–N(2) 1.938(1), Ge(1)–N(3) 1.831(1), S(1)–Cu(1) 2.143(8), Cu(1)–Cl(1) 2.087(2); N(3)–Ge(1)–N(1) 112.2(5), N(3)–Ge(1)–N(2) 112.0(5), N(1)–Ge(1)–N(2) 96.6(4), N(3)-Ge(1)-S(1) 116.30(4), S(1)-Cu(1)-Cl(1) 178.04(2). Data collection temperature: 100 K.

Conflicts of Interest

There are no conflicts to declare

Notes and References

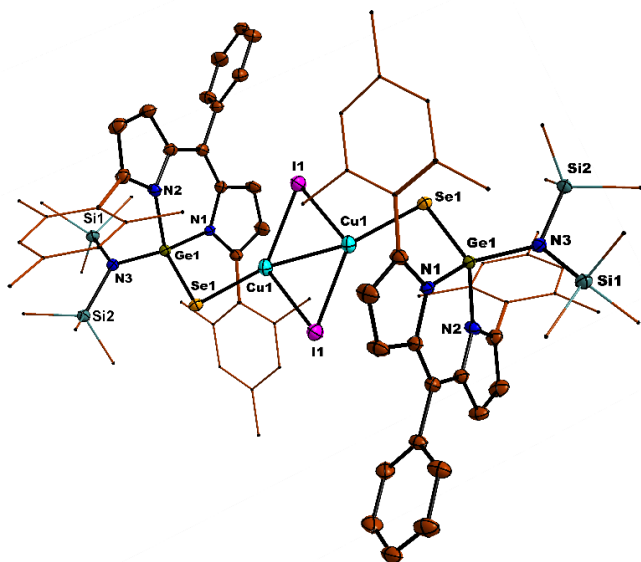1. Y. K. Loh and S. Aldridge, *Angew. Chem. Int. Ed.*, 2021, **60**, 8626–8648.

Figure 4. Molecular structure of selenogermaamide stabilized copper(I) iodide complex **19** with thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–Se(1) 2.234(6), Ge(1)–N(1) 1.928(2), Ge(1)–N(2) 1.931(3), Ge(1)–N(3) 1.853(3), Se(1)–Cu(1) 2.349(5), Cu(1)–I(1) 2.566(5), Cu(1)–I(1) 2.632(4), Cu1-Cu1 2.581(8); N(3)–Ge(1)–N(1) 110.98(2), N(3)–Ge(1)–N(2) 105.98(2), N(1)–Ge(1)–N(2) 94.50 (1), Ge(1)-Se(1)-Cu(1) 102.18(2), I(1)-Cu(1)-I(1) 120.47(2), Se(1)-Cu(1)-I(1) 133.05(2). Data collection temperature: 100 K.

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