Air and water stable germacarbonyl compounds†‡

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Germacarbonyl compounds are the germanium analogs of carbonyl compounds requiring 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 thiogermaone 4, thiogermaacid 6, selenogermacid 7, thiogermaester 9, selenogermamida 12, and selenogermaamide 13 with Ge=E bonds (E = S, Se). Compounds 12 and 13 can react under ambient 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.

The desulphurization and deselenation of tetrathiogermolane and tetrathioselenogermolane ([Tbt(Tip)Ge(E)2]; E = S and Se), gave germanothiophenol and germanoselenolene ([Tbt(Tip)Ge=E]; E = S (vi) and Se (vii), respectively). Germatellurones ([Tbt(R)Ge(Te)]; R = Tip (viii), Dis (ix)) were synthesized by the oxidation of the corresponding kinetically stabilized germynes [Tbt(R)Ge] with elemental tellurium. The desulphurization of tetraoxygenolane [Tbt(Dip)(Sn(Si)3)] by PPh3 afforded...

Chart 1 Examples of heavy ketones.
stannanethione \([\text{Tbt}(\text{Dipp})\text{Sn}=\text{S}]\) \((x)\). Stannaneselenone and stannanetellurone \([L_2\text{Sn}=\text{E}]\; E=\text{Se} \,(\text{xi}), \; E=\text{Te} \,(\text{xii})\) were isolated through the reaction of alkyl stannylene \([L_2\text{Sn}]\) with elemental selenium and tellurium \((L=\text{CH}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{N-8})\). These seminal studies have spurred interest in heavy carbonyl compounds; a variety of reports on synthesis and characterization is found in contemporary literature.\(^1\)\(^2\) However, there is no example of a heavy carbonyl compound that is stable in air and water to the best of our knowledge.

With the objective to develop 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 \((E=\text{S, Se})\). Consequently, the synthesis of the first examples of air and water stable thiogermanone \([\text{DPMGe(S)}\text{Ph}]\) \((\text{a})\), selenogermaamide \([\text{DPMGe(S)}\text{N}(\text{TMS})_2\text{]})\) \((\text{b})\), thiogermaester \([\text{DPMGe(S)}\text{OEt}]\) \((\text{c})\), selenogermaester \([\text{DPMGe(Se)}\text{OEt}]\) \((\text{d})\), thiogermaacid and selenogermaacid chlorides. The treatment of phenyl germylene \([\text{DPMGePh}]\) \((\text{e})\) with excess amounts of elemental sulphur and selenium occurred smoothly in toluene at room temperature for 1 h to afford thiogermaone \([\text{DPMGe(S)}\text{Ph}]\) \((\text{f})\) in 95% and 93% yields (Scheme 1). THF and DCM as solvents instead of toluene did not offer germaones \((\text{b, c})\) cleanly. As phenyl germylene \((\text{e})\) did not react with elemental tellurium at room temperature or high \((60 \, {^\circ}\text{C})\) temperature, telluromerone was not isolable. Similarly, the reactions of compound \((\text{f})\) with nitrous oxide, \(N\)-(methyl)morpholine-N-oxide, and pyridine-N-oxide also did not occur, prohibiting the synthesis of germaone with a Ge=O bond. A possible reason for this could be the bulkiness of the mesityl groups protecting the germylene center. Monoanionic N-heterocyclic ligand stabilized gemerenones have offered gemerenones indirectly, which means that gemerlyne reacted with \(\text{N}_2\text{O}\) to form a \(\mu\)-oxo dimer and the reaction of this dimer with a suitable Lewis acid afforded germaamido.\(^4\)\(^{}\)\(^5\) Considering this aspect, it is anticipated that the reaction of gemerlyne \((\text{g})\) with an oxygen transfer agent does not occur due to the steric effect posed by the mesityl groups for the \(\mu\)-oxo dimer formation. Concerning the reaction with elemental tellurium, the large size of tellurium may prohibit its interaction with the germanium(n) center heavily guarded by bulky mesityl groups.

The synthesis of thiogermaaldehyde and selenogermaaldehyde was tried; this requires a gemerlyne hydride precursor. The reactions of monochlorogermylene \((\text{h})\) with various hydride sources, such as \(\text{NaBH}_4\), \(\text{LiAlH}_4\), K-selectride, and \(\text{NaH}\), did not result in the anticipated gemerlyne hydride. The reactions of gemerlyne hydride oxide \([\text{DPMGeOH}^\text{xe}]\) \((\text{i})\) with elemental sulphur and selenium at room temperature in toluene were checked to isolate thiogermaacarbonylic and selenogermaacarbonylic acids. These reactions afforded thiogermaacarbonylic acid \([\text{DPMGe(S)}\text{OH}]\) \((\text{j})\) in 95% and 96% yields after 20 min (Scheme 1). Similarly, under the same reaction conditions, thiogermaester \([\text{DPMGe(S)}\text{OEt}]\) \((\text{h})\) and selenogermaester \([\text{DPMGe(Se)}\text{OEt}]\) \((\text{k})\) were also synthesized from gemerlyne ethoxide \([\text{DPMGeOEt}^\text{xe}]\) \((\text{m})\) in 97% and 96% yields (Scheme 1). Finally, the synthesis of thiogermaamide and selenogermaamide was tried; the required aminoamergerlyne \((\text{n})\) was obtained in 97% yield through the reaction of monochlorogermylene \((\text{h})\) with \(\text{LiN(TMS)}_2\) at \(-20 \, {^\circ}\text{C}\) for 12 h in toluene (see ESI; Scheme S2\(\text{e}\)). The reactions of aminoamergerlyne \((\text{a})\) with excess amounts of elemental sulphur and selenium in toluene at \(60 \, {^\circ}\text{C}\) for 12 h resulted in thiogermaamid \([\text{DPMGe(S)}\text{N(TMS)}_2\text{]})\) \((\text{b})\) and selenogermaamido \([\text{DPMGe(Se)}\text{N(TMS)}_2\text{]})\) \((\text{c})\) in 95% and 94% yields (Scheme 1). The steric crowding due to the bulky N(TMS)\(_2\) group of gemerlyne \((\text{a})\)

### Scheme 1 Synthesis of germerlynealdehyde compounds.

With the knowledge that dipyrrinate stabilized mono-
chlorogermylenes are air and water stable,\(^6\)\(^\text{ab}\) we studied the utility of \([\text{DPMGeCl}]\) \((\text{a})\) to afford air and water stable thiogermaacid and selenogermaacid chlorides. The treatment of compound \((\text{a})\) with excess elemental sulphur/selenium in toluene \((12 \, {^\circ}\text{C}, \text{rt})\) gave no product. At a high temperature \((60 \, {^\circ}\text{C})\), the desired thiogermaacetyl and selenogermaacetyl chlorides were formed along with an inseparable unidentified side product. It is anticipated that the \(-1\) effect of chlorine may be the reason for this result; therefore, compounds with other functional groups were reacted with chalcogens. Phenyli gemerlyne \([\text{DPMGePh}]\) \((\text{a})\) was synthesized in 95% yield as an air and water stable solid through the reaction of gemerlyne \((\text{a})\) with phenyl lithium at \(-20 \, {^\circ}\text{C}\) in toluene for 12 h (see ESI; Scheme S1\(\text{f}\)). As the handling of phenyl lithium requires an inert atmosphere, phenyl gemerlyne \((\text{a})\) was synthesized under a nitrogen atmosphere using a dried solvent. As anticipated, the reactions of compound \((\text{a})\) under ambient conditions with stoichiometric amounts of elemental sulphur and selenium occurred smoothly in toluene at room temperature for 1 h to afford thiogermaone \([\text{DPMGe(S)}\text{Ph}]\) \((\text{a})\) in 95% and 93% yields (Scheme 1). THF and DCM as solvents...
may justify the high-temperature requirement to form thio-
germaamide 12 and selenogermaamide 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 the bulky DPM ligand to protect the polar Ge=S bonds (E = S, Se). The air and water stability of these germacarbonyl compounds was monitored by $^1$H NMR spectroscopy [see ESI; Fig. S7, S8, S11, S12, S16, S19, S20, S24, S25, S28, S29, S38, S39, S43, and S44†]. The air stability was checked for up to 10 days and it was found that all the compounds were stable. Concerning 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 indicated stability refers to the duration for which the compounds show no detectable sign of decomposition). The thiogermaoxylic and selenogermacarboxylic acids displayed poor water stability; selenogermaoxylic acid 7 is stable for 6 h, while thiogermaoxylic acid 6 is not stable and produces DPMH (2%) after just 10 min of water addition. It is anticipated that two electronegative atoms, such as oxygen and S/Se attached to germanium, are responsible for this observation. These atoms make germanium more electrophilic; therefore, compounds 6 and 7 are more reactive toward water than the other compounds. Among all the germacarbonyl compounds, selenogermaoxylic compounds are more stable than the corresponding thiogermaoxylic compounds, perhaps due to the stronger Ge=Se bond in selenogermaoxylic compounds than the Ge=S bond in thiogermaoxylic compounds (Table 1)†. Theoretical calculations on thiogermaoxane 3, selenogermaoxane 4, thiogermaamide 12, and selenogermaamide 13, offer evidence for this assumption; the Wirburg bond index (WBI) for the Ge=S bond in compounds 3 (1.457) and 12 (1.419) is marginally lower than that of compounds 4 (1.484) and 13 (1.439) with a Ge=Se bond.

Furthermore, to explain the observed stability of the germacarbonyl compounds, the NPA charges of the atoms in the Ge=E bond and the nature of the HOMO of dipyrirrate stabilized thiogermaamide 12 (E = S) and selenogermaamide 13 (E = Se) were analyzed and compared with those of aminotropiniminate and amidinate stabilized thio- and selenogermaamides (see computational details in the ESI†). As no significant differences were seen, it was concluded that these electronic properties could not explain the observed air and water stability of dipyrirrate compounds with Ge=E bonds. Therefore, it is anticipated that the steric protection offered by the mesityl groups of the dipyrirrate ligand may provide air and water stability. To test this, the isolation of $^{19}$PDMGe=S(N(TMS)$_2$)$_2$ with phenyl groups(1,10),(993,987)

| 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 |
| DPMGe[S(N(TMS)$_2$)$\rightarrow$CuCl] (14) | 10 | 0.125 |
| DPMGe[S(N(TMS)$_2$)$\rightarrow$CuBr] (16) | 10 | 1 |
| DPMGe[S(N(TMS)$_2$)$\rightarrow$CuI] (17) | 10 | 3 |
| DPMGe[Se(N(TMS)$_2$)$\rightarrow$CuCl] (15) | 10 | 0.125 |
| DPMGe[Se(N(TMS)$_2$)$\rightarrow$CuBr] (18) | 10 | 0.50 |
| DPMGe[Se(N(TMS)$_2$)$\rightarrow$CuI] (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 compounds 13 and 16 reveals that they 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.

Furthermore, to explain the observed stability of the germacarbonyl compounds, the NPA charges of the atoms in the Ge=E bond and the nature of the HOMO of dipyrirrate stabilized thiogermaamide 12 (E = S) and selenogermaamide 13 (E = Se) were analyzed and compared with those of aminotropiniminate and amidinate stabilized thio- and selenogermaamides (see computational details in the ESI†). As no significant differences were seen, it was concluded that these electronic properties could not explain the observed air and water stability of dipyrirrate compounds with Ge=E bonds. Therefore, it is anticipated that the steric protection offered by the mesityl groups of the dipyrirrate ligand may provide air and water stability. To test this, the isolation of $^{19}$PDMGe=S(N(TMS)$_2$)$_2$ with phenyl groups (1.484) and (1.419) resulted in dimeric thiogermaamide 3–4, 6–7, 9–10, and 12–13, we started to scrutinize their ability to stabilize transition metal complexes;$^{19}$ The reactions of compounds 3–4, 6–7, and 9–10 with excess amounts of 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)$_2$)$_2$ (12) with an equimolar amount of Cu(i)Cl at room temperature in toluene for 30 min resulted in a monomeric thiogermaamide stabilized copper(i) chloride complex [DPMGe[S(N(TMS)$_2$)$_2$ → CuCl] (14) in 89% yield (see ESI; Scheme S3†). 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)$_2$)$_2$ → CuBr]$_2$ and [DPMGe[S(N(TMS)$_2$)$_2$ → CuI]$_2$ with a Cu$_2$X$_2$ core in 94% and 90% yields, respectively (X = Br (16) and I (17)) (see ESI; Scheme S3†). Similarly, equimolar reactions of selenogermaamide DPMGe[Se(N(TMS)$_2$)$_2$ 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 \([\text{DPMGe(Se)N(TMS)2}] \rightarrow \text{CuX} \) \(15\) (yield 95%) and \([\text{DPMGe(Se)N(TMS)}] \rightarrow \text{CuX}_2 \) \(X = \text{Br} \) \(18\) (yield 92%), \(I \) \(19\) (yield 94%), respectively (see ESI; Scheme S4†). 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. The polar Ge=S/Se bond of germacarbonyl compounds should become further polarized after forming complexes with copper halides; this anticipation is supported by the decreased WBI values of the Ge=S/Se bond(s) in complexes \(14\) (1.135) and \(19\) (1.205) compared to those of their precursors \(12\) (1.419) and \(13\) (1.439), respectively. The electron-donating and bulky nature of the \([\text{Me₅Si}]_2\text{N}\) substituent in compounds \(12\) and \(13\) is expected to stabilize the largely polarized Ge=S/Se bond(s) of Cu(i) halide complexes more efficiently.

Thiogermaamide \(12\) and selenogermaamide \(13\), apart from reacting independently with CuX \((X = \text{Cl}, \text{Br}, \text{I})\), showed a novel aspect of selective binding towards a particular copper halide when a mixture of copper halides is present (Scheme 2). The reaction of thiogermaamide \(12\) with an equimolar mixture of CuX \((X = \text{Cl}, \text{Br}, \text{I})\) in toluene for 15 min at room temperature exclusively gave compound \(14\) by reacting with CuCl only (Scheme 2). In contrast, selenogermaamide \(13\), under the same reaction conditions, reacted selectively with CuBr and gave compound \(18\) (Scheme 2). Even when thiogermaamide \(12\) was reacted with a mixture of CuX containing one equivalent 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 \(14\) (Scheme 2). The result was the same 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 \(18\) (Scheme 2). Pearson’s HSAB principle may better explain the observed selectivity. Among compounds \(12\) and \(13\), the Ge=S bond of thiogermaamide \(12\) is more polarized than that of selenogermaamide \(13\) \((\text{vide supra})\). The NPA charge on the sulphur \((−0.826)\) of compound \(12\) is higher than that on the selenium \((−0.685)\) of compound \(13\) (see computational details in the ESI†). These factors suggest that the softness of the sulphur in compound \(12\) is less than that of compound \(13\)’s selenium atom. For the copper(i) halides, copper(i) has the least softness when attached to chlorine (see computational details in the ESI†). Considering all these aspects, it is anticipated that the softness of sulphur in compound \(12\) closely matches the softness of copper(i) in CuCl rather than the copper(i) atom of CuBr/CuI. Extending the same argument to compound \(13\), the softness of its selenium matches the copper(i)’s softness in CuBr. Furthermore, compounds \(12\) and \(13\) did not react with AgX \((X = \text{Cl}, \text{Br}, \text{I})\) 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 feature 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, these copper(i) complexes’ stability was studied using \(^1\text{H} \) NMR spectroscopy (see ESI; Fig. S49, S50, S54, S55, S60, S61, S65, S66, S70, S71, S76, and S77†). The complexes were stable in air up to the monitored period of 10 days. Regarding 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 moving 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 1).

The compounds \(3–4, 6–7, 9–10, \) and \(12–13\) are well soluble in toluene, tetrahydrofuran, dichloromethane, and chloroform. The thiogermaamide and selenogermaamide stabilized copper(i) complexes \(14–19\) have bad solubility in tetrahydrofuran and toluene. The thiogermaamide stabilized copper(i) complexes \(14, 16, \) and \(17\) are well soluble in dichloromethane; however, their selenium analogs \(15, 18, \) and \(19\) are poorly soluble. The newly synthesized compounds \(2–4, 6–7, \) and \(9–19\) were characterized in the solution state through multinuclear NMR spectroscopic techniques \((^{1}\text{H}, ^{13}\text{C}, ^{29}\text{Si}, ^{77}\text{Se})\). In the \(^1\text{H} \) NMR spectra of compounds \(3–4, 6–7, 9–10, \) and \(12–13\), almost all the resonances are slightly downfield shifted compared to those of their germene precursors \(2, 5, 8, \) and \(11\), respectively. This shift is due to increase in the germanium atoms’ formal oxidation state from +2 to +4 (in compounds \(2, 5, 8, \) and \(11\)) to +4 (in compounds \(3–4, 6–7, 9–10, \) and \(12–13\)) owing to their attachment to an electronegative sulphur/selenium atom. The OH proton of thiogermaacarboxylic acid \(6\) and selenogermaacarboxylic acid \(7\) resonated at 1.77 and 1.79 ppm, respectively, which was downfield shifted compared to that of germene hydroxide \(5\) (1.21 ppm). The trimethylsilyl protons of aminogermylene \(11\) were seen as two singlets \((-0.46 \) and \(-0.25 \) ppm); in

![Scheme 2](image-url)
comparison, these protons of thiogermaamide (−0.05 ppm) 12 and selenogermaamide (0.02 ppm) 13 appeared as a broad singlet. Almost all the resonances of thi- and selenogermaamide stabilized copper(i) complexes 14, 16, 17 and 15, 18, 19 showed downfield shifts compared to those of thiogermaamide 12 and selenogermaamide 13, respectively. This effect is due to the donation of a lone pair of electrons from the sulphur/selenium atom of the Ge−E bond to the copper atom (E = S/Se). Akin to compounds 12 and 13, the trimethylsilyl protons of the monomeric 14−15 and dimeric 16−19 copper(i) halide complexes resonate as a broad singlet (between −0.06 and 0.01 ppm). In the $^{13}$C NMR spectra of compounds 2 (23 signals), 3 (22) 4 (21), 6 (18), 7 (16), 9 (22), 10 (21), 11 (16), 12 (21), 13 (20), 14 (21), 15 (25), 16 (21), 17 (20), 18 (19), and 19 (20) different number of signals were observed. 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 single resonance (−21.8 (12), −21.9 (13), −21.8 (14), −21.9 (15), −21.8 (16), −21.9 (17), −21.9 (18), and −21.9 ppm (19)). As the selenium resonances of compounds 4 (−386 ppm), 7 (−340 ppm), 10 (−379 ppm), 13 (−178 ppm), 15 (−237 ppm), 18 (−228 ppm), and 19 (−235 ppm) are in between the resonances of [H$_2$Ge$_2$Se (−612 ppm) with a Ge–Se single bond and [Tbt(Tip)GeSe]$^i$ (940.6 ppm)$^{34}$ having an electronically unperturbed Ge=Se double bond, their Ge=Se bonds should be polarized with partial positive and negative charges on the germanium and selenium atoms, respectively (see ESI; Table S2‡). 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 the bulky DPM ligand bestowed. In the IR spectra of compounds 6 and 7, the hydroxy group’s stretching band was seen at 3612.69 and 3612.05 cm$^{-1}$, respectively; in comparison, the OH stretching band of compound 5 was detected at 3627 cm$^{-1}$ (Fig. S80 and S81; see ESI†). The UV-vis spectra of thiogerma carbonyl compounds 3, 6, 9, and 12 (Fig. S82‡), selenogerma carbonyl compounds 4, 7, 10, and 13 (Fig. S83‡), and thi/o selenogermaamide stabilized copper(i) complexes 14, 18, and 19 (Fig. S84‡) were recorded in toluene at room temperature. All these compounds showed an absorption maximum in the visible region between 505 and 525 nm (Table S3‡). Preliminary theoretical studies on germa carbonyl compounds 12 and 13 showed that the absorptions are essentially due to π$_{\text{pyrroles}}$ → π$^*$$_{\text{dipyrrole}}$ (~82%) and π$_{\text{Mes}}$ → π$^*$$_{\text{dipyrrole}}$ (~15%) transitions. A computational study on copper complex 18 revealed that the observed absorption maximum is due to multiple transitions; d$_{\text{Cu}}$ → π$^*$$_{\text{dipyrrole}}$ (34.3%) and d$_{\text{Cu}}$ + n$_{\text{H}}$ + n$_{\text{Se}}$ → π$^*$$_{\text{dipyrrole}}$ (14.1%) transitions contribute majorly, and all other transitions have below 5% contributions.

**X-ray crystal structures of compounds 2−4, 9, 11−14, 16−17, and 19**

Molecular structures of germynes (2 and 11), germacarbonyl compounds (3, 4, 9, 12, and 13), and metal complexes (14 (Fig. 1), 16, 17, and 19 (Fig. 2)) were confirmed by single-crystal X-ray diffraction analysis. The Ge–X bond in compounds 3 (1.928(6) Å; X = C$_{\text{Ph}}$), 4 (1.933(2) Å; X = C$_{\text{Ph}}$), 12 (1.843(3) Å; X = N$_{\text{TMS}}$), and 13 (1.837(7) Å; X = N$_{\text{TMS}}$) is shorter compared to the corresponding bond in compounds 2 (2.001(2) Å; X = C$_{\text{Ph}}$) and 11 (1.924(2) Å; X = N$_{\text{TMS}}$). This effect is due to the higher electrophilicity of the germanium atom in compounds 3, 4, and 12−13 than that in germynes 2 and 11; the electrophilicity is increased by the electron-negative chalcogen atom doubly bonded to germanium. The Ge=S bonds in thiogerma nane 3 (2.052(2) Å), thiogerma ster 9 (2.058(5) Å), and thiogerma mide 12 (2.062(1) Å) are shorter than that in aminotrop imine ligand stabilized thiogerma mide LGe(S)Ph (xix) (2.102(7) Å)$^{16}$ and thiogerma ster LGe(S)O'Bu (xvi) (2.076(1) Å)$^{19}$ and thiogerma mide LGe(S)N(SiMe$_3$)$_2$ (xvii) (2.083(1) Å), respectively$^{24}$ (L = (Bu)$_2$ATI; ATI = aminotrop imine). Furthermore, the Ge=S bond of compound 3 is much shorter than the Ge=S single bond (2.239(1) Å)$^7$ 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 thiogerma nane Tbt(Tip)Ge=S (vi)$^{24}$ 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=S bond of compounds 4 (2.195(3) Å) and 13 (2.194(1) Å) is shorter than that in ATI ligand stabilized selenogerma mide (xiii) (2.235(4) Å)$^{16}$ and selenogerma mide (xvii) (2.222(1) Å)$^{24}$ respectively. The Ge=S bond of compound 4 is much shorter than the Ge=Se single bond (2.433(1) Å) in compound [Tbt(Mes)GeSe] and marginally longer than the Ge=Se bond (2.180(2) Å) in the kinetically stabilized selenogerma mide [Tbt(Tip)Ge=Se] (vii)$^{25}$.

Due to the coordination of the sulphur atom of the Ge=S bond with Lewis acid (CuCl/CuBr/CuI), the Ge=S bond of thiogerma mide 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

![Fig. 1](image-url) The molecular structure of thiogerma mide stabilized copper(i) chloride complex 14 with thermal ellipsoids at a 40% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−S(11) 2.132(7), Ge(1)−N(11) 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(11) 122.2(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) 116.3(0), and S(1)−Cu(1)−Cl(1) 178.0(2). Data collection temperature: 100 K.
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, respectively (X = Cl, Br, I).

Data availability
The experimental and computational data associated with this article are provided in the ESI.‡

Author contributions
P. M. carried out the experimental studies and drafted the manuscript. P. S. and P. C. J. helped P. M. during (a) dipyrromethene synthesis and (b) monitoring the air and water stability of compounds reported in the manuscript. D. S. assisted P. M. during the crystallographic studies on compounds 14, 16, and 17. H. K. assisted P. M. with the UV-vis spectroscopic studies. P. M. and P. S. carried out the theoretical calculations; G. M. helped them analyze the computational data. S. N. corrected the manuscript.

Conflicts of interest
There are no conflicts to declare.

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Notes and references
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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 thiogermanone 3, selengemeranone 4, thiogermaoxylic acid 6, selengermacarbonylic acid 7, thiogermaester 9, and selengergaamster 10 did not bind with copper(i) halides, thiogermaamide 12 and selenogermaamide 13 did react under 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 1H NMR spectroscopy; the stability of these compounds is due to the precise thermodynamic and kinetic stabilizations provided by a bulky
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