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Donor–acceptor-stabilised germanium analogues of acid chloride, ester, and acyl pyrrole compounds: synthesis and reactivity

Acid chlorides and esters are basic and important organic compounds. Such compounds of germanium (a heavier element in the carbon family) were not known until now; a text-book wisdom. However, germaacid chloride, germaester, and N-germaacyl pyrrole with Ge(O)Cl, Ge(O)OSiPh$_3$, and Ge(O)NC$_4$H$_4$ moieties, respectively, are successfully isolated and structurally characterized using donor–acceptor-stabilisation. Despite such stabilisation, these germanium compounds can react further and afford interesting products. Like acid chlorides, germaacid chloride undergoes nucleophilic substitution with various nucleophiles; for example, its reaction with LiC≡CPh, has afforded germaynone (a germanium analogue of ynone).

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Donor–acceptor-stabilised germanium analogues of acid chloride, ester, and acyl pyrrole compounds: synthesis and reactivity†‡

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Germaacid chloride, germaester, and *N*-germaacyl pyrrole compounds were not known previously. Therefore, donor–acceptor-stabilised germaacid chloride (i-Bu)$_2$ATIGe(O)(Cl) → B(C$_6$F$_5$)$_3$ (**1**), germaester (i-Bu)$_2$ATIGe(O)(OSiPh$_3$) → B(C$_6$F$_5$)$_3$ (**2**), and *N*-germaacyl pyrrole (i-Bu)$_2$ATIGe(O)(NC$_4$H$_4$) → B(C$_6$F$_5$)$_3$ (**3**) compounds, with Cl–Ge=O, Ph$_3$SiO–Ge=O, and C$_4$H$_4$N–Ge=O moieties, respectively, are reported here. Germaacid chloride **1** reacts with PhCCLi, KOt-Bu, and RLi (R = Ph, Me) to afford donor–acceptor-stabilised germaynone (i-Bu)$_2$ATIGe(O)(CCPh) → B(C$_6$F$_5$)$_3$ (**4**), germaester (i-Bu)$_2$ATIGe(O)(Ot-Bu) → B(C$_6$F$_5$)$_3$ (**5**), and germanone (i-Bu)$_2$ATIGe(O)(R) → B(C$_6$F$_5$)$_3$ (R = Ph **6**, Me **7**) compounds, respectively. Interconversion between a germaester and a germaacid chloride is achieved; reaction of germaesters **2** and **5** with TMSCl gave germaacid chloride **1**, and **1** reacted with Ph$_3$SiOLi and KOt-Bu to produce germaesters **2** and **5**. Reaction of *N*-germaacyl pyrrole **3** with thiophenol produced a donor–acceptor-stabilised germaacyl thioester (i-Bu)$_2$ATIGe(O)(SPh) → B(C$_6$F$_5$)$_3$ (**10**). Furthermore, the attempted syntheses of germaamides and germacarboxylic acids are also discussed.

Introduction

The carbonyl group (C=O) in organic compounds such as ketones [RC(O)R], aldehydes [RC(O)H], acid halides [RC(O)X], esters [RC(O)OR], amides [RC(O)NR$_2$], carboxylic acids [RC(O)OH], and acid anhydrides [RC(O)OC(O)R] is of great importance in organic chemistry (R = alkyl/aryl group; X = halogen). The significance of these carbon compounds provides inspiration for the synthesis of their heavier analogues,[1–3] but the synthetic efforts are typically hampered by the lability of the M=O bond (M = Si, Ge, Sn, Pb). The instability of this bond stems from the σ-bond polarisation and poor π-type overlap between M and O atoms, which usually leads to oligomerisation/polymerisation of compounds containing such M=O bonds.[4–6] Strategies that utilise tailor-made ligands and/or provide donor–acceptor

stabilisation to M/O atoms have been applied to address the aforementioned problems and have yielded various stable compounds containing M=O bonds.[7–11] Thus, silanones (silaketones) and germanones (germaketones) with formal Si=O and Ge=O bonds, respectively, were successfully isolated, and the variety of silanones exceeds that of the germanones.[7–10] In addition to silanones, silicon analogues of aldehyde, ester, amide, formyl chloride, carboxylic acid, and acid anhydride compounds were also synthesised *via* various methods mainly by the groups of Driess, Roesky, Baceiredo, and Kato.[12] Very recently, Aldridge and co-workers reported the generation of a silicon analogue of an acid chloride [(*N*-nacnac)^{Ar}Si(Cl)=O (**I**)] through the reaction of the silylene (*N*-nacnac)^{Ar}SiCl with N$_2$O (Chart 1) [(*N*-nacnac)^{Ar} = HC{(Me$_2$N)C(Ar)N}$_2$; Ar = 2,6-i-Pr$_2$C$_6$H$_3$]. The metathesis reactions of **I** with K[Et$_3$BH] and KOt-Bu afforded a silaaldehyde [(*N*-nacnac)^{Ar}Si(H)=O → BEt$_3$ (**II**)]

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† Dedicated to Prof. V. Chandrasekhar on the occasion of his 60th birthday.

‡ Electronic supplementary information (ESI) available: Experimental section, UV-vis spectra of compounds **1**, **2**, and **10**; molecular structure determination of compounds **D1**, **D3–D5**, **1–7**, **9**, and **10**; computational details (PDF). CIFs for compounds **D1**, **D3–D5**, **1–7**, **9**, and **10**, are deposited with the Cambridge Structural Database (CSD). CCDC 1564828–1564834, 1564836, and 1851011–1851015. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc05380d


Chart 1 Silicon analogues of an acid chloride **I**, aldehyde **II**, and ester **III**.

and a silaester [(N-nacnac)^{Ar}Si(Ot-Bu)=O (**III**)], respectively (Chart 1).[12a] Surprisingly, such analogues of germanium [LGe(O)Y] [L = a monoanionic ligand; Y = H (germaaldehyde), Cl (germaacid chloride), OR (germaester), NR$_2$ (germaamide), OH (germacarboxylic acid), and (OGe(O)L) germaacid anhydride] are not yet known, perhaps due to the difficulty in adding an electron-withdrawing Y atom/group to the germanium atom in light of the already heavily polarised Ge=O bond. Owing to our continued interest in the chemistry of germanium, we were able to isolate the Lewis acid (LA) complexes (i-Bu)$_2$ATIGe(i-Pr)=O → LA (LA = B(C$_6$F$_5$)$_3$ (**IV**), ZnCl$_2$ (**V**), SnCl$_2$ (**VI**), and GeCl$_2$ (**VII**)) of a germanone[10] starting from a germanium-μ-oxo dimer [ATI = aminotroponiminate, a monoanionic bidentate ligand]. We now understand that this synthetic protocol is exploitable for the synthesis of hitherto unknown germaacid chlorides and germaesters. Consequently, we report in this article the isolation and reactivity of the first examples of a donor–acceptor-stabilised germaacid chloride (i-Bu)$_2$ATIGe(O)(Cl) → B(C$_6$F$_5$)$_3$ (**1**), germaester (i-Bu)$_2$ATIGe(O)(OSiPh$_3$) → B(C$_6$F$_5$)$_3$ (**2**), and N-germaacyl pyrrole (i-Bu)$_2$ATIGe(O)(NC$_4$H$_4$) → B(C$_6$F$_5$)$_3$ (**3**). Compound **3** was obtained during our search for stable germaamides.

To synthesise a germaacid chloride, oxidation of the germylene monochloride[13] (i-Bu)$_2$ATIGeCl (**G1**) with N$_2$O was carried out in tetrahydrofuran at room temperature. However, germylene **G1** did not react with N$_2$O at room temperature, and therefore, this reaction was performed at higher temperatures. Germylene **G1** reacted with N$_2$O at 60 °C in tetrahydrofuran and afforded the germanium μ-oxo dimer {(i-Bu)$_2$ATIGe(Cl)(μ-O)}$_2$ (**D1**) after 2 h as a yellow solid in 60% yield (Scheme 1).[5,14] It appears that 60 °C is the optimum temperature for this reaction; higher temperatures afforded the ATI ligand salt [ATIH]$^+$(Cl)$^-$, and lower temperatures resulted in lower yields of μ-oxo dimer **D1**. Based on the successful conversion of a germanium μ-oxo dimer {(i-Bu)$_2$ATIGe(i-Pr)(μ-O)}$_2$ (**D**) containing Ge–C bonds into donor–acceptor-stabilised germanones **IV–VII** through the reaction of **D** with Lewis acids, we planned to react germanium μ-oxo dimer **D1** containing Ge–Cl bonds with

B(C$_6$F$_5$)$_3$. To our surprise, treatment of μ-oxo dimer **D1** with two equivalents of B(C$_6$F$_5$)$_3$ in toluene for 2 h at room temperature yielded the first example of a donor–acceptor-stabilised germaacid chloride (i-Bu)$_2$ATIGe(O)(Cl) → B(C$_6$F$_5$)$_3$ (**1**) in quantitative yield (Scheme 1). This accomplishment inspired us to determine whether hitherto unknown germaesters and germaamides could also be isolated using this synthetic strategy of reacting suitable germanium μ-oxo dimers with Lewis acids. Thus, to synthesise a germaester, a germylene siloxide[15] (i-Bu)$_2$ATIGeOSiPh$_3$ (**G2**) was reacted with N$_2$O in tetrahydrofuran at 60 °C for 2 h to obtain the germanium μ-oxo dimer {(i-Bu)$_2$ATIGe(OSiPh$_3$)(μ-O)}$_2$ (**D2**). The reaction of μ-oxo dimer **D2** containing Ge–OSiPh$_3$ bonds with two equivalents of B(C$_6$F$_5$)$_3$ in toluene at room temperature afforded the first example of a donor–acceptor-stabilised germaester, namely, (i-Bu)$_2$ATIGe(O)(OSiPh$_3$) → B(C$_6$F$_5$)$_3$ (**2**) (Scheme 2), and demonstrated the suitability of the germanium μ-oxo dimer route for the preparation of germaesters. To extend this route for the synthesis of germaamides, a germanium μ-oxo dimer with Ge–NR$_2$ moieties is required. Two such germanium μ-oxo dimers, {(i-Bu)$_2$ATIGeN(H)Ph(μ-O)}$_2$ (**D3**) and {(i-Bu)$_2$ATIGeN(Me)Ph(μ-O)}$_2$ (**D4**), were obtained through the reaction of the amidogermylenes (i-Bu)$_2$ATIGeN(H)Ph (**G3**) and (i-Bu)$_2$ATIGeN(Me)Ph (**G4**) with N$_2$O at 60 °C for 2 h in tetrahydrofuran (Scheme 3). However, the reaction of μ-oxo dimers **D3** and **D4** with two equivalents of B(C$_6$F$_5$)$_3$ resulted in the amine → borane adducts PhNH$_2$ → B(C$_6$F$_5$)$_3$ and Ph(Me)NH → B(C$_6$F$_5$)$_3$, respectively, along with an unidentified oily material instead of the expected germaamides (Scheme 3). These reactions suggest that the synthetic route discussed above is not suitable for the isolation of donor–acceptor-stabilised germaamides. On the basis of the products obtained, it was thought that the lone pairs of electrons on the nitrogen atoms of the NR$_2$ moieties in **D3** and **D4** interfered with the expected reaction of these compounds (**D3** and **D4**) with B(C$_6$F$_5$)$_3$. To confirm this hypothesis, a germanium μ-oxo dimer containing amino functional groups with nitrogen atoms that cannot donate lone pairs of electrons to Lewis acids was synthesised and used. As a pyrrole substituent (Py; NC$_4$H$_4$) can satisfy the required criterion, the germanium μ-oxo dimer {(i-Bu)$_2$ATIGe(NC$_4$H$_4$)(μ-O)}$_2$ (**D5**) with two Ge–NC$_4$H$_4$ moieties was synthesised in quantitative yield by the reaction of
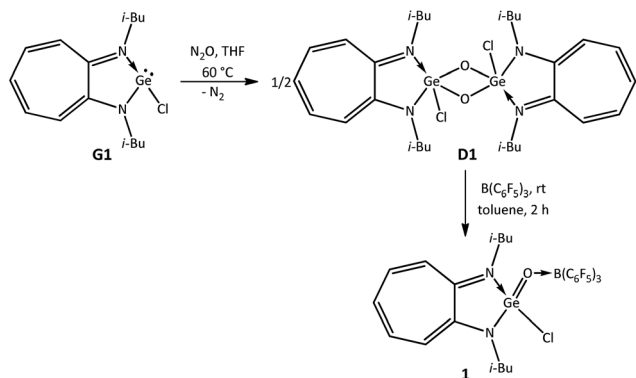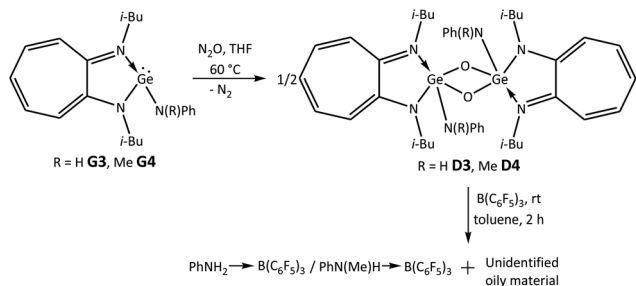

Scheme 1 Synthesis of donor−acceptor-stabilised germaacid chloride **1**. *Notes*: (a) in the alphanumerical numbering pattern, **G** denotes germylene, and **D** denotes germanium μ-oxo dimer, and (b) products with a Ge=O → B(C$_6$F$_5$)$_3$/Ge-OTMS → B(C$_6$F$_5$)$_3$ moiety are given a linear/arbitrary numerical numbering pattern (starting from **1**).
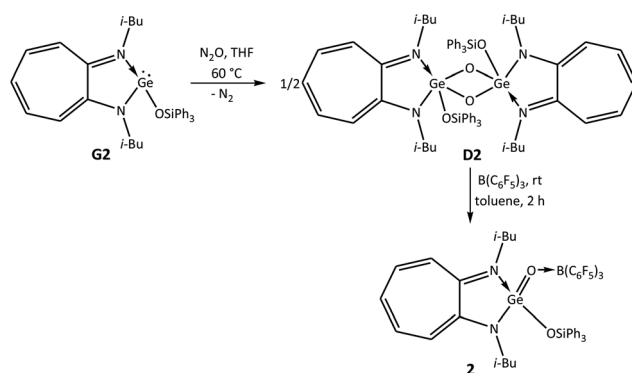
Scheme 2 Synthesis of donor−acceptor-stabilised germaester **2**.

Scheme 3 Attempted synthesis of donor–acceptor-stabilised germaamides that resulted in amine → borane adducts.

the *N*-germylene pyrrole (i-Bu)$_2$ATIGe(NC$_4$H$_4$) (**G5**) with N$_2$O in tetrahydrofuran at 60 °C for 2 h (Scheme 4).[16] Treatment of μ-oxo dimer **D5** with two equivalents of B(C$_6$F$_5$)$_3$ in toluene at room temperature resulted in the first donor–acceptor-stabilised *N*-germaacyl pyrrole, (i-Bu)$_2$ATIGe(O)(NC$_4$H$_4$) → B(C$_6$F$_5$)$_3$ (**3**) in quantitative yield (Scheme 4). The feasibility of isolating *N*-germaacyl pyrrole **3** as a stable species proves that the aforementioned hypothesis of the interference of lone pairs of electrons on the nitrogen atoms of the NR$_2$ moieties in μ-oxo dimers **D3** and **D4** is factually valid.

In all the reactions, germanium μ-oxo dimers **D1**–**D5** were reacted with the Lewis acid B(C$_6$F$_5$)$_3$.[17] To understand the utility of other Lewis acids for the successful conversion of germanium μ-oxo dimers **D1**, **D2**, and **D5** to the corresponding donor–acceptor-stabilised germaacid chloride, germaester, and *N*-germaacyl pyrrole, a range of Lewis acids (such as BF$_3$, GeCl$_2$, and SnCl$_2$) were screened. However, all of these reactions were typically unsuccessful until now (see the ESI‡ for details). Surprisingly, the germanium-μ-oxo dimer {(i-Bu)$_2$ATIGe(i-Pr)(μ-O)}$_2$ (**D**) with Ge–i-Pr bonds was insensitive to the nature of the Lewis acid used.[10] Thus, it reacted smoothly with B(C$_6$F$_5$)$_3$, ZnCl$_2$, SnCl$_2$, and GeCl$_2$ to afford the donor–acceptor-stabilised germanones **IV**, **V**, **VI**, and **VII**, respectively.[10]

As the germanium analogues of acid halides, esters, and amides were previously unknown, there has been no reactivity study on them. Therefore, the reactivity of the donor–acceptor-stabilised germaacid chloride **1**, germaester **2**, and *N*-germaacyl

Scheme 4 Synthesis of donor–acceptor-stabilised *N*-germaacyl pyrrole **3**.

pyrrole **3** was studied with great interest to understand how these compounds behave chemically. It was found that germaacid chloride **1** can react with various lithium salts and afford clean products. Thus, through reaction of **1** with lithium phenylacetylide in toluene for 12 h, a unique example of a germaynone (i-Bu)$_2$ATIGe(O)(CCPh) → B(C$_6$F$_5$)$_3$ (**4**) was obtained (Scheme 5). Notably, until now, there has been no example of a silaynone. Furthermore, this reaction reveals that the chloride attached to the germaacyl moiety can be replaced with other functional groups, a reactivity omnipresent among acid chlorides in organic chemistry. Germaacid chloride **1**, a heavier analogue of acid halides, exhibits reactivity similar to that of acid halides and silaacid chloride;[12a] therefore, this reactivity of **1** was further exploited. The lithium and potassium salts of triphenylsilanol and *t*-butanol reacted with **1** to result in germaesters **2** and (i-Bu)$_2$ATIGe(O)(O*t*-Bu) → B(C$_6$F$_5$)$_3$ (**5**), respectively (Scheme 5), which is another route for the isolation of germaesters in addition to that shown in Scheme 2.

In a similar fashion, alternate synthetic protocols can be suggested for *N*-germaacyl pyrrole **3** and germanones. For example, treatment of **1** with lithium pyrrol-1-ide and phenyl/ methyl lithium yielded *N*-germaacyl pyrrole **3** and the germanones (i-Bu)$_2$ATIGe(O)(Ph) → B(C$_6$F$_5$)$_3$ (**6**)/(i-Bu)$_2$ATIGe(O)(Me) → B(C$_6$F$_5$)$_3$ (**7**) as products, respectively (Scheme 5). Thus, from germaacid chloride **1**, germaesters, *N*-germaacyl pyrrole, and germanones can be derived without the need to isolate the corresponding germanium-μ-oxo dimers. This route was also attempted for the possible isolation of germaamides, and the reactions of germaacid chloride **1** with the lithium salts PhN(H) Li and PhN(Me)Li were carried out. However, these reactions faced the same fate as that of the abovementioned reactions carried out for the isolation of germaamides (shown in Scheme 3) by yielding amine → borane adducts only.

However, another reaction of germaacid chloride **1** with lithium bis(trimethylsilyl)amide, which aimed again at obtaining the elusive germaamide, occurred differently and resulted in the germaimine (i-Bu)$_2$ATIGe(NTMS)(OTMS) → B(C$_6$F$_5$)$_3$ (**9**) in quantitative yield (Scheme 6). This result reveals that the desired germaamide [**8**] was formed as an intermediate, which then underwent 1,3-silyl migration to form the stable compound **9** (Scheme 6).

Reactivity studies with donor–acceptor-stabilised germaesters **2** and **5** demonstrated that an interconversion between these germaesters and germaacid chloride **1** is achievable. Germaesters **2** and **5** reacted with a slight excess of Me$_3$SiCl in
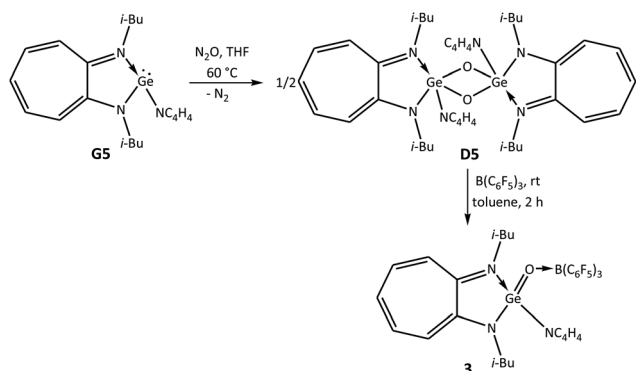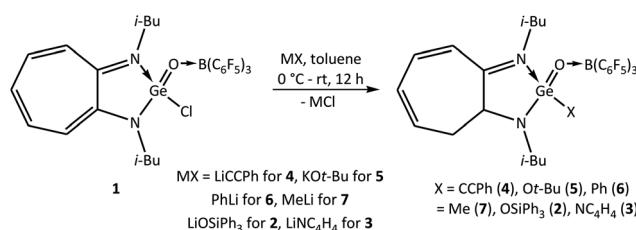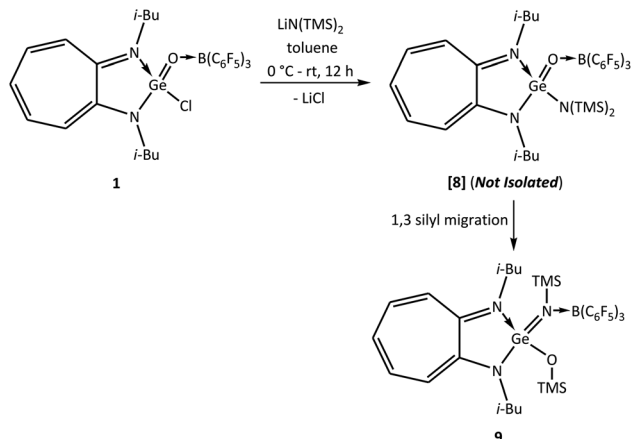
Scheme 5 Reactions of germaacid chloride **1** with various lithium/ potassium salts.
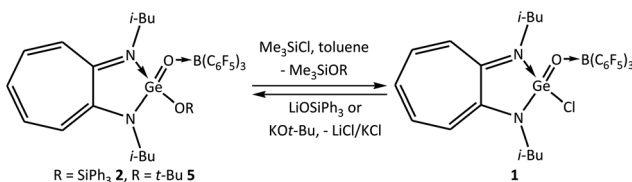
Scheme 6 Reaction of germaacid chloride **1** with lithium bis(-trimethylsilyl)amide.

toluene at room temperature and offered germaacid chloride **1** (Scheme 7). As mentioned above (Scheme 5), reactions of germaacid chloride **1** with one equivalent of LiOSiPh$_3$ and KOt-Bu in toluene at room temperature generated the germaesters **2** and **5**, respectively (Scheme 7). This type of interconversion is not known among the analogous silicon compounds.

The reactivity studies on *N*-germaacyl pyrrole **3** demonstrated that the thiophenoxide moiety of thiophenol can substitute the pyrrolide of **3**. Accordingly, the reaction of *N*-germaacyl pyrrole **3** with thiophenol at room temperature in toluene for 6 h resulted in the first example of a germaacyl thioester (i-Bu)$_2$ATIGe(O)(SPh) → B(C$_6$F$_5$)$_3$ (**10**) in quantitative yield (Scheme 8).

Considering this reaction, the feasibility of substituting the pyrrolide of **3** with hydroxide from a suitable precursor was investigated, as this might lead to the first example of a donor–acceptor-stabilised germacarboxylic acid. However, the reaction of **3** with water in a 1 : 1 molar ratio for 2 h in toluene resulted in [ATIH]$^+$[(OH)(B(C$_6$F$_5$)$_3$)]$^-$ and not the expected germacarboxylic acid (Scheme S1; see the ESI‡). The commonality in all of the abovementioned reactions of donor–acceptor-stabilised germaacid chloride **1**, germaester **2**, and *N*-germaacyl pyrrole **3** is that these reactants undergo nucleophilic substitution in the presence of suitable substrates without any damage to the Ge═O → B(C$_6$F$_5$)$_3$ moiety.

The germanium-μ-oxo dimers **D1** and **D3–D5**, germaacid chloride **1**, germaesters **2** and **5**, *N*-germaacyl pyrrole **3**, germaynone **4**, germanones **6** and **7**, and germaacyl thioester **10** are

Scheme 7 Interconversion between germaesters **2/5** and germaacid chloride **1**.
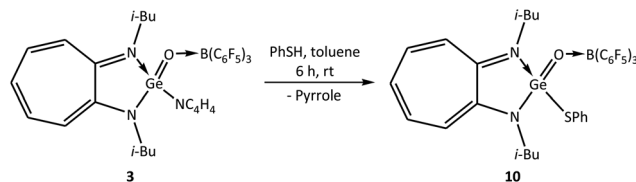
Scheme 8 Reaction of *N*-germaacyl pyrrole **3** with thiophenol.

stable at room temperature in an inert atmosphere of dinitrogen. All these compounds are freely soluble in common organic solvents, such as toluene, chloroform, and dichloromethane. Though the germanium-μ-oxo dimers **D1–D5** are also freely soluble in tetrahydrofuran, products **1–7** and **10**, containing a Ge═O → B(C$_6$F$_5$)$_3$ moiety, decompose even in tetrahydrofuran dried over a potassium mirror to afford [ATIH]$^+$[(OH)(B(C$_6$F$_5$)$_3$)]$^-$.

Compounds **D1**, **D3–D5**, **1–7**, and **10** were characterised through multinuclear NMR spectroscopic (^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{29}Si) and single-crystal X-ray diffraction studies in the solution and solid states, respectively (see the ESI‡ for details). In the ^{1}H NMR spectra of **D1** and **D5**, all the resonances are shifted slightly downfield in comparison to those of the precursor molecules, germylene monochloride **G1** and *N*-germylene pyrrole **G5**, respectively. This shifting is due to the attachment of germanium atoms to electronegative oxygen atoms and the concomitant increase in the formal oxidation state of germanium atoms from +2 to +4. The resonances of the seven-membered ring protons in **1–7** and **10** are shifted downfield in comparison to the corresponding protons in germanium-μ-oxo dimer **D1**. Owing to the increased electrophilicity of the germanium atom in the Ge═O → B(C$_6$F$_5$)$_3$ moiety (of **1–7** and **10**) in comparison to the germanium atoms in the Ge(μ-O)$_2$Ge moiety of **D1**, these shifts are expected. In the ^{13}C NMR spectra of **D1**, **D3–D5**, **1–7**, and **10**, the expected numbers of signals were observed. In the ^{11}B NMR spectra of **1–6**, and **10**, singlet resonances at −2.46, −2.61, −2.72, −2.79, −2.44, −3.12, and −2.73 ppm were observed, respectively (Table 1). In comparison, B(C$_6$F$_5$)$_3$ and the donor–acceptor-stabilised germanone (i-Bu)$_2$ATIGe(O)(i-Pr) → B(C$_6$F$_5$)$_3$ (**IV**) showed singlet resonances at −2.30 ppm[18,19] and −4.52 ppm,[10] respectively. These data reveal that the resonances in **1–6** and **10** are in between the resonances of B(C$_6$F$_5$)$_3$ and **IV**. These results suggest that the electron donation by the germaacyl oxygen atom to the boron atom in **1–6**, and **10** is reduced relative to that in **IV** due to the electron-withdrawing effect of the Cl, OSiPh$_3$, NC$_4$H$_4$, CCPh, Ot-Bu, Ph, and SPh atom/group on the germanium atom, respectively (**IV** has an electron-donating i-Pr group on the germanium atom). The donor–acceptor-stabilised silaaldehyde L'Si(H)═O → B(C$_6$F$_5$)$_3$ (**VIII**),[12g] silaformyl chloride IPr·SiH(Cl)═O → B(C$_6$F$_5$)$_3$ (**IX**),[12c] silaacid anhydride [{PhC(t-BuN)$_2$}Si{═O → B(C$_6$F$_5$)$_3$}O–Si(H){═O → B(C$_6$F$_5$)$_3$}(Nt-Bu)(HNt-Bu)CPh] (**X**),[12d] monoalumoxane L*Al═O → B(C$_6$F$_5$)$_3$ (**XI**),[20] and boraacid chloride IPr → B(Cl)═O → B(C$_6$F$_5$)$_3$ (**XII**)[21] have B(C$_6$F$_5$)$_3$ as the acceptor in the M═O → B(C$_6$F$_5$)$_3$ moiety (M = Si **VIII**, **IX**, **X**; Al **XI**; B **XII**) [L' = HC[CMeN(Ar)]$_2$ IPr = 1,3-

Table 1 Comparison of the ^{11}B and ^{19}F NMR spectral resonances of boron and fluorine atoms and the O–B bond distances in compounds **1–6** and **10** with $B(C_6F_5)_3$ and other related compounds of group **13–14** elements with an M=O → $B(C_6F_5)_3$ moiety(s) (M = Ge, Si, Al, B)

S. no.	Compound	^{11}B NMR chemical shift (ppm)	^{19}F NMR chemical shift (ppm)	O–B bond length (Å)	Reference
1	Germanone, (i-Bu)$_2$ATIGe(i-Pr)(O) → $B(C_6F_5)_3$ (**IV**)	−4.52[a]	(−134, −161, and −166)[a]	1.473(4)	10
2	Silaaldehyde, L'Si(H)=O → $B(C_6F_5)_3$ (**VIII**)	−4.70[b]	(−132, −162, and −165)[b]	1.503(3)	12g
3	Silaformyl chloride, IPr·SiH(Cl)=O → $B(C_6F_5)_3$ (**IX**)	−5.28[c]	(−134, −163, and −168)[c]	1.492(3)	12c
4	Silaacid anhydride, [{PhC(t-BuN)$_2$}Si{=O→$B(C_6F_5)_3$}O–Si(H){=O→$B(C_6F_5)_3$}(Nt-Bu)(HNt-Bu)CPh] (**X**)	(−3.99, and −5.46)[c]	(−134, −135, −164, −165, −167, and −168)[c]	1.493(3), and 1.488(3)	12d
5	Monoalumoxane, L*Al=O → $B(C_6F_5)$ (**XI**)	−4.83[d]	(−134, −164, and −166)[d]	1.444(3)	20
6	Boraacid chloride, IPr → B(Cl)=O → $B(C_6F_5)$ (**XII**)	−2.7[e]	(−131, −160, and −165)[e]	1.518(3)	21
7	$B(C_6F_5)_3$	−2.30[a]	(−127, −143, and −160)[a]	—	19
8	Germaacid chloride, (i-Bu)$_2$ATIGe(O)(Cl) → $B(C_6F_5)_3$ (**1**)	−2.46[a]	(−133, −159, and −165)[a]	1.493(5)	This work
9	Germaester, (i-Bu)$_2$ATIGe(O)(OSiPh$_3$) → $B(C_6F_5)_3$ (**2**)	−2.61[a]	(−132, −160, and −165)[a]	1.497(3)	This work
10	N-Germaacyl pyrrole, (i-Bu)$_2$ATIGe(O)(NC$_4$H$_4$) → $B(C_6F_5)_3$ (**3**)	−2.72[a]	(−133, −159, and −165)[a]	1.494(6)	This work
11	Germaynone, (i-Bu)$_2$ATIGe(O)(CCPh) → $B(C_6F_5)_3$ (**4**)	−2.79[a]	(−133, −161, and −165)[a]	1.489(4)	This work
12	Germaester, (i-Bu)$_2$ATIGe(O)(Ot-Bu) → $B(C_6F_5)_3$ (**5**)	−2.44[a]	(−132, −160, and −165)[a]	1.505(3) and 1.502(3)	This work
13	Germanone, (i-Bu)$_2$ATIGe(O)(Ph) → $B(C_6F_5)_3$ (**6**)	−3.12[a]	(−133, −160, and −165)[a]	1.481(3)	This work
14	Germaacyl thioester, (i-Bu)$_2$ATIGe(O)(SPh) → $B(C_6F_5)_3$ (**10**)	−2.73[a]	(−133, −160, and −165)[a]	1.501(5)	This work

[a] In CDCl$_3$. [b] In CD$_2$Cl$_2$. [c] In THF-d$_8$. [d] In C$_6$D$_6$/THF-d$_8$. [e] In C$_6$D$_6$.

bis(2,6-diisopropylphenyl)imidazol-2-ylidene, L* = Et$_2$-NCH$_2$CH$_2$NC(Me)CHC(Me)NCH$_2$CH$_2$NEt$_2$]. It may therefore be appropriate to compare the boron and fluorine resonances of these compounds with those of **1–6** and **10** (Table 1). These resonances in compounds **VIII**, **IX**, **X**, **XI**, and **XII** are shifted upfield with respect to the corresponding resonances of $B(C_6F_5)_3$ (Table 1), which indicates the shielding of boron and fluorine atoms due to electron donation by oxygen atoms. This result is similar to that observed for compounds **1–6** and **10**, containing a Ge=O → $B(C_6F_5)_3$ moiety (Table 1), but as revealed by the ^{11}B NMR spectral data (Table 1), the magnitude of the shielding in these compounds is lower than that in compounds **VIII**, **IX**, **X**, and **XI**. In the ^{29}Si NMR spectra of germaester **2**, a signal at −13.62 ppm for the SiPh$_3$ group is shifted downfield in comparison to that in germylene **G2** (−24.72 ppm).[15]

In a preliminary study of optical properties, the UV-vis spectra of compounds **1**, **2**, and **10** were recorded in toluene at room temperature. Compounds **1**, **2**, and **10** showed an absorption maximum in the visible region at approximately 420 nm (Fig. 1). Theoretical studies suggested that these absorptions in compounds **1**, **2**, and **10** are essentially due to $\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$, $\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$, and $n_{(F)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$ transitions, respectively (Table S1; see the ESI‡ for details). Furthermore, there are two high-energy transitions in each of these compounds with λ_{max} values of approximately 350 and 285 nm

(Fig. 1), which are due to multiple transitions (Table S1; see the ESI‡ for details). The optical properties of compounds with formal M=O → LA moieties (M = Ge, Si) have rarely been studied. For germanone **VII** with a Ge=O → GeCl$_2$ moiety, optical properties have been reported. In comparison to compounds **1**, **2**, and **10**, the absorption maximum of **VII** in the visible region (437 nm) is slightly redshifted, and this absorption is due to a HOMO[$s^{nb}_{Ge_2} + p^{nb}_{(N,O,Cl)} + \pi_{(C=C)}$]→LUMO[$\pi^*_{(ATI)}$]
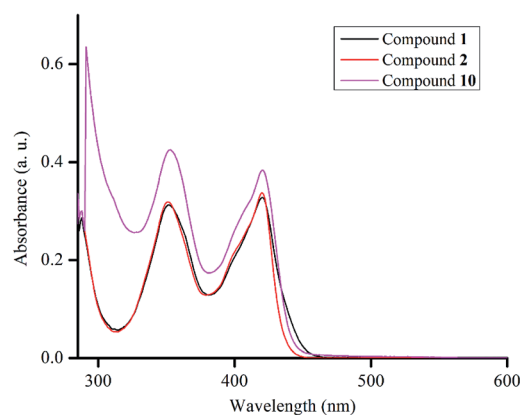

Fig. 1 UV-vis spectra of compounds **1**, **2**, and **10** (30 μM solution) in toluene.

transition. Most likely, a different Lewis acid in compound **VII** altered the composition of the HOMO.

The structures of compounds **D1, D3–D5, 1–7, 9**, and **10** in the solid state were determined by single-crystal X-ray diffraction analysis (Fig. 2–4 and S53–S62, Tables S2–S5, and Experimental section; see the ESI‡).[22] Compounds **1–4** and **6** crystallised in the triclinic space group $P\bar{1}$ (Tables S3 and S4; see the ESI‡). Compounds **5, 7**, and **10** crystallised in the monoclinic, orthorhombic, and monoclinic space groups $P2_1/n$, $P2_12_12_1$, and $P2_1/c$, respectively (Table S4; see the ESI‡).

The molecular structures of compounds **1–7** and **10** [Fig. 2 (**1**), 3 (**4**), 4 (**10**), S57 (**2**), S58 (**3**), S59 (**5**), S60 (**6**), and S61 (**7**)‡] confirmed the presence of a (Y)Ge=O → B(C₆F₅)₃ moiety [Y = Cl (**1**), OSiPh₃ (**2**), NC₄H₄ (**3**), CCPh (**4**), O*t*-Bu (**5**), Ph (**6**), Me (**7**), and SPh (**10**)]. In these compounds, the germanium atom has a distorted tetrahedral geometry with two ATI ligand nitrogens, one germaacyl oxygen, and one Cl (**1**), O (**2**), N (**3**), C (**4**), O (**5**), C (**6**), C (**7**), or S (**10**) atom. The average length of the Ge–N$_{ligand}$ bonds in compounds **1** (1.838 Å), **2** (1.848 Å), and **3** (1.843 Å) is shorter than that in their precursors **D1** (1.931 Å), **D2** (1.946 Å), and **D5** (1.942 Å), respectively. Similarly, the Ge–Y bond in compounds **1** (2.117(1) Å; Y = Cl), **2** (1.719(2) Å; Y = OSiPh₃), and **3** (1.820(4) Å; Y = NC₄H₄) is also shorter than that in compounds **D1** (2.20(8) Å), **D2** (1.767(3) Å), and **D5** (1.892(3) Å), respectively. These differences are due to the electrophilicity of the oxygen atom in the Ge=O → B(C₆F₅)₃ moiety of compounds **1, 2**, and **3** being higher than that of the oxygen atoms in the Ge(μ-O)₂Ge moiety of **D1, D2**, and **D5**, which makes the germanium atom in the former set of compounds more electrophilic than that in the latter set. Though these effects are observed in germanone **IV**, in comparison to the electron-donating i-Pr group bound to the germanium atom of germanone **IV**, the Cl, OSiPh₃, NC₄H₄, CCPh, and SPh atom/group
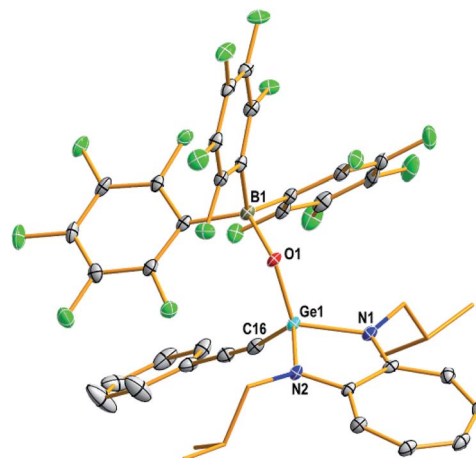

Fig. 3 Molecular structure of germaynone **4** with thermal ellipsoids at the 50% probability level. All hydrogen atoms and a solvent molecule (dichloromethane) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–O1 1.708(2), O1–B1 1.489(4), Ge1–C16 1.856(3), Ge1–N1 1.860(2), Ge1–N2 1.845(2); O1–Ge1–N1 114.10(1), O1–Ge1–N2 110.17(1), O1–Ge1–C16 113.63(12), B1–O1–Ge1 131.46(2), N2–Ge1–N1 86.91(1), N1–Ge1–C16 112.42(2), N2–Ge1–C16 116.98(1). Data collection temperature: 100 K.

bound to the germanium atom in germaacid chloride **1**, germaester **2**, *N*-germaacyl pyrrole **3**, germaynone **4**, and germaacyl thioester **10**, respectively, exert electron-withdrawing (+I) effects and compete for the germanium atom's electron density, thus increasing the interaction between the germanium and oxygen atoms of the Ge=O bond. Therefore, the length of the formal Ge=O bond in compounds **1** (1.698(2) Å), **2** (1.696(2) Å), **3** (1.695(3) Å), **4** (1.708(2) Å), and **10** (1.698(3) Å) is shorter than that in germanones **IV** (1.718(2) Å), **V** (1.724(2) and 1.728(2) Å), **VI** (1.728(5) Å), and **VII** (1.718(2) Å).[10] These data also reveal that relative to the polarisation of the Ge=O bond in germanone

Fig. 2 Molecular structure of germaacid chloride **1** with thermal ellipsoids at the 50% probability level. All hydrogen atoms and a solvent molecule (dichloromethane) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–O1 1.698(2), O1–B1 1.493(5), Ge1–Cl1 2.117(1), Ge1–N1 1.831(3), Ge1–N2 1.846(3); O1–Ge1–N1 111.60(1), O1–Ge1–N2 116.79(1), O1–Ge1–Cl1 112.25(9), B1–O1–Ge1 134.6(2), N2–Ge1–N1 87.46(1), N1–Ge1–Cl1 116.19(1), N2–Ge1–Cl1 110.52(1). Data collection temperature: 100 K.
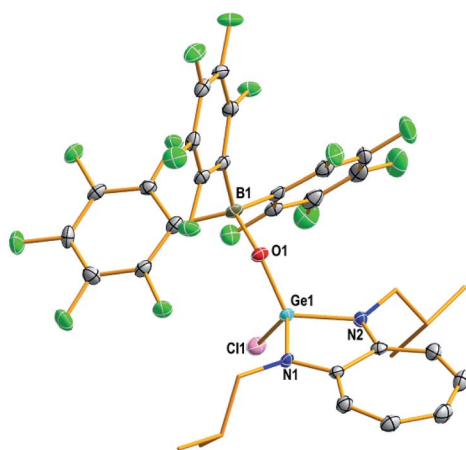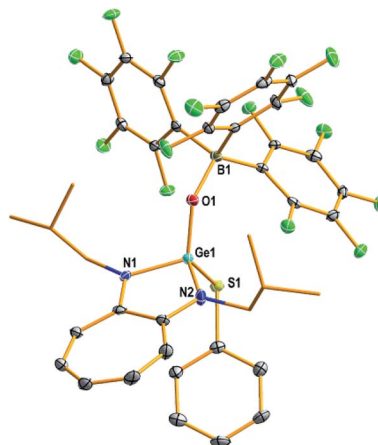

Fig. 4 Molecular structure of germaacyl thioester **10** with thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–O1 1.698(3), O1–B1 1.501(5), Ge1–S1 2.199(2), Ge1–N1 1.864(4), Ge1–N2 1.866(4); O1–Ge1–S1 116.19(1), B1–O1–Ge1 144.0(3), N2–Ge1–N1 85.72(2). Data collection temperature: 100 K.

IV,[10] the same bonds in germaacid chloride 1, germaester 2, N-germaacyl pyrrole 3, germaynone 4, and germaacyl thioester 10 are less polarised due to the electron-withdrawing effect of the Cl, OSiPh$_3$, NC$_4$H$_4$, CCPh, and SPh atoms/groups bound to the germanium atom, respectively. A consequence of the increased interaction between the germanium and oxygen atoms of the germaacyl bond in these compounds is the reduced Lewis basicity of the oxygen atom. This result is reflected in the interaction of this oxygen atom with the Lewis acid B(C$_6$F$_5$)$_3$, where the O → B bond in compounds 1 (1.493(5) Å), 2 (1.497(3) Å), 3 (1.494(6) Å), 4 (1.489(4) Å), and 10 (1.501(5) Å) is longer than the corresponding bond in germanone IV (1.473(4) Å).[10] The O → B bond lengths observed in these compounds are similar to those observed in analogous silicon derivatives (VIII 1.503(3), IX 1.492(3), and X 1.493(3) and 1.488(3); M = Si) and boraacid chloride (XII 1.518(3); M = B) with an M=O → B(C$_6$F$_5$)$_3$ bond (Table 1).[12g,12c,12d,21] However, in the mono-alumoxane[20] XI with an Al=O → B(C$_6$F$_5$)$_3$ bond, the O → B bond is shorter (1.444(3) Å) than those in compounds 1–4, 10, VIII, IX, X, and XII. All the bonding aspects discussed here are supported by theoretical studies (vide infra). Furthermore, the Ge=O bond (vide supra) in compounds 1–4 and 10 is slightly longer than the Ge=O bond in the base-stabilised germanones [L″L^{D}Ge=O] (L″ = [CH{(C=CH$_2$)(CMe)(NAr)2}]; L^D = [{(Me)CN(Me)}$_2$C] (XIII), [{(Me)CN(i-Pr)}$_2$C] (XIV), 4-(Me$_2$N)–C$_5$H$_4$N (XV)) without an acceptor at an oxygen atom (1.646(2)–1.672(3) Å)[8] and shorter than the Ge–O single bonds in germanium-μ-oxo dimers D1, D2, and D5 (1.848(2)–1.787(3) Å).

The nature of the Ge=O bond in compounds 1–3 and 10 was analysed through natural bond orbital (NBO)[23,24] studies, and the details are provided in Table S6 (see the ESI‡). The Ge–O σ-bond in compounds 1 and 10 is formed by the overlap of the sp$^{2.59}$ and sp^2 hybrid orbitals of germanium with the sp$^{1.62}$ and sp$^{2.66}$ hybrid orbitals of oxygen, respectively (Fig. 5 and Table S6; see the ESI‡). In compounds 2 and 3, the sp$^{2.53}$ and sp$^{2.43}$ hybrid orbitals of germanium overlap with the sp$^{2.89}$ and sp$^{2.57}$ hybrid orbitals of oxygen to form the Ge–O bond, respectively (Fig. 5 and Table S6; see the ESI‡). MO calculations also reveal the presence of Ge–O bonds in compounds 1–3 and 10, and these bonds are deeply buried (Figure S63, see the ESI‡).

NBO second-order perturbation theory analysis reveals that in germaacid chloride 1, the sigma bond between germanium and oxygen is formed by the donation of the lone pair of electrons on the oxygen atom to the σ* orbital of the Ge–Cl bond (Fig. 6a; 79.3 kcal mol^{-1}). The lone pair of electrons on the oxygen atom also interacts with the π* orbitals of the Ge–N$_{ATI}$ bonds (Fig. 6b; 100.3 kcal mol^{-1} and Fig. 6c; 52.8 kcal mol^{-1}). However, in addition to these interactions, there are two strong stabilising interactions between the sp$^{3.82}$ (Fig. 6d; 44.8 kcal mol^{-1}) and sp$^{0.29}$ (Fig. 6e; 43.6 kcal mol^{-1}) orbitals of oxygen and the π* orbital of the Ge–N$_4$ bond. Compounds 2, 3, and 10, instead of showing the aforementioned n (lone pair of electrons on oxygen) to σ*/π* orbital interactions, showed strong NBO donor–acceptor interactions from the s, p or sp^x orbitals of oxygen atoms to vacant s, p or sp^x orbitals of the germanium atoms [Fig. 6f–h (2), Fig. 6i–l (3), and Fig. 6m–p (10)]. However, in compound 10, a moderately strong NBO donor–acceptor interaction was found

sp$^{2.59}$(Ge)–sp$^{1.62}$(O)   sp$^{2.43}$(Ge)–sp$^{2.57}$(O)   sp^2(Ge)–sp$^{2.66}$(O)
Ge(14.05%)–O(85.95%)   Ge(15.01%)–O(84.99%)   Ge(15.79%)–O(84.21%)
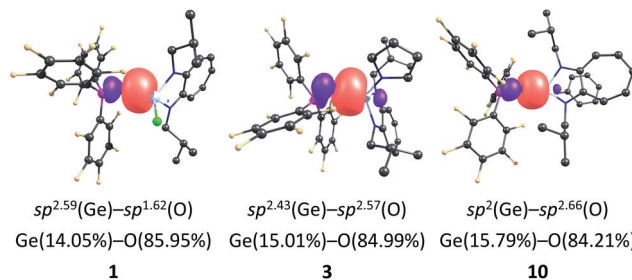1   3   10

Fig. 5 NBO calculated Ge–O σ-bond in germaacid chloride 1, N-germaacyl pyrrole 3, and germaacyl thioester 10. The hybridisations of the germanium and oxygen orbitals involved in the overlap are mentioned along with the percentage contributions of the constituent atoms to the Ge–O bond.

between the p orbital of oxygen and the σ* orbital of the Ge–S bond (27.9 kcal mol^{-1}) (Fig. 6q). In comparison, germanone IV showed three σ interactions: two O → Ge interactions and one O → σ*(Ge–C$_{i-Pr}$) interaction; these interactions result in a total stabilisation energy of 236.3 kcal mol^{-1}.[10] Thus, the total stabilisation energy due to the donor–acceptor interactions in compounds 1 (320.8 kcal mol^{-1}), 2 (284.7 kcal mol^{-1}), 3 (303.7 kcal mol^{-1}), and 10 (329.2 kcal mol^{-1}) is higher than that in germanone IV, which is due to the difference in the nature of the atoms/moieties bound to germanium atom in these compounds (–Cl, –OSiPh$_3$, –NC$_4$H$_4$, and –SPh, respectively) instead of an i-Pr group. The Wiberg bond index (WBI) calculations for compounds 1, 3, and 10 also showed a slightly increased bond order for the Ge=O bond (0.74–0.76) relative to that in germanone IV (0.70)[10] (Table S6; see the ESI‡). A similar bond order (0.7955) was calculated for silaaldehyde II (with BEt$_3$ as an acceptor bound to the oxygen atom); for silaacid chloride I and silaester III (without any acceptor bound to the oxygen atom), the calculated WBI values are 1.0993 and 1.0441, respectively.[12a] In compounds 1, 2, and 10, the HOMO is localised on the phenyl ring of the B(C$_6$F$_5$)$_3$ moiety (Fig. S64; see the ESI‡), and in compound 3, it is localised on the pyrrole ring, which also reveals the stabilisation of the formal Ge=O bonds in these compounds (Fig. S64; see the ESI‡). Furthermore, NBO donor–acceptor interactions between oxygen and boron atoms can be observed in all these compounds (Fig. S65; see the ESI‡); the stabilisation energies due to these interactions are 280.3 kcal mol^{-1}, 315.6 kcal mol^{-1}, 296.3 kcal mol^{-1}, and 294.6 kcal mol^{-1} in compounds 1 (Fig. S65a‡), 2 (Fig. S65b‡), 3 (Fig. S65c‡), and 10 (Fig. S65d‡), respectively. All these stabilisation energies are lower than that observed in germanone IV (334.9 kcal mol^{-1}),[10] indicating the reduced electron donation from oxygen atoms to boron atoms in compounds 1–3, and 10.

As none of the monoanionic ligands, such as β-diketiminate and amidinate ligands, are known to stabilise compounds with formal Ge=O bonds, it is of interest to examine how the bulky monoanionic aminotroponiminate (ATI) ligand used in the present study helps to stabilise various compounds with formal Ge=O bonds. NBO second-order perturbation theory analysis reveals the existence of donor–acceptor interactions between (a) sp^x orbitals of nitrogen atoms of the ATI ligand to vacant s,
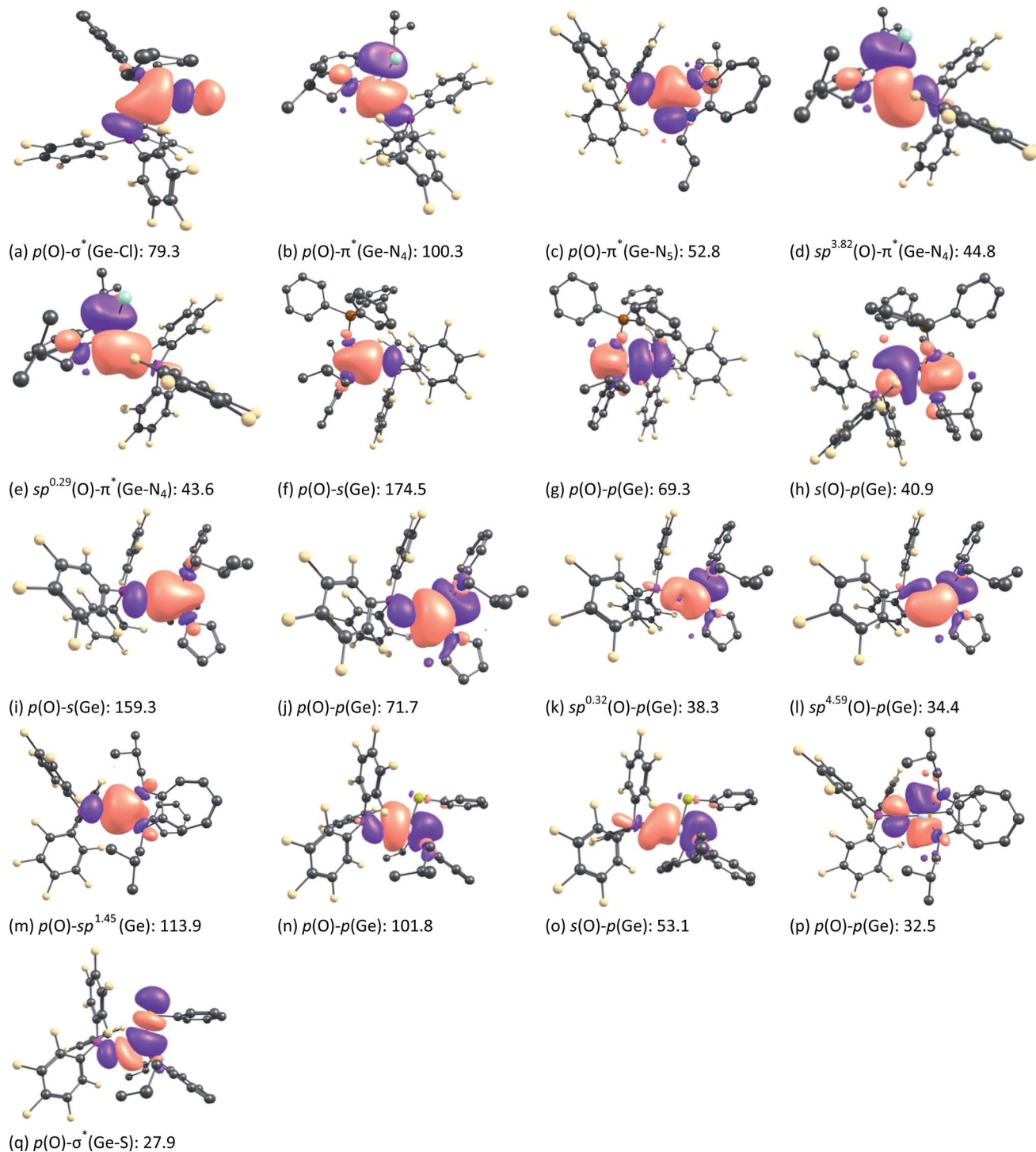
(a) $p(O)$-σ^*(Ge-Cl): 79.3

(b) $p(O)$-π^*(Ge-N$_4$): 100.3

(c) $p(O)$-π^*(Ge-N$_5$): 52.8

(d) $sp^{3.82}$(O)-π^*(Ge-N$_4$): 44.8

(e) $sp^{0.29}$(O)-π^*(Ge-N$_4$): 43.6

(f) $p(O)$-s(Ge): 174.5

(g) $p(O)$-p(Ge): 69.3

(h) $s(O)$-p(Ge): 40.9

(i) $p(O)$-s(Ge): 159.3

(j) $p(O)$-p(Ge): 71.7

(k) $sp^{0.32}$(O)-p(Ge): 38.3

(l) $sp^{4.59}$(O)-p(Ge): 34.4

(m) $p(O)$-$sp^{1.45}$(Ge): 113.9

(n) $p(O)$-p(Ge): 101.8

(o) $s(O)$-p(Ge): 53.1

(p) $p(O)$-p(Ge): 32.5

(q) $p(O)$-σ^*(Ge-S): 27.9

Fig. 6 Pictorial view of NBO donor−acceptor interactions between p or sp^x (x = 3.82, 0.29) orbitals of oxygen and the σ* orbital of the Ge−Cl bond/π* orbitals of the Ge−N$_{ATI}$ bonds in compound **1** (a−e), s or p orbitals of oxygen and s or p orbitals of germanium in compound **2** (f−h), p or sp^x (x = 0.32, 4.59) orbitals of oxygen and s or p orbitals of germanium in compound **3** (i−l), s or p orbitals of oxygen and p or sp$^{1.45}$ orbitals of germanium in compound **10** (m−p), and p orbital of oxygen and σ* orbital of Ge−S bond in compound **10** (q). Energy values are given in kcal mol^{-1}. Hydrogen atoms are omitted for clarity. The cut−off interaction energies for LP → LP* and LP → BD* are ≥30 kcal mol^{-1} and 20 kcal mol^{-1}, respectively.

p or sp^x orbitals of germanium in compounds **1–3** and **10** (Fig. S66a, b, S67a–d, S68a–d, and S69a–d; see the ESI‡); (b) N$_{ATI}$ orbitals to the σ* orbital of the Ge–Cl bond in compound **1** (Fig. S66c and d; see the ESI‡) and N$_{ATI}$ orbitals to the σ* orbital of the Ge–S bond in compound **10** (Fig. S69e and f; see the ESI‡); and (c) s or p orbitals of the chlorine atom to π* orbitals of Ge–

N_{ATI} bonds in compound **1** (Fig. S66e and f; see the ESI‡). Owing to the interactions of types (b) and (c), the energies of the σ* orbital of the Ge–Cl bond in compound **1**, π* orbitals of the Ge–N_{ATI} bonds in compound **1**, and the σ* orbital of the Ge–S bond in compound **10** are lower, and these orbitals are available for accepting electrons donated by the O atom of the Ge=O bond. Further, energy decomposition analysis (EDA)[25] was performed using {Y–Ge=O → B(C$_6$F$_5$)$_3$} (Y = Cl (**1**), OSiPh$_3$ (**2**), NC$_4$H$_4$ (**3**), SPh (**10**)) as one fragment and the {ATI} ligand as another fragment with frozen geometries obtained from DFT calculations; the results are summarised in Table S7 (see the ESI‡). The large interaction energy (E_{int}) observed for these compounds arises essentially due to the favourable ΔE_{orb} term that describes the stabilising interaction between the ATI ligand and the Y–Ge=O → B(C$_6$F$_5$)$_3$ moiety (Y = Cl (**1**), OSiPh$_3$ (**2**), NC$_4$H$_4$ (**3**), SPh (**10**)).

Conclusions

Donor–acceptor-stabilised germaacyl chloride (i-Bu)$_2$-ATIGe(O)(Cl) → B(C$_6$F$_5$)$_3$ (**1**), germaester (i-Bu)$_2$-ATIGe(O)(OSiPh$_3$) → B(C$_6$F$_5$)$_3$ (**2**), and *N*-germaacyl pyrrole (i-Bu)$_2$ATIGe(O)(NC$_4$H$_4$) → B(C$_6$F$_5$)$_3$ (**3**) compounds were successfully isolated as stable species for the first time. Compounds **1**, **2**, and **3** can undergo nucleophilic substitution reactions without any disturbance to the Ge=O → B(C$_6$F$_5$)$_3$ moiety to afford germaynone (i-Bu)$_2$ATIGe(O)(CCPh) → B(C$_6$F$_5$)$_3$ (**4**), germaester (i-Bu)$_2$ATIGe(O)(O*t*-Bu) → B(C$_6$F$_5$)$_3$ (**5**), germanone (i-Bu)$_2$ATIGe(O)(R) → B(C$_6$F$_5$)$_3$ (R = Ph **6**, Me **7**), and germaacyl thioester (i-Bu)$_2$ATIGe(O)(SPh) → B(C$_6$F$_5$)$_3$ (**10**) compounds in good yields. Interestingly, through the reactivity of **1** and **2**, the feasibility to interconvert germaesters and germaacid chlorides is exposed. Attempts were also made to synthesise germaamides and germacarboxylic acids, and it is anticipated that the wisdom obtained during these endeavours will offer new directions to the isolation of these compounds as stable species in the near future.

Author contributions

M. K. S. carried out all the experimental studies and drafted the manuscript. S. S. and P. M. helped M. K. S. with some of the experimental studies. The theoretical studies were carried out by G. M., who also wrote the theoretical section of the manuscript. B. P. assisted G. M. with some of the theoretical calculations/write-up. S. N. and G. R. corrected the experimental and theoretical write-ups of the manuscript, respectively.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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