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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)OSiPh3, and Ge(O)NC6H4 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).
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-Bu₂ATIGe(O)Cl) → B(C₆F₅)₃ (1), germaester (i-Bu₂ATIGe(O)(OSiPh₂) → B(C₆F₅)₃ (2), and N-germaacyl pyrrole (i-Bu₂ATIGe(O)(NC₄H₄) → B(C₆F₅)₃ (3) compounds, with Cl–Ge=O, Ph₃Si=Ge=O, and C₃H₄N–Ge=O moieties, respectively, are reported here. Germaacid chloride 1 reacts with PhClLi, KOt-Bu, and RLi (R = Ph, Me) to afford donor–acceptor-stabilised germylamine (i-Bu₂ATIGe(O)(CCPh) → B(C₆F₅)₃ (4), germaester (i-Bu₂ATIGe(O)(Ot-Bu) → B(C₆F₅)₃ (5), and germanone (i-Bu₂ATIGe(O)(R) → B(C₆F₅)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 TMSCI gave germaacid chloride 1, and 1 reacted with Ph₃SiOLi and KOt-Bu to produce germaesters 2 and 5. Reaction of N-germaacyl pyrrole 3 with phenol produced a donor–acceptor-stabilised germaacyl thioester (i-Bu₂ATIGe(O)(SPh) → B(C₆F₅)₃ (10). Furthermore, the attempted syntheses of germaamides and germanocarboxylic 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)NR₂], carboxylic acids [RC(O)OH], and acid anhydrides [RC(O)C(O)R] is of great importance in organic chemistry (R = alkyl/aryl group; X = halogen). The significance of these carbon bonds provides inspiration for the synthesis of their heavier analogues, 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. 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. Thus, silanones (sila-ketones) 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. 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. Very recently, Aldridge and co-workers reported the generation of a silicon analogue of an acid chloride [(N-naacac)²Si(Cl)=O (I)] through the reaction of the silylene (N-naacac)²SiCl with N₂O (Chart 1) [(N-naacac)²Ar = HC[(Me₂N)₂C(Ar)=N]₂; Ar = 2,6-i-Pr₂C₆H₃]. The metathesis reactions of I with K[ET₃BH] and KOt-Bu afforded a silaaldehyde [(N-naacac)²ArSi(H)=O → BET₃ (II)]
and a silaester \([\text{N-nacnac}]^2\text{Si(Ot-Bu)}=\text{O}\) (III), respectively (Chart 1)\(^{29}\). Surprisingly, such analogues of germanium \([\text{LGe(O)}\ Y]\) \([\text{L} = \text{a monoanionic ligand}; \ Y = \text{H (germaaldehyde), Cl (germaacid chloride), OR (germaester), NR}^2 (\text{germanamide}, \ \text{OH (germacarboxylic acid), and } \text{OGF}^2\text{OL (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 \([\text{i-Bu}_2\text{ATIGe(i-Pr)}=\text{O}] \rightarrow \text{LA} (\text{LA} = \text{B(C}_6\text{F}_5)_2\text{(IV), ZnCl}_2\text{(V), SnCl}_2\text{(VI), and GeCl}_2\text{(VII)})\] of a germanone\(^{28}\) starting from a germanium-\(\mu\)-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 germametastases. Consequently, we report in this article the isolation of germaamides, a germanium \(\mu\)-oxo dimer with \(\text{Ge}^\equiv\text{O}\) bond. This accomplishment inspired us to determine whether hitherto unknown germametastases and germaamides could also be isolated using this synthetic strategy of reacting suitable germanium \(\mu\)-oxo dimers with Lewis acids. Thus, to synthesise a germaester, a germylene siloxide \([\text{i-Bu}_2\text{ATIGeOSiPh}_3\text{(G2)}]\) was reacted with \(\text{N}_2\text{O}\) in tetrahydrofuran at \(60^\circ\text{C}\) for 2 h to obtain the germanium \(\mu\)-oxo dimer \([\text{(i-Bu)}_2\text{ATIGe(OSiPh}_3\text{(µ-O)})_2\text{(D2)}]\). The reaction of \(\mu\)-oxo dimer D2 containing Ge-OsiPh3 bonds with two equivalents of \(\text{B(C}_6\text{F}_5)_3\) in toluene at room temperature afforded the first example of a donor–acceptor-stabilised germaester, namely, \([\text{(i-Bu)}_2\text{ATIGe(O)(OSiPh}_3\text{(µ-O)})_2\text{(D3)}]\) and \([\text{(i-Bu)}_2\text{ATIGeN(Me)Ph(µ-O)})_2\text{(D4)}]\) (Scheme 2). These reactions suggest that the synthetic route discussed above is not suitable for the isolation of donor–acceptor-stabilised germametastases. On the basis of the products obtained, it was thought that the lone pairs of electrons on the nitrogen atoms of the \(\text{NR}^2\) moieties in D3 and D4 interfered with the expected reaction of these compounds (D3 and D4) with \(\text{B(C}_6\text{F}_5)_3\). To confirm this hypothesis, a germanium \(\mu\)-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; \(\text{NC}_4\text{H}_4\)) can satisfy the required criterion, the germanium \(\mu\)-oxo dimer \([\text{(i-Bu)}_2\text{ATIGeNC}_4\text{H}_4(µ-O)})_2\text{(D5)}\] with two Ge–\(\text{NC}_4\text{H}_4\) moieties was synthesised in quantitative yield by the reaction of

\[
\begin{align*}
\text{G1} & \quad \text{N}_2\text{O, THF, 60°C, 2 h} \\
\text{D1} & \quad \text{B(C}_6\text{F}_5)_3, \text{rt, toluene, 2 h} \\
\text{D1} & \quad \text{B(C}_6\text{F}_5)_3, \text{rt, toluene, 2 h} \\
\text{D2} & \quad \text{B(C}_6\text{F}_5)_3, \text{n, toluene, 2 h} \\
\text{D2} & \quad \text{B(C}_6\text{F}_5)_3, \text{n, toluene, 2 h}
\end{align*}
\]

Scheme 1  Synthesis of donor–acceptor-stabilised germaacid chloride 1. Notes: (a) in the alphanumerical numbering pattern, G denotes germylene, and D denotes germanium \(\mu\)-oxo dimer, and (b) products with a Ge\equivO \rightarrow B(C\text{F}_5)_3Ge-OTMS \rightarrow B(C\text{F}_5)_3 moiety are given a linear/arithmetical numerical numbering pattern (starting from 1).
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 $\mu$-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$_4$) $\rightarrow$ 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 the aforementioned hypothesis of the interconversion of lone pairs of electrons on the nitrogen atoms of the NR$_2$ moieties in $\mu$-oxo dimers D3 and D4 is factually valid.

In all the reactions, germanium $\mu$-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 $\mu$-oxo dimers D1, D2, and D5 to the corresponding donor–acceptor-stabilised germaamide chloride, germaester, and $N$-germaacyl pyrrole, a range of Lewis acids (such as BF$_3$, GeCl$_2$, and SnCl$_4$) 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(O)(μ-O)$_2$(D) with Ge–i-Pr bonds was insensitive to the nature of the Lewis acid used.$^{18}$ 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 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)$_3$ATIGe(O)(CCPh) $\rightarrow$ B(C$_6$F$_5$)$_3$ (4) was obtained (Scheme 5). Notably, until now, there has been no example of a silynone. 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;$^{12}$ therefore, this reactivity of 1 was further exploited. The lithium and potassium salts of triphenylsilyl and $t$-butanol reacted with 1 to result in germaesters 2 and (i-Bu)$_2$ATIGe(O)(Of-Bu) $\rightarrow$ 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 germa-\(\text{no}n\)es (i-Bu)$_3$ATIGe(O)(Ph) $\rightarrow$ B(C$_6$F$_5$)$_3$ (6)(i-Bu)$_2$ATIGe(O)(Me) $\rightarrow$ 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 $\rightarrow$ 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) $\rightarrow$ 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 germesters 2 and 5 demonstrated that an interconversion between these germesters and germaacid chloride 1 is achievable. Germesters 2 and 5 reacted with a slight excess of Me$_3$SiCl in...
thioester (i-Bu)2ATIGe(O)(SPh)

3

substitute the pyrrolide of

strated that the thiophenoxide moiety of thiophenol can

not known among the analogous silicon compounds.

and

in toluene at room temperature generated the germaesters

1

maacid chloride

1

maacid chloride

2

N

1

–oxo dimers

Scheme 7

Interconversion between germaesters 2/5 and germaacid chloride 1.

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(C6F5)3 moiety, decompose even in tetrahydrofuran dried over a potassium mirror to afford [ATIH][[OH](B(C6F5)3)].

Compounds D1, D3–D5, 1–7, and 10 were characterised through multinuclear NMR spectroscopic (1H, 11B, 13C, 29F, and 29Si) and single-crystal X-ray diffraction studies in the solution and solid states, respectively (see the ESI† for details). In the 1H 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(C6F5)3 moiety (of 1–7 and 10) in comparison to the germanium atoms in the Ge(μ-O)2Ge moiety of D1, these shifts are expected. In the 13C NMR spectra of D1, D3–D5, 1–7, and 10, the expected numbers of signals were observed. In the 11B 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(C6F5)3 and the donor-acceptor-stabilised germanone (i-Bu)2ATIGe(O)(i-Pr) → B(C6F5)3 (IV) showed singlet resonances at -2.30 ppm18,19 and -4.52 ppm,20 respectively. These data reveal that the resonances in 1–6 and 10 are in between the resonances of B(C6F5)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, OSiPh3, NC4H4, 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 silaalddehyde L’Si(H)=O → B(C6F5)3 (VIII),27c silaformyl chloride IPr-SiH(Cl)=O → B(C6F5)3 (IX),27c silaacid anhydride [(PhC(i-Bu)2)2Si]=O → B(C6F5)3-O-Si(H)=O = B(C6F5)3(Nr-Bu)[(HNr-Bu)2CPH](X),27d monoalumoxane L’Si=O → B(C6F5)3 (XI),20 and boracac acid chloride IPr → B(Cl)=O → B(C6F5)3 (XII)21 have B(C6F5)3 as the acceptor in the M=O → B(C6F5)3 moiety [M = Si VIII, IX, X; Al XI; B XII] [L’ = HC[CMeN(Ar)]] 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$_6$F$_5$)$_3$ and other related compounds of group 13–14 elements with an M=O → B(C$_6$F$_5$)$_3$ 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$_6$F$_5$)$_3$ (IV) | $-4.52^a$ | $(-134$, $-161$, and $-166)^a$ | 1.473(4) | 10 |
| 2      | Silaaldheyde, L'Si(H)=O → B(C$_6$F$_5$)$_3$ (VIII) | $-4.70^a$ | $(-132$, $-162$, and $-165)^a$ | 1.503(3) | 12g |
| 3      | Silaformyl chloride, IPr-SiH(Cl)=O → B(C$_6$F$_5$)$_3$ (IX) | $-5.28^e$ | $(-134$, $-163$, and $-166)^f$ | 1.492(3) | 12c |
| 4      | Silaacid anhydride, [[PhC(Ph-Bu)][Si(=O)B(C$_6$F$_5$)$_3$]-O-Si(Ph)]-[=O=B(C$_6$F$_5$)$_3$]-[i-(Ph-Bu)]-[H:N-Bu]-[H:N-Bu]-[CPh] (X) | $(3.99$, and $-5.46)^e$ | $(-134$, $-135$, $-164$, $-165$, $-166$, and $-169)^f$ | 1.493(3), and 1.488(3) | 12d |
| 5      | Monoalumoxane, L*Al=O → B(C$_6$F$_5$)$_3$ (XI) | $-4.83^d$ | $(-134$, $-164$, and $-166)^e$ | 1.444(3) | 20 |
| 6      | Boraacid chloride, IPr-B(C$_6$F$_5$) =O → B(C$_6$F$_5$)$_3$ (XII) | $-2.7^f$ | $(-131$, $-160$, and $-165)^f$ | 1.518(3) | 21 |
| 7      | B(C$_6$F$_5$)$_3$ | $-2.30^a$ | $(-127$, $-143$, and $-160)^a$ | $-$ | 19 |
| 8      | Germaacid chloride, [i-Bu]$_2$ATIGe(O)(Cl) → B(C$_6$F$_5$)$_3$ (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$_6$F$_5$)$_3$ (2) | $-2.61^d$ | $(-132$, $-160$, and $-165)^a$ | 1.497(3) | This work |
| 10     | N-Germaacetyl pyrrole, [i-Bu]$_2$ATIGe(O)(NC$_4$H$_4$) → B(C$_6$F$_5$)$_3$ (3) | $-2.72^a$ | $(-133$, $-159$, and $-165)^a$ | 1.494(6) | This work |
| 11     | Germanone, [i-Bu]$_2$ATIGe(O)(CCPh) → B(C$_6$F$_5$)$_3$ (4) | $-2.79^a$ | $(-133$, $-161$, and $-165)^a$ | 1.489(4) | This work |
| 12     | Germanone, [i-Bu]$_2$ATIGe(O)(O=Bu) → B(C$_6$F$_5$)$_3$ (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$_6$F$_5$)$_3$ (6) | $-3.12^a$ | $(-133$, $-160$, and $-165)^a$ | 1.481(3) | This work |
| 14     | Germaacid thioester, [i-Bu]$_2$ATIGe(O)(SPh) → B(C$_6$F$_5$)$_3$ (10) | $-2.73^d$ | $(-133$, $-160$, 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$_5$/THF-d$_8$. $^e$ In C$_6$D$_6$. $^f$ In C$_6$D$_6$. $^g$ In C$_6$D$_6$.

bis(2,6-diisopropylphenyl)imidazol-2-ylidine, L$^*$ = Et$_2$-NCH$_2$CH$_2$N(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$_6$F$_5$)$_3$ (Table 1), which indicates the shielding of boron and fluorine atoms by electron donation by oxygen atoms. This result is similar to that observed for compounds 1–6 and 10, containing a Ge=O → B(C$_6$F$_5$)$_3$ 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 $^{25}$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). 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 $\pi(C_6F_5) \rightarrow \pi^*(ATT)$, $\pi(C_6F_5) \rightarrow \pi^*(ATT)$ and $\pi(F) + \pi(C_6F_5) \rightarrow \pi^*(ATT)$ transitions, respectively (Table S1; see the ESI$^*$ for details). Furthermore, there are two high-energy transitions in each of these compounds with $\lambda_{max}$ 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$^{[a,b]}$ + LUMO$^{[a,c]}$ → LUMO$^{[a,b]}$. The 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 S3–S62, Tables S2–S5, and Experimental section; see the ESI†). Compounds 1–4 and 6 crystallised in the triclinic space group P1 (Tables S3 and S4; see the ESI†). Compounds 5, 7, and 10 crystallised in the monoclinic space groups P21/n, P212121, and P21/c, respectively (Table S4; see the ESI†).

The molecular structures of compounds 1–7 and 10 [Fig. 2 (1), 3 (4), 4 (10), S37 (2), S58 (3), S59 (5), S60 (6), and S61 (7)] confirmed the presence of a YGe=O → B(C6F5)3 moiety [Y = Cl (1), OSIh3 (2), NC6H4 (3), CCPh (4), Oc-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 germanacyl 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=Nligand 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 (1.179 (2) Å; Y = OSIh3), and 3 (1.820(4) Å; Y = NC6H4) 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 germainone IV, in comparison to the electron-donating i-Pr group bound to the germanium atom of germainone IV, the Cl, OSIh3, NC6H4, CCPh, and SPh atom/group bound to the germanium atom in germaacid chloride 1, germaester 2, N-germaacyl pyrrole 3, germynone 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 germainones 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). These data also reveal that relative to the polarisation of the Ge=O bond in germainone

![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–C1l 2.117(1), Ge1–N1 1.831(5), Ge1–N2 1.846(3), O1–Ge1–N1 111.60(1), O1–Ge1–N2 116.79(1), O1–Ge1–C1l 112.25(9), B1–O1–Ge1 134.6(2), N2–Ge1–N1 87.46(1), N1–Ge1–C1l 116.19(1), N2–Ge1–C1l 110.52(1). Data collection temperature: 100 K.](Image 357x119 to 500x284)

![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.](Image 14x290 to 26x354)
IV, the same bonds in germacrylic chloride 1, germaester 2, N-germacrylic pyrrole 3, germarynone 4, and germaeryl thiocyste 10 are less polarised due to the electron-withdrawing effect of the Cl, OSiPh₃, NC₃H₄, CCPF, and SPh atoms/groups bound to the germanium atom, respectively. A consequence of the increased interaction between the germanium and oxygen atoms of the gemacryl 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(C₆F₅)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 gemacryl IV (1.473(4) Å). 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 boracryl chloride [XII 1.518(3); M = B] with an M=O → B(C₆F₅)₃ bond (Table 1). However, in the monolamoxane XI with an Al=O → B(C₆F₅)₃ bond, the O → B bond is shorter (1.441(4) 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 was slightly longer than the Ge=O bond in the base-stabilised germanones [L²⁺Ge=O]²⁻ + CH [(C=CH₂)(CMe)[NAr]2] 1⁻ = [([{MeCN(Me)]Cl₂]} III, [([MeCN(i-Pr)]₂Cl] (XIV), 4-(Me₂N)ₐ-C₆H₄N (XV)] without an acceptor at an oxygen atom (1.646(2)–1.672(3) Å) and shorter than the Ge–O single bonds in gemacryl-m-o xo 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) 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 sp² and sp³ hybrid orbitals of germanium with the sp³ and sp³.66 hybrid orbitals of oxygen, respectively (Fig. 5 and Table S6; see the ESI†). In compounds 2 and 3, the sp².53 and sp².43 hybrid orbitals of germanium overlap with the sp³ and sp³.57 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 germacrylic 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–NₓTAI 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 sp³ and sp³.29 (Fig. 6d; 44.8 kcal mol⁻¹) and sp³.29 (Fig. 6d; 43.6 kcal mol⁻¹) orbitals of oxygen and the π* orbital of the Ge–Nₓ bond. Compounds 2, 3, and 10, instead of showing the aforementioned n lone pair of electrons on oxygen) to σ*π n orbital interactions, showed strong NBO donor-acceptor interactions from the s, p, or sp³ orbitals of oxygen atoms to vacant s, p or sp³ 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 between the p orbital of oxygen and the σ* orbital of the Ge–S bond (27.9 kcal mol⁻¹) (Fig. 6g). In comparison, germarynone IV showed three σ interactions: two O → Ge interactions and one O → σ*(Ge–CₓPy) interaction; these interactions result in a total stabilisation energy of 236.3 kcal mol⁻¹. 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 germarynone IV, which is due to the difference in the nature of the atoms/moieties bound to germanium atom in these compounds (–Cl, –OSiPh₃, –NC₃H₄, 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 germarynone IV (0.70) (Table S6; see the ESI†). A similar bond order (0.7955) was calculated for silaalddehyde II (with BEt₃ 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. In compounds 1, 2, and 10, the HOMO is localised on the phenyl ring of the B(C₆F₅)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 germarynone IV (334.9 kcal mol⁻¹), 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) sp³ orbitals of nitrogen atoms of the ATI ligand to vacant s,
p or sp* orbitals of germanium in compounds 1–3 and 10 (Fig. S66a, b, S67a–d, S68a–d, and S69a–d; see the ESI‡); (b) N<sub>AX</sub> orbitals to the σ* orbital of the Ge–Cl bond in compound 1 (Fig. S66c and d; see the ESI‡) and N<sub>AX</sub> 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–Cl/Ge–S bonds.
N\textsubscript{ATI} bonds in compound 1 (Fig. S66e and f; see the ESI\textsuperscript{‡}). Owing to the interactions of types [b] and [c], the energies of the \(\sigma^*\) orbital of the Ge–Cl bond in compound 1, \(\pi^*\) orbitals of the Ge–N\textsubscript{ATI} bonds in compound 1, and the \(\sigma^*\) 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)\textsuperscript{25} was performed using \{Y–Ge=O \rightarrow B(C\textsubscript{6}F\textsubscript{5})\subscript{3}\} (Y = Cl (1), OSI\textsubscript{Ph} (2), NC\textsubscript{2}H\textsubscript{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\textsuperscript{‡}).

Conclusions

Donor–acceptor-stabilised germaacetyl chloride ([i-Bu]\textsubscript{2}ATIGe(O)(OSiPh\textsubscript{3})] (1), germaester ([i-Bu]\textsubscript{2}ATIGe(O)(OSiPh\textsubscript{3})] (2), and N-germaacetyl pyrrole ([i-Bu]\textsubscript{2}ATIGe(O)(NC\textsubscript{2}H\textsubscript{4})] (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 \rightarrow B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} moiety to afford germaonyle (i-Bu)\textsubscript{2}ATIGe(O)(CCPh) \rightarrow B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (4), germaester (i-Bu)\textsubscript{2}ATIGe(O)(OR=Bu) \rightarrow B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (5), germaester (i-Bu)\textsubscript{2}ATIGe(O)(OR=Ph) \rightarrow B(C\textsubscript{6}F\textsubscript{5})\textsubscript{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 germaacarboxylic 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.

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