Showcasing research from Professor S. Nagendran’s laboratory, Department of Chemistry, Indian Institute of Technology Delhi (IIT Delhi), New Delhi, India.

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).

As featured in:

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

Mahendra Kumar Sharma, a Soumen Sinhababu, b Pritam Mahawar, c a Goutam Mukherjee, d,b Bhawana Pandey, d,b Gopalan Rajaraman and Selvarajan Nagendran c,a

Germaacid chloride, germaester, and N-germaacyl pyrrole compounds were not known previously. Therefore, donor–acceptor-stabilised germaacid chloride (i-Bu2ATIGe(O)(Cl) → BC6F5, 1), germaester (i-Bu2ATIGe(O)(OSiPh3) → BC6F53, 2), and N-germaacyl pyrrole (i-Bu2ATIGe(O)(NC6H4-H2) → BC6F53, 3) compounds, with Cl–Ge=O, Ph3SiO–Ge=O, and C6H4N–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 germaynone (i-Bu2ATIGe(O)(CCPh) → BC6F53, 4), germaester (i-Bu2ATIGe(O)(O)(Bu) → BC6F53, 5), and germanone (i-Bu2ATIGe(O)(R) → BC6F53 (R = Ph, 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 Ph3SiOLi 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-Bu2ATIGe(O)(SPh) → BC6F53 (10)). Furthermore, the attempted syntheses of germaamides and germa carboxylic 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)OC(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 (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. 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-naac]2Si(Cl) = O (I)] through the reaction of the silylene (N-naac)2SiCl with N2O (Chart 1) [[N-naac]2Ar = HC([Me2N]C[Ar]N)2; R = 2,6-iPr2C6H3]. The metathesis reactions of I with K[Et3BH] and KOT-Bu afforded a silaaldehyde [[N-naac]2ArSi(H) = O → BEt3 (II)]

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

a Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110 016, India. E-mail: ssisin@chemistry.iitd.ac.in
b Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

† 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 1564826–1564834, 1564836, and 1851011–1851015. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc05380d
and a silaester \([N\text{-nacnac}]^\text{Si}(\text{Ot-Bu})\equiv \text{O}\) (III), respectively (Chart 1).

Surprisingly, such analogues of germanium \([L\text{Ge}(\text{O})\ Y]\) \(L = \text{a monoanionic ligand}; \ Y = \text{H (germaaldehyde), Cl (germaacid chloride), OR (germaester), NR}_2\) (germaaamide), OH (germacarboxylic acid), and \([\text{OGe(O)OL}]\) 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 \(\text{Ge}=\text{O}\) bond. Owing to our continued interest in the chemistry of germanium, we were able to isolate the Lewis acid (LA) complexes \((i-\text{Bu})_2\text{ATIGe}(\text{i-Pr})\) (1), germaester \((i-\text{Bu})_2\text{ATIGeO}(\text{OSiPh}_3)\) \to B\([C_6F_5]_3\) (2), and \(N\)-germaacyl pyrrole \((i-\text{Bu})_2\text{ATIGeO}(\text{N}C_4\text{H}_4)\) \to B\([C_6F_5]_3\) (3). Compound 3 was obtained during our search for stable germaamides.

To synthesise a germaacid chloride, oxidation of the germylene monochloride\(^{13}\) \((i-\text{Bu})_2\text{ATIGeCl}\) (G1) with \(N\text{O}_2\) was carried out in tetrahydrofuran at room temperature. However, germylene G1 did not react with \(N\text{O}_2\) at room temperature, and therefore, this reaction was performed at higher temperatures. Germylene G1 reacted with \(N\text{O}_2\) at 60 °C in tetrahydrofuran and afforded the germanium \(\mu\)-oxo dimer \([\{i-\text{Bu}\}2\text{ATIGeCl}(\mu\text{-O}\})_2\) (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 \(\text{ATI}\) ligand salt \([\text{ATI}H]^+\text{Cl}^−\), and lower temperatures resulted in lower yields of \(\mu\)-oxo dimer D1. Based on the successful conversion of a germanium \(\mu\)-oxo dimer \([\{i-\text{Bu}\}_2\text{ATIGe}(\mu\text{-Pr})\](\mu\text{-O})\] (D) containing Ge–C bonds into donor–acceptor-stabilised germanones IV–VII through the reaction of D with Lewis acids, we planned to react geranium \(\mu\)-oxo dimer D1 containing Ge–Cl bonds with B\([C_6F_5]_3\). To our surprise, treatment of \(\mu\)-oxo dimer D1 with two equivalents of B\([C_6F_5]_3\) in toluene for 2 h at room temperature yielded the first example of a donor–acceptor-stabilised germaacid chloride \([i-\text{Bu}]_2\text{ATIGeO}(\text{Cl})\) \to B\([C_6F_5]_3\) (1) in quantitative yield (Scheme 1). This accomplishment inspired us to determine whether hitherto unknown germaesters and germamides 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\(^{15}\) \([i-\text{Bu}]_3\text{ATIGeOSiPh}_3\) (G2) was reacted with \(N\text{O}_2\) in tetrahydrofuran at 60 °C for 2 h to obtain the germanium \(\mu\)-oxo dimer \([\{i-\text{Bu}\}_2\text{ATIGeOSiPh}_3\}(\mu\text{-O})\] (D2). The reaction of \(\mu\)-oxo dimer D2 containing Ge–OSiPh\(_3\) bonds with two equivalents of B\([C_6F_5]_3\) in toluene at room temperature afforded the first example of a donor–acceptor-stabilised germaester, namely, \([i-\text{Bu}]_3\text{ATIGeO}(\text{OSiPh}_3)\) \to B\([C_6F_5]_3\) (2) (Scheme 2), and demonstrated the suitability of the germanium \(\mu\)-oxo dimer route for the preparation of germaesters. To extend this route for the synthesis of germamides, a germanium \(\mu\)-oxo dimer with \(\text{Ge}NR_2\) moieties is required. Two such germanium \(\mu\)-oxo dimers, \([\{i-\text{Bu}\}_2\text{ATIGeN}(\text{H})\text{Ph}(\mu\text{-O})\] (D3) and \([\{i-\text{Bu}\}_2\text{ATIGeN}(\text{Me})\text{Ph}(\mu\text{-O})\] (D4), were obtained through the reaction of the amidogermynes \([i-\text{Bu}]_2\text{ATIGeN}(\text{H})\text{Ph}\) (G3) and \([i-\text{Bu}]_2\text{ATIGeN}(\text{Me})\text{Ph}\) (G4) with \(N\text{O}_2\) at 60 °C for 2 h in tetrahydrofuran (Scheme 3). However, the reaction of \(\mu\)-oxo dimers D3 and D4 with two equivalents of B\([C_6F_5]_3\) resulted in the amine → borane adducts \(\text{PhNH}_2\to B\([C_6F_5]_3\) and \(\text{Ph}(\text{Me})\text{NH}\to B\([C_6F_5]_3\), respectively, along with an unidentifiable oily material instead of the expected germamides (Scheme 3). These reactions suggest that the synthetic route discussed above is not suitable for the isolation of donor–acceptor-stabilised germamides. 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 B\([C_6F_5]_3\). 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 \([\{i-\text{Bu}\}_2\text{ATIGeN}C_4\text{H}_4(\mu\text{-O})\] (D5) with two Ge–NC\(_4\text{H}_4\) 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 \(\mu\)-oxo dimer, and (b) products with a Ge=O → B\([C_6F_5]_3\)/Ge-OTMS → B\([C_6F_5]_3\) moiety are given a linear/arbitrary numerical numbering pattern (starting from 1).

**Scheme 2** Synthesis of donor–acceptor-stabilised germaester 2.
the N-germylene pyrrole (i-Bu)₂ATIGe(NC₄H₄) (G5) with N₂O in tetrahydrofuran at 60 °C for 2 h (Scheme 4). Treatment of μ-oxo dimer D5 with two equivalents of B(C₆F₅)₃ in toluene at room temperature resulted in the first donor–acceptor-stabilised N-germaacetyl pyrrole, (i-Bu)₂ATIGe(O)(NC₄H₄) → B(C₆F₅)₃ (3) in quantitative yield (Scheme 4). The feasibility of isolating N-germaacyl pyrrole as a stable species proves that the aforementioned hypothesis of the interference of lone pairs of electrons on the nitrogen atoms of the NR₂ 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(C₆F₅)₃. 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 germaacetyl chloride, germaester, and N-germaacyl pyrrole, a range of Lewis acids (such as BF₃, GeCl₂, and SnCl₄) were screened. However, all of these reactions were typically unsuccessful until now (see the ESI† for details). Surprisingly, the germanium-μ-oxo dimers (i-Bu)₂ATIGe(μ-Pr)(μ-O)₂ (D) with Ge–i-Pr bonds was insensitive to the nature of the Lewis acid used. Thus, it reacted smoothly with B(C₆F₅)₃, ZnCl₂, SnCl₂, and GeCl₂ to afford the donor–acceptor-stabilised germanones IV, V, VI, and VII, respectively.

As the germaanalogues 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 germaaynone (i-Bu)₂ATIGe(O)(CCPH) → B(C₆F₅)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; thus, 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)₂ATIGe(O)(Or-Bu) → B(C₆F₅)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/phenyl methyl lithium yielded N-germaacetyl pyrrole 3 and the germanones (i-Bu)₂ATIGe(O)(Ph) → B(C₆F₅)₃ (6) (i-Bu)₂ATIGe(O)(Me) → B(C₆F₅)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 germaamine (i-Bu)₂ATIGe(NTMS)(OTMS) → B(C₆F₅)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 Me₃SiCl in
germaacyl pyrrole 3

substitute the pyrrolide of thiophenol can not known among the analogous silicon compounds.

in toluene at room temperature generated the germaesters 4

maacid chloride 1

from a suitable precursor was

N

demonstrated that the thiophenoxide moiety of thiophenol can

Interconversion between germaesters 4 and 5 is

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 [ATTIH]⁺[OH](B(C₆F₅)₃)⁻.

Compounds D1, D3–D5, 1–7, and 10 were characterised through multinuclear NMR spectroscopic (¹H, ¹¹B, ¹³C, ¹⁹F, 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, germanylene monochloride G1 and N-germanyle 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 electropositivity 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 ppm¹⁰,¹⁳ and −4.52 ppm,¹⁰ 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 silaaldehyde L’Si(H)=O → B(C₆F₅)₃ (VIII),¹²⁷ silaformyl chloride IPr-SiH(Cl) =O → B(C₆F₅)₃ (IX),¹²⁷ silaacid anhydride [(PhC(t-Bu)N)₂]⁺Si(=O) → B(C₆F₅)₃-O-Si(H)=O → B(C₆F₅)₃(Nr-Bu)(HNr-Bu)CPh) (X),¹³⁴ monoalumoxane L’Al=O → B(C₆F₅)₃ (XI),¹³⁰ and boraacid chloride IPr → B(Cl)=O → B(C₆F₅)₃ (XII)¹³¹ have B(C₆F₅)₃ as the acceptor in the M=O → B(C₆F₅)₃ moiety [M = Si VIII, IX, X; Al VII, 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$_6$F$_5$)$_3$ and other related compounds of group 13–14 elements with an M=O $\rightarrow$ B(C$_6$F$_5$)$_3$ moiety (M = Ge, Si, Al, B)

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Compound</th>
<th>$^{11}$B NMR chemical shift (ppm)</th>
<th>$^{19}$F NMR chemical shift (ppm)</th>
<th>O–B bond length (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Germanone, (i-Bu)$_2$ATIGe(i-Pr)(O) $\rightarrow$ B(C$_6$F$_5$)$_3$ (IV)</td>
<td>$-4.52^a$</td>
<td>$(-134, -161, and -166)^a$</td>
<td>$1.473(4)$</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Silaaldhyde, L’Si(H)=O $\rightarrow$ B(C$_6$F$_5$)$_3$ (VII)</td>
<td>$-4.70^a$</td>
<td>$(-132, -162, and -165)^a$</td>
<td>$1.503(3)$</td>
<td>12a</td>
</tr>
<tr>
<td>3</td>
<td>Silaformyl chloride, IPr-SiH(Cl)=O $\rightarrow$ B(C$_6$F$_5$)$_3$ (IX)</td>
<td>$-5.28^a$</td>
<td>$(-134, -163, and -167)^a$</td>
<td>$1.492(2)$</td>
<td>12c</td>
</tr>
<tr>
<td>4</td>
<td>Silaacyclic anhydride, ${[PhC(i-BuN)]_2SiO=O=B(C_6F_5)_3}$-SiO=O $\rightarrow$ B(C$_6$F$_5$)$_3$ (X)</td>
<td>$(-3.99, and -5.46)^a$</td>
<td>$(-134, -135, -164, -165, -167$, and -168$)^a$</td>
<td>$1.493(3)$ and $1.488(3)$</td>
<td>12d</td>
</tr>
<tr>
<td>5</td>
<td>Monoalumoxane, L’*Al=O $\rightarrow$ B(C$_6$F$_5$)$_3$ (XI)</td>
<td>$-4.83^a$</td>
<td>$(-134, -164, and -166)^a$</td>
<td>$1.444(3)$</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>Boraacid chloride, IPr-B(Cl)=O $\rightarrow$ B(C$_6$F$_5$)$_3$ (XII)</td>
<td>$-2.7^a$</td>
<td>$(-131, -160, and -165)^a$</td>
<td>$1.518(3)$</td>
<td>21</td>
</tr>
<tr>
<td>7</td>
<td>B(C$_6$F$_5$)$_3$</td>
<td>$-2.30^a$</td>
<td>$(-127, -143, and -160)^a$</td>
<td>—</td>
<td>19</td>
</tr>
<tr>
<td>8</td>
<td>Germaniacid chloride, (i-Bu)$_2$ATIGe(C)(Cl) $\rightarrow$ B(C$_6$F$_5$)$_3$ (1)</td>
<td>$-2.46^a$</td>
<td>$(-133, -159, and -165)^a$</td>
<td>$1.493(5)$</td>
<td>This work</td>
</tr>
<tr>
<td>9</td>
<td>Germanium, (i-Bu)$_2$ATIGe(O)(i-Pr)(O) $\rightarrow$ B(C$_6$F$_5$)$_3$ (2)</td>
<td>$-2.61^a$</td>
<td>$(-132, -160, and -165)^a$</td>
<td>$1.497(3)$</td>
<td>This work</td>
</tr>
<tr>
<td>10</td>
<td>N-Germanacyl pyrrole, (i-Bu)$_2$ATIGe(O)(NC$_4$H$_4$) $\rightarrow$ B(C$_6$F$_5$)$_3$ (3)</td>
<td>$-2.72^a$</td>
<td>$(-133, -159, and -165)^a$</td>
<td>$1.494(6)$</td>
<td>This work</td>
</tr>
<tr>
<td>11</td>
<td>Germanone, (i-Bu)$_2$ATIGe(O)(CCPh) $\rightarrow$ B(C$_6$F$_5$)$_3$ (4)</td>
<td>$-2.79^a$</td>
<td>$(-133, -161, and -165)^a$</td>
<td>$1.489(4)$</td>
<td>This work</td>
</tr>
<tr>
<td>12</td>
<td>Germanium, (i-Bu)$_2$ATIGe(O)(Or-Bu) $\rightarrow$ B(C$_6$F$_5$)$_3$ (5)</td>
<td>$-2.44^a$</td>
<td>$(-132, -160, and -165)^a$</td>
<td>$1.505(3)$ and $1.502(3)$</td>
<td>This work</td>
</tr>
<tr>
<td>13</td>
<td>Germanone, (i-Bu)$_2$ATIGe(O)(Ph) $\rightarrow$ B(C$_6$F$_5$)$_3$ (6)</td>
<td>$-3.12^a$</td>
<td>$(-133, -160, and -165)^a$</td>
<td>$1.481(3)$</td>
<td>This work</td>
</tr>
<tr>
<td>14</td>
<td>Germanacyle thioester, (i-Bu)$_2$ATIGe(O)(SPh) $\rightarrow$ B(C$_6$F$_5$)$_3$ (10)</td>
<td>$-2.73^a$</td>
<td>$(-133, -160, and -165)^a$</td>
<td>$1.501(5)$</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$ 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$_3$CH$_2$NC(Me)CH(Me)NCH$_2$CH$_2$N(Et)$_2$. 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 VII, 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 due to electron donation by oxygen atoms. This result is similar to that observed for compounds 1–6 and 10, containing a Ge=O $\rightarrow$ 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 VII, IX, X, and XI. In the $^{29}$Si NMR spectra of germane 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 $\pi(CF_3)\rightarrow\pi^*_{(ATT)}$, $\pi(CF_3)\rightarrow\pi^*_{(ATT)}$, and $n(p)+\pi(CF_3)\rightarrow\pi^*_{(ATT)}$ 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 $\rightarrow$ LA moieties (M = Ge, Si) have rarely been studied. For germanone VII with a Ge=O $\rightarrow$ 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[$\pi_{(ATT)}^* + \pi_{(N,O,Cl)}^* + \pi_{(C=Cl)}^* \rightarrow$ LUMO[$\pi_{(ATT)}^*$]
The molecular structures of compounds 1–7 and 10 [Fig. 2 (1), 3, 4, 6, 7, 9, 10] confirmed the presence of a \( \text{Y} \)Ge=O → B(C_6F_5)_3 moiety \( \text{Y} = \text{Cl} (1), \text{OSiPh}_3 (2), \text{NC}_3H_4 (3), \text{CCPh} (4), \text{OCBu} (5), \text{Ph} (6), \text{Me} (7), \) and \( \text{SPh} (10) \). In these compounds, the germanium atom has a distorted tetrahedral geometry with two ATI lig!##d nitrogens, one germaacyl oxygen, and one Cl (1), O (2), N (3), C (4), O (5), C (6), or S (10) atom. The average length of the Ge\(-\text{N}{\text{ligand}}\) bonds in compounds 1 (1.838 Å), 2 (1.848 Å), and 3 (1.843 Å) is shorter than that in their precursors \( \text{D1} (1.931 \text{ Å}), \text{D2} (1.946 \text{ Å}), \) and \( \text{D5} (1.942 \text{ Å}) \), respectively. Similarly, the Ge\(-\text{Y} \) bond in compounds 1 (2.117(1) Å; \( \text{Y} = \text{Cl} \)), 2 (1.719(2) Å; \( \text{Y} = \text{OSiPh}_3 \)), and 3 (1.820(4) Å; \( \text{Y} = \text{NC}_3H_4 \)) is also shorter than that in compounds \( \text{D1} (2.20(8) \text{ Å}), \text{D2} (1.767(3) \text{ Å}), \) and \( \text{D5} (1.892(3) \text{ Å}) \), respectively. These differences are due to the electrophilicity of the oxygen atom in the Ge\(-\text{O} \) → B(C_6F_5)_3 moiety of compounds 1, 2, and 3 being higher than that of the oxygen atoms in the Ge\(\mu\text{-O})Ge moiety of \( \text{D1}, \text{D2}, \) and \( \text{D5} \), 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 germa!##none IV, the Cl, OSiPh_3, NC_3H_4, 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\(-\text{O} \) bond. Therefore, the length of the formal Ge\(-\text{O} \) 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). These data also reveal that relative to the polarisation of the Ge\(-\text{O} \) bond in germaacid chloride 1, the Ge\(\mu\text{-O})Ge moiety of \( \text{D1}, \text{D2}, \) and \( \text{D5} \), and the Ge\(-\text{N}\) bonds in compounds 1, 2, and 3 make the Germanium atom more electrophilic, thus increasing the interaction between the germanium and oxygen atoms of the Ge\(-\text{O} \) bond.

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–Cl6 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–Cl6 113.63(12), B1–O1–Ge1 151.46(2), N2–Ge1–N1 86.91(1), N1–Ge1–Cl6 112.42(2), N2–Ge1–Cl6 116.98(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–Cl6 1.708(2), Ge1–N1 1.832(3), Ge1–N2 1.724(2), O1–Ge1–N1 111.60(1), O1–Ge1–N2 116.79(1), O1–Ge1–Cl6 112.25(9), B1–O1–Ge1 134.6(2), N2–Ge1–N1 87.46(1), N1–Ge1–Cl6 116.19(1), N2–Ge1–Cl6 110.52(1). Data collection temperature: 100 K.
IV,10 the same bonds in germaacid chloride 1, germaester 2, N-
germaacryl pyrrole 3, germahyone 4, and germaacryl thioester 10
are less polarised due to the electron-withdrawing effect of the
Cl, OSIPh3, NC6H4i, CCPh, and SP atoms/groups bound to the
germanium atom, respectively. A consequence of the increased
interaction between the germanium and oxygen atoms of the
germaacid 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 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
boracaid chloride [XII 1.518(3); M = B] with an M=O → 
B(C6F5)3 bond (Table 1).12g,12d,12c,21 However, in the mono-
alumoxane20 XI with an Al=O → B(C6F5)3 bond, the O → B
bond is shorter (1.441(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 germanenes
[L52Ge=O=O] â = [CH([C=CH2](Me)[NAr]2)]; 1â = [([Me
CN][Me2]2)Cl] (XIII), [(MeCN][Pr],[Me]2Cl] (XIV), 4-Me2N-C6H4N
(VX) without an acceptor at an oxygen atom (1.646(2)–1.672(3)
Å) and shorter than the Ge–O single bonds in germanium–mu-oxid
dimers D1, D2, and D5 (1.848(2)–1.787(3) Å).22

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
sp2.59 and sp bonding orbitals of germanium with the sp².62 and
sp².66 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 sp².49 and sp².57 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†).22

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–NATI 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 sp²3.82 (Fig. 6d; 44.8 kcal mol⁻¹) and
sp²0.29 (Fig. 6e; 43.6 kcal mol⁻¹) orbitals of oxygen and the π*
orbital of the Ge-N 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 sp² orbitals of oxygen atoms
to vacant s, p, or sp² orbitals of the germanium atoms (Fig. 6f–h
[2], Fig. 6i–1 [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, germaacid IV
showed three σ interactions: two O → Ge interactions and one O →
σ*(Ge–C–Pr) interaction; these interactions result in a total
stabilisation energy of 236.3 kcal mol⁻¹.10 Thus, the total stabilisa-
tion 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 germaacid IV, which is due to the difference in the nature of
the atoms/moieties bound to germanium atom in these
compounds (–Cl, –OSiPh3, –NC6H4i, and –SPh, respectively)
instead of an i-Pr group. The Wiberg bond index (WBI) calcula-
tions 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
germaacid IV (0.70) (Table S6; see the ESI†). A similar bond
order (0.7955) was calculated for silicaaldehyde II (with B=O as
an acceptor bond to the oxygen atom); for silicaaldehyde I and
c렇iaenser III (without any acceptor bond to the oxygen atom),
the calculated WBI values are 1.0993 and 1.0441, respectively.22
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 germaacid 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) sp² orbitals of nitrogen atoms of the ATI ligand to vacant s,
The text mentions the interaction of 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\(^+\)); N\(_{\text{ATI}}\) orbitals to the \(\sigma^*\) orbital of the Ge–Cl bond in compound 1 (Fig. S66c and d; see the ESI\(^+\)) and N\(_{\text{ATI}}\) orbitals to the \(\sigma^*\) 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 \(\pi^*\) orbitals of Ge–Cl bond. The 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.

Fig. 6  Pictorial view of NBO donor–acceptor interactions between p or sp\(^x\) (\(x = 3.82, 0.29\)) orbitals of oxygen and the \(\sigma^*\) orbital of the Ge–Cl bond/\(\pi^*\) orbitals of the Ge–N\(_{\text{ATI}}\) 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 \(\sigma^*\) orbital of Ge–S bond in compound 10 (q). Energy values are given in kcal mol\(^{-1}\).
the isolation of these compounds as stable species in the
obtained during these endeavours will expose germaesters and germaacid chlorides is exposed. B(C6F5)3 (R)
accepting electrons donated by the O atom of the Ge–DST (New Delhi, India, for funding (EMR/2017/005519)
and DST-FIST for establishing single-crystal X-ray diffraction (SR/FST/CSII-027/2014) and HRMS (SR/FST/CS-1-195/2008) facil-
ies in the Department of Chemistry, IIT Delhi.

Conclusions

Donor–acceptor-stabilised germaacial chloride (i-Bu)2ATIGe(O)(O)(Cl) → B(C6F5)3 (1), germaester (i-Bu)2ATIGe(O)(OSiPh3) → B(C6F5)3 (2), and N-germaacial pyrrole (i-Bu)2ATIGe(O)(NC4H4) → B(C6F5)3 (3) compounds were successfully isolated as stable species for the first time. Compounds 1, 2, and 3 can undergo nucleophilic substitution reactions with any disturbance to the Ge=O → B(C6F5)3 moiety to afford germaonoyone (i-Bu)2ATIGe(O)(NC4H4), germaester (i-Bu)2ATIGe(O)(OC6H5), and germaester (i-Bu)2ATIGe(O)(OR)-Bu → B(C6F5)3 (5), germaester (i-Bu)2ATIGe(O)(OR)-Bu → B(C6F5)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

M. K. S., P. M. and S. S. thank the Indian Institute of Technology Delhi (IITD), New Delhi, India, and the University Grants Commission (UGC), New Delhi, India, for research fellowships. S. N. thanks the SERB, Department of Science and Technology (DST), New Delhi, India, for funding (EMR/2017/005519) and DST-FIST for establishing single-crystal X-ray diffraction (SR/FST/CSII-027/2014) and HRMS (SR/FST/CS-1-195/2008) facilities in the Department of Chemistry, IIT Delhi.

Notes and references


22 CCDC 1564828 contains the crystallographic data for this paper.

