Germanium Compounds

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The Preparation of Complexes of Germanone from a Germanium μ-Oxo Dimer

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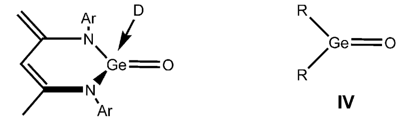
Dedicated to Professor T. K. Chandrashekar on the occasion of his 60th birthday

Abstract: *Complexes of germanone containing formal Ge=O→M bonds (M = Zn, B, Ge, Sn) were isolated and characterized. The compounds were prepared through a novel synthetic route using a germanium μ-oxo dimer **3** as the starting material. This method circumvents the need to employ germanones to prepare complexes of germanones.*

Germanones are heavier analogues of ketones ($R_2C{=}O$) and contain Ge=O bonds.[1–3] As a result of a high electronegativity difference and poor pπ–pπ overlap between oxygen and germanium atoms, the Ge=O bond is weak and reactive.[1–5] Therefore, compounds containing Ge=O bonds can be easily polymerized or oligomerized unless suitable steric and/or electronic stabilizations are available. For example, oxygenation of $Ge[N(SiMe_3)_2]_2$ affords the germanium μ-oxo dimer $[\{[(Me_3Si)_2N]_2GeO\}_2]$ and not the corresponding germanone.[6] Oxidative addition of oxygen (from an oxygen source) to stable germylenes is the typical approach for the isolation of stable germanones.[2,3] Driess and co-workers isolated germanones [LL′Ge=O] **I**–**III** (for all complexes $L = [CH\{(C{=}CH_2)(CMe)(NAr)_2\}]$, with Ar = 2,6-*i*-$Pr_2C_6H_3$; $L' = [\{(Me)CN(Me)\}_2C]$ (**I**), $L' = [\{(Me)CN(i\text{-}Pr)\}_2C]$) (**II**), $L' = 4\text{-}(Me_2N)\text{-}C_5H_4N$ (DMAP) (**III**); Figure 1) through the reaction of the corresponding germylenes [LL′Ge] with N_2O.[2] Tamao and co-workers synthesized germanone [$R_2Ge{=}O$] (**IV**; R = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl; Figure 1) by the oxygenation of a bulky germylene [R_2Ge].[3] As oxygen atoms in Ge=O bonds of germanones are electron rich, they can act as Lewis bases and form adducts/complexes with Lewis acids. Nevertheless, none of the germanones have been reported to form such stable complexes to date.[1–5] This issue has been successfully addressed in this Communication through the isolation of zinc, boron, germanium, and tin complexes (**4**, **5**, **6**, and **7**) of a germanone. Interestingly, this has been achieved through the use of a readily isolable germanium μ-oxo dimer $[\{(i\text{-}Bu)_2(ATI)Ge(i\text{-}Pr)(\mu\text{-}O)\}_2]$ (**3**; ATI = aminotroponiminate) as an alternate precursor to the synthetically challenging germanones.



IV

D = [{(Me)CN(Me)}$_2$C] (**I**)
[{(Me)CN(*i*-Pr)}$_2$C] (**II**)
4-(Me$_2$N)-C$_5$H$_4$N (**III**)
Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$

R = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl

Figure 1. Structure of germanones **I**–**IV**. The donor ligand (D) corresponds to ligand L′.

To isolate complexes of germanone, we planned to synthesize germanone $[(i\text{-}Bu)_2(ATI)Ge(O)(i\text{-}Pr)]$ [**A**] and react it with Lewis acids. To synthesize germanone [**A**], the following strategy was designed: a) conversion of germylene monochloride **1** into alkyl germylene **2**, and b) oxygenation of compound **2** to obtain compound [**A**]. Accordingly, alkyl germylene complex **2** was synthesized through a 1:1 reaction of germylene monochloride[7a] **1** with the Grignard reagent *i*-PrMgCl (2 M in tetrahydrofuran) in hexane at −78 °C (Scheme 1). After workup, compound **2** was isolated as a dark brown solid in 91 % yield. Compound **2** is stable under an inert atmosphere and soluble in common solvents, such as pentane, hexane, and toluene. However, **2** decomposes rapidly in chlorinated solvents such as chloroform and dichloromethane. With the successful isolation of compound **2**, its reaction with N_2O in tetrahydrofuran at room temperature for 15 min was carried out. Instead of the formation of desired compound [**A**], this reaction resulted in the formation of the germanium μ-oxo dimer $[\{(i\text{-}Bu)_2(ATI)Ge(i\text{-}Pr)(\mu\text{-}O)\}_2]$ (**3**, 86 % yield; Scheme 1).[7b–e] Compound **3** is stable under an inert atmosphere of nitrogen. As germanone [**A**] did not form, we thought of using germanium μ-oxo dimer **3** as a germanone substitute for the preparation of complexes of germanone [**A**]. Thus, reaction of compound **3** (1 equiv) with $ZnCl_2$ (2 equiv) in tetrahydrofuran at room temperature was carried out for 4 h. To our surprise, this reaction afforded the desired germanone-stabilized zinc chloride complex **4** as a yellow solid in 94 % yield (Scheme 2). To investigate whether compound **3** reacts in this manner only in the

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Supporting information for this article (including the experimental section, photophysical studies, computational details, and details of X-ray structural analysis) can be found under: http://dx.doi.org/10.1002/anie.201601445.

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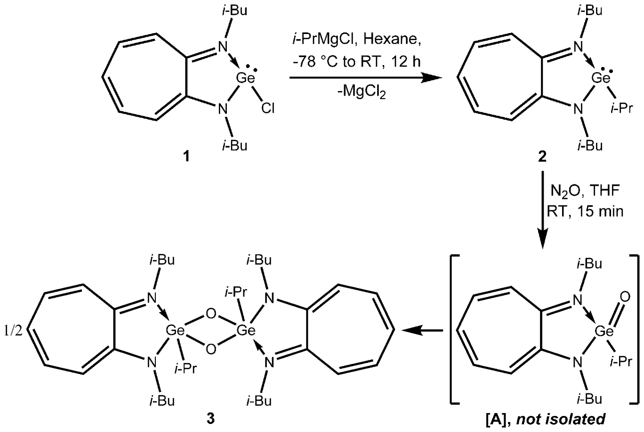
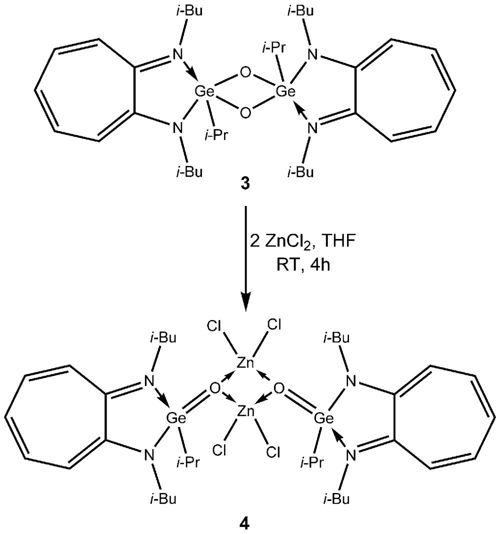
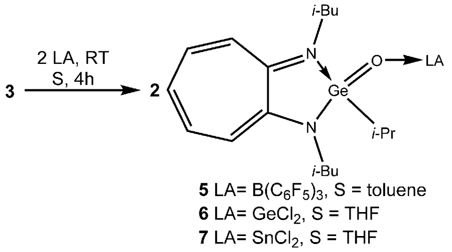


Scheme 1. Synthesis of *iso*-propyl germylene **2** and germanium μ-oxo dimer **3**.



Scheme 2. Synthesis of germanone-stabilized zinc chloride complex **4** through the reaction of germanium μ-oxo dimer **3** with zinc chloride.

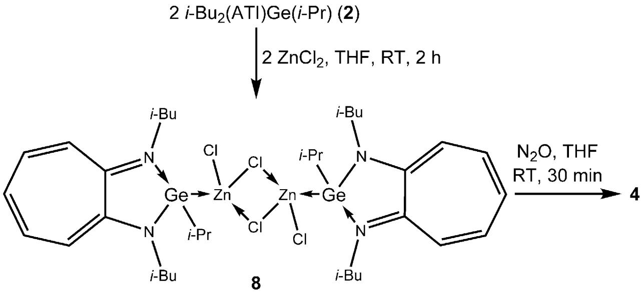


Scheme 3. Synthesis of germanone-stabilized boron, germanium, and tin complexes (**5**, **6**, and **7**).

presence of $ZnCl_2$, its reactions with other Lewis acids were carried out. Interestingly, reactions of compound **3** with $B(C_6F_5)_3$, $GeCl_2\cdot(1,4\text{-dioxane})$, and $SnCl_2$ at room temperature for 4 h gave germanone-stabilized boron(III) (**5**), germanium(II) (**6**), and tin(II) (**7**) complexes in 92 %, 94 %, and 93 % yields, respectively (Scheme 3). Thus, these reactions disclosed the generality of this route for the synthesis of complexes of germanone.

The reactions of compound **3** with Lewis acids can be considered to proceed through two different pathways: i) germanium μ-oxo dimer **3** first gets converted into germanone [**A**] in the reaction medium and then compound [**A**] forms complexes with Lewis acids; or ii) the oxygen atoms of germanium μ-oxo dimer **3** coordinate with Lewis acids, followed by dissociation of the Ge–O bonds as a result of the increased electrophilicity of oxygen atoms, affording complexes of germanone. To determine the most probable pathway, ^1H diffusion-ordered spectroscopy (DOSY) NMR studies at room temperature in $CDCl_3$ were carried out on compound **3**.[8] DOSY NMR studies revealed that germanium μ-oxo dimer **3** does not dissociate to germanone [**A**], as the calculated molecular weight of 720 g mol^{-1} is very close (−0.9 % error) to the molecular weight of compound **3** (726.2 g mol^{-1}; see Figure S1 in the Supporting Information). This conclusion is supported by theoretical studies where a prohibitively high energy requirement of 48.3 kcal mol^{-1} for the dissociation of germanium μ-oxo dimer **3** to the corresponding germanone [**A**] has been computed. On the basis of these, it can be proposed that complexes of germanone are formed through pathway ii (see Scheme S1 for a plausible mechanism). Furthermore, to evaluate the donor strength of germanone [**A**], as a representative study, reaction of complex **5** with a large excess of a strong donor (DMAP) was carried out at room temperature for 2 h in $CDCl_3$. Interestingly, no displacement of germanone [**A**] by DMAP was detected. This result reveals the strong binding of germanone [**A**] with a Lewis acid ($B(C_6F_5)_3$) and provides evidence for its stability.

The possibility to obtain complexes of germanone through oxygenation of a germylene→Lewis acid adduct, such as, germylene zinc chloride complex **8** (Scheme 4), was also examined. Compound **8** was synthesized as an orange solid in 96 % yield through an equimolar reaction of compound **2** with $ZnCl_2$ in tetrahydrofuran at room temperature for 2 h (Scheme 4). More remarkably, the reaction of compound **8** with N_2O occurred cleanly in tetrahydrofuran at room temperature for 30 min and afforded the zinc chloride complex **4** of germanone in 98 % yield (Scheme 4). Thus, this is another facile route for isolation of complexes of germanone that avoids the requirement of germanone as starting material.



8

Scheme 4. Synthesis of germylene zinc chloride complex **8** and its reaction with N_2O to afford the germanone-stabilized zinc chloride complex **4**.

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Compound **4** is poorly soluble in chloroform, dichloromethane, acetonitrile, and dimethyl sulfoxide. Compounds **5**–**8** are less soluble in toluene, but are freely soluble in tetrahydrofuran, chloroform, and dichloromethane. Compounds **4**–**8** are stable at room temperature under an inert atmosphere. Compounds **2**–**8** were characterized in solution using NMR (^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{119}Sn) spectroscopic studies. In the ^{1}H NMR spectrum of compound **2**, the resonance signals for the methyl protons of the *iso*-butyl and *iso*-propyl groups appeared as two doublets ($\delta = 0.98, 1.30$ ppm) and one doublet ($\delta = 0.78$ ppm), respectively. Signals for the methine protons of the *iso*-butyl and *iso*-propyl groups were seen as a multiplet in the range of $\delta = 2.06$–2.15 and 0.94–1.04 ppm, respectively. The diastereotopic methylene protons of the *iso*-butyl groups resonated as two double doublets ($\delta = 2.89$ and 3.00 ppm). Signals for the five seven-membered ring protons appeared as a triplet ($\delta = 5.86$ ppm), a doublet ($\delta = 5.93$ ppm), and a multiplet ($\delta = 6.45$–6.52 ppm). Compound **3** showed a similar splitting pattern for the *iso*-butyl and *iso*-propyl protons except the methylene protons which appear as a multiplet ($\delta = 3.63$–3.78 ppm). Signals for its seven-membered ring protons appeared as a triplet (6.32 ppm), a doublet (6.62 ppm), and a pseudotriplet (7.02 ppm). This splitting pattern of seven-membered ring protons is retained in compounds **4** ($\delta = 7.04$, 7.25, and 7.50 ppm), **6** ($\delta = 7.11$, 7.20, and 7.58 ppm), and **7** ($\delta = 7.06$, 7.16, and 7.55 ppm). Uniquely, these protons in compound **5** appeared as a multiplet ($\delta = 7.07$–7.23 ppm) and a doublet (7.57 ppm). The signals for the protons of the seven-membered ring in compounds **4**–**7** are downfield shifted in comparison to those of compound **3** and this is due to the electrophilicity of oxygen atoms upon binding with Lewis acids. This effect is also seen with the methine proton of the *iso*-propyl group in these compounds (**4**–**7**). Specifically, whereas the signal for this proton in compound **3** appears at $\delta = 1.19$–1.32 ppm, in compounds **4**, **5**, **6**, and **7** it is detected at $\delta = 2.52$, 2.31–2.41, 2.56–2.66, and 2.41–2.51 ppm, respectively. Compound **8** showed a splitting pattern similar to that of compound **2**. The ^{13}C NMR spectra of compounds **2**–**4** and **6**–**8** showed ten signals, whereas compound **5** showed thirteen signals as a result of the additional carbon atoms of the C_6F_5 groups. In the ^{11}B NMR spectrum of compound **5**, a resonance signal at $\delta = -4.52$ ppm is detected. The free Lewis acid $B(C_6F_5)_3$ showed a resonance signal at $\delta = -2.3$ ppm.[9] Similarly, through an examination of the ^{19}F NMR spectra, significant differences are evident in the chemical shifts of the signals for the fluorine atoms in compound **5** ($\delta = -134$, -161, and -166 ppm) and $B(C_6F_5)_3$ ($\delta = -128$, -143, and -160 ppm).[10] Additional evidence for the stability of complexes of germanone in solution was obtained through ^{1}H DOSY NMR experiments on compounds **4**–**5** (see Figure S2 for a representative example). The calculated molecular weights of 1032 and 847 g mol^{-1} for compounds **4** and **5** with +3.3 % and −3.2 % errors against their molecular weights of 998.8 and 875.1 g mol^{-1} support the structural integrity of these complexes in solution, respectively. In the ^{119}Sn NMR spectrum of compound **7**, a resonance signal at $\delta = -151$ ppm is detected which is considerably upfield shifted in comparison to that detected for $\mathrm{IPr}\rightarrow\mathrm{SnCl_2}$ ($\delta = -68.7$ ppm) ($\mathrm{IPr} = (\mathrm{HCNAr})_2\mathrm{C}$:, $\mathrm{Ar} = 2{,}6\text{-}{}^{i}\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$).[11] Representative optical spectroscopic studies were also carried out on compound **6** (see the Supporting Information for details). In the UV/Vis absorption spectrum, compound **6** absorbs at $\lambda = 283$, 365, and 437 nm (Figure S3). In the steady-state emission spectroscopic studies, compound **6** emits at $\lambda = 498$ nm when excited at a wavelength of $\lambda = 430$ nm (Figure S4). Time-resolved emission studies showed that the emission is fluorescence-based (excited state lifetime 0.69 ns, $\chi^2 = 1.16$). Theoretical studies show that the absorption maxima in the visible region is due to the HOMO–LUMO transition (Table S1, Figure S5).

Compounds **3**–**8** were further characterized by single-crystal X-ray diffraction studies (see the Supporting Information for details).[16] Compound **3** crystallized in the triclinic space group $P\bar{1}$ (Table S2). The germanium atoms are pentacoordinate with distorted square pyramidal geometries (geometry index $\tau = 0.042$; $\tau = 1$ for trigonal bipyramidal geometry, $\tau = 0$ for square pyramidal geometry; Figure S6).[12] In the planar Ge_2O_2 four-membered ring, Ge−O bond lengths (1.818(3) and 1.823(3) Å) are almost identical.[7b–e] Complexes **4**–**7** of germanone crystallized in the monoclinic, monoclinic, orthorhombic, and triclinic space groups $P2_1/c$, $P2_1/c$, $Pccn$, and $P\bar{1}$, respectively (Table S2). The molecular structures of these compounds (see Figure 2 and Figure 3 for compounds **4** and **6**, Figure S7 for compound **5**, and Figure S8 for compound **7**) reveal the presence of tetracoordinate germanium centers with distorted tetrahedral environments of two nitrogen, one carbon, and one oxygen atoms. The lengths of Ge=O bonds in compounds **4** (1.724(2) and 1.728(2) Å), **5** (1.718(2) Å), **6** (1.718(2) Å), and **7** (1.728(5) Å) are longer than Ge=O bonds in germanones **I** (1.672(3) Å), **III** (1.646(2) Å), and **IV** (1.6468(5) Å).[2,3] The Ge=O bonds in compounds **4**–**7** are shorter than Ge−O single bonds in compound **3**, and therefore, are intermediate between Ge−O single and Ge=O double bonds. This is mainly due to donation of the lone pair of electrons on the oxygen atoms to acceptor atoms in Lewis acids. Compound **4** possess a planar four-membered Zn_2O_2 ring (Figure 2). The chlorine atoms attached to zinc atoms are perpendicularly oriented with respect to the Zn_2O_2 ring (dihedral angle between planes containing Zn_2O_2 and Zn_2Cl_4 moieties is 88.35(12)°). The metallylene centers in compounds **6** (Ge) and **7** (Sn) adopt distorted trigonal-pyramidal geometries with two chlorine and one oxygen atoms. The sum of bond angles around the Ge and Sn atoms in compounds **6** (288.83°) and **7** (277.49°) are indicative of the presence of a stereochemically active lone pair of electrons.[13] The molecular structure of compound **8** is shown in Figure S9. Compound **8** crystallized in the triclinic space group $P\bar{1}$ and has a planar Zn_2Cl_2 four-membered ring with μ-bridged chlorine atoms. The germanium atoms are tetracoordinate and adopt distorted tetrahedral geometries with two nitrogen atoms, one carbon atom, and one zinc atom.

The NBO analysis (see the Supporting Information for details) reveals that in compounds **4**–**7**, Ge−O σ bonds are formed through the overlap of germanium sp$^{2.5}$ orbitals (approximately) and oxygen sp^{2} orbitals (approximately; see Table S3 for the precise orbital types). The ionicity of the Ge−O bond in compound **4** is 70.6 % with 14.7 % and 85.3 % contributions from germanium and oxygen, respectively. The

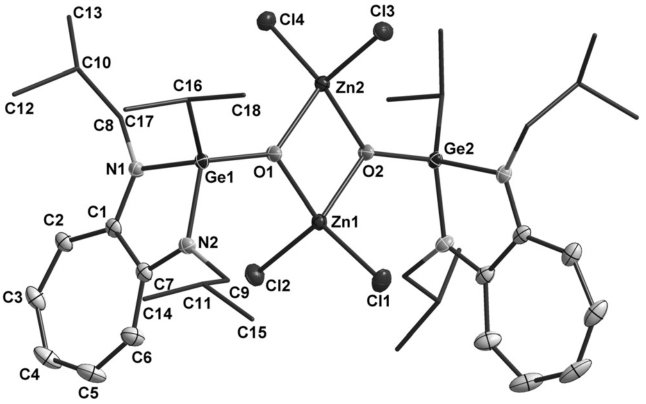

Figure 2. Molecular structure of compound **4** with thermal ellipsoids set at 30% probability.[16] All hydrogen atoms and one solvent molecule (acetonitrile) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–O1 1.724(2), Ge2–O2 1.728(2), Zn1–O1 1.995(2), Zn2–O1 2.003(2), Ge1–C16 1.933(3), Ge1–N1 1.870(2), Ge1–N2 1.876(3); O1-Ge1-N1 112.71(1), O1-Ge1-N2 109.48(1), O1-Ge1-C16 112.87(1), Ge1-O1-Zn1 125.16(1), Ge1-O1-Zn2 135.48(1), N1-Ge1-N2 85.73(1). Data collection temperature: 150 K.

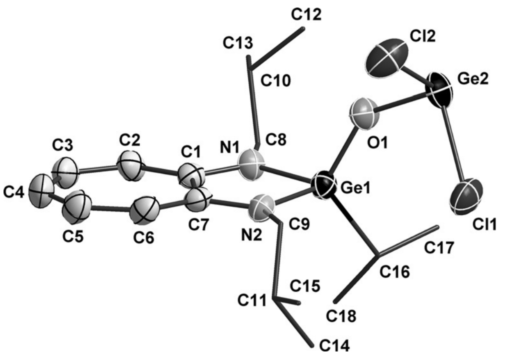

Figure 3. Molecular structure of compound **6** with thermal ellipsoids set at 30% probability.[16] All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–O1 1.718(2), Ge2–O1 1.816(2), Ge2–Cl1 2.346(2), Ge2–Cl2 2.300(2), Ge1–C16 1.954(3); Ge1-O1-Ge2 138.15(15), O1-Ge1-C16 116.79(13), O1-Ge2-Cl1 97.11(8) O1-Ge2-Cl2 97.03(9), Cl2-Ge2-Cl1 94.68(5) O1-Ge1-N(1) 110.32(11), O1-Ge1-N2 109.92(12). Data collection temperature: 298 K.

ionicities of Ge–O bonds in compounds **5**–**7** are almost the same as that in compound **4**, whereas in germanone [**A**] (used as a model compound; Figure S10), it is 59.5% (Table S3). In compound **4**, the Zn–O bond is formed by the overlap of the zinc sp$^{3.35}$ orbital and the oxygen sp$^{1.96}$ orbital. The ionicity of the Zn–O bond is 93.2% and contributions from oxygen and zinc are 96.62% and 3.38%, respectively. The boron sp$^{3.69}$ orbital overlaps with the oxygen sp$^{0.80}$ orbital to form a B–O σ bond in compound **5**. In compounds **6** and **7**, the germanium sp$^{14.06}$ orbital (Ge2) and the tin sp$^{15.69}$ orbital overlap with sp$^{2.25}$ and sp$^{2.96}$ orbitals of oxygens to form Ge2–O and Sn–O σ bonds, respectively. The ionicities of Ge2–O (82.4%) and Sn–O (87.4%) σ bonds are close to each other. The ionicity of the B–O bond (63.3%) in compound **5** is the lowest among O→LA bond ionicities (LA = Lewis acid) in compounds **4**–**7** (see Table S3). These discussions suggest that although the nature of the Ge–O bond remains almost same, the nature of the O→LA bond varies with respect to the Lewis acid used.

In the second-order perturbation theory analysis, strong O→Ge and O→B donor–acceptor interactions were detected for compound **5** (Figure S11 a–d). The oxygen sp$^{12.13}$ orbital and germanium sp$^{1.96}$ orbital overlap to give a σ interaction which is stabilized by 113.8 kcal mol^{-1} (Figure S11a). Another σ interaction between the oxygen sp$^{12.13}$ orbital and the germanium p orbital is stabilized by 81.0 kcal mol^{-1} (Figure S11b). The O→B donor–acceptor interaction is stabilized by 334.9 kcal mol^{-1} through the overlap of the oxygen sp$^{0.38}$ orbital with the boron sp$^{3.94}$ orbital (Figure S11c). The σ interaction between the oxygen sp$^{12.13}$ orbital and the Ge–C$_{i\text{-Pr}}$ antibonding orbital is stabilized by 41.5 kcal mol^{-1} (Figure S11d). In compound **6**, the lone pair of electrons on germanium (Ge2) occupies the sp$^{0.13}$ orbital and interacts with the Ge1–O antibonding orbital (4.8 kcal mol^{-1}; Figure S12a), whereas the lateral overlap (π interaction) of the oxygen sp$^{4.56}$ orbital with the Ge1–C$_{i\text{-Pr}}$ antibonding orbital is stabilized by 5.8 kcal mol^{-1} (Figure S12b). The oxygen sp$^{4.34}$ orbital laterally overlaps with the Ge2–Cl2 antibonding orbital to give a π interaction (3.1 kcal mol^{-1}; Figure S12c). A π antibonding interaction (2.8 kcal mol^{-1}) is also observed between the oxygen sp$^{4.56}$ orbital and the Ge2–Cl1 antibonding orbital (Figure S12d). Compound **7** shows similar donor–acceptor interactions as seen in compound **6** (Figure S13 a–d).

The Wiberg bond index (WBI) values of Ge=O bonds in complexes **4**–**7** of germanone fall between 0.60 and 0.72 (Table S3). In comparison, the WBI values for Ge=O bonds in compounds [**A**] and **IV** are 1.08 and 1.25, respectively. This reveals the presence of very highly polarized Ge=O bonds in compounds **4**–**7**. Further, it should be mentioned that with an increase in the strength of the Lewis acidity of the acceptor, the strength of the O→LA bond increases (i.e., O→B (**5**) > O→Ge (**6**) > O→Sn (**7**); Table S3). As the ionicity of the O–Zn bond in compound **4** is very high (see above), an atoms in molecules (AIM) calculation was carried out to probe its nature further. The magnitude of charge density $\rho(r_c)$ (0.059) at the bond critical point (r_c) and the positive sign of the Laplacian of charge density ($\bigtriangledown^2\rho(r_c)$) suggest a closed-shell interaction between oxygen and zinc in compound **4**. However, the dominance of potential energy density ($V(r_c)$) over kinetic energy density ($G(r_c)$) reveals that it is an intermediate interaction, that is, the Zn–O bond is a coordinate bond with some degree of ionization.[14,15]

In conclusion, we have demonstrated the facile synthesis of hitherto unknown complexes of germanone as stable species through the reaction of the germanium μ-oxo dimer **3** with Lewis acids without the need to prepare the synthetically challenging germanones. In addition, another convenient route to isolate complexes of germanone, starting from germylene→Lewis acid adducts, was also shown.

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[16] CCDC 1430542 (**3**), 1430543 (**4**), 1430544 (**5**), 1430545 (**6**), 1430546 (**7**), and 1435773 (**8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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