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The reactivity of NOBF₄ towards silylene, disilene, germylene, stannylenes has been described. Smooth syntheses of compounds of composition [PhC(NtBu)₂E(= O \rightarrow BF₃)N(SiMe₃)₂, E = Si (3) and Ge (4)] were accomplished from the corresponding tetrylenes. An unusual heterocycle (10) featuring B, Sn, N, P, and O atoms was obtained from the reaction with a stannylene, while a 1,2-vicinal anti addition of fluoride was observed with a disilene (12).

Unlike ketones, their higher homologues (E=O, E: Si-Pb) are oligomeric or polymeric in nature due to the unfavourable overlapping between $p_{\pi}(E)$ and $p_{\pi}(O)$ orbitals as well as large electronegativity difference between the E and O atoms. To harness the reactivity of Si=O or Ge=O bonds, the synthetic chemists devised the donor-acceptor concept and reported a good number of compounds featuring a Si=O/Ge=O double bond, where an additional donor like N-heterocyclic carbene (NHC) or 4-(dimethylamino)pyridine (4-DMAP) is coordinated to the silicon/germanium atom.¹ The entrée of the first bonafide heavy ketone was noted by the isolation of a germanone (G) (Scheme 1) by Tamao and coworkers,² who used an immensely bulky ligand, 1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl (Eind) to provide the kinetic and thermodynamic stabilization to the Ge=O double bond. Since then many compounds with E=O bond (E = Si, Ge) have been isolated (selected examples are given in Scheme 1).³⁻¹¹

NOBF₄ is a known nitrosating reagent for the synthesis of transition metal nitrosyl complexes.¹² Our interest to study the reactivity of NOBF₄ towards compounds with low-valent silicon and germanium atoms emanates from the three recent publications by the groups of Braunschweig, Inoue, and Schulz, where boron- and silicon-carbonyl complexes have been isolated.¹³ Therefore, the question arises whether the analogous reactions with NOBF₄ can furnish the hitherto unknown main-group nitrosyl complexes.

While our investigations of $NOBF_4$ with compounds with low-valent silicon, germanium and tin atoms did not render the formation of main-group nitrosyl complexes, it unravels the diverse reactivity tapestry of $NOBF_4$ towards such species. In this paper, we report the convenient access towards compounds with BF_3 coordinated silicon/germanium–oxygen partial multiple bonds starting from the amidinatesilylene/ germylene, which can be deemed as analogues of acetamide by using $NOBF_4$ as an oxygen donor. We have also found the formation of an unprecedented tin heterocycle with five-fused rings based on B, F, O, N, P, Sn atoms. Analogous reaction with a disilene led to the first vicinal fluorination of a Si—Si double bond.

The reaction of silylene, $[PhC(NtBu)_2SiN(SiMe_3)_2]$ (1),¹⁴ with NOBF₄ in toluene afforded the formation of $[{PhC(NtBu)_2SiN(SiMe_3)_2}]$ (3) and $[PhC(NtBu)_2SiF_2N(SiMe_3)_2]$ (5) with the concomitant elimination of N₂O and BF₃ (Scheme 2). The

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Scheme 1 Selected examples of silanones (A-F) and germanones (G-I).



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²⁹Si NMR spectrum of **3** shows a signal at δ –13.39 ppm for the Si=O bond, which is consistent with the four-coordinated silicon atom.¹⁵ The ²⁹Si NMR spectrum of 5 displays a doublet resonance at -62.71 ppm with the ${}^{1}J_{Si-F}$ coupling constant of 186.81 Hz. The upfield shift is consistent with the increase of the coordination number around the Si center. Analogous reaction with $[PhC(NtBu)_2GeN(SiMe_3)_2]^{16}$ (2) also led to the formation of the Ge=O multiply bound compound [{PhC(NtBu)2GeN (SiMe₃)₂}OBF₃] (4) and the oxidative addition product, [PhC $(NtBu)_2GeF_2N(SiMe_3)_2$ (6) (Scheme 2). 3 crystallizes in the monoclinic space group P_n (Fig. 1). The Si–O bond length in 3 is 1.566(8) Å, which is slightly longer than those in **B** (1.523(3) Å),^{3a} **D** $(1.533(1) \text{ Å})^5$ and E (1.537(3) Å),⁶ but well comparable with the Lewis acid stabilized silanone, **F** (1.5568(14) Å).¹⁰ 4 also crystallizes in the monoclinic space group P_n and is shown in Fig. 1. The Ge–O bond length is of 1.677(9) Å, which is slightly longer than that in G (1.6468(5) Å),² but matching well with Lewis acid/base stabilized germanones (1.67-1.71 Å).^{1g-h},11 Notwithstanding the coordination of the oxygen atom to the BF₃, the B–O bond lengths in 3 (1.445(13) Å) and 4 (1.443(18) Å) are significantly shorter than typical B-O single bond (~1.5 Å).¹⁷ 5 and 6 crystallize in the monoclinic space group $P2_1/c$, where the central Si or Ge atom is five coordinated acquiring distorted trigonal bipyramidal geometry (Fig. 1). The Si-F bond distances are 1.6126(15) and 1.6476(15) Å, which is well matched with $[{PhC(NtBu)_2SiFN(SiMe_3)_2}C_6F_4(CF_3)]$ $(1.640(3) \text{ Å})^{18}$ and $[{PhC(NtBu)_2SiFCl}C_6F_4(CF_3)] (1.633(3)\text{Å})^{19}$ and the Ge-F bond distances are 1.725(4) and 1.775(3) Å.

We have carried out quantum mechanical calculations at the M06/def2-TZVPP//BP86/def2-SVP level of theory to explore the stability and bonding of the compounds 3 and 4 as compared to the hypothetical compounds without the Lewis acid BF₃ (3' and 4').²⁰ The calculated Si–O and Ge–O bond length in 3 and 4 are slightly elongated compared to the experimental values

(Fig. S1a, ESI[†]). The Si-O and Ge-O bond in 3' (1.573 Å) and 4' (1.680 Å) are elongated as compared to those in 3 (1.566(8) Å) and 4 (1.677(9) Å), and the Si–N1 and Si–N2 bond in 3′ (1.896 Å and 1.895 Å) and 4' (2.016 Å) are also elongated as compared to those in 3 (1.796(10) and 1.805(10)Å) and 4 (1.913(11) Å and 1.904(10) Å) (Fig. S1, ESI⁺). The Si-O and Ge-O single bond lengths in the compounds with tetracoordinated silicon and germanium are 1.63 Å-1.76 Å^{6,21*a*,22*a*} and 1.78 Å-1.87 Å^{11,22*b*} respectively. The Si-O and Ge-O bond lengths in tricoordianted Si and Ge complexes, where Si-O and Ge-O bonds are considered as typical double bonds, are 1.533 Å-1.543 Å^{5,6,21a} and 1.646 Å² respectively. The Si-O and Ge-O bond lengths in 3' (1.573 Å), in 4' (1.680 Å), 3 (1.566(8) Å) and 4 (1.677(9) Å) are in between corresponding single and double bond lengths, and it is much closer to double bond lengths in 3' and 4' and matches well with those in tetracoordinated silanoic silyl ester $(1.579 \text{ Å})^{21b}$ as well as Lewis acid coordinated Si=O $(1.580 \text{ Å})^8$ and Ge=O (1.698 Å and 1.708 Å).¹¹

The Natural Bond Orbital (NBO)²⁰ analysis indicate that the compounds 3' and 4' show significant hyperconjugative donoracceptor interactions (66.2 kcal mol⁻¹ and 67.0 kcal mol⁻¹, respectively) from the lone pair of oxygen to the Si–N σ^* orbitals as compared to those present in 3 (25.9 kcal mol⁻¹) and 4 $(22.24 \text{ kcal mol}^{-1})$ (Table S3, ESI[†]). The high positive natural charge on E (2.45 e in Si and 2.32 e in Ge) and a high negative natural charge on the oxygen atom (-1.17 e-1.13 e) indicate a highly polarized E-O bond in compounds 3 and 4 (Table S2, ESI[†]). The Energy Decomposition Analysis combined with Natural Orbital for Chemical Valence (EDA-NOCV)²⁰ analysis indicate that the Si-O bond in 3 and 3' and Ge-O bond in 4 and 4' can be best represented by charge separated electron sharing Si⁺-O⁻ and Ge⁺-O⁻ σ -bonds (A in Scheme S1, ΔE_1 in Table S7, ESI[†]). The lone pair of electrons from oxygen atoms involves in two hyperconjugative interaction with the antibonding Si-N σ^* - molecular orbitals. The deformation densities ($\Delta \rho_2$ and $\Delta \rho_3$) which are the difference between the charge densities of fragments before and after bond formation, corresponding to the hyperconjugative interactions are given in Fig. 2 (3 and 4), Fig. S5 (3') and S6 (4') (ESI^{\dagger}). The extent of hyperconjugative interaction is less in 3 and 4 compared to that in 3' and 4'



Fig. 1 The molecular structures of **3–6** (ellipsoids are shown at the probability level of 30%). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): For **3**, Si1-O1 1.566(8), O1-B1 1.445(13), B1-F1 1.360(14), B1-F2 1.370(14), B1-F6 1.434(15); N1-Si2-O3 112.3(5), Si2-O3-B7 140.6(7). For **4**, Ge1-O1 1.677(9), O1-B1 1.443(18), B1-F1 1.348(18), B1-F2 1.425(16), B1-F3 1.337(19); Ge1-O1-B1 131.6(8), N3-Ge1-O1 110.4(4). For **5**, Si1-F1 1.6126(15), Si1-F2 1.6476(15); F1-Si1-F2 90.91(7). For **6**, Ge1-F1 1.725(4), Ge1-F2 1.775(3); F1-Ge1-F2 88.96(19).



Fig. 2 Plots of deformation densities $\Delta \rho_n$ and the associated orbital stabilization energies ΔE (in kcal mol⁻¹) of (a). **3** and (b). **4** calculated at the BP86/TZ2P level of theory. The isosurface value for the deformation densities is 0.003 for $\Delta \rho_1$ and 0.001 for $\Delta \rho_2$ and $\Delta \rho_3$. The direction of charge flow is from red to blue.

 $(\Delta E_2 + \Delta E_3)$ are -67.7 kcal mol⁻¹ for 3' and -51.9 kcal mol⁻¹ for 4' (Table S7 and Fig. S5 and S6, ESI[†]) and -43.8 kcal mol⁻¹ for 3 and -28.7 kcal mol⁻¹ for 4 (Table S7, ESI[†] and Fig. 2). The hyperconjugative interactions in two different directions resulted in a partial multiply bonded character of the Si–O (3' and 3) and Ge–O bonds (4' and 4). The EDA-NOCV results are correlating well with the NBO and MO analyses.

When we performed the analogous reaction with [PhC $(NtBu)_2SnN(SiMe_3)_2$]^{23*a*} (7), we were able to obtain only the difluorostannane [PhC($NtBu)_2SnF_2N(SiMe_3)_2$] (8), which is analogous to 5 and 6 (Scheme 3). The result is in contrast to the reaction of [PhC($NtBu)_2SnNMe_2$] with C_5F_5N , which led to the σ -bond metathesis between NMe₂ and F moieties.^{23*b*} A subsequent theoretical paper also supported the result and predicted the less scope of oxidative addition of a Sn(π) center.^{23*c*} The ¹¹⁹Sn NMR of 8 exhibits a doublet at δ –396.66 ppm with a coupling constant of 2784.8 Hz, which is in agreement with the Sn-F coupling constant of 3100 Hz reported for LSnF [L = HC{CMeN(2,6-*i*Pr₂-C₆H₃)}].²⁴ 8 crystallizes in the monoclinic space group $P2_1/c$, where the Sn centre is five coordinated (Scheme 3).

To explore the possibility of the formation of a Sn=O doubly bonded compound, we further used another system of stannylene aided with -PPh₂ group (9) to stabilize an intermolecular Sn=O multiply bound compound. Very surprisingly, the reaction of 9 with NOBF₄ afforded an unusual cyclic compound **10** (Scheme 4) along with some unidentified products. The



Scheme 3 Synthesis and molecular structure of 8 (ellipsoids are shown at the probability level of 30%). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Sn1-N3 2.008(4), Sn1-F1 2.072(3), Sn1-F2 2.138(3); F1-Sn1-F2 83.45(15).



Scheme 4 Synthesis and molecular structure of **10** (ellipsoids are shown at the probability level of 30%). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Sn1-O1 2.134(4), Sn1-O1 2.110(4), Sn1-F3 1.941(4), O1-B1 1.370(8), B1-O3 1.322(8), O3-B2 1.472(8), B2-N4 1.581(8), N4-P1 1.623(5), P1-N3 1.638(5), N3-O2 1.447(6), O2-Sn1 2.035(4).

molecular structure of **10** discloses a system with five-fused rings consists of Sn, B, O, P, N atoms. The bond distances of Sn1–O1 are 2.110(4) and 2.134(4) Å, respectively. Comparing the Sn–O bond lengths with **J**,²⁵ one Sn–O of **10** can be assigned as the coordination bond while the other one is a Sn–O single bond. It is noteworthy to mention that this is the first example of such a heterocyclic compound based on Sn, B, O, N and P atoms. The ¹¹⁹Sn NMR and ³¹P NMR spectra display resonances at δ –549.39 (¹ J_{Sn-F} = 4638 Hz) and 20.67 ppm, respectively.

To check the generality of our methodology, we used several other low valent group 14 compounds (Scheme 5) to investigate the reactivity pattern with NOBF₄. The reaction of $(Cp^*)_2$ Ge with NOBF₄ afforded $[Cp^*Ge]^+[BF_4]^-$ (11), which was previously isolated through the reaction of $(Cp^*)_2$ Ge and HBF₄.²⁶ The reaction of IPr (1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) with NOBF₄ led to the previously reported IPr \rightarrow BF₃ adduct (13)²⁷ formation. Both 11 and 13 were isolated and



Scheme 5 Synthesis of **11–13**. (IPr = 1,3-bis(2,6-diisopropylphenyl) imidazole-2-ylidene). The molecular structure of **12** (ellipsoids are shown at the probability level of 30%). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Si1-Si1 2.475(6), Si1-F1 1.649(5), Si1-N1 1.732(7); N1-Si1-Si1 119.6(3), F1-Si1-Si1 101.2(2), N1-Si1-F1 102.6(3).

characterized by single crystal X-ray diffraction studies (see the ESI, \dagger Fig. S8).

Further, upon reaction of $Cp*SiN(TMS)_2 = SiN(TMS)_2Cp*$ disilene²⁹ with NOBF₄, a difluorinated compound **12** was isolated. The 1,2-fluoride addition to a disilene is not known. In fact, there is only one example of disilene-fluoride compound reported by Marschner and coworkers, where a disilene potassium fluoride adduct was isolated.²⁸ The molecular structure of **12** displays the placement of two fluoride atoms opposite to each other on different silicon centres (Scheme 5).

In summary, we have demonstrated diverse reactivity of $NOBF_4$ towards silylene, disilene, germylenes, stannylenes *etc.* The reactions with silylene and germylene led to benzamidinatosila- (3) and germa-acetamide (4), where $NOBF_4$ serves as a OBF_3 donor, whereas a stannylene with $N(Dipp)PPh_2$ moiety (9) afforded an unprecedented fused heterocycle (10). Another interesting reaction is the vicinal anti fluorination (12) of Jutzi's disilene upon reacting with $NOBF_4$. All the compounds are reproducible under the same reaction conditions.

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Conflicts of interest

There are no conflicts to declare.

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