Reactivity of NHI-Stabilized Heavier Tetrylenes towards CO$_2$ and N$_2$O

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A heteroleptic amino(imino)stannylene (TMS$_2$N)(I^{t}BuN)Sn: (TMS = trimethylsilyl, I^{t}Bu = C[(N–^{t}Bu)CH]$_2$) as well as two homoleptic NHI-stabilized tetrylenes, (I^{t}BuN)$_2$E: (NHI = N-heterocyclic imine, E = Ge, Sn) are presented. VT-NMR investigations of (I^{t}BuN)$_2$Sn: (2) reveal an equilibrium between the monomeric stannylene at room temperature and the dimeric form at −80 °C as well as in the solid state. Upon reaction of the homoleptic tetryl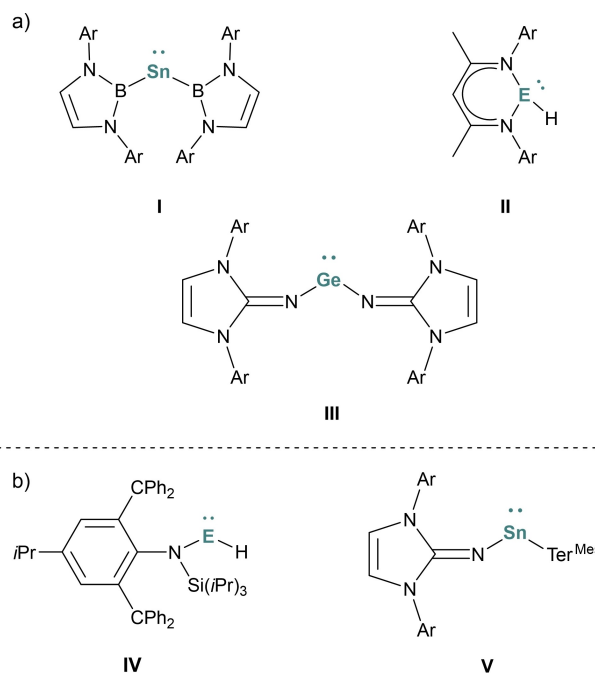enes with CO$_2$, both compounds insert two equivalents of CO$_2$, however differing bonding modes can be observed. (I^{t}BuN)$_2$Sn: (2) inserts one equivalent of CO$_2$ into each Sn–N bond, giving carbamato groups coordinated κ^2O,O' to the metal center. With (I^{t}BuN)$_2$Ge: (3), the Ge–N bonds stay intact upon activation, being bridged by one molecule of CO$_2$ respectively, forming 4-membered rings. Furthermore, the reactivity of 2 towards N$_2$O was investigated, resulting in partial oxidation to form stannylene dimer [((I^{t}BuN)$_3$SnO)(I^{t}BuN)Sn:]$_2$ (6).

Introduction

One of the most pressing goals in contemporary chemical research is the utilization of CO$_2$ as a source of a C$_1$ building block. This is due to its ubiquity and status as a greenhouse gas. CO$_2$ as well as N$_2$O, contribute significantly to climate change, due to their considerable heat-trapping potency.[1] One approach to curb global warming, is the utilization of these climate critical gases in the production of value added chemicals, which can be achieved with the use of transition-metal compounds as catalysts.[2] However, due to their often costly and toxic nature, there have been efforts towards more economically viable alternatives. As such, metal-free systems as well as abundant main-group element compounds have been investigated.[3] Pertinent to this, low valent group 14 compounds are of interest, since they have been shown to mimic the reactivity of transition metal complexes when isolated in a low oxidation state.[3a,4] In particular, heavier tetrylenes R$_2$E: (E = Si, Ge, Sn) demonstrated considerable potential in this respect due to their ambiphilic nature and small HOMO-LUMO gap. For example the uptake of CO$_2$ and N$_2$O by diborylstannylene [(CHDippN)$_2$B]$_2$Sn: I (Dipp = 2,6-iPr$_2$(C$_6$H$_3$) and N-heterocyclic tetrylene hydrides CH[(CMe)(DippN)]$_2$EH II, the formation of a

germanone (IDippN)$_2$Ge=O (IDipp = C[(N–Dipp)CH]$_2$) upon reaction of (IDippN)$_2$Ge: III with N$_2$O with subsequent O-atom transfer, or the catalytic reduction of CO$_2$ to methanol by tetrylene hydride complexes N(Ar)(Si^{i}Pr$_3$)EH (Ar = C$_6$H$_2$Pr^i{C(H)Ph$_2$}$_2$-4,2,6, E = Ge, Sn) IV have been reported (cf. Scheme 1).[5]

With our recently reported aryl(imino)stannylene (^{Mes}Ter)(IDippN)Sn: V (^{Mes}Ter = 2,6-Mes$_2$C$_6$H$_3$), which showed catalytic activity in CO$_2$ hydroboration with HBpin, we could showcase the notable suitability of NHI (N-heterocyclic imine) ligated stannylenes for small molecule activation and catalysis.[6] Here, the zwitterionic nature of the Sn–Imine bond due to

Scheme 1. Selected tetrylenes E$_2$R (E = Ge, Sn) capable of activating CO$_2$ and/or N$_2$O (a),[5a,b,e–g] as well as catalytic reduction of CO$_2$ (b)[5d,6] (Ar = Dipp = 2,6-iPr$_2$(C$_6$H$_3$), ^{Mes}Ter = 2,6-Mes$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$(C$_6$H$_2$),).

distinct properties of the NHI ligand allows activation and subsequent reduction of CO_2 under mild conditions. In comparison, amine or NHCP (N-heterocyclic phospinidine) substituted congeners were not able to reduce CO_2. NHIs are exceptionally strong π- as well as σ-donors and also allow facile modification of their steric demand at the endocyclic nitrogen moieties and backbone, making them excellent ligands for an electrophilic metal center.[7] With this in mind, we set out to further expand the library of NHI stabilized tetrylenes and explore their capabilities in small molecule activation.

Results and Discussion

Heteroleptic stannylene $(TMS_2N)(I^tBuN)Sn$: **1** $(I^tBu = C[(N-^tBu)CH]_2)$ was synthesized via a ligand exchange reaction with Lappert's stannylene[8] $(TMS_2N)_2Sn$: with protonated ligand, $(I^tBuN)H$ at room temperature (Scheme 2a) and characterized by standard NMR and SC-XRD techniques (see SI). Subsequent introduction of a second equivalent of $(I^tBuN)H$ to **1** gave bis-NHI-substituted stannylene $(I^tBuN)_2Sn$: **2**, however in poor yield and purity. Alternatively, introduction of two equivalents lithiated ligand, $(I^tBuN)Li$ to $SnCl_2 \cdot$ dioxane with one additional equivalent of DMAP lead to the formation of **2** more selectively. In a similar manner, the analogous germylene $(I^tBuN)_2Ge$: (**3**) could be obtained by the reaction of $GeCl_2 \cdot$ dioxane with $(I^tBuN)Li$ (Scheme 2b). It should be noted that parent amino-germylene $(TMS_2N)_2Ge$: showed no reactivity towards $(I^tBuN)H$.

The ^{119}Sn-NMR Signal of **2** (122.07 ppm) is significantly up-field shifted compared to **1** (401.35 ppm) as well as $(TMS_2N)_2Sn$: (767 ppm), but within the range of previously reported two-coordinate, NHI-stabilized stannylenes (−208.0–967.8 ppm).[6,8–9] While solution state ^1H-NMR characterization shows one set of signals attributed to the ligand indicating a symmetrical molecule, the solid state structure of **2** exhibits a dimer with two distinct ligand environments (Figure 1). The compound
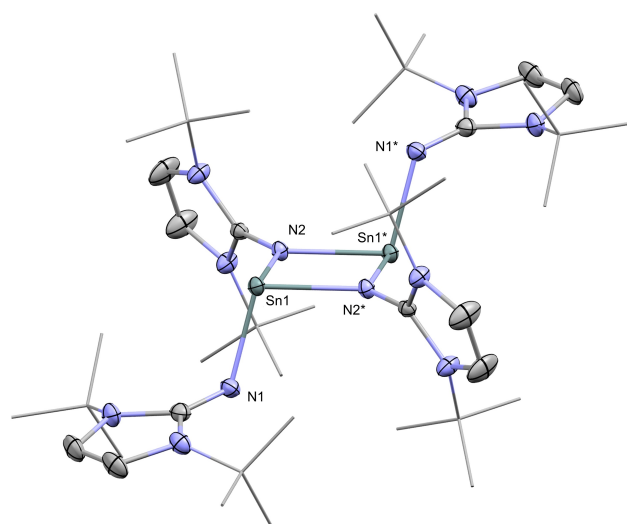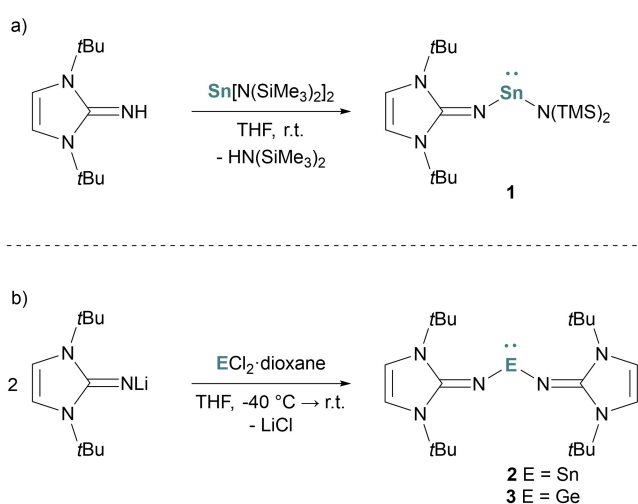

Figure 1. Molecular structure of Stannylene **2** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–N1 2.0985(16), Sn1–N2 2.1841(16), Sn1–N2* 2.1880(16), N2–Sn1–N2* 75.96(6), Sn1–N2–Sn1* 104.04(6).

displays a nearly planar Sn_2N_2 ring (sum of internal bond angles = 359.5°) with terminal ligand moieties trans oriented in respect to the Sn_2N_2 ring, and two imines bridging the Sn centers. The Sn–N bond lengths are in the range of previously reported amido- and iminato-stannylene single bonds (2.041(2)–2.227(7) Å).[6,9c,10]

In order to elucidate the structure of **2** in solution, VT-NMR experiments in toluene-d_8 were conducted (Figure 2). ^1H- and ^{119}Sn-NMR measurements show the gradual appearance of a second species upon cooling, with an approximate 1:1 ratio at −80°C (determined by ^1H-NMR integral ratios, cf. Figure S18). The new ^{119}Sn signal displays further up-field at 130.6 ppm, while the ^1H-NMR shows the emergence of two new distinct sets of ligand signals, as expected according to the molecular

a)

b)

2 E = Sn
3 E = Ge

Scheme 2. a) Synthesis of heteroleptic stannylene **1** via ligand exchange of Lappert's stannylene with free $(I^tBuN)H$. b) Homoleptic tetrylenes **2** and **3** obtained via imination of $ECl_2 \cdot$ dioxane with $(I^tBuN)Li$ ($I^tBu = C[(N-^tBu)CH]_2$, E = Sn, Ge).
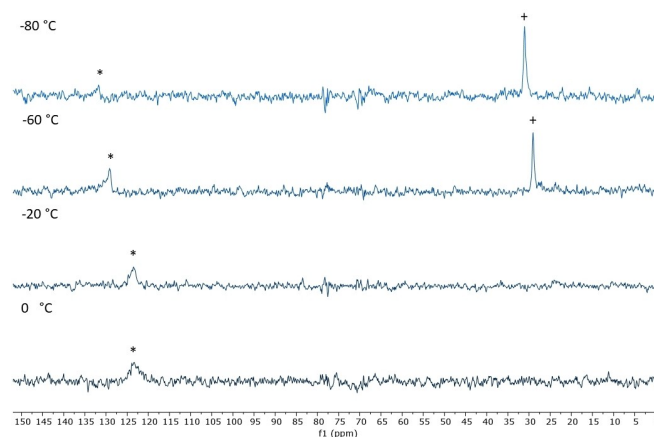

Figure 2. Truncated variable temperature ^{119}Sn NMR spectra of stannylene **2** in Toluene-d_8 at −80°C, −60°C, −20°C and 0°C. (* = signals corresponding to monomeric stannylene, + = signals corresponding to di-stannylene). For experimental details and corresponding 1H NMR spectra see supporting information.

structure of **2** in the solid state. This confirms an equilibrium between the monomer and dimer of **2** in solution, with the monomer being the preferred form at room temperature.

Germylene **3** displays a monomeric molecular structure in solution as well as in solid state, according to ^{1}H-NMR and SC-XRD characterization (Figure 3). Compared to previously reported germylene (IDippN)$_2$Ge: (**III**), Ge–N bond lengths of 1.8739(17) Å are elongated and the Ge–N–Ge angle of 94.17(9) is more acute (**III**: 1.819(15) Å, 99.48(10)°). Overall, **3** is highly symmetrical with the imidazole rings being perpendicular to the N–Ge–N moiety (Ge1–N1–C1–N2 = 90°).

With **1**–**3** in hand, we wanted to explore their reactivity towards small molecules, in particular CO_2 and N_2O. Both homoleptic tetrylenes **2** and **3** reacted with 1 bar of CO_2 at room temperature instantaneously to give colorless crystals suitable for SC-XRD analysis (Scheme 3). In contrast, **1** did not selectively react with CO_2, likely due to decomposition of the amido-ligand via silyl migration, a commonly observed phenomenon when utilizing silyl-amido-ligands.[11]

Stannylene **2** inserts one molecule of CO_2 into each Sn–N bond, giving a distorted seesaw structure with both carbamato groups coordinated κ^2O,O' around the metal center (Compound **4**, Figure 4, Sn1–O 2.1578(15)–2.2410(15) Å). The ^{1}H- as well as the

Figure 4. Molecular structure of compound **4**. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–O1 2.1846(16), Sn1–O2 2.2054(15), Sn1–O3 2.1578(15), Sn1–O4 2.2410(15), O1–Sn1–O2 59.79(5), O1–Sn1–O3 83.71(6).

^{13}C-NMR spectroscopic analysis confirms a quantitative conversion and a ^{13}C-NMR signal at 167.40 ppm, characteristic for the formation of a tin-carbamate carbon (161.6–175.6 ppm)[6,12] can be observed. Compound **4** shows very poor solubility in THF and C_6H_6 but is soluble in acetonitrile, nevertheless no ^{119}Sn-NMR signal could be observed. The insertion of CO_2 is irreversible and **2** could not be recovered upon heating or under reduced pressure.

Germylene **3** also irreversibly activates two equivalents of CO_2 to give compound **5**. Here, the Ge–N bonds stay intact, and we observe a N,O coordination mode as opposed to the O,O mode as seen in **4**. This is presumably due to the higher bond strength of Ge–N bonds (364 kJ/mol) compared to Sn–N bonds (324 kJ/mol).[13] The central germanium is surrounded by the ligands in a distorted seesaw fashion, with an almost perpendicular O–Ge–O angle (94.4(3)°) and nearly planar four membered metallacycles (sum of internal bond angles = 178.4°) (*cf.* Figure 5).

Reaction of **2** with N_2O gives bis-stannylene [((I^{t}BuN)$_3$SnO)(I^{t}BuN)Sn:]$_2$ (**6**) with a central Sn_2N_2 ring (Scheme 4). The +II oxidation state is retained by the central Sn atoms, which are bridged by imine moieties similarly to stannylene **2**. However, the other two Sn centers get oxidized and form stannanolate (IDippN)$_3$SnO– ligands. We propose that
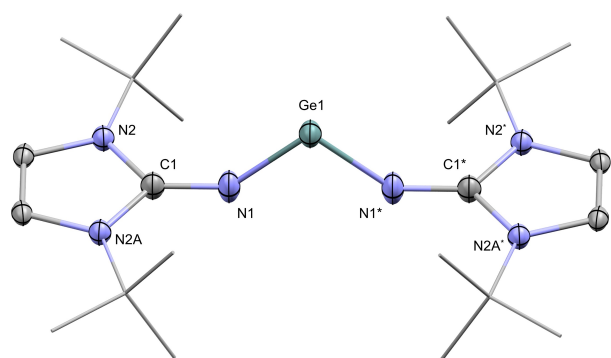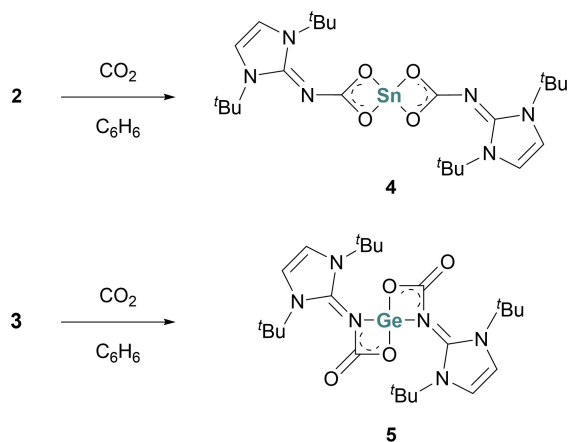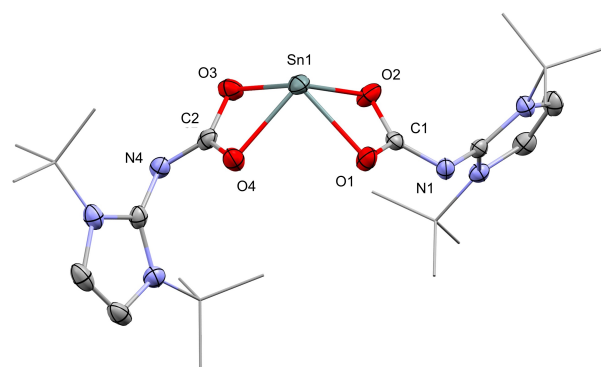

Figure 3. Molecular structure of compound **3** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ge1–N1 1.8738(17), Ge1–N1* 1.8739(17), N1–Ge–N1* 94.17(9), Ge1–N1–C1–N2 90.000(1).

Scheme 3. Reaction of tetrylenes **2** and **3** with 1 bar of CO_2 in benzene at room temperature.
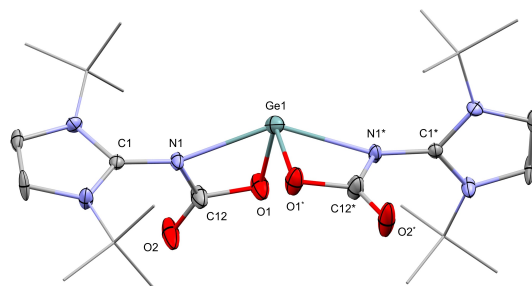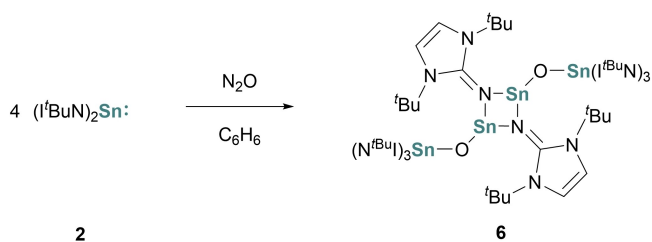

Figure 5. Molecular structure of compound **5** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ge1–O1 1.904(5), Ge1–N1 2.288(5), O1*–Ge1–O1 94.4(3), O1–Ge1–N1 63.64(18), O1–Ge1–N1* 91.25(19).

Scheme 4. Reaction of tetrylene **2** with 1 bar of N_2O in benzene at room temperature.

the initial step in the mechanism is the formation of a transient stannone intermediate, as suggested for the reaction of **1** and N_2O. This transient stannone reacts with one equivalent of **2** giving the final product **6** after dimerising (a proposed mechanism is in the SI, Figure S22)[5a] Pertinently, the formation of a silanolate-ligated bis-stannylene when $(TMS_2N)_2Sn:$ was treated with CO_2 as well as NHI ligand rearrangements have been reported.[11a,14] The ^1H- and ^{13}C-NMR spectra show two sets of signals corresponding to the distinct ligand environments. Due to the low solubility of compound **6** in most common NMR solvents and only slight solubility in acetonitrile, no ^{119}Sn-NMR signal could be observed. The molecular structure of **6** displays a planar Sn_2N_2 ring (sum of internal bond angles = 360.0°) with Sn—N bond lengths (Sn2—N1 2.185(6) Å, Sn2—N1* 2.173(6) Å) shorter than **2** and the stannanolate moieties *trans* oriented to the ring center (Figure 6).

Treatment of **1** as well as **3** with N_2O, lead to the formation of mostly protonated ligand and indeterminable decomposition products. The reaction outcome for **3** and N_2O is in stark contrast to the previously reported reaction of $(IDippN)_2Ge:$ with N_2O, which leads to the isolation of a stable germanone.[5c] This is likely due to the $I^{tBu}N$ ligands not offering sufficient kinetic protection to the polarized Ge=O bond compared to the more sterically imposing IDippN. The comparison of **1** and **2** in terms of small molecule activation showcases once again the benefits of utilizing the robust NHI ligand system for the stabilization of low valent tin compounds, enabling selective reactivity.
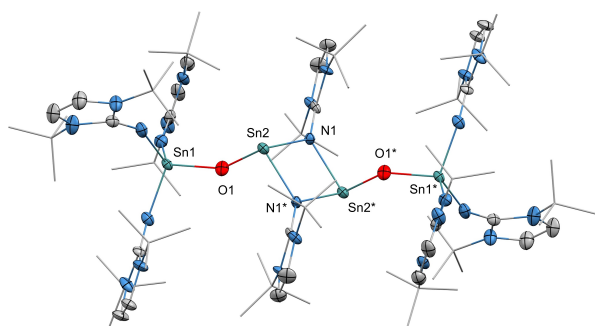
Conclusions

The isolation and reactivity of three novel NHI-stabilized tetrylenes has been reported. While the heteroleptic amino(imino)stannylene $(TMS_2N)(I^{tBu}N)Sn:$ (**1**) does not selectively react with N_2O or CO_2, the homoleptic congener $(I^{tBu}N)_2Sn:$ (**2**) shows defined activation of both small molecules. Also, the reaction of $(I^{tBu}N)_2Ge:$ (**3**) with CO_2 could be observed, which led to a rare bonding mode (N,O) for germanium. These tetrylenes expand the library of low valent group 14 compounds capable of small molecule activation and the investigation of their reactivity towards a broader substrate scope as well as their potential catalytic applications is currently underway.

Acknowledgements

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Figure 6. Molecular structure of compound **6**. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: **1**: Sn1—O1 1.930(6), Sn2—O1 2.022(7), Sn2—N1 2.185(6), Sn2—N1* 2.173(6), O1—Sn2—N1 98.8(2), O1—Sn2—N1* 97.0(3), Sn2—N1—Sn2* 102.4(3), N1—Sn2—N1* 77.6(3).

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