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Synthesis and Structures of Homoleptic Germlyenes and Stannylenes with Sulfonimidamide Ligands †

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An unusual series of germlyenes and stannylenes with homoleptic symmetric and unsymmetric N-substituted sulfonimidamide ligands PhSO(NiPr)(NH*i*Pr) **1** and PhSO(NMes)(NH*i*Pr) **2** have been prepared by protonolysis reaction of Lappert's metallylenes [M(HMDS)₂] (M = Ge or Sn) with two equivalents of the appropriate sulfonimidamide. The homoleptic germlyenes [PhSO(NiPr)₂]₂Ge **3** and [PhSO(NMes)(NiPr)]₂Ge **4**, and stannylenes [PhSO(NiPr)₂]₂Sn **5** and [PhSO(NMes)(NiPr)]₂Sn **6** were fully characterized by NMR spectroscopy and by X-ray diffraction analysis. DFT calculations have been performed to understand the electronic properties brought by sulfonimidamide ligand.

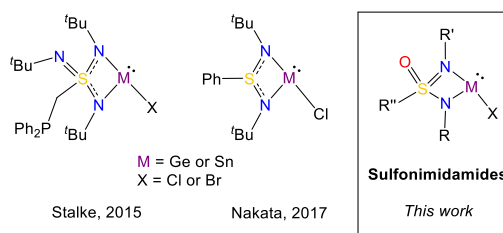
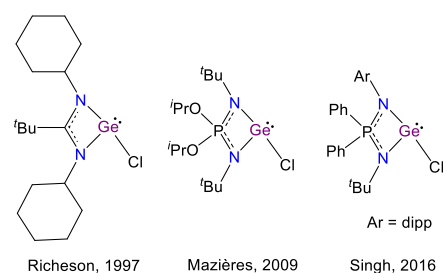
Introduction

The synthesis of germlyenes and stannylenes, group 14 elements exhibiting a +II oxidation state, was extensively studied over the last decades which allowed to obtain a wide range of tetrylenes with well-defined electronic and steric properties.¹ Since the leading work by Lappert and co-workers, who synthesized the first stable germlyenes and stannylenes,² a plethora of studies on the modification of the architecture of ligands have been reported, highlighting the steric and electronic influences of ligand substituents on the corresponding tetrylenes.^{1,3.}

At the end of the 90's, the amidinate ligand emerged as an important tool to prepare a large variety of stable tetrylenes applied in various fields (Figure 1).³ For instance, amidinato-tetrylenes have been used as strong σ-donating ligands for transition metal catalysts, thanks to the extensive work of Driess and co-workers.⁴ Recently, several related ligand systems with phosphorus- and sulfur-centers provided access to new families of stable tetrylenes (Figure 1).⁵ Nevertheless, in almost all cases, these ligands are symmetrical which prevents the

introduction of asymmetry in the architecture.⁶ It is important to note that, germlyenes and stannylenes featuring an asymmetric unit remain scarce compared to the overall contribution of carbene analogues.

In this context, we were interested in easily accessible asymmetric amidinate analogue ligands, allowing to synthesize stable chiral tetrylenes. For this purpose, promising candidates are sulfonimidamides⁷ in which a chiral center can be introduced at the sulfur atom, whereas only one example of such a sulfonimidamide as ligand has been reported to date.^{7d} Here we report the synthesis of an unusual series of germlyenes (**3-4**) and stannylenes (**5-6**) with homoleptic symmetric and unsymmetric N-substituted sulfonimidamide ligands (Figure 1).



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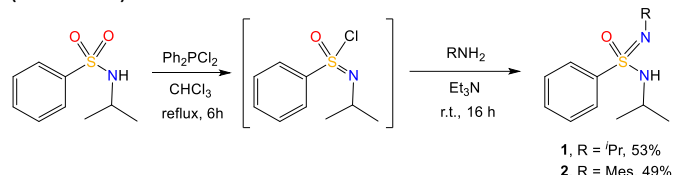
† This article is dedicated to the memory of the late Dr. Jean-Pierre Férézou.

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Fig. 1 Selected examples of phosphorus- and sulfur- analogues of amidinato-tetrylenes, and the present work.

Results and discussion

Sulfonimidamides **1** and **2** have been prepared according the method reported by the group of Chen in 2015, from *iso*-propylbenzenesulfonamide in 53 % and 49 % yield respectively (Scheme 1).⁹



Scheme 1 Synthesis of sulfonimidamides **1-2**.

Both compounds were isolated as air- and moisture-stable white powders, and characterized in the solid state by X-ray crystallography (Figure 2).

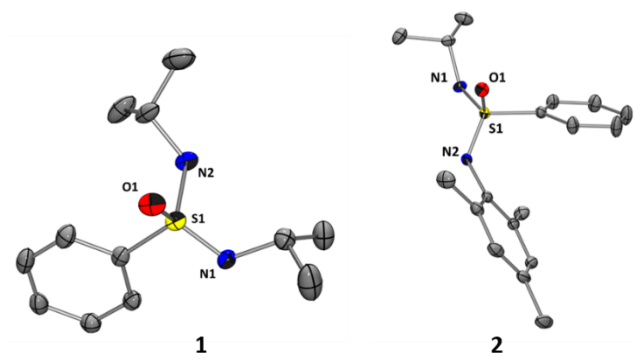
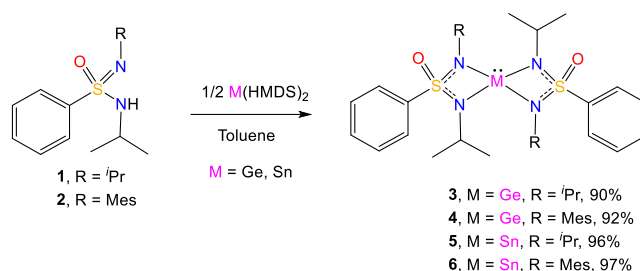


Fig. 2 Molecular structures of **1** and **2**. Thermal ellipsoids represent 30 % probability. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and bond angles [deg] for **1**: S1–O1 1.4562(15), S1–N1 1.501(2); S1–N2 1.628(2); N1–S1–O1 123.44(11); N2–S1–O1 103.97(10); N1–S1–N2 109.70(11). Selected bond distances [Å] and bond angles [deg] for **2**: S1–O1 1.4486(9), S1–N1 1.6032(10); S1–N2 1.5343(10); N1–S1–O1 110.08(5); N2–S1–O1 121.31(6); N1–S1–N2 103.75(5).

As expected, sulfonimidamides **1** and **2** exhibit two different S–N bond lengths [**1**: 1.628(2) and 1.501(2) Å, **2**: 1.6032(10) and 1.5343(10) Å], while in solution the two N-*i*Pr fragments of **1** are equivalent, in agreement with a fast tautomerization process as reported by Johnson et al. in 1979.¹⁰

In order to prepare the corresponding tetrylenes, the first approach was the deprotonation of sulfonimidamide ligands with lithiated bases and subsequent reaction with one or half an equivalent of dichlorometallylene, but the formation of the expected heteroleptic or homoleptic metallylenes was not observed. Thus, protonolysis reactions were considered,^{6d,10} according to the previous work of Guzyr in 2006.^{7d} Germylenes **3** and **4** (Scheme 2) were obtained by reaction of the

corresponding sulfonimidamide with half an equivalent of Lappert's germylene [Ge(HMDS)₂] in toluene overnight at room temperature.



Scheme 2 Synthesis of germylenes **3-4** and stannylenes **5-6**.

After extraction with pentane and elimination of all solvents, germylenes **3** and **4** were isolated as air- and moisture-sensitive white powders in 90 % and 92 % yields respectively. Single crystals of **3** and **4** were obtained from a pentane solution at -20 °C, or from a benzene solution at room temperature, respectively. X-ray diffraction analysis showed the homoleptic germylenes with a sawhorse-like geometry, with N1 and N1' in the axial positions and N2 and N2' sitting in the equatorial plane, similarly to other homoleptic germylenes¹¹ and stannylenes¹² with amidinate ligands (Figure 3).

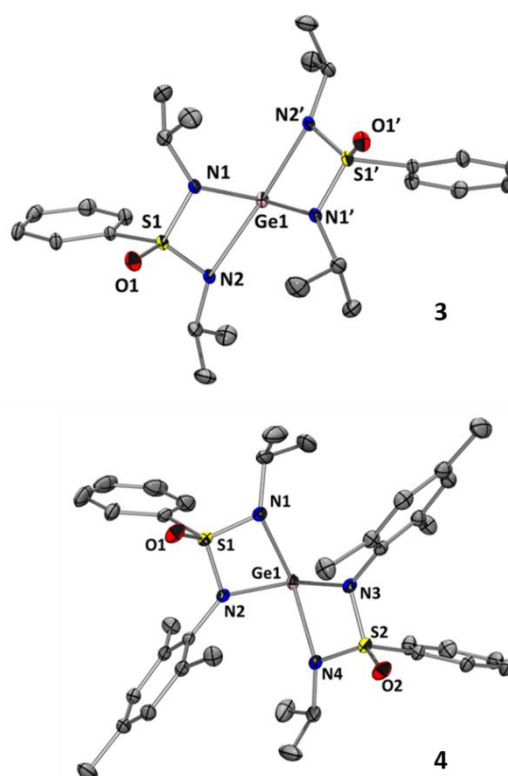


Fig. 3 Molecular structures of **3** and **4**. Thermal ellipsoids represent 30 % probability. Hydrogen atoms and solvent molecule (for **4**) have been omitted for clarity. Selected bond distances [Å] and bond angles [deg] for **3**: Ge1–N1 2.0085(12); Ge1–N2 2.3241(12); S1–O1 1.4484(11), S1–N1 1.5757(12); S1–N2 1.5445(13); N1–Ge1–N1' 97.90(7); N1–Ge1–N2 65.17(5); N1–Ge1–N2' 94.31(5); S1–N1–Ge1 103.84(6);

S1–N2–Ge1 91.95(6); N1–S1–O1 115.67(7); N2–S1–O1 120.81(7); N1–S1–N2 97.64(6). Selected bond distances [Å] and bond angles [deg] for **4**: Ge1–N1 2.2635(11); Ge1–N2 2.0318(10); S1–O1 1.4415(11), S1–N1 1.5505(12); S1–N2 1.5845(11); Ge1–N3 2.0273(10); Ge1–N4 2.2257(12); S2–N3 1.5842(11); S2–N4 1.5512(12); N1–Ge1–N2 65.37(4); N1–Ge1–N3 87.85(4); N1–Ge1–N4 134.89(5); S1–N1–Ge1 93.71(5); S1–N2–Ge1 102.00(5); N1–S1–O1 121.34(7); N2–S1–O1 115.98(6); N1–S1–N2 95.90(6).

The molecular structures of **3** and **4** indicate two types of nitrogen-germanium distances [2.0085(12) Å and 2.3241(12) Å for **3**, 2.0273(10)/2.0328(10) Å and [2.2257(12) /2.2635(11) Å for **4**] in agreement with equatorial and axial bonds respectively, as observed for penta-coordinated species. The equatorial Ge–N bonds are in the usual range for a Ge–N bond distance reported for amidinate-stabilized germynes (1.95 – 2.07 Å).^{5,13} Due to the presence of two different nitrogen centers at the axial and equatorial positions, the two S–N bonds are also inequivalent. Indeed, the S–N_{equatorial} bonds are long like a single bond 1.5757(12) Å for **3** [1.5845(11)/1.5842(11) Å for **4**] while the other ones (S–N_{axial}) are shorter [1.5445(13) Å for **3**, 1.5505(12) /1.5512(12) Å for **4**] in agreement with a S=N double bond character. Again, ¹H NMR spectroscopy of **3** shows only one set of signals for the iPr-groups, indicating a fast isomerization in solution. Moreover, due to the unsymmetrical character of ligand **2** leading to a stereogenic sulfur atom, ¹H NMR spectrum of **4** shows the formation of two diastereomers in a 82:18 ratio.

To prepare the corresponding tin(II) derivatives, the same procedure by protonolysis reaction was employed with Lappert's stannylene. Stannylenes **5** and **6** (Scheme 1) were obtained by the reaction of sulfonimidamides with half an equivalent of [Sn(HMDS)₂] in toluene at room temperature. The formation of stannylenes **5-6** is faster than that of germynes **3-4**, and was completed in 20 minutes. After evaporation and elimination of volatiles, compounds **5** and **6** were isolated as air- and moisture-sensitive white powders in 96 % and 97 % yields respectively. Single crystals of **5** and **6** were obtained from a benzene solution at room temperature, and their structures were determined by X-ray diffraction analysis (Figure 4). Once again, the molecular structures show the homoleptic stannylenes in a sawhorse-like geometry as observed with the germylene compounds, with two types of nitrogen-tin distances : 2.202(5) and 2.208(5) Å for **5** and 2.229(2) and 2.240(2) Å for **6**, corresponding to the equatorial bonds, and 2.389(5) and 2.426(5) Å for **5** and 2.342(2) and 2.347(2) Å for **6** corresponding to the axial bonds.¹⁴ ¹H NMR spectroscopy of **5** shows again only one set of signals for the iPr-groups, corroborating a fast isomerization in solution. Interestingly, ¹H NMR spectroscopy of **6** exhibits the presence of only one diastereomer. ¹¹⁹Sn NMR resonance at –487 and –530 ppm for **5** and **6** respectively confirms the tetra-coordinate nature of these stannylenes in solution, slightly upfield in comparison with the chemical shifts of homoleptic bis-amidinate stannylenes.^{14c}

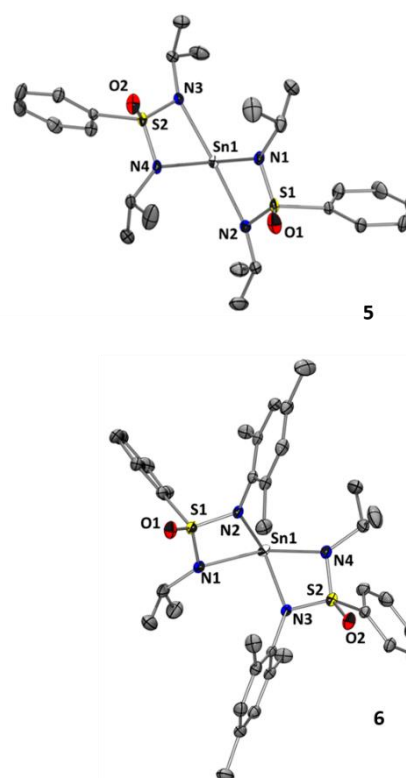


Fig. 4 Molecular structures of **5** and **6**. Thermal ellipsoids represent 30 % probability. Hydrogen atoms and solvent molecule (for **6**) have been omitted for clarity. Selected bond distances [Å] and bond angles [deg] for **5**: Sn1–N1 2.202(5); Sn1–N2 2.426(5); S1–O1 1.442(5), S1–N1 1.572(6); S1–N2 1.539(6); Sn1–N3 2.389(5); Sn1–N4 2.208(5); S2–N3 1.558(5); S2–N4 1.563(6); N1–Sn1–N2 61.2(2); N1–Sn1–N3 92.78(19); N1–Sn1–N4 94.0(2); S1–N1–Sn1 104.0(3); S1–N2–Sn1 95.7(3); N1–S1–O1 116.0(3); N2–S1–O1 119.1(3); N1–S1–N2 99.0(3). Selected bond distances [Å] and bond angles [deg] for **6**: Sn1–N1 2.342(2); Sn1–N2 2.229(2); S1–O1 1.444(2), S1–N1 1.553(2); S1–N2 1.576(2); Sn1–N3 2.240(2); Sn1–N4 2.347(2); S2–N3 1.576(2); S2–N4 1.558(2); N1–Sn1–N2 61.54(8); N1–Sn1–N3 88.24(8); N1–Sn1–N4 125.94(9); S1–N1–Sn1 97.52(11); S1–N2–Sn1 101.43(10); N1–S1–O1 120.28(13); N2–S1–O1 116.90(12); N1–S1–N2 96.85(12).

DFT calculations were undertaken to gain further insight into electronic properties of these new metallaylenes, consistent to a large extent with those observed experimentally. Indeed, we find a sawhorse-like geometry around the metal. In all the studied molecules, two types of axial and equatorial Ge/N (and Sn/N) bonds exist. It is with compound **3** that there is the most deviation from the experimental one while respecting the trend (Δ GN: 0.5/0.4 Å). For the other systems, the deviation is very weak (Δ GN between 0.01 and 0.09 Å). For the S–N distance, the agreement is even better with a bond length difference of less than 0.05 Å. The AIM calculation shows a Bond Critical Point (BCP) between Ge/Sn and sulfonimidate nitrogens with a very low electron density value (between +0.05 and 0.09 eÅ⁻³), the Laplacian of the charge density $\nabla^2\rho$ is positive with negative electron density energy H ($H=G+V$, sum of kinetic energy density

and potential energy density). Typically, the bond is not covalent, but rather highly polarized. It is classified as "intermediate type". The different values show non-equivalent M-N bonds, but still the same in nature. In these systems, the HOMO (mainly s orbital) is well-localized on the germanium/tin atom in interaction with the symmetrical combination of delocalized π sulfonimidamide. The vacant orbital on the metal can be described as a σ^* orbital localized in a Sn p-type orbital. Figure 5 illustrates the HOMO and LUMO+5 orbitals by using compound **5** as an example.

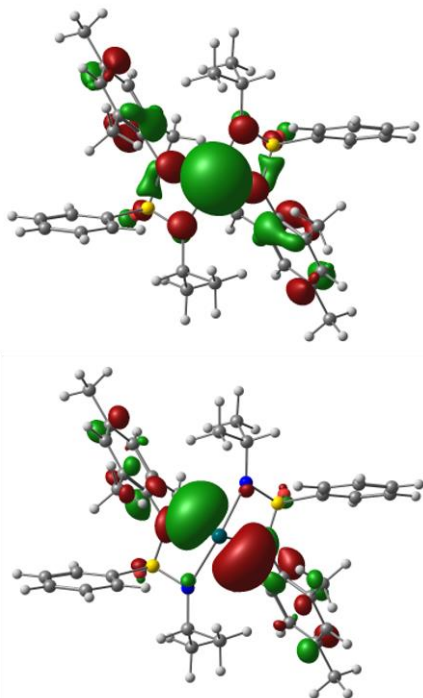


Fig. 5 HOMO (up) and LUMO+5 (down) for compound **5**.

It is interesting to notice a strong stabilization of the electronic system when switching from Ge to Sn derivatives, especially in regard to the previously mentioned vacant orbital. For instance, if we compare compounds **3** and **5**, we have a slight stabilization of the HOMO (0.4 eV) but a substantial stabilization of the vacant one (from 0.61 to -0.03 eV) indicating a high electrophilic character of tin derivatives that might have to be exploited.

Conclusions

Two sulfonimidamides, symmetric **1** and unsymmetric **2**, were successfully synthesized and used for the stabilization of low valent group 14 elements. The homoleptic germlylenes and stannylenes have been obtained by protonolysis reactions with $\text{Ge}(\text{HMDS})_2$ or $\text{Sn}(\text{HMDS})_2$ and the corresponding sulfonimidamide. These new metallylenes, **3-6**, have been characterized by NMR spectroscopy and X-ray diffraction analysis. Molecular structures show different bond lengths for germanium-nitrogen or tin-nitrogen interatomic distances. However, fast isomerization is observed in solution by ^1H NMR spectroscopy at room temperature.

Finally, DFT calculations have been performed to understand the electronic properties brought by the sulfonimidamide on the metallylene, indicating a high electrophilic character of the tin derivatives.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Experimental

General Procedures.

All manipulations with air-sensitive products were performed in dry and oxygen-free atmosphere by using standard Schlenk-line and glovebox techniques. Solvents were purified with the MBraun SBS-800 purification system. The Lappert germanium(II) and tin (II) derivatives were prepared according to literature procedures.² All reagents were obtained from commercial suppliers unless otherwise statement.

Characterizations.

NMR spectra were recorded with the following spectrometers: ^1H , Bruker Avance II 300 (300.18 MHz); ^{13}C , Bruker Avance II 300 (75.48 MHz) at 298 K. Mass spectrometry (MS) spectra were measured on a Maldi micro MX microMass in an anthracene matrix (ratio product/matrix : 1/100). High-resolution MS (HR-MS) spectra were measured with a GCT Premier Waters in DCI mode (CH_4). Melting points were measured with a sealed capillary using the Stuart automatic melting point SMP40 apparatus. Single-crystal X-ray data were collected at low temperature (193(2)K) on a Bruker-AXS APEX II Quazar diffractometer equipped with a 30W air-cooled microfocus source (**4** and **6**) or on a Bruker-AXS PHOTON100 D8 VENTURE diffractometer (**1**, **2**, **3** and **5**), using $\text{MoK}\alpha$ radiation ($\lambda = 0.71037 \text{ \AA}$). The structure were solved by the direct method (SHELXS-97)¹⁵ or by intrinsic phasing method (SHELXT)¹⁶ and refined by full-matrix least-squares method on F2.¹⁷ All non-H atoms were refined with anisotropic displacement parameters.

CCDC-2254658 (**1**), CCDC-2254659 (**2**), CCDC-2254660 (**3**), CCDC-2254661 (**4**), CCDC-2254662 (**5**) and CCDC-2254663 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of (1): Hexachloroethane (264 mg, 1.11 mmol, 1.1 eq) was added to a solution of triphenylphosphine (293 mg, 1.11 mmol, 1.1 eq) in CHCl_3 (10 mL) at room temperature. The solution was heated at reflux for 6 h. Then, the mixture was allowed to return at room temperature and triethylamine (210 μL , 1.52 mmol, 1.5 eq) was added, the mixture was stirred for 30 min at room temperature. *N*-iso-propylbenzenesulfonamide (200 mg, 1.01 mmol, 1 eq) was dissolved in CHCl_3 and added on the mixture. Finally, after stirring the mixture for 30 min at room temperature iso-propylamine (260 μL , 3.03 mmol, 3 eq) was added and the solution stirred overnight at room temperature. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (Eluent: Petroleum Ether/Ethyl Acetate: 4/6, Rf = 0.78) to give a white solid (129 mg) in 53 % yield. Crystals were obtained by slow evaporation in ethyl acetate. M.p.: 66 °C; ^1H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 1.07 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$); 1.12 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$); 3.62 (sept., $^3J_{\text{HH}} = 6.5$ Hz, 2H, $\text{N-CH}(\text{CH}_3)_2$), 5.09 (s, 1H, NH), 6.98–7.08 (m, 3H, CH_{Ar}), 8.09–8.13 (m, 2H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, C_6D_6 , 25 °C): δ 25.4 ($\text{CH}(\text{CH}_3)_2$); 25.5 ($\text{CH}(\text{CH}_3)_2$); 45.5 ($\text{CH}(\text{CH}_3)_2$); 128.0 (C_{Ar}); 128.6 (C_{Ar}); 131.3 (C_{Ar}); 143.3 ($\text{C}_{\text{Ar/q}}$). HRMS m/z (%): 241.1380 ($[\text{M} + 1]^+$) calcd for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{OS}$ ($[\text{M} + 1]^+$) 241.1375.

Synthesis of (2): Hexachloroethane (264 mg, 1.11 mmol, 1.1 eq) was added to a solution of triphenylphosphine (293 mg, 1.11 mmol, 1.1 eq) in CHCl_3 (10 mL) at room temperature. The solution was heated at reflux for 6 h. Then, the mixture was allowed to return at room temperature and triethylamine (210 μL , 1.52 mmol, 1.5 eq) was added, the mixture was stirred for 30 min at room temperature. *N*-iso-propylbenzenesulfonamide (200 mg, 1.01 mmol, 1 eq) was dissolved in CHCl_3 and added on the mixture. Finally, after stirring the mixture for 30 min at room temperature 2,4,6-Trimethylaniline (426 μL , 410 mg, 3.03 mmol, 3 eq) was added and the solution stirred overnight at room temperature. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (Eluent: Petroleum Ether/Ethyl Acetate: 4/6, Rf = 0.80) to give a white solid (157 mg) in 49 % yield. Crystals were obtained by slow evaporation in ethyl acetate. M.p.: 93 °C; ^1H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 0.60 (d, $^3J_{\text{HH}} = 6.5$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$); 0.84 (d, $^3J_{\text{HH}} = 6.5$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$); 2.15 (s, 3H, CH_3); 2.53 (s, 6H, CH_3); 3.41 (sept., $^3J_{\text{HH}} = 6.5$ Hz, 1H, $\text{N-CH}(\text{CH}_3)_2$), 5.11 (s, 1H, NH), 6.84 (s, 2H, CH_{Ar}), 6.98–7.02 (m, 3H, CH_{Ar}), 8.04–8.07 (m, 2H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, C_6D_6 , 25 °C): δ 20.6 (CH_3); 20.9 (CH_3); 23.0 ($\text{CH}(\text{CH}_3)_2$); 24.1 ($\text{CH}(\text{CH}_3)_2$); 46.0 ($\text{CH}(\text{CH}_3)_2$); 127.6 (C_{Ar}); 128.7 (C_{Ar}); 129.5 (C_{Ar}); 131.4 (C_{Ar}); 132.2 ($\text{C}_{\text{Ar/q}}$); 134.1 ($\text{C}_{\text{Ar/q}}$); 138.3 ($\text{C}_{\text{Ar/q}}$); 144.3 ($\text{C}_{\text{Ar/q}}$). HRMS m/z (%): 317.1697 ($[\text{M} + 1]^+$) calcd for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{OS}$ ($[\text{M} + 1]^+$) 317.1688.

Synthesis of (3): KHMDS (85.8 mg, 0.43 mmol, 2 eq) was added to $\text{GeCl}_2 \cdot \text{dioxane}$ (49.7 mg, 0.215 mmol, 1 eq) in Et_2O at room temperature. The mixture was stirred for 2 hours and *N,N'*-di-iso-propylbenzenesulfonimidamide (1) (154 mg, 0.43 mmol, 2

eq) in Et_2O was added at the same temperature. After 16 h, the solvent was removed under reduced pressure and the resulting solid was extract with pentane. The solvent was removed under reduced pressure to give a white solid in 90 % yield (107 mg). Crystallization from pentane at –25 °C gave colourless crystals suitable for X-ray study. M.p.: 105 °C (decomposition); ^1H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 1.33 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$); 1.40 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$); 3.64 (sept., $^3J_{\text{HH}} = 6.6$ Hz, 4H, $\text{N-CH}(\text{CH}_3)_2$), 6.96–7.08 (m, 6H, CH_{Ar}), 7.89–7.91 (m, 4H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, C_6D_6 , 25 °C): δ 24.6 ($\text{CH}(\text{CH}_3)_2$); 25.4 ($\text{CH}(\text{CH}_3)_2$); 47.4 ($\text{CH}(\text{CH}_3)_2$); 128.9 (C_{Ar}); 129.1 (C_{Ar}); 131.4 (C_{Ar}); 141.9 ($\text{C}_{\text{Ar/q}}$). MS m/z (%): 552 (M^+).

Synthesis of (4): KHMDS (43 mg, 0.215 mmol, 2 eq) was added to $\text{GeCl}_2 \cdot \text{dioxane}$ (25 mg, 0.108 mmol, 1 eq) in Et_2O at room temperature. The mixture was stirred for 2 hours and *N*-iso-propyl-*N'*-mesitylbenzenesulfonimidamide (2) (68 mg, 0.215 mmol, 2 eq) in Et_2O was added at the same temperature. After 16 h, the solvent was removed under reduced pressure and the resulting solid was extract with pentane. The solvent was removed under reduced pressure to give a white solid in 92 % yield (70 mg). Crystallization from benzene at room temperature gave colourless crystals suitable for X-ray study. M.p.: 108 °C (decomposition); *Isomer A*: ^1H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 0.72 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$); 0.91 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$); 2.05 (s, 6H, CH_3); 3.23 (sept., $^3J_{\text{HH}} = 6.5$ Hz, 4H, $\text{N-CH}(\text{CH}_3)_2$), 6.89–6.93 (m, 6H, CH_{Ar}), 7.70–7.73 (m, 4H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, C_6D_6 , 25 °C): δ 20.8 (CH_3); 23.8 ($\text{CH}(\text{CH}_3)_2$); 25.2 ($\text{CH}(\text{CH}_3)_2$); 46.8 ($\text{CH}(\text{CH}_3)_2$); 128.9 (C_{Ar}); 131.6 (C_{Ar}); 134.0 (C_{Ar}); 135.9 ($\text{C}_{\text{Ar/q}}$); 140.1 ($\text{C}_{\text{Ar/q}}$). *Isomer B*: ^1H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 1.26 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$); 1.45 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$); 2.02 (s, 6H, CH_3); 3.69 (sept., $^3J_{\text{HH}} = 6.5$ Hz, 4H, $\text{N-CH}(\text{CH}_3)_2$), 6.97–7.05 (m, 6H, CH_{Ar}), 7.80–7.83 (m, 4H, CH_{Ar}). MS m/z (%): 704 (M^+).

Synthesis of (5): *N,N'*-di-iso-propylbenzenesulfonimidamide (1) (60 mg, 0.25 mmol, 2 eq) was dissolved in C_6D_6 (0.4 mL) and added to $\text{Sn}(\text{HMDS})_2$ (55 mg, 0.125 mmol, 1 eq) at room temperature. The mixture was stirred 20 min at room temperature and the solvent was removed under reduced pressure. The solid was extracted with pentane (3x3 mL) to give a white solid in 96 % yield (72 mg). Crystallization from benzene at room temperature gave colourless crystals suitable for X-ray study. M.p.: 117 °C (decomposition); ^1H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 1.26 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$); 1.54 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$); 3.61 (sept., $^3J_{\text{HH}} = 6.6$ Hz, 4H, $\text{N-CH}(\text{CH}_3)_2$), 6.96–7.11 (m, 6H, CH_{Ar}), 7.90–7.92 (m, 4H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, C_6D_6 , 25 °C): δ 25.1 ($\text{CH}(\text{CH}_3)_2$); 25.8 ($\text{CH}(\text{CH}_3)_2$); 47.0 ($\text{CH}(\text{CH}_3)_2$); 128.9 (C_{Ar}); 129.0 (C_{Ar}); 131.1 (C_{Ar}); 142.3 ($\text{C}_{\text{Ar/q}}$). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, C_6D_6 , 25 °C): δ -487. MS m/z (%): 598 (M^+).

Synthesis of (6): *N*-iso-propyl-*N'*-mesitylbenzenesulfonimidamide (2) (60 mg, 0.19 mmol, 2 eq) was dissolved in C_6D_6 (0.4 mL) and added to $\text{Sn}(\text{HMDS})_2$ (42 mg, 0.09 mmol, 1 eq) at room temperature. The mixture was stirred 20 min at room temperature and the solvent was removed under reduced

pressure to give a white solid in 97 % yield (69 mg). Crystallization from benzene at room temperature gave colourless crystals suitable for X-ray study. M.p. : 118 °C (decomposition); ^1H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 0.80 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$); 0.86 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$); 1.80 (s, 6H, CH_3); 2.08 (s, 6H, CH_3); 3.26 (sept., $^3J_{\text{HH}} = 6.5$ Hz, 2H, $\text{N-CH}(\text{CH}_2)_2$), 3.42 (s, 6H, CH_3); 6.63 (s, 4H, CH_{Ar}), 6.89–6.97 (m, 6H, CH_{Ar}), 7.68–7.71 (m, 4H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, C_6D_6 , 25 °C): δ 19.3 ($\text{CH}(\text{CH}_3)_2$); 20.5 (CH_3); 22.1 ($\text{CH}(\text{CH}_3)_2$); 24.1 (CH_3); 24.9 (CH_3); 46.3 ($\text{CH}(\text{CH}_3)_2$); 127.7 (C_{Ar}); 128.5 (C_{Ar}); 128.7 (C_{Ar}); 130.3 (C_{Ar}); 130.9 (C_{Ar}); 134.0 ($\text{C}_{\text{Ar/q}}$); 134.9 ($\text{C}_{\text{Ar/q}}$); 136.7 ($\text{C}_{\text{Ar/q}}$); 141.0 ($\text{C}_{\text{Ar/q}}$); 141.5 ($\text{C}_{\text{Ar/q}}$). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, C_6D_6 , 25 °C): δ -530. MS m/z (%): 750 (M^+).

Notes and references

‡ CCDC-2254658 (1), CCDC-2254659 (2), CCDC-2254660 (3), CCDC-2254661 (4), CCDC-2254662 (5) and CCDC-2254663 (6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- The methyl groups in *ortho*-position and the hydrogen in *meta*-position of the mesityl substituent appear as baseline signals at room temperature and variable temperatures ^1H NMR analysis demonstrated that increasing temperature to +70 °C could provide significantly better broad signals resulting from a free movement of the mesityl group (see supporting information).