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Article

Stannylenes and Germylenes Stabilized by Tetradentate Bis(amidine) Ligands with a Rigid Naphthalene Backbone [†]

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[†] This paper is dedicated to the memory of Dr. Jean-Pierre Férézou.

Abstract: An unusual series of germylenes and stannylenes stabilized by new tetradentate bis(amidine) ligands RNC(R')N-linker-NC(R')NR with a rigid naphthalene backbone has been prepared by protonolysis reaction of Lappert's metallylenes [M(HMDS)₂] (M = Ge or Sn). Germylenes and stannylenes were fully characterized by NMR spectroscopy and X-ray diffraction analysis. DFT calculations have been performed to clarify the structural and electronic properties associated with tetradentate bis(amidine) ligands. Stannylene **L₁Sn** shows reactivity through oxidation, oxidative addition, and transmetalation reactions, affording the corresponding gallium and aluminum derivatives.

Keywords: amidine; ligand; metallylene



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1. Introduction

Amidines have been employed as ligands for numerous metallic and semi-metallic elements [1], and one of their best features is the ability to adjust both steric and electronic properties, leading to many substitution patterns of the CN₂ framework [2–4]. In recent years, the trend has shifted to develop bulkier systems to stabilize a broader range of metal centers or to control the complex geometry via rigid coordination, as seen with bridged bis(amidine) ligands.

Amidinate ligands have shown a remarkable ability to stabilize low-valent main group elements, such as tetrylenes, forming planar NCN-Ge^(II) and NCN-Sn^(II) four-membered rings [5]. The first bis(amidinato)germylene, reported by Richeson et al. in 1997, exhibited one chelating and one dangling amidinate ligand, with the three-coordinate germanium center adopting a trigonal-pyramidal geometry (Figure 1) [6]. Using the same synthetic method, Karsch et al. reported in 1998 a bis(amidinato)germylene with both amidinate ligands acting as chelates due to the less hindered substituents on the nitrogen atoms [7]. On the other hand, the first mono- and bis-(amidinato)stannylenes were reported by Tolman et al. in 2002, using a *N*-silylated benzamidinate ligand (Figure 1) [8].

More recently, the first tetrylenes with 1,4-phenylene (**I**) and 1,4-cyclohexylene (**II**) bridged bis(amidine) ligands were reported by Jones et al. in 2020 [9]. In 2021, the same group reported a bis-germylene and a bis-stannylene with a dibenzofurandiyl-linked Dipp-substituted bis(amidine) ligand (**III**) [10]. In the same year, Kretschmer et al. reported bis-germylenes and bis-stannylenes using a terphenyl-linked bis(amidine) ligand (**IV**) [11].

It is important to note that all these examples correspond to amidine fragments connected through the carbon atom, and only one bis-germylene with a bis(amidine) ligand nitrogen connected via a 1,3-phenylene bridge has been synthesized by Jones et al. (V) [10]. The main characteristic of bridged bis(amidine) ligands exhibited is that the amidine functionalities act as independent ligands, allowing the convenient preparation of stable bis-metallaylenes. Moreover, there is no report of a bis(amidine) system acting as a tetradentate ligand with both amidine moieties coordinated to the same metal center. We therefore considered the hypothesis that such a bis(amidine) system could influence the stabilization and the reactivity of the corresponding tetraylenes.

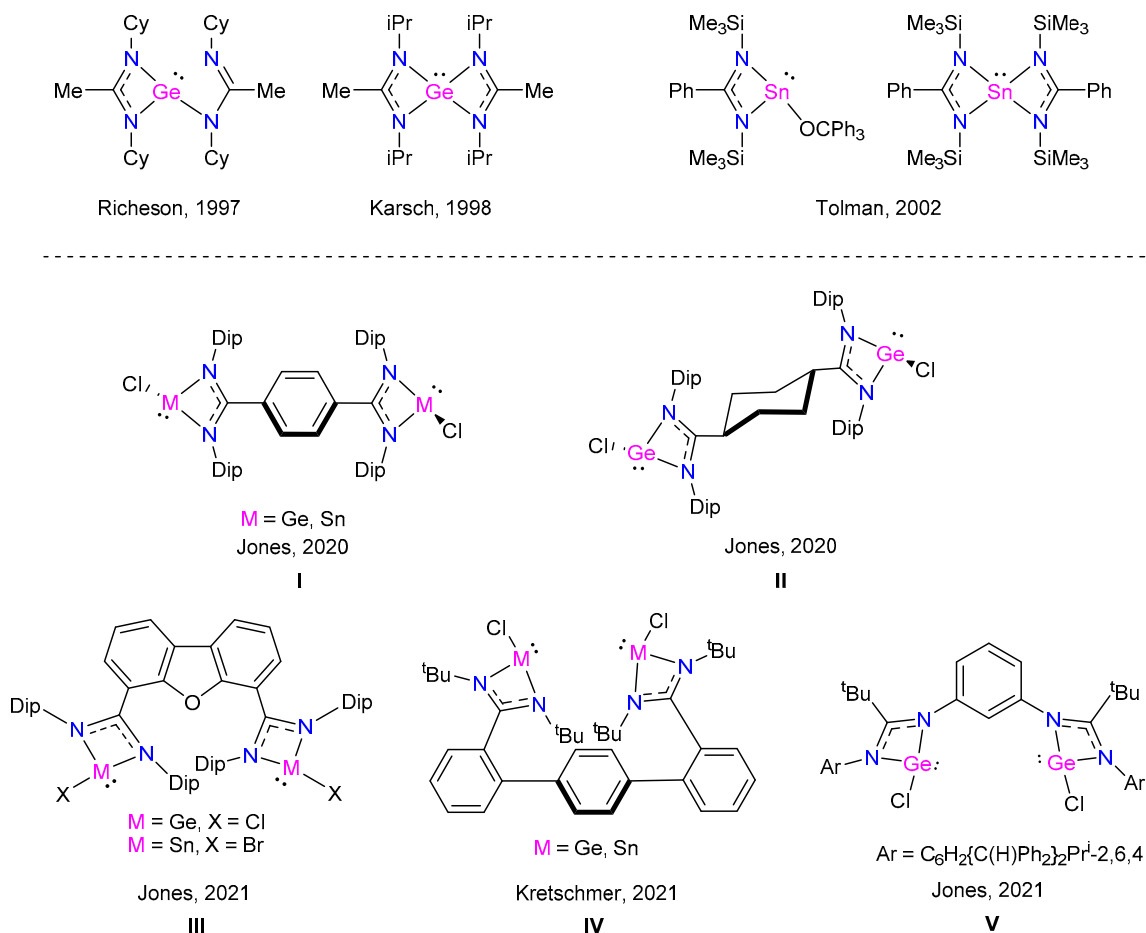


Figure 1. Examples of germylenes and stannylenes with bis(amidine) ligands [6–11].

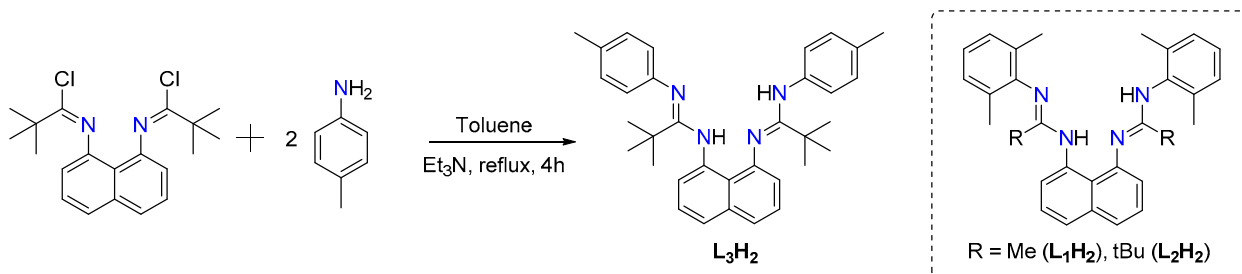
Herein, we report the synthesis and structural characterization of novel stannylene and germylene compounds stabilized by naphthalene-linked bis(amidine) ligands, with the amidine functionalities connected to the naphthalene bridge through the nitrogen atoms. In addition, the reactivity of synthesized stannylenes was explored in oxidation, oxidative addition, and transmetalation reactions.

2. Results and Discussion

2.1. Synthesis of Bis(amidine) Ligands with a Rigid Naphthalene Backbone

Bis(amidine) ligands **L₁H₂** and **L₂H₂**, with a rigid planar 1,8-diaminonaphthalene linker, were prepared following the reported procedures [12,13], while the synthesis of **L₃H₂** was carried out through the reaction between one equivalent of *N,N'*-(naphthalene-1,8-diyl)bis(2,2-dimethylpropanimidoyl chloride) and two equivalents of *p*-tolylamine in dry toluene under reflux for 4 h in the presence of Et₃N (Scheme 1). **L₃H₂** was isolated as yellow crystals in 63% yield and characterized by NMR spectroscopy. The ¹H NMR

spectrum shows two NH signals at 9.43 and 8.50 ppm, similar to those previously reported bis(amidine) ligands [13,14]. In addition, CH₃ resonances of *p*-tolyl and *t*butyl fragments appear as singlets at 2.05 and 2.01 ppm and at 1.38 and 1.23 ppm, respectively. The ¹³C NMR spectrum also exhibits two different C=N groups at 161.3 and 160.7 ppm, confirming the non-symmetrical character of L₃H₂ ligand in solution due to NH⋯N hydrogen bonds.



Scheme 1. Synthesis of ligand L₃H₂.

The presence of an intramolecular hydrogen bond between the N-H group and the nitrogen atom of the amidine moiety [N1-(H1)⋯N(3) 1.95(5) Å] is confirmed in the solid-state structure of ligand L₃H₂ (Figure 2), in line with similar observations for ligands L₁H₂ and L₂H₂ [12,13].

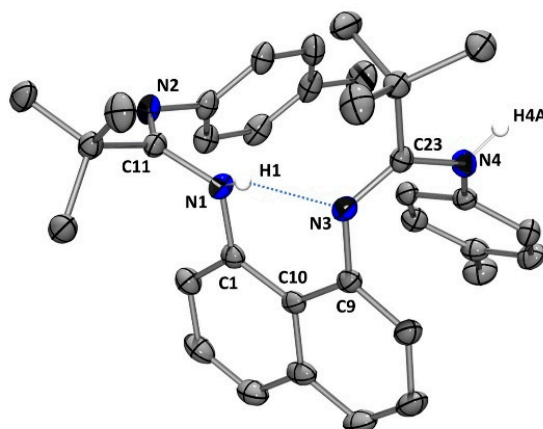
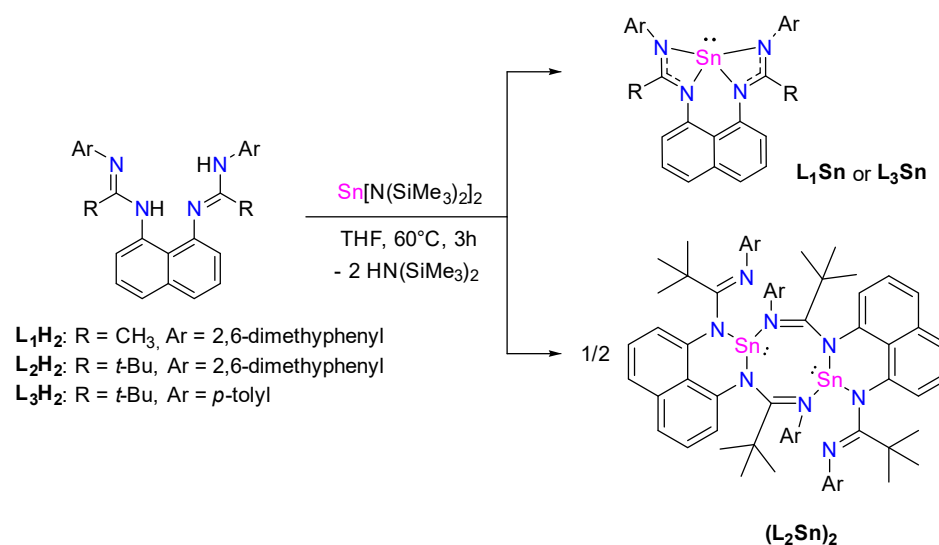


Figure 2. Molecular structure of L₃H₂. Thermal ellipsoids are represented with a 30% probability. Hydrogen atoms (except H1 and H4A) have been omitted for clarity. Selected bond distances [Å] and bond angles [deg]: N(1)-C(11) 1.421(5); N(2)-C(11) 1.272(5); N(3)-C(23) 1.286(5); N(4)-C(23) 1.373(5); N1-(H1)⋯N(3) 1.95(5); N(1)-C(11)-N(2) 122.5(3); N(3)-C(23)-N(4) 126.1(3).

2.2. Synthesis of Stannylenes L₁₋₃Sn

The synthesis of stannylene L₁₋₃Sn was carried out using protonolysis reactions due to the simplicity of the procedure [15–17]. Therefore, the corresponding bis(amidine) ligand L₁₋₃H₂ reacted with one equivalent of Sn(HMDS)₂ in dry THF at 60 °C for 3 h (Scheme 2). Stannylene L₁Sn was isolated as colorless crystals from a pentane solution at −30 °C in 77% yield. The formation of L₁Sn was confirmed by ¹H, ¹³C, and ¹¹⁹Sn NMR spectroscopy and mass spectrometry. The ¹H NMR spectrum shows a singlet at 1.97 ppm with an integration of 6 H, corresponding to the two amidine methyl groups, and a singlet at 2.18 ppm with an integration of 12 H, corresponding to the methyl groups of 2,6-dimethylphenyl fragments. This observed NMR pattern agrees with a symmetrical structure around the tin center. The ¹³C NMR spectrum shows a characteristic signal for the NCN fragment at 169.0 ppm, similar to those (amidinato)stannylenes previously reported [8,15,16,18]. In the ¹¹⁹Sn NMR spectrum, a resonance at −276.7 ppm confirms the tetracoordinated nature of the tin atom, comparable to that of reported homoleptic four-coordinated bis(amidinate) tin(II) [15]. L₃H₂

also reacts with $\text{Sn}(\text{HMDS})_2$ in the same manner to give the corresponding tetracoordinated stannylene L_3Sn , as shown by the NMR analysis. Indeed, the ^1H NMR spectrum shows a singlet at 1.30 ppm that integrates for 18 H, corresponding to the amidine *t*-butyl groups, and a singlet at 2.29 ppm that integrates for 6 H, corresponding to the *p*-tolyl methyl groups. The ^{13}C NMR spectrum shows a characteristic signal for the NCN fragment at 177.5 ppm. The symmetrical tetracoordination of the tin center is also confirmed by a resonance at -254.9 ppm in the ^{119}Sn NMR spectrum. In contrast, the use of the bulky bis(amidinate) ligand L_2H_2 leads to the formation of a dimeric structure $(\text{L}_2\text{Sn})_2$.



Scheme 2. Synthesis of stannylene L_{1-3}Sn .

Stannylene L_1Sn was characterized in the solid state by single-crystal X-ray diffraction analysis (Figure 3). The molecular structure indicates a four-coordinate tin center with a distorted square-based pyramidal geometry. A few stannylenes with unbridged bis(amidinate) ligands display a similar geometry [16]. The acute N1–Sn–N2 and N3–Sn–N4 angles of 57.38° and 57.74° are comparable to values previously recorded for Sn^{II} amidinate complexes [15,18].

The coordinates of the experimental solid-state structure are consistent with the calculated values in DFT (see Supplementary Materials for more information). Indeed, the modeling calculates values between 2.27 and 2.42 Å for the Sn–N bonds, probably due to steric repulsion, and angles at the tin atom of 56° . Moreover, the energy of molecular orbitals of this species (computed using DFT) shows an electrophilic character (the first vacant orbital on the Sn atom is computed at -0.60 eV) and a potential nucleophilicity, as the HOMO centered on the non-bonding pair of tin is rather accessible (-5.42 eV) (Figure 4).

The modeling demonstrates that this compound can be obtained from the bis(amidinate) ligand through the addition of $\text{Sn}(\text{HMDS})_2$. Indeed, starting from the resulting complex, a prototropic shift can occur, leading to the facile formation of the corresponding RSnH (TS = 21.63 kcal/mol) (see Supplementary Materials for more information). Subsequently, the elimination of HMDS results in the obtaining of L_1Sn , exhibiting a higher but consistent kinetic rate with the applied experimental conditions ($60^\circ\text{C}/3$ h).

Because of the poor solubility of stannylene dimer $(\text{L}_2\text{Sn})_2$ in common organic solvents, the NMR characterization cannot be obtained once crystallized. Nevertheless, the X-ray diffraction analysis shows an eight-membered cyclic structure with a Sn···Sn distance of 3.7311(5) Å (Figure 5). Each Sn center has a trigonal pyramidal geometry with a sum of angles around the Sn atom of 272° . Interestingly, the tin atoms are coordinated to both nitrogen atoms directly linked to the naphthalene core and, simultaneously, to one of the nitrogen atoms from another amidinate fragment. Unfortunately, providing theoretical arguments for the formation of dimer $(\text{L}_2\text{Sn})_2$ is challenging. Indeed, calculations reveal an

energetically favorable reaction pathway ($\Delta G = -27.74$ kcal/mol) to obtain the corresponding monomer. We can postulate that the presence of the 2,6-dimethylphenyl and *t*butyl groups in the ligand introduces significant steric hindrance, inhibiting the arrangement of a tetracoordinated tin center and thereby influencing the preferential formation of the dimer.

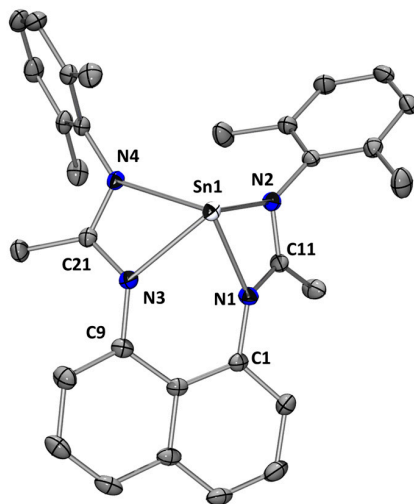


Figure 3. Molecular structure of L_1Sn . Thermal ellipsoids are represented with a 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and bond angles [deg]: Sn(1)–N(1) 2.2435(17); Sn(1)–N(2) 2.3327(17); Sn(1)–N(3) 2.2232(17); Sn(1)–N(4) 2.3181(16); N(1)–C(11) 1.326(3); N(2)–C(11) 1.328(3); N(3)–C(21) 1.328(3); N(4)–C(21) 1.329(3); N(3)–Sn(1)–N(1) 72.57(6); N(3)–Sn(1)–N(4) 57.74(6); N(1)–Sn(1)–N(4) 107.35(6); N(3)–Sn(1)–N(2) 112.07(6); N(1)–Sn(1)–N(2) 57.38(6); N(4)–Sn(1)–N(2) 95.29(6); N(1)–C(11)–N(2) 111.85(17); N(3)–C(21)–N(4) 111.37(17).

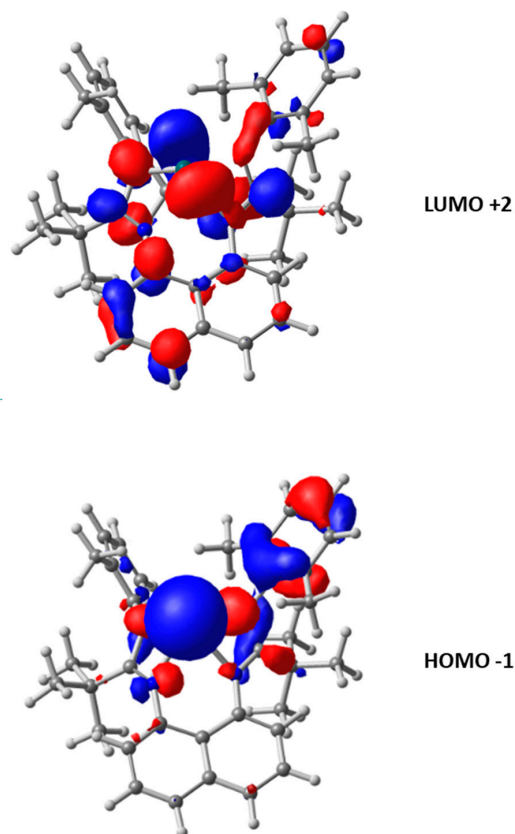


Figure 4. LUMO +2 (up) and HOMO –1 (down) for L_1Sn .

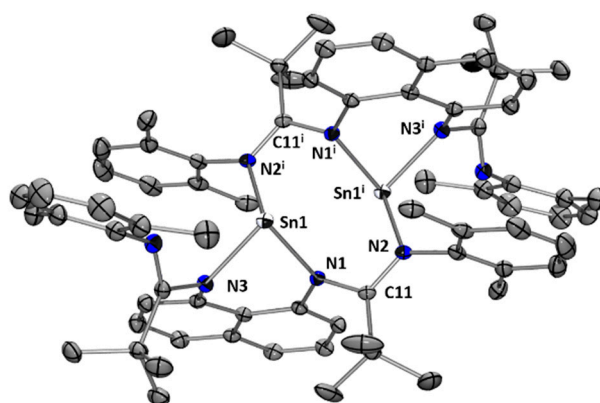
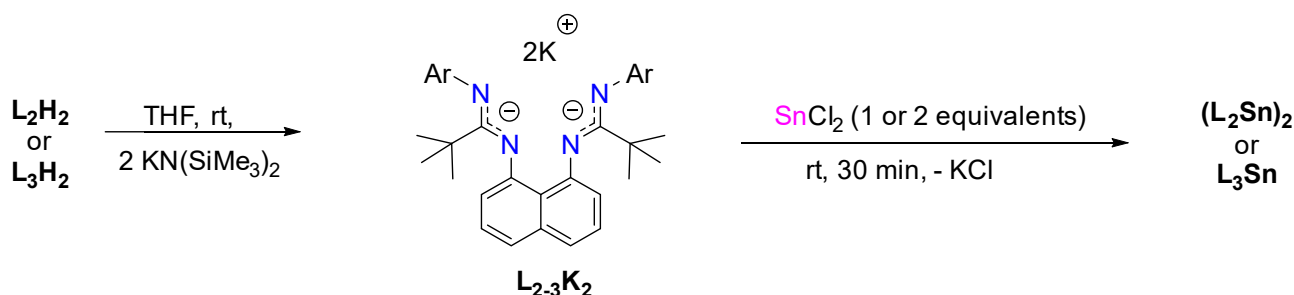


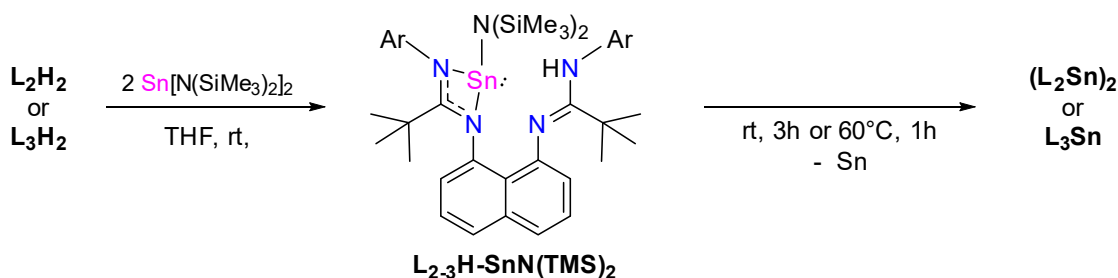
Figure 5. Molecular structure of $(L_2Sn)_2$. Thermal ellipsoids are represented with a 30% probability. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond distances [Å] and bond angles [deg]: Sn(1)–N(1) 2.243(2); Sn(1)–N(2ⁱ) 2.327(2); Sn(1)–N(3) 2.144(3); C(11)–N(1) 1.378(4); C(11)–N(2) 1.309(4); N(1)–Sn(1)–N(3) 78.80(9); N(3)–Sn(1)–N(2ⁱ) 97.73(9); N(1)–Sn(1)–N(2ⁱ) 95.21(9); C(11)–N(1)–Sn(1) 112.43(18); N(1)–C(11)–N(2) 114.2(3).

Stannylene L_3Sn and dimer $(L_2Sn)_2$ can also be prepared through the reaction of deprotonated bis(amidine) ligand (L_2K_2 or L_3K_2) with one equivalent of $SnCl_2$. The same products, $(L_2Sn)_2$ and L_3Sn , were also obtained using two equivalents of $SnCl_2$, instead of the expected bis-stannylenes L_2Sn_2 and L_3Sn_2 (Scheme 3).



Scheme 3. Synthetic routes to obtain $L_{2-3}Sn$ from deprotonated bis(amidine) ligands.

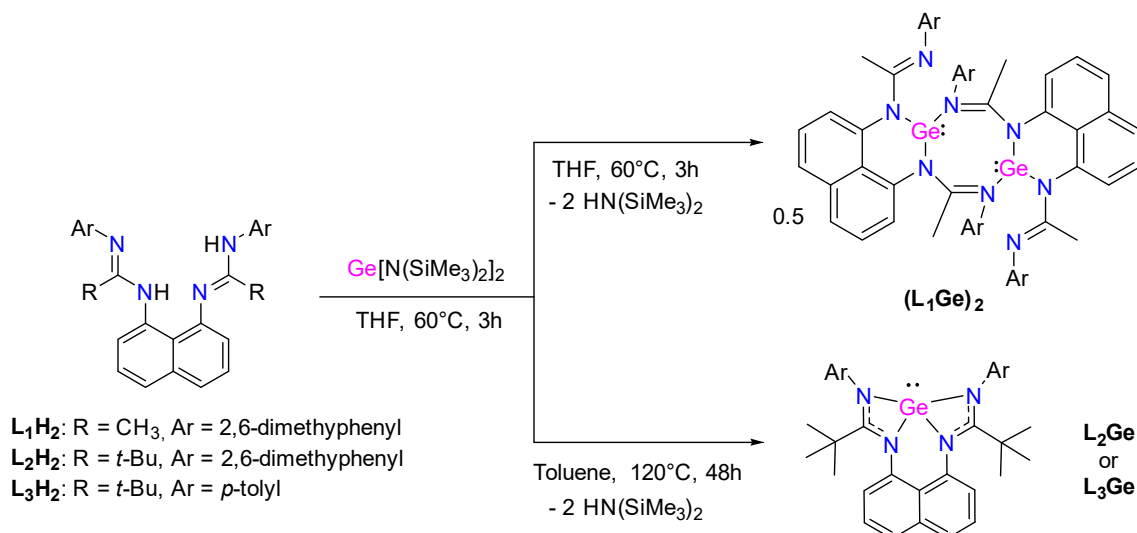
Other attempts to synthesize bis-stannylenes L_2Sn_2 and L_3Sn_2 , by reacting the corresponding ligand (L_2H_2 or L_3H_2) with two equivalents of $Sn(HMDS)_2$ (via protonolysis reactions), have also failed (Scheme 4). In both cases, at room temperature, the formation of an intermediate $LH-SnN(TMS)_2$ was first detected by 1H NMR spectroscopy. The subsequent heating at 60 °C for 1 h affords the corresponding stannylenes $(L_2Sn)_2$ or L_3Sn (44% and 61% yield, respectively), accompanied by the formation of H-HMDS and a black solid of Sn^0 as by-products.



Scheme 4. Synthetic routes to obtain $L_{2-3}Sn$ by protonolysis.

2.3. Synthesis of Germylenes Stabilized by Bis(amidine) Ligands

Following the same synthetic strategy, we have considered the reaction of bis(amidinato) ligands $L_{1-3}H_2$ with $Ge(HMDS)_2$. In the case of L_1H_2 , only dimer $(L_1Ge)_2$ was obtained as yellow crystals in 42% yield (Scheme 5). Because of poor solubility, it was only possible to characterize $(L_1Ge)_2$ by an X-ray diffraction analysis. The eight-membered cyclic molecular structure of $(L_1Ge)_2$ exhibits two trigonal pyramidal Ge centers with a Ge–Ge distance of 3.4984(3) Å (Figure 6).



Scheme 5. Synthesis of germylenes $L_{1-3}Ge$.

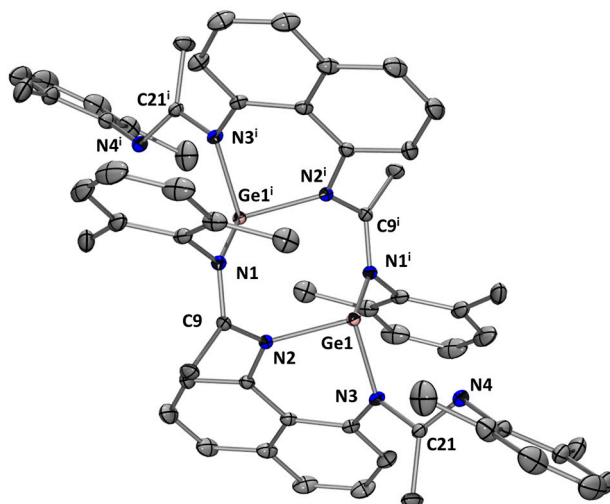


Figure 6. Molecular structure of $(L_1Ge)_2$. Thermal ellipsoids are represented with a 30% probability. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond distances [Å] and bond angles [deg]: Ge(1)–N(1ⁱ) 2.0961(11); Ge(1)–N(2) 2.0048(10); Ge(1)–N(3) 1.9332(10); C(9)–N(1) 1.3074(16); C(9)–N(2) 1.3740(16); N(3)–Ge(1)–N(2) 87.48(4); N(3)–Ge(1)–N(1ⁱ) 95.69(4); N(2)–Ge(1)–N(1ⁱ) 96.79(4); N(1)–C(9)–N(2) 116.31(11); C(9)–N(2)–Ge(1) 112.38(8).

The reaction of L_2H_2 with $Ge(HMDS)_2$ afforded germylene L_2Ge after heating at 110 °C for 48 h to complete the reaction (Scheme 5). Germylene L_2Ge was isolated as yellow crystals from a pentane solution at $-30^\circ C$ in 52% yield. The 1H NMR spectrum shows a singlet at 1.60 ppm with an integration of 18 H, corresponding to the t butyl groups, and a singlet at 2.18 ppm with an integration of 12 H, corresponding to the methyl groups of the 2,6-dimethylphenyl substituent. In addition, the ^{13}C NMR spectrum shows the

characteristic signal for the NCN fragment at 170.9 ppm. These data are in agreement with a symmetrical tetracoordinated germanium center in solution. However, in the solid state, the X-ray diffraction analysis of **L₂Ge** shows a tri-coordinated germanium atom with a distorted trigonal pyramidal geometry. Here, the coordination is through the two nitrogen atoms of the naphthalene bridge and one nitrogen atom of amidine moiety, leaving the remaining nitrogen atom dangling (Figure 7). The N–C distances [1.275(5)–1.417(5) Å] indicate an electron delocalization within the NCN fragments, and due to the bulky nature of the *t*butyl substituents, they are in opposite directions to each other, distorting the naphthalene ring.

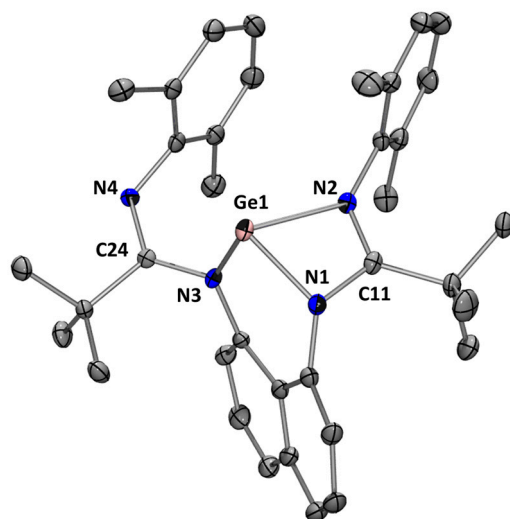


Figure 7. Molecular structure of **L₂Ge**. Thermal ellipsoids are represented with a 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and bond angles [deg]: Ge(1)–N(1) 1.969(3); Ge(1)–N(2) 2.073(3); Ge(1)–N(3) 1.912(3); C(11)–N(2) 1.308(5); C(11)–N(1) 1.374(5); C(24)–N(4) 1.275(5); C(24)–N(3) 1.417(5); N(1)–Ge(1)–N(2) 64.89(13); N(1)–Ge(1)–N(3) 90.95(13); N(2)–Ge(1)–N(3) 102.00(13); N(1)–C(11)–N(2) 108.0(3); N(3)–C(24)–N(4) 124.0(3).

2.4. Reactivity of Stannylenes **L₁Sn**

Several tests of reactivity were carried out with stannylenes **L₁Sn**, which is easy to obtain in good yields. We first considered the activation of small molecules such as ethylene, NH₃, and CO₂, but without any success because of no reactions, despite the multiple conditions evaluated (temperature, time, and pressure).

However, when exposed to N₂O (five bars) in THF solution, **L₁Sn** slowly reacts (3 h at 70 °C) to give a dimeric amidinate-stannoxane **1a**, which was isolated as colorless crystals in 46% yield (Scheme 6). Compound **1a** is moderately soluble in THF, and the ¹H NMR signals tend to be broadened. Therefore, the coupling of signals in the aromatic region cannot be clearly seen, but the integration is as expected, with two broad singlets at 2.07 and 1.85 ppm that integrate for 12 H, corresponding to the methyl groups of the 2,6-dimethylphenyl fragment. In addition, a resonance at 1.76 ppm, integrating for 12 H and corresponding to the methyl groups of the amidine moieties, was observed. The characteristic signal of the carbon amidinate fragments in the ¹³C NMR spectrum resonates at 168.7 ppm. In addition, a ¹¹⁹Sn chemical shift at −494.5 ppm was observed, consistent with reported stannoxane dimers [19]. The crystal structure of **1a** shows a dinuclear species with a central planar Sn₂O₂ ring with two hexacoordinated tin atoms in a distorted pseudo-octahedral geometry (Figure 8). The O–Sn distances (~2.000 Å), Sn–Sn contact (2.9779(2) Å), and O–Sn–O angles (84.01°) are in the range of other dimeric tin amidinate-stannoxanes reported [19].

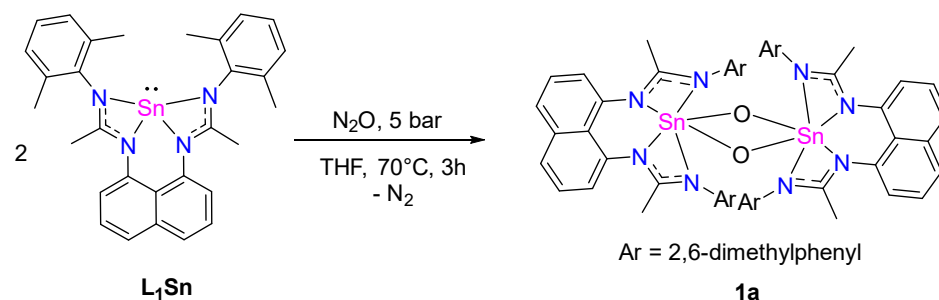
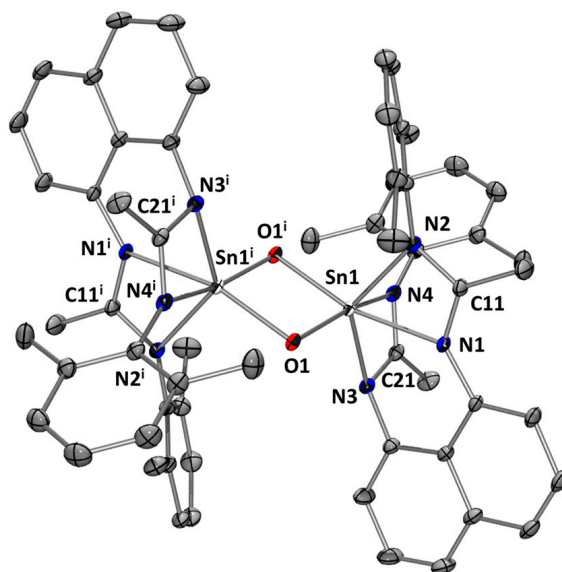
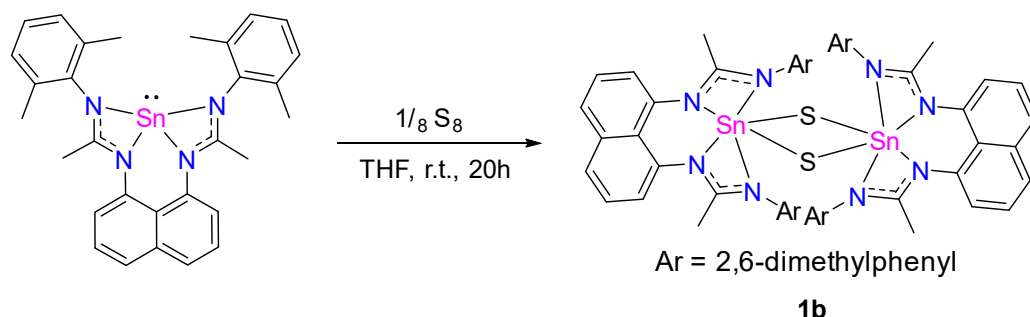
Scheme 6. Synthesis of **1a**.

Figure 8. Molecular structure of **1a**. Thermal ellipsoids are represented with a 30% probability. Hydrogens and solvent molecules have been omitted for clarity. Selected bond distances [Å] and bond angles [deg]: Sn(1)–N(1) 2.2236(10); Sn(1)–N(2) 2.1644(11); Sn(1)–N(3) 2.1423(10); Sn(1)–N(4) 2.2742(10); Sn(1)–O(1) 2.0079(9); Sn(1)–O(1ⁱ) 1.9996(8); Sn(1)–Sn(1ⁱ) 2.97787(19); C(11)–N(1) 1.3285(16); C(11)–N(2) 1.3415(16); C(21)–N(4) 1.3113(17); C(21)–N(3) 1.3439(17); O(1)–Sn(1)–O(1ⁱ) 84.01(4); Sn(1)–O(1)–Sn(1ⁱ) 95.98(4); N(1)–C(11)–N(2) 110.50(11); N(3)–C(21)–N(4) 112.95(11).

Usually, stannylenes readily react with chalcogenides [6,20–25], and therefore we have investigated the reaction of **L₁Sn** with elemental sulfur (Scheme 7). After the reaction mixture had been stirred at room temperature for 4 h, ¹H, and ¹¹⁹Sn NMR spectroscopy showed a mixture of new signals and starting stannylene. In the ¹¹⁹Sn NMR spectrum, next to the resonance of **L₁Sn**, a new signal appears at −371 ppm, which evolves to a resonance singlet at −648.0 ppm after 24 h, corresponding to dimer **1b**. After purification, **1b** was isolated as pale-yellow crystals from a THF solution at −30 °C in 51% yield. The dimeric structure of **1b** has been determined by an X-ray diffraction analysis, revealing a central planar Sn₂S₂ ring with the two tin centers in a distorted pseudo-octahedral geometry (Figure 9). The S–Sn distances are ~2.400 Å and Sn–Sn contact is 3.3847(10) Å [25], longer than that observed for the di-oxygen analog dimer **1a** due to the size of the sulfur atom.

In addition, compound **1b** was characterized by NMR spectroscopy. The ¹H NMR spectrum exhibits broadened signals. In the ¹³C NMR spectrum, the characteristic signal of the NCN fragment appears at 167.4 ppm. In the ¹¹⁹Sn NMR spectrum, a very high field chemical shift at −648.0 ppm is observed, a resonance signal that is more high-field shifted than those of previously reported Sn₂S₂-bridged dimeric complexes [26,27].



Scheme 7. Synthetic route to obtain **1b**.

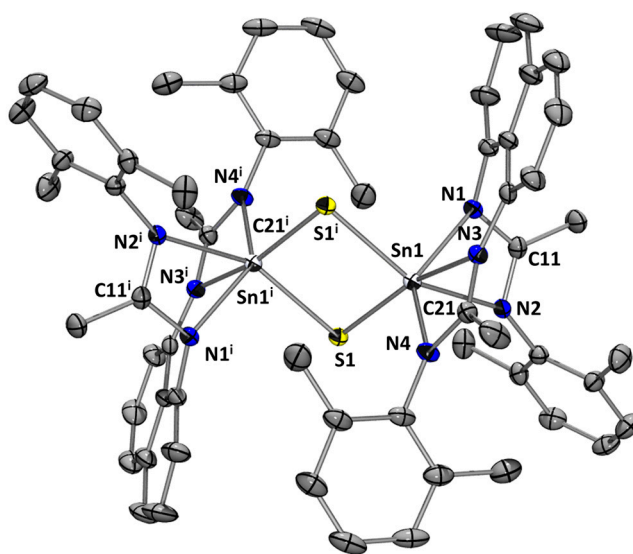
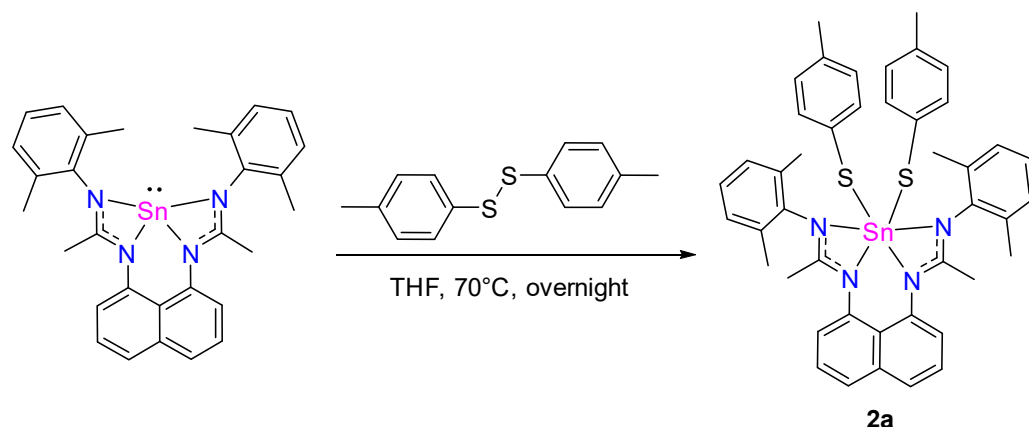


Figure 9. Molecular structure of **1b**. Thermal ellipsoids are represented with a 30% probability. Hydrogen atoms and solvent molecules have been omitted for clarity. The asymmetric unit contains two independent but very similar molecules; data for only one molecule are discussed. Selected bond distances [Å] and bond angles [deg]: Sn(1)-N(1) 2.130(4); Sn(1)-N(2) 2.374(3); Sn(1)-N(3) 2.240(3); Sn(1)-N(4) 2.198(4); Sn(1)-S(1) 2.4172(14); Sn(1)-S(1') 2.4585(13); C(11)-N(1) 1.345(6); C(11)-N(2) 1.315(5); C(21)-N(3) 1.332(5); C(21)-N(4) 1.328(5); Sn(1)-S(1)-Sn(1') 87.92(4); S(1)-Sn(1)-S(1') 92.08(4); N(1)-C(11)-N(2) 112.8(4); N(3)-C(21)-N(4) 110.9(4).

L₁Sn reacts with *p*-tolyl disulfide in THF at 70 °C overnight via an oxidative addition reaction with a tin insertion into the S–S bond (Scheme 8) to give a hexacoordinate Sn^(IV) species **2a** [22]. This molecule presents a characteristic ¹¹⁹Sn chemical shift at −456.7 ppm, consistent with a hexacoordinated tin center [24]. In addition, the X-ray diffraction analysis of **2a** reveals a monomeric Sn^(IV) species in a distorted octahedral coordination sphere that included the four nitrogen atoms of the two chelating amidinates and the two *p*-tolyl sulfur fragments (Figure 10). The equivalence of C–N bond lengths within NCN frameworks and their magnitudes (1.301 to 1.361 Å) indicate that the π electrons within the ligands are delocalized.

3,5-di-*tert*-butyl-ortho-quinone also reacts with **L₁Sn** to afford the corresponding [4 + 1]-cycloadduct **2b** (Scheme 9). The ¹H NMR spectrum reveals the characteristic signals of the quinone group in the aromatic region, doublets at 6.57 and 6.39 ppm (*J*_{HH} = 2.4 Hz), and two singlets at 1.06 and 1.16 ppm, corresponding to the CH₃ groups of *t*butyl in the aliphatic area. Also, the signals corresponding to the amidine CH₃ groups' moieties integrating for 6 H as a singlet at 2.00 ppm and to the CH₃ groups of 2,6-dimethylphenyl moieties integrating for 12 H as a singlet at 2.08 ppm, respectively, are observed. The ¹¹⁹Sn NMR spectrum shows a singlet at −512.2 ppm, in agreement with the cycloadduct structure.

The mass analysis (DCI/CH₄) spectrum exhibits a peak at 786.29, which corresponds to [M]⁺ of compound **2b**, evidencing its formation.



Scheme 8. Synthesis of **2a**.

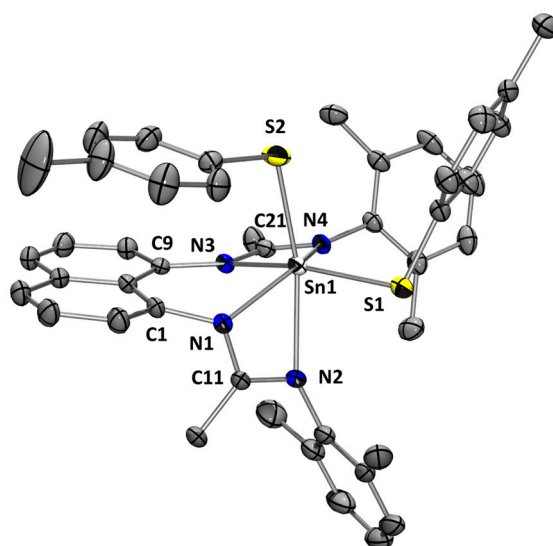
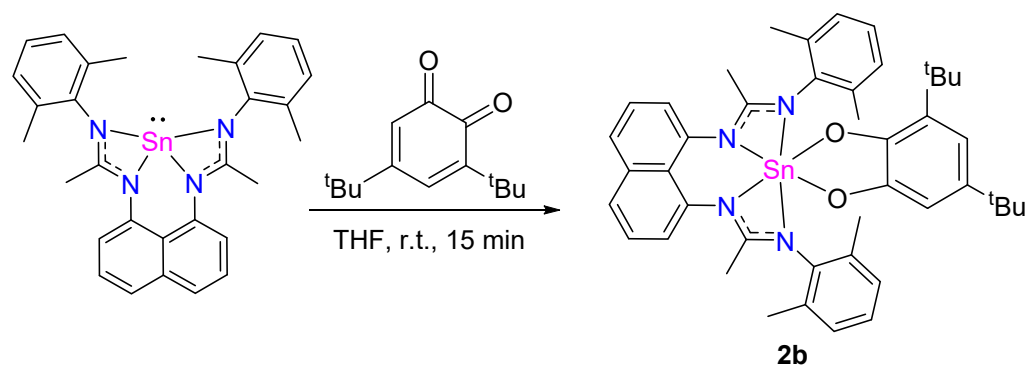
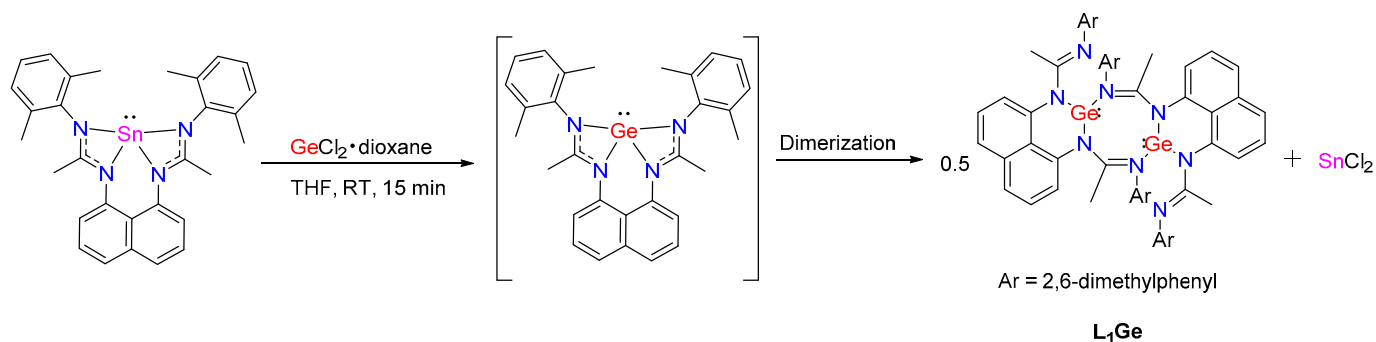
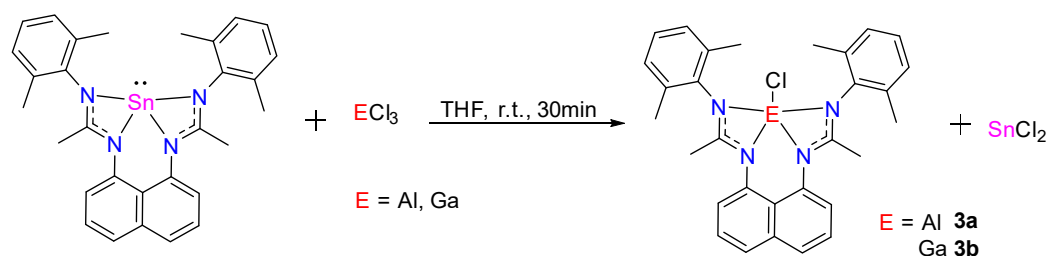


Figure 10. Molecular structure of **2a**. Thermal ellipsoids are represented with a 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and bond angles [deg]: Sn(1)–N(1) 2.132(3); Sn(1)–N(2) 2.411(3); Sn(1)–N(3) 2.230(3); Sn(1)–N(4) 2.180(3); Sn(1)–S(1) 2.4297(15); Sn(1)–S(2) 2.4483(16); C(11)–N(1) 1.361(4); C(11)–N(2) 1.301(4); C(21)–N(3) 1.334(4); C(21)–N(4) 1.337(4); N(1)–Sn(1)–N(4) 132.96(11); N(1)–Sn(1)–N(3) 78.01(11); N(3)–Sn(1)–N(4) 59.72(10); N(1)–Sn(1)–N(2) 58.27(11); N(2)–Sn(1)–N(4) 97.20(12); N(2)–Sn(1)–N(3) 86.71(11); N(1)–Sn(1)–S(1) 111.48(9); N(4)–Sn(1)–S(1) 102.83(8); N(3)–Sn(1)–S(1) 158.14(7); N(2)–Sn(1)–S(1) 82.44(9); N(1)–Sn(1)–S(2) 105.90(9); N(4)–Sn(1)–S(2) 97.26(9); N(3)–Sn(1)–S(2) 94.06(9); N(2)–Sn(1)–S(2) 163.67(8); S(1)–Sn(1)–S(2) 101.67(7); N(2)–C(11)–N(1) 113.5(3); N(3)–C(21)–N(4) 110.6(3).

As reported by So et al., an amidinatogermylene can act as a good ligand to form a germylene→ECl₂-type adduct with GeCl₂ and SnCl₂ [28]. In contrast, **L₁Sn** reacts with GeCl₂(dioxane) in THF at room temperature via a transmetalation reaction to give a germylene dimer (**L₁Ge**)₂ (Scheme 10). The ¹¹⁹Sn NMR spectrum shows a resonance at −214.0 ppm, in agreement with the formation of SnCl₂ [29].

Scheme 9. Synthesis of **2b**.Scheme 10. Synthesis of **L₁Ge** by transmetalation reaction.

Transmetalation reactions were also observed with AlCl_3 and GaCl_3 , affording the corresponding $\text{Al}^{(\text{III})}$ **3a** and $\text{Ga}^{(\text{III})}$ -chlorides **3b**, and in both cases, forming one equivalent of SnCl_2 (Scheme 11). The modeling confirms an exergonic reaction (-18.92 kcal/mol) during this “metal” exchange process. **L₁Sn** reacts with AlCl_3 quickly in THF at room temperature for 30 min to give **3a**, which was isolated as a white solid in 83% yield. The ^1H NMR spectrum shows, in the aromatic region, the expected resonances and integrals, and in the aliphatic area, two singlets at 2.33 and 1.90 ppm, integrating for 12 H, corresponding to the methyl groups of 2,6-dimethylphenyl fragments and a singlet at 2.13 ppm (6 H) related to the $-\text{CH}_3$ of the amidine groups. In the ^{13}C NMR spectrum, the characteristic NCN signal is observed at 176.4 ppm. The symmetry of the ^1H and ^{13}C NMR spectra are in agreement with a pentacoordinated aluminum complex. Using the same experimental conditions, **L₁Sn** also reacts with GaCl_3 to give $\text{Ga}^{(\text{III})}$ -chloride **3b**, which was isolated as colorless crystals from a pentane solution at -30°C in 88% yield. Gallium chloride **3b** was fully characterized by NMR spectroscopy (very similar to that of **3a**) and by X-ray diffraction analysis. The molecular structure of **3b** (Figure 11) shows a pentacoordinated gallium center with a distorted square-based pyramidal geometry. The Ga–Cl bond distance of 2.183 Å is in the range expected for such compounds [30].

Scheme 11. Synthesis of **3a** and **3b** via transmetalation reactions.

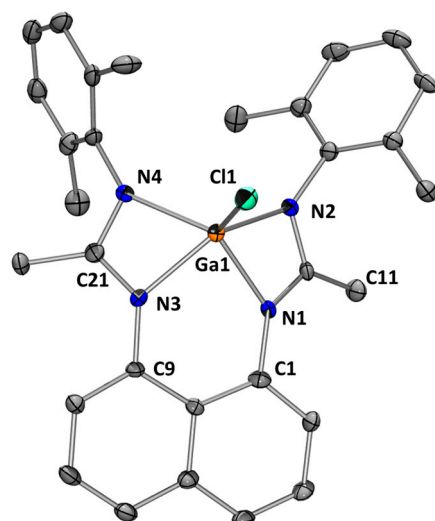


Figure 11. Molecular structure of **3b**. Thermal ellipsoids are represented with a 30% probability. Hydrogens have been omitted for clarity. Selected bond distances [Å] and bond angles [deg]: Ga(1)–N(1) 1.984(4); Ga(1)–N(2) 2.017(4); Ga(1)–N(3) 1.981(4); Ga(1)–N(4) 2.051(4); Ga(1)–Cl(1) 2.1828(14); N(1)–Ga(1)–N(3) 85.32(15); C(11)–N(1) 1.320(5); C(11)–N(2) 1.345(6); C(21)–N(3) 1.327(6); C(21)–N(4) 1.342(6); N(2)–Ga(1)–N(3) 139.06(16); N(1)–Ga(1)–N(2) 65.43(16); N(3)–Ga(1)–N(4) 65.69(15); N(1)–Ga(1)–N(4) 130.88(15); N(2)–Ga(1)–N(4) 112.06(16); N(3)–Ga(1)–Cl(1) 110.32(12); N(1)–Ga(1)–Cl(1) 115.30(11); N(2)–Ga(1)–Cl(1) 107.98(12); N(4)–Ga(1)–Cl(1) 111.79(12); N(1)–C(11)–N(2) 108.5(4); N(3)–C(21)–N(4) 110.1(4).

3. Materials and Methods

3.1. General Comments

All manipulations were performed under an inert argon or nitrogen atmosphere using standard Schlenk-line and glovebox techniques. Dry, oxygen-free solvents were employed. Reagents were obtained from commercial suppliers unless otherwise stated. *N*-(2,6-dimethylphenyl)acetamide [31], *N*-(2,6-dimethylphenyl)acetimidoyl chloride [29], *N,N'*-(naphthalene-1,8-diyl)bis(2,2-dimethylpropanamide) [13], *N,N'*-(naphthalene-1,8-diyl)bis(2,2-dimethylpropanimidoyl chloride) [13], *L*₁ [12], and *L*₂ [13] were synthesized following reported procedures. The Lappert's germanium(II) and tin(II) derivatives were prepared according to the literature procedures [32]. The 1D and 2D NMR spectra were recorded with the following spectrometers for ¹H, ¹³C, and ¹¹⁹Sn: Bruker Avance II 300 MHz, Avance III HD 400 MHz, and Avance I and II 500 MHz spectrometers. The chemical shift has been counted positively versus the low field and expressed in part per million (ppm). The mass spectrometric analysis was performed using three techniques: direct chemical ionization (DCI-CH₄) methods recorded on a GCT Premier Waters mass spectrometer (Headquarters, MN, USA); electrospray ionization (ESI, Los Angeles, CA, USA) recorded on a Waters Xevo G2 Q-TOF mass spectrometer; and a Maldi micro-MX micro-mass in a pyrene matrix (ratio of product/matrix 1/100). Melting points were measured with capillary Electrothermal Stuart SMP40 apparatus, and samples were prepared in the glovebox before the analysis. FT-IR spectra were measured on a Thermo Nicolet 6700 (Waltham, MA, USA) Nexus and recovered in a solid state (KBr). Single-crystal X-ray data were collected at a low temperature (193(2)K) on a Bruker APEX II Quazar (Billerica, MA, USA) diffractometer equipped with a 30W air-cooled microfocus source [(*L*₂Sn)₂, *L*₂Ge, **2a** and **3b**] or on a Bruker D8 VENTURE diffractometer equipped with a PHOTON III detector [*L*₃H₂, *L*₁Sn, (*L*₁Ge)₂, **1a** and **1b**] using MoK α radiation (λ = 0.71037 Å). The structures were solved by the intrinsic phasing method (SHELXT) [33] and refined by the full-matrix least-squares method on F2 [34]. All non-H atoms were refined with anisotropic displacement parameters and all the hydrogen atoms were refined isotropically at calculated positions using a riding model. For **2a**, some solvent molecules were highly disordered and difficult to model correctly. Therefore, the SQUEEZE function of PLATON [35] was used to eliminate the contribution

of the electron density of those solvent molecules from the intensity data. Calculations were performed with the Gaussian 16 suite of programs [36] using the density functional method B3LYP with dispersion (D3) [37–40]. Tin atoms were treated with a Stuttgart–Dresden pseudopotential in combination with its adapted basis set [41]. All other atoms have been described with a 6–31G(d,p) basis set. Geometry optimizations were carried out without any symmetry restrictions. Frequency calculations were undertaken to confirm the nature of the stationary points, yielding one imaginary frequency for transition states (TS) and all of them were positive for minima. The connectivity of the transition states and their adjacent minima was confirmed by intrinsic reaction coordinate (IRC) calculations [42,43].

3.2. Synthesis

Synthesis of L₃H₂. *p*-toluidine (591 mg, 5.6 mmol) was added to a solution of *N,N'*-(naphthalene-1,8-diyl)bis(2,2-dimethylpropanimidoyl chloride) (1 g, 2.8 mmol) in dry toluene (50 mL). Then, Et₃N (559 mg, 5.6 mmol) was added to the mixture. The reaction was stirred for 4 h under reflux. All volatiles were removed under reduced pressure. The solid residue was taken up in 40 mL of Et₂O and washed with 25 mL of a saturated solution of Na₂CO₃. Then, the organic layer was washed with water (3 × 30 mL) and dried over Na₂SO₄. After that, the solvent was removed, and the crude product was recrystallized with CH₂Cl₂/pentane (1:2). Yellow crystals were obtained (63% yield). **Melting point:** 116–122 °C. **¹H NMR** (DMSO-*d*₆, 500 MHz): δ 9.43 (s, 1H, NH); 8.50 (s, 1H, NH); 7.26 (d, *J*_{HH} = 6.5 Hz, 1H, aryl); 6.94 (d, *J*_{HH} = 7.9 Hz, 1H, aryl); 6.88–6.83 (m, 3H, aryl); 6.80 (m, 3H, aryl); 6.66 (d, *J*_{HH} = 8.1 Hz, 2H, aryl); 6.58–6.51 (m, 2H, aryl); 6.32–6.20 (m, 2H, aryl); 2.05 (s, 3H, CH₃); 2.01 (s, 3H, CH₃); 1.38 (s, 9H, C(CH₃)₃); 1.23 (s, 9H, C(CH₃)₃). **¹³C{¹H} NMR** (DMSO-*d*₆, 125 MHz): δ 161.3 (C=N); 160.7 (C=N); 147.2 (aryl, C); 146.5 (aryl, C); 138.6 (aryl, C); 137.2 (aryl, C); 135.6 (aryl, C); 131.2 (aryl, C); 130.4 (aryl, C); 128.7 (aryl, CH); 128.0 (aryl, CH); 127.7 (aryl, CH); 124.8 (aryl, CH); 121.4 (aryl, CH); 120.9 (aryl, CH); 119.8 (aryl, CH); 116.5 (aryl, C); 114.8 (aryl, CH); 28.8 (C(CH₃)₃); 28.3 (C(CH₃)₃); 20.3 (CH₃). **IR** (KBr, cm^{−1}): 3373 (νNH); 1623 (νC=N). **ESI *m/z*:** 504.33 ([M]⁺).

3.2.1. General Synthetic Procedure of Metallylenes

THF (5 mL) was added to a mixture of one equiv. of MCl₂ (M = Sn or Ge) and two equiv. of K[N(SiMe₃)₂]₂ in a 20 mL vial inside the glovebox. The mixture was stirred for 30 min at room temperature. After this time, a white precipitate was obtained. The mixture was filtered, and the solution was added to one equiv. of the corresponding L_{1–3}H₂, stirring at 60 °C for 3 h. Then, all the volatiles were removed and the residual solid was washed with pentane (3 × 5 mL).

L₁Sn. Colorless crystals were obtained by recrystallization from pentane at −30 °C (77% yield). **Melting point:** 202 °C (decomposition). **¹H NMR** (THF-*d*₈, 500 MHz): δ 7.42 (dd, *J*_{HH} = 8.2, 1.1 Hz, 2H, C₁₀H₆); 7.31–7.27 (m, 2H, C₁₀H₆); 7.07 (dd, *J*_{HH} = 7.5, 1.1 Hz, 2H, C₁₀H₆); 6.96 (d, *J*_{HH} = 7.4 Hz, 4H, C₆H₃); 6.83 (t, *J*_{HH} = 7.5 Hz, 2H, C₆H₃); 2.18 (s, 12H, CH₃); 1.97 (s, 6H, CH₃). **¹³C{¹H} NMR** (THF-*d*₈, 125 MHz): δ 169.0 (NCN); 145.3 (C₆H₃_{ipso}); 144.5 (C₁₀H₆_{ipso}); 138.6 (C₁₀H₆_{ipso}); 134.4 (C₆H₃_{ipso}); 128.8 (C₆H₃); 126.4 (C₁₀H₆); 124.8 (C₆H₃); 123.4 (C₁₀H₆); 119.8 (C₁₀H₆); 20.0 (CH₃); 17.9 (CH₃). **¹¹⁹Sn{¹H} NMR** (THF-*d*₈, 186 MHz): δ −276.7. **ESI *m/z*:** 565.15 ([M]⁺); 449.27 ([M − Sn]⁺).

(L₂Sn)₂. Yellow crystals (44% yield). **Melting point:** 243 °C (decomposition). **MS** (Maldi-TOF) *m/z*: 649.3 ([M/2, monomer]⁺). Meaningful solution state spectroscopic data for the compound could not be obtained for the compound as it shows negligible solubility in normal non-coordinating deuterated solvents once crystallized.

L₃Sn. Yellow solid (61% yield). **Melting point:** 189 °C (decomposition). **¹H NMR** (THF-*d*₈, 400 MHz): δ 7.38 (d, *J*_{HH} = 7.5 Hz, 2H, C₁₀H₆); 7.24–7.19 (m, 2H, C₁₀H₆); 7.09 (d, *J*_{HH} = 7.1 Hz, 2H, C₁₀H₆); 7.05 (d, *J*_{HH} = 8.0 Hz, 4H, C₆H₄); 6.97 (d, *J*_{HH} = 8.2 Hz, 4H, C₆H₄); 2.29 (s, 6H, CH₃); 1.30 (s, 18H, C(CH₃)₃). **¹³C{¹H} NMR** (THF-*d*₈, 125 MHz): δ 177.5 (NCN); 146.7 (C₆H₄_{ipso}); 145.7 (C₁₀H₆_{ipso}); 138.4 (C₁₀H₆_{ipso}); 133.0 (C₆H₄_{ipso}); 130.4 (C₆H₄); 126.3 (C₁₀H₆); 124.9 (C₆H₄); 123.4 (C₁₀H₆); 121.3 (C₁₀H₆); 43.6 (C(CH₃)₃); 31.8 (C(CH₃)₃);

21.0 (CH₃). ¹¹⁹Sn{¹H} NMR (THF-d₈, 186 MHz): δ −254.9. MS (Maldi-TOF) *m/z*: 621.2 ([M]⁺); 503.4 ([M-Sn]⁺).

(L₁Ge)₂. Yellow crystals (42% yield). **Melting point**: 259 °C (decomposition). MS (Maldi-TOF) *m/z*: 519.14 ([M/2, monomer]⁺). Meaningful solution state spectroscopic data for the compound could not be obtained for the compound as it shows negligible solubility in normal non-coordinating deuterated solvents once crystallized.

L₂Ge. Toluene was used instead of THF as solvent. Yellow crystals were obtained by recrystallization from pentane at −30 °C. (52% yield). **Melting point**: 199 °C (decomposition). ¹H NMR (C₆D₆, 300 MHz): δ 6.98–6.91 (m, 2H, C₁₀H₆); 6.89–6.81 (m, 2H, C₁₀H₆); 6.62 (d, *J*_{HH} = 7.7 Hz, 4H, C₆H₃); 6.47–6.40 (m, 2H, C₆H₃); 6.33 (d, *J*_{HH} = 6.3 Hz, 2H, C₁₀H₆); 2.18 (s, 12H, CH₃); 1.60 (s, 18H, C(CH₃)₃). ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 170.9 (NCN); 151.8 (C₆H_{3ipso}); 148.8 (C₁₀H_{6ipso}); 139.7 (C₁₀H_{6ipso}); 138.5 (C₆H_{3ipso}); 128.3 (C₆H₃); 126.3 (C₁₀H₆); 120.4 (C₆H₃); 114.9 (C₁₀H₆); 108.8 (C₁₀H₆); 41.9 (C(CH₃)₃); 30.6 (C(CH₃)₃); 19.7 (CH₃).

Synthesis of 1a. In a J. Young valve NMR tube, a THF (0.4 mL) solution of L₁Sn (30 mg, 0.053 mmol) was exposed to 5 bar of N₂O. The reaction was monitored by NMR and proceeded quantitatively after 3 h at 70 °C. Colorless crystals were observed and separated from the solution by filtration. Then, the crystals were washed with pentane (3 × 2 mL). Colorless crystals were obtained (46% yield). **Melting point**: 204 °C. ¹H NMR (THF-d₈, 500 MHz): δ 7.42 (d, *J*_{HH} = 6.4 Hz, 4H, C₁₀H₆); 7.26 (t, *J*_{HH} = 7.8 Hz, 4H, C₁₀H₆); 7.13 (d, *J*_{HH} = 6.8 Hz, 4H, C₁₀H₆); 7.01 (s, 4H, C₆H₃); 6.92–6.83 (m, 8H, C₆H₃); 2.07 (s, 12H, CH₃); 1.85 (s, 12H, CH₃); 1.76 (s, 12H, CH₃). ¹³C{¹H} NMR (THF-d₈, 125 MHz): δ 168.7 (NCN); 143.6 (C₆H_{3ipso}); 142.7 (C₁₀H_{6ipso}); 138.5 (C₁₀H_{6ipso}); 137.0 (C₁₀H_{6ipso}); 135.3 (C₆H_{3ipso}); 128.7 (C₆H₃); 128.3 (C₆H₃); 126.3 (C₁₀H₆); 125.7 (C₆H₃); 124.8 (C₁₀H₆); 120.6 (C₁₀H₆); 19.8 (CH₃); 19.0 (CH₃); 15.8 (CH₃). ¹¹⁹Sn{¹H} NMR (THF-d₈, 186 MHz): δ −494.5. MS (Maldi-TOF) *m/z*: 1161.26 ([M]⁺); 583.13 ([M/2, monomer]⁺).

3.2.2. General Reactivity Evaluation Procedure

THF was added to a mixture of one equiv. of L₁Sn and one equiv. of S₈, *p*-tolylidysulfide, 3,5-di-*tert*-butyl-*o*-benzoquinone, AlCl₃, or GaCl₃, accordingly. The mixture was stirred for the corresponding time and temperature. Then, the solvent was removed and the residual solid was washed with pentane (3 × 0.5 mL).

1b. Stirred overnight at room temperature. Pale-yellow crystals were obtained by recrystallization from THF at −30 °C (51% yield). **Melting point**: 229 °C (decomposition). ¹H NMR (THF-d₈, 300 MHz): δ 7.40 (d, *J*_{HH} = 7.5 Hz, 4H, C₁₀H₆); 7.22 (t, *J*_{HH} = 7.8 Hz, 4H, C₁₀H₆); 7.11–7.02 (m, 4H, C₁₀H₆); 6.93 (bs, 12H, C₆H₃); 2.11 (br s, 24H, CH₃); 1.75 (s, 12H, CH₃). ¹³C{¹H} NMR (THF-d₈, 125 MHz): δ 167.4 (NCN); 142.7 (C₁₀H_{6ipso}); 138.2 (C₁₀H_{6ipso}); 135.9 (C₆H_{3ipso}); 128.8 (C₆H₃); 126.4 (C₁₀H₆); 125.7 (C₆H₃); 124.8 (C₁₀H₆); 121.5 (C₁₀H₆); 19.7 (CH₃); 16.4 (CH₃). ¹¹⁹Sn{¹H} NMR (THF-d₈, 186 MHz): δ −648.0. MS (Maldi-TOF) *m/z*: 1193.10 ([M]⁺); 597.04 ([M/2, monomer]⁺).

2a. Stirred overnight at 70 °C. Pale-brown crystals (51% yield). **Melting point**: 199 °C. ¹H NMR (THF-d₈, 500 MHz): δ 7.40 (dd, *J*_{HH} = 8.1, 1.1 Hz, 2H, C₁₀H₆); 7.25–7.21 (m, 2H, C₁₀H₆); 7.17 (dd, *J*_{HH} = 7.5, 1.2 Hz, 2H, C₁₀H₆); 7.05–6.96 (m, 6H, C₆H₃); 6.63 (d, *J*_{HH} = 8.1 Hz, 4H, C₆H₄); 6.44 (d, *J*_{HH} = 7.9 Hz, 4H, C₆H₄); 2.19 (s, 12H, CH₃); 2.09 (s, Sn satellite: *J*_{HSn} = 7.3 Hz, 6H, CH₃); 1.79 (s, Sn satellite: *J*_{HSn} = 2.4 Hz, 6H, CH₃). ¹³C{¹H} NMR (THF-d₈, 125 MHz): δ 168.8 (NCN); 143.8 (Sn satellite: *J*_{CSn} = 5.2 Hz, C₁₀H_{6ipso}); 143.3 (Sn satellite: *J*_{CSn} = 7.2 Hz, C₆H₃); 138.4 (Sn satellite: *J*_{CSn} = 3.3 Hz, C₁₀H_{6ipso}); 136.1 (Sn satellite: *J*_{CSn} = 12.8 Hz, C₆H₄); 135.6 (Sn satellite: *J*_{CSn} = 3.1 Hz, C₆H₃); 135.5 (C₆H_{4ipso}); 131.4 (C₆H_{4ipso}); 129.2 (C₆H₃); 129.0 (Sn satellite: *J*_{CSn} = 6.6 Hz, C₆H₄); 127.6 (C₁₀H_{6ipso}); 126.4 (C₁₀H₆); 126.4 (C₆H₃); 125.2 (C₁₀H₆); 121.1 (Sn satellite: *J*_{CSn} = 11.2 Hz, C₁₀H₆); 21.1 (CH₃); 19.9 (CH₃); 16.4 (Sn satellite: *J*_{CSn} = 21.40 Hz, CH₃). ¹¹⁹Sn{¹H} NMR (THF-d₈, 186 MHz): δ −456.7. MS (Maldi-TOF) *m/z*: 687.13 ([M − S(tolyl)]⁺); 565.05 ([M − 2 S(tolyl)]⁺).

2b. Stirred for 15 min at room temperature. White solid (96% yield). **Melting point**: 240 °C (decomposition). ¹H NMR (THF-d₈, 500 MHz): δ 7.65–7.62 (m, 2H, C₁₀H₆);

7.44–7.39 (m, 4H, C₁₀H₆); 6.98–6.92 (m, 6H, C₆H₃); 6.57 (d, $J_{\text{HH}} = 2.4$ Hz, 1H, C₆H₂); 6.39 (d, $J_{\text{HH}} = 2.4$ Hz, 1H, C₆H₂); 2.08 (s, 12H, CH₃); 2.00 (s, Sn satellite: $J_{\text{HSn}} = 3.5$ Hz, 6H, CH₃); 1.16 (s, 9H, C(CH₃)₃); 1.06 (s, 9H, C(CH₃)₃). **¹³C{¹H} NMR** (THF-d₈, 125 MHz): δ 171.6 (NCN); 151.3 (Sn satellite: $J_{\text{CSn}} = 5.1$ Hz, C₆H_{2ipso}); 147.1 (Sn satellite: $J_{\text{CSn}} = 3.3$ Hz, C₆H_{2ipso}); 142.0 (Sn satellite: $J_{\text{CSn}} = 3.9$ Hz, C₁₀H_{6ipso}); 140.9 (Sn satellite: $J_{\text{CSn}} = 7.5$ Hz, C₆H_{3ipso}); 138.7 (C₆H_{2ipso}); 138.5 (C₁₀H_{6ipso}); 136.1 (C₆H_{3ipso}); 134.1 (C₆H_{2ipso}); 129.1 (C₆H₃); 127.1 (C₆H₃); 126.7 (C₁₀H₆); 126.1 (C₁₀H_{6ipso}); 126.0 (C₁₀H₆); 121.2 (Sn satellite: $J_{\text{CSn}} = 11.6$ Hz, C₁₀H₆); 111.5 (C₆H₂); 110.3 (Sn satellite: $J_{\text{CSn}} = 40.2$ Hz, C₆H₂); 35.3 (C(CH₃)₃); 34.9 (C(CH₃)₃); 32.4 (C(CH₃)₃); 30.2 (C(CH₃)₃); 19.1 (CH₃); 15.5 (Sn satellite: $J_{\text{CSn}} = 33.7$ Hz, CH₃). **¹¹⁹Sn{¹H} NMR** (THF-d₈, 186 MHz): δ −512.2. **ESI m/z** : 786.29 ([M]⁺).

3a. Stirred for 30 min at room temperature. White solid (85% yield). **Melting point:** 124 °C. **¹H NMR** (THF-d₈, 500 MHz): δ 7.46 (dd, $J_{\text{HH}} = 8.3, 1.1$ Hz, 2H, C₁₀H₆); 7.35–7.31 (m, 2H, C₁₀H₆); 7.24 (dd, $J_{\text{HH}} = 7.5, 1.2$ Hz, 2H, C₁₀H₆); 7.02–6.90 (m, 6H, C₆H₃); 2.33 (s, 6H, CH₃); 2.13 (s, 6H, CH₃); 1.90 (s, 6H, CH₃). **¹³C{¹H} NMR** (THF-d₈, 125 MHz): δ 176.4 (NCN); 141.9 (C₁₀H_{6ipso}); 141.8 (C₁₀H_{6ipso}); 140.6 (C₆H_{3ipso}); 138.4 (C₁₀H_{6ipso}); 135.8 (C₆H_{3ipso}); 135.1 (C₆H_{3ipso}); 129.4 (C₆H₃); 128.8 (C₆H₃); 126.6 (C₁₀H₆); 126.2 (C₆H₃); 124.1 (C₁₀H₆); 123.9 (C₁₀H_{6ipso}); 117.8 (C₁₀H₆); 19.9 (CH₃); 19.3 (CH₃); 15.6 (CH₃). **²⁷Al{¹H} NMR** (THF-d₈, 130 MHz): δ 69.4.

3b. Stirred for 30 min at room temperature. Colorless crystals were obtained from recrystallization with pentane at −30 °C (88% yield). **Melting point:** 209 °C (decomposition). **¹H NMR** (THF-d₈, 500 MHz): δ 7.46 (dd, $J_{\text{HH}} = 8.3, 1.1$ Hz, 2H, C₁₀H₆); 7.34–7.30 (m, 2H, C₁₀H₆); 7.20 (dd, $J_{\text{HH}} = 7.5, 1.2$ Hz, 2H, C₁₀H₆); 7.03–6.90 (m, 6H, C₆H₃); 2.34 (s, 6H, CH₃); 2.12 (s, 6H, CH₃); 1.98 (s, 6H, CH₃). **¹³C{¹H} NMR** (THF-d₈, 125 MHz): δ 172.3 (NCN); 142.9 (C₁₀H_{6ipso}); 141.9 (C₆H_{3ipso}); 138.6 (C₁₀H_{6ipso}); 136.1 (C₆H_{3ipso}); 135.5 (C₆H_{3ipso}); 128.8 (C₆H₃); 126.4 (C₁₀H₆); 126.4 (C₆H₃); 124.3 (C₁₀H₆); 123.1 (C₁₀H_{6ipso}); 118.3 (C₁₀H₆); 19.8 (CH₃); 15.1 (CH₃). **MS** (Maldi-TOF) m/z : 551.06 ([M]⁺); 517.04 ([M − Cl]⁺); 449.10 ([M − GaCl]⁺).

3.3. X-ray Data

CCDC-2303009 (L₃H₂), CCDC-2266345 (L₁Sn), CCDC-2266346 [(L₂Sn)₂], CCDC-2266347 [(L₁Ge)₂], CCDC-2266348 (L₂Ge), CCDC-2266349 (1a), CCDC-2266350 (1b), CCDC-2266351 (2a), and CCDC-2266352 (3b) 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.

4. Conclusions

Three tetradentate bis(amidine) ligands RNC(R')N-linker-NC(R')NR with a rigid naphthalene linker L_{1–3} were successfully used for the stabilization of metallylenes. The corresponding stannylenes and germylenes (L₁Sn and L₁Ge) have been prepared by protonolysis reaction of Lappert's metallylenes [M(HMDS)₂] (M = Ge or Sn) and were fully characterized by NMR spectroscopy and X-ray diffraction analysis. Structures in the solid state show either a monomer or a dimer depending on the different substituents of the amidine moiety, demonstrating that the nature of the bis(amidine) system can influence the stabilization and the reactivity of the corresponding tetrylenes. DFT calculations have been performed in order to define the electronic properties associated with tetradentate ligands. The reactivity of stannylene L₁Sn was explored in oxidation, oxidative addition, and transmetalation reactions to form in particular the corresponding gallium and aluminum derivatives.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29020325/s1>, NMR spectra, crystal structure refinements, and computational investigations (PDF).

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