

# N-Heterocyclic Carbene and Cyclic (Alkyl)(amino)carbene Adducts of Germanium(IV) and Tin(IV) Chlorides and Organyl Chlorides

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A study on the reactivity of *N*-heterocyclic carbenes (NHCs) and the cyclic (alkyl)(amino)carbene cAAC<sup>Me</sup> with selected germanium(IV) and tin(IV) chlorides and organyl chlorides is presented. The reactions of the NHCs Me<sub>2</sub>Im<sup>Me</sup>, *i*Pr<sub>2</sub>Im<sup>Me</sup> and Dipp<sub>2</sub>Im with the methyl chlorides ECl<sub>2</sub>Me<sub>2</sub> afforded the adducts NHC·ECl<sub>2</sub>Me<sub>2</sub> (E=Ge (1), Sn (2)), NHC=Me<sub>2</sub>Im<sup>Me</sup> (a), *i*Pr<sub>2</sub>Im<sup>Me</sup> (b), Dipp<sub>2</sub>Im (c). The reaction of Me<sub>2</sub>Im<sup>Me</sup> with GeCl<sub>4</sub> led to isolation of Me<sub>2</sub>Im<sup>Me</sup>·GeCl<sub>4</sub> (3), the reaction of *i*Pr<sub>2</sub>Im<sup>Me</sup> with SnCl<sub>4</sub> in THF afforded the THF adduct *i*Pr<sub>2</sub>Im<sup>Me</sup>·SnCl<sub>4</sub>·THF (4). Dipp<sub>2</sub>Im·GeCl<sub>2</sub>Me<sub>2</sub> (1c) isomerized into the backbone coordi-

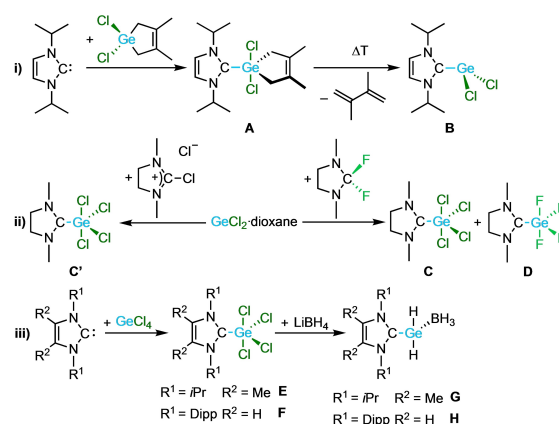
nated imidazolium salt [Dipp<sub>2</sub>Im·GeClMe<sub>2</sub>][Cl] (5) upon thermal treatment. The reactions of cAAC<sup>Me</sup> with (i) ECl<sub>2</sub>R<sub>2</sub> (E=Ge, Sn) gave the adducts cAAC<sup>Me</sup>·ECl<sub>2</sub>R<sub>2</sub> (R=Me: E=Ge (6); Sn (7); Ph: E=Ge (8)), with (ii) GeClMe<sub>3</sub> and GeCl<sub>4</sub> the salts [cAAC<sup>Me</sup>·GeMe<sub>3</sub>][Cl] (9) and [cAAC<sup>Me</sup>Cl][GeCl<sub>3</sub>] (10), and (iii) with SnCl<sub>4</sub> the salt [cAAC<sup>Me</sup>Cl][SnCl<sub>3</sub>] (11) and the adduct cAAC<sup>Me</sup>·SnCl<sub>4</sub> (12). Reduction of 2a with KC<sub>8</sub> afforded the NHC-stabilized stannylene Me<sub>2</sub>Im<sup>Me</sup>·SnMe<sub>2</sub> 13, reduction of 7 with either KC<sub>8</sub> or 1,4-bis-(trimethylsilyl)-1,4-dihydropyrazin in the presence of SnCl<sub>2</sub>Me<sub>2</sub> yielded cAAC<sup>Me</sup>·SnMe<sub>2</sub>·SnMe<sub>2</sub>Cl<sub>2</sub> (14).

## Introduction

*N*-heterocyclic carbenes (NHCs)<sup>[1]</sup> and cyclic (alkyl)(amino)carbenes (cAACs)<sup>[1,2]</sup> have a major impact in main group chemistry and their use allowed to realize molecular scaffolds and reaction pathways which would not be feasible without the support of this type of ligand. Their use as such ligands is mainly due to their tunable ambiphilicity and steric properties.<sup>[2b,3]</sup> In the recent years, we investigated the synthesis and the reactivity of different silicon<sup>[4]</sup> and tin compounds.<sup>[5]</sup> For group 14, especially NHC silicon chemistry is well developed<sup>[1g-j,2c,6]</sup> and a wide range of Si(IV) precursors such as NHC·SiCl<sub>x</sub><sup>[7]</sup> and cAAC·SiCl<sub>x</sub><sup>[8]</sup> are already known. For the higher homologues Ge and Sn, common precursors are subvalent adducts L·ECl<sub>2</sub> (L=NHC, cAAC; E=Ge, Sn) which can be prepared from the corresponding carbenes and commercially available GeCl<sub>2</sub>·dioxane<sup>[9]</sup> and SnCl<sub>2</sub><sup>[7a,9b,e,10]</sup> respectively. The reaction of different carbenes with ECl<sub>4-n</sub>R<sub>n</sub> (E=Ge, Sn; n=0–4) to yield the corresponding adducts NHC·ECl<sub>4-n</sub>R<sub>n</sub> was also used as a starting point into germanium<sup>[11]</sup> and tin chemistry.<sup>[7a,12]</sup>

It has been demonstrated on several occasions that these compounds are potential starting materials for carbene stabilized subvalent tetrel compounds. For example, Baines *et al.*

reported the Ge(IV) chloride adduct *i*Pr<sub>2</sub>Im·GeCl<sub>2</sub>(DMB) (DMB = 2,3-dimethyl-2-butenyl; R<sub>2</sub>Im = 1,3-di-organyl-imidazolin-2-ylidene) (Scheme 1, A), which was synthesized starting from GeCl<sub>2</sub>(DMB) and *i*Pr<sub>2</sub>Im, and subsequently converted into the Ge(II)-adduct *i*Pr<sub>2</sub>Im·GeCl<sub>2</sub> (Scheme 1, B).<sup>[11a]</sup> Another interesting example was reported by Rösenthaler *et al.* who reacted <sup>5</sup>Me<sub>2</sub>ImF<sub>2</sub> (2,2-difluoro-1,3-dimethylimidazolidine; “<sup>5</sup>n” denotes saturated backbone) with GeCl<sub>2</sub>·dioxane, yielding both, <sup>5</sup>Me<sub>2</sub>Im·GeCl<sub>4</sub> (Scheme 1, C) and <sup>5</sup>Me<sub>2</sub>Im·GeF<sub>4</sub> (Scheme 1, D).<sup>[11b]</sup> Based on this research, Rivard *et al.* reacted the NHC salt [Dipp<sub>2</sub>ImCl][Cl] with GeCl<sub>2</sub>·dioxane, which led selectively to <sup>5</sup>Me<sub>2</sub>Im·GeCl<sub>4</sub> (Scheme 1, C'). In addition, the adducts *i*Pr<sub>2</sub>Im<sup>Me</sup>·GeCl<sub>4</sub><sup>[11d]</sup> (R<sub>2</sub>Im<sup>Me</sup> = 1,3-di-organyl-4,5-dimethyl-imidazolin-2-ylidene Scheme 1, E) and Dipp<sub>2</sub>Im·GeCl<sub>4</sub><sup>[11c]</sup> (Scheme 1, F) were reported, which were synthesized starting from GeCl<sub>4</sub>



**Scheme 1.** (i) Synthesis of *i*Pr<sub>2</sub>Im·GeCl<sub>2</sub>(DMB) (A) and *i*Pr<sub>2</sub>Im·GeCl<sub>2</sub> (B); (ii) Synthesis of <sup>5</sup>Me<sub>2</sub>Im·GeCl<sub>4</sub> (C and C') and <sup>5</sup>Me<sub>2</sub>Im·GeF<sub>4</sub> (D); (iii) Synthesis of *i*Pr<sub>2</sub>Im·GeCl<sub>4</sub> (E) and Dipp<sub>2</sub>Im·GeCl<sub>4</sub> (F) and subsequent reaction with LiBH<sub>4</sub> to yield *i*Pr<sub>2</sub>Im·GeH<sub>2</sub>·BH<sub>3</sub> (G) and Dipp<sub>2</sub>Im·GeH<sub>2</sub>·BH<sub>3</sub> (H).

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and the NHCs  $iPr_2Im^{Me}$  and  $Dipp_2Im$  (1,3-bis-(2,6-di-isopropylphenyl)-imidazolin-2-ylidene) respectively. Reduction with  $LiBH_4$  afforded the borane-stabilized adducts  $iPr_2Im^{Me} \cdot GeH_2 \cdot BH_3^{[11d]}$  (Scheme 1, G) and  $Dipp_2Im \cdot GeH_2 \cdot BH_3^{[11c]}$  (Scheme 1, H). Similarly, the reaction of  $Dipp_2Im$  with  $SnCl_4$  afforded the corresponding Sn(IV) compound  $Dipp_2Im \cdot SnCl_4$  (Figure 1, I).<sup>[11c]</sup>

Sn(IV) adducts were already reported previously by Boese *et al.* in 1995, who reacted  $R_2Im^{Me}$  ( $R=Me, Et, iPr$ ) with  $SnCl_2Ph_2$  to isolate the corresponding compounds  $R_2Im^{Me} \cdot SnCl_2Ph_2$  (Figure 1, J).<sup>[7a]</sup> In addition, an adduct of  $SnCl_2Me_2$  was realized by coordination of the NHC  $DMP_2Im^{Me}$  ( $DMP=2,3$ -dihydro-1,3-di-3'-methoxypropyl) to give the adduct  $DMP_2Im^{Me} \cdot SnCl_2Me_2$  (Figure 1, K).<sup>[12]</sup> In the course of our work on the reactivity of NHCs with  $SiCl_2Ph_2$  to yield  $iPr_2Im \cdot SiCl_2Ph_2$  and the rearrangement of this adduct into a backbone coordinated ("abnormal" coordination) adduct  $[(^a iPr_2ImH)_2SiPh_2]^+ 2[Cl]^-$  ("*ab*" denotes "abnormal" coordination mode of the NHC)<sup>[4c]</sup> we synthesized the NHC adducts  $iPr_2Im \cdot SnCl_2R_2$  ( $R=Me, Ph$ ; Figure 1, L) starting from  $iPr_2Im$  and  $SnCl_2R_2$ . However, the corresponding rearrangement was not observed, most probably due to the larger Lewis-acidity of the tin compounds.<sup>[5]</sup> As the number of such NHC (or cAAC) adducts of E(IV) halides or organohalides are rather limited, and to explore the possibility whether adducts  $NHC \cdot EX_2R_2$  ( $E=Ge, Sn$ ) are prone to rearrangement into the abnormally coordinated isomers and thus pave the way to germanium and tin tethered bis(carbene) ligands,<sup>[4c]</sup> we further explored this type of adducts and report our results here.

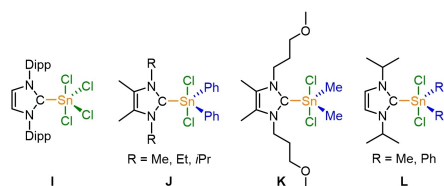
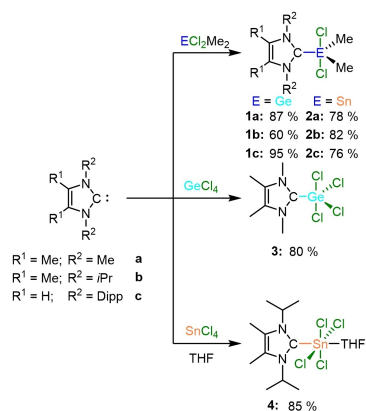


Figure 1. Selected NHC–Sn(IV) adducts.



Scheme 2. Synthesis of the NHC-stabilized adducts of  $GeCl_2Me_2$  (**1a–c**),  $SnCl_2Me_2$  (**2a–c**),  $GeCl_4$  (**3**) and  $SnCl_4$  (**4**).

## Results and Discussion

We started our investigations with the reaction of Lewis-acidic Ge(IV) and Sn(IV) halides with different NHCs. The reaction of  $ECl_2Me_2$  ( $E=Ge, Sn$ ), with the NHCs  $Me_2Im^{Me}$  (**a**),  $iPr_2Im^{Me}$  (**b**) and  $Dipp_2Im$  (**c**) in *n*-hexane at room temperature led to the corresponding adducts  $NHC \cdot ECl_2Me_2$  (**1a–2c**) as colorless solids in fair to high yields (60–95%; Scheme 2). Similarly, the reaction of  $GeCl_4$  with  $Me_2Im^{Me}$  in *n*-hexane at room temperature afforded  $Me_2Im^{Me} \cdot GeCl_4$  (**3**) as a colorless solid in 80% yield (Scheme 2). In contrast, the formation of the tin adduct  $Me_2Im^{Me} \cdot SnCl_4$  was not observed due to decomposition of the carbene to unknown salts with  $[Me_2Im^{Me}H]^+$  cations. However, the reaction of  $iPr_2Im^{Me}$  with  $SnCl_4$  in THF led to formation of  $iPr_2Im^{Me} \cdot SnCl_4 \cdot THF$  (**4**) as a colorless solid in 85% yield (Scheme 2).

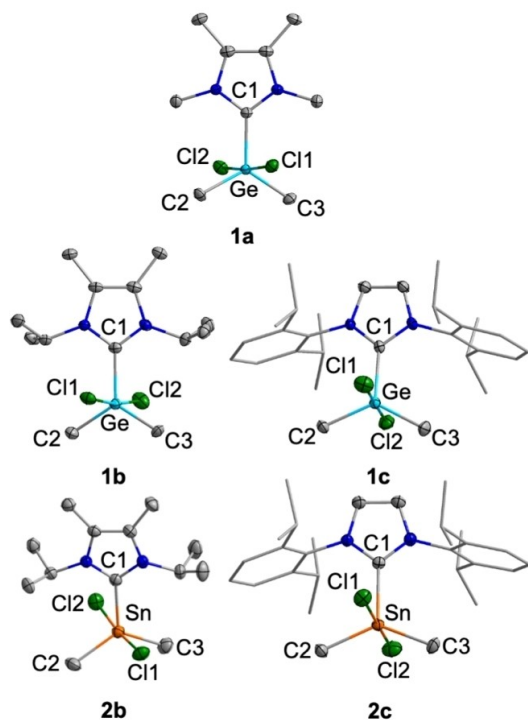
Adduct formation of these compounds is evident from  $^1H$ ,  $^{13}C\{^1H\}$  and  $^{119}Sn\{^1H\}$  NMR spectroscopy (Table 1) as well as elemental analysis. In the  $^{13}C\{^1H\}$  NMR spectra, the NCN carbene carbon resonances of the adducts **1a–2c** (155.8 ppm to 165.9 ppm), are ca. 50 ppm high-field shifted compared to the corresponding uncoordinated carbene (see Table 1) due to coordination of the Lewis-acid. The Sn(IV) adducts **2a–c** revealed characteristic resonances in the  $^{119}Sn$  NMR spectra in a range from  $-227.8$  ppm to  $-217.6$  ppm, similar to the  $^{119}Sn$  NMR shift for  $iPr_2Im \cdot SnCl_2Me_2$  ( $\delta_{119Sn} = -227.0$  ppm) reported previously.<sup>[5]</sup> The NCN resonance of **3** at 153.6 ppm in the  $^{13}C\{^1H\}$  NMR spectrum is almost identical to that of literature known  $iPr_2Im \cdot GeCl_4^{[11d]}$  (155.7 ppm). The additional THF coordination in the six-coordinate tin adduct  $iPr_2Im^{Me} \cdot SnCl_4 \cdot THF$  (**4**) led to a low-field shift in the  $^{13}C\{^1H\}$  NMR spectrum of the NCN resonance to 160.1 ppm and to a high-field shift of the corresponding  $^{119}Sn\{^1H\}$  resonance to  $-446.5$  ppm (cf. 146.7 ppm and  $-422.6$  ppm for  $Dipp_2Im \cdot SnCl_4$ ).<sup>[11c]</sup>

Crystals suitable for X-ray diffraction were obtained for the compounds **1a–c** (benzene, 6 °C), **2b, 2c** (benzene, rt) (Figure 2), **3** (toluene, rt) and **4** (THF layered with *n*-hexane,  $-30$  °C) (Figure 3). The adducts crystallized in the monoclinic space groups  $P2_1/c$  (**1c**) and  $P2_1/n$  (**2b** and **2c**), in the triclinic space group  $P\bar{1}$  (**4**) as well as in the orthorhombic space groups  $Pbca$  (**1a**),  $Pca2_1$  (**1b**) and  $P2_12_1$  (**3**), respectively, with one molecule in the asymmetric unit. Selected bonding parameter are summarized in Table 2. All adducts, except for **4**, adopt a trigonal bipyramidal arrangement of the ligands at the Ge or Sn

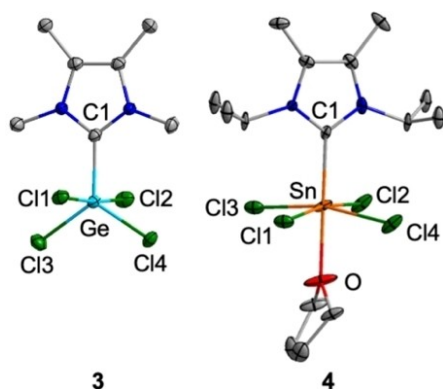
Table 1. Selected  $^{13}C\{^1H\}$  and  $^{119}Sn\{^1H\}$  NMR chemical shifts (ppm) of the compounds  $NHC \cdot ECl_2Me_2$  (**1a–2c**),  $Me_2Im^{Me} \cdot GeCl_4$  (**3**),  $iPr_2Im^{Me} \cdot SnCl_4 \cdot THF$  (**4**) and related compounds (\*), recorded in  $C_6D_6$ , unless otherwise noted.

		$Me_2Im^{Me}$	$iPr_2Im^{Me}$	$Dipp_2Im$
<b>1a–c</b>	$\delta^{13}C$	155.8	157.5	160.5
	$\delta^{13}C$	160.0	162.6	165.9
	$\delta^{119}Sn$	$-222.5$	$-227.8$	$-217.6$
<b>3</b>	$\delta^{13}C$	153.6	155.7 <sup>*(11d)</sup>	156.5 <sup>*(a)(11c)</sup>
	$\delta^{13}C$	/	160.1	146.7 <sup>*(11c)</sup>
<b>4</b>	$\delta^{13}C$	/	$-446.5$	$-422.6$ <sup>*(11c)</sup>
	$\delta^{119}Sn$	/	(THF adduct)	
free NHC	$\delta^{13}C$	212.4	207.6	220.1

[a] Recorded in  $CD_2Cl_2$ .



**Figure 2.** Molecular structures of  $\text{Me}_2\text{Im}^{\text{Me}} \cdot \text{GeCl}_2\text{Me}_2$  (**1a**),  $i\text{Pr}_2\text{Im}^{\text{Me}} \cdot \text{GeCl}_2\text{Me}_2$  (**1b**),  $\text{Dipp}_2\text{Im} \cdot \text{GeCl}_2\text{Me}_2$  (**1c**),  $i\text{Pr}_2\text{Im}^{\text{Me}} \cdot \text{SnCl}_2\text{Me}_2$  (**2b**) and  $\text{Dipp}_2\text{Im} \cdot \text{SnCl}_2\text{Me}_2$  (**2c**) in the solid-state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at the 50% probability level and Dipp groups are shown as wire-and-stick models. Selected bond lengths and angles are given in Table 2.



**Figure 3.** Molecular structures of  $\text{Me}_2\text{Im}^{\text{Me}} \cdot \text{GeCl}_4$  (**3**), and  $i\text{Pr}_2\text{Im}^{\text{Me}} \cdot \text{SnCl}_2\text{Me}_2 \cdot \text{THF}$  (**4**) in the solid-state. Hydrogen atoms and solvent molecules (**4**: THF) are omitted for clarity. Atomic displacement ellipsoids are set at 50% probability. Selected bond lengths and angles are given in Table 2.

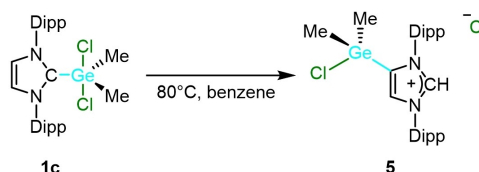
atom with two chloride substituents in axial positions and the remaining substituents at equatorial sites. The C1–E distances of **1a–c** and **2b–c** (Table 2) are within  $3\sigma$  in the range of the corresponding distances in other NHC coordinated Ge(IV) (C1–Ge: 1.987(2) Å–1.9921(14) Å)<sup>[11a–c]</sup> and Sn(IV) (C1–Sn: 2.1773(19) Å–2.203(3) Å) compounds reported previously.<sup>[5,11c,12]</sup> The axial chlorides are slightly tilted towards the carbene with

C1–E–Cl2 angles ranging from 172.39(2)° to 179.45(2)° and C1–Cl distances in the range from 2.9679(30) Å (**3**) to 3.1704(16) Å (**1c**) for the germanium compounds and 3.1251(50) Å (**12**) to 3.5048(29) Å (**7**) for the tin compounds. Non-bonding intra-ligand interactions between the carbene carbon  $p_\pi$ -orbitals and the lone pairs of the chloride ligands Cl1 and Cl2 might be the reason for this distortion. Such non-bonding interactions might additionally stabilize the compounds, as has been noticed for NHC complexes of early transition metals in their high to highest oxidation states before.<sup>[13]</sup>

The structure of compound **4** reveals an octahedral coordination sphere at the central tin atom with the NHC as well as one THF ligand coordinated *trans* to each other and the chloride substituents occupying the remaining coordination sites. From the angles C1–Sn–Cl2 (170.23(4)°) and Cl3–Sn–Cl4 (165.73(3)°) it can be concluded that the chloride substituents are slightly bent towards the THF ligand.

Recently, our group has demonstrated that  $i\text{Pr}_2\text{Im} \cdot \text{SiCl}_2\text{Ph}_2$  rearranges to the backbone-coordinated and silicon-bridged compound  $[(^i\text{Pr}_2\text{Im})_2 \cdot \text{SiPh}_2]^{2+} + 2[\text{Cl}]^-$  upon heating.<sup>[4c]</sup> However, so far we did not observe similar reactivity for the related tin compounds reported herein.<sup>[5]</sup> Furthermore, we did not observe the controlled formation of Ge(II) or Sn(II) compounds  $\text{NHC} \cdot \text{ECl}_2$  after heating benzene solutions of  $\text{NHC} \cdot \text{ECl}_2\text{Me}_2$  to reflux for several days. However, the Ge(IV) adduct **1c** isomerized after heating in benzene to give a colorless precipitate of the salt  $[\text{Dipp}_2\text{Im} \cdot \text{GeClIme}_2][\text{Cl}]$  (**5**), which was isolated in 71% yield (Scheme 3). It has been demonstrated previously that abnormal coordination is often thermodynamically favored.<sup>[1,2]</sup> The abnormal coordination of **5** is evident from  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. The signal sets of the Dipp groups are doubled in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra due to the asymmetry of **5**. Two characteristic resonances in the  $^1\text{H}$  NMR spectrum are indicative for a change in the coordination mode, namely one singlet with an intensity of one for the remaining backbone proton at 7.68 ppm and a second singlet for the new imidazolium proton were observed at 12.2 ppm. The NCN resonance in the  $^{13}\text{C}\{^1\text{H}\}$  NMR is shifted from 160.5 ppm (**1c**) to 146.0 ppm (**5**).

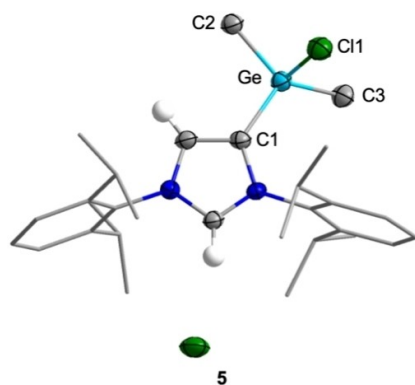
Crystals of **5** suitable for X-ray diffraction were obtained by cooling an at reflux saturated benzene solution of the compound to room temperature (Figure 4). Compound **5** crystallizes in the triclinic space group  $P\bar{1}$  with two molecules in the asymmetric unit. The structure reveals a tetrahedral coordination sphere at germanium, which deviates from the five-coordinated nature of the other adducts reported here,



**Scheme 3.** Thermal induced isomerization of  $\text{Dipp}_2\text{Im} \cdot \text{GeCl}_2\text{Me}_2$  (**1c**) into the abnormal coordinated salt  $[\text{Dipp}_2\text{Im} \cdot \text{GeClIme}_2][\text{Cl}]$  (**5**).

**Table 2.** Selected bond lengths [Å] and angles [°] of the NHC adducts **1 a–c**, **2 b**, **2 c**, **3** and **4**.

trigonal bipyramidal	E–C1	E–Cl1	E–Cl2	E–C2	E–C3	Cl1–E–Cl2	C2–E–C3
(1a) Me <sub>2</sub> Im <sup>Me</sup> ·GeCl <sub>2</sub> Me <sub>2</sub>	1.9803(18)	2.4513(5)	2.4910(5)	1.9395(17)	1.9305(18)	175.292(17)	121.29(8)
(1b) <i>i</i> Pr <sub>2</sub> Im <sup>Me</sup> ·GeCl <sub>2</sub> Me <sub>2</sub>	1.984(3)	2.5348(9)	2.3634(9)	1.950(4)	1.933(3)	172.58(4)	118.41(16)
(1c) Dipp <sub>2</sub> Im <sup>Me</sup> ·GeCl <sub>2</sub> Me <sub>2</sub>	1.9987(15)	2.3603(4)	2.5199(4)	1.9355(16)	1.9386(17)	179.445(17)	128.20(7)
(2b) <i>i</i> Pr <sub>2</sub> Im <sup>Me</sup> ·SnCl <sub>2</sub> Me <sub>2</sub>	2.189(3)	2.5540(7)	2.5638(7)	2.122(3)	2.121(3)	172.39(2)	125.83(13)
(2c) Dipp <sub>2</sub> Im·SnCl <sub>2</sub> Me <sub>2</sub>	2.202(2)	2.5692(6)	2.5107(6)	2.115(2)	2.122(2)	178.11(2)	132.16(10)
trigonal bipyramidal	E–C1	E–Cl1	E–Cl2	E–Cl3	E–Cl4	Cl1–E–Cl2	Cl3–E–Cl4
(3) Me <sub>2</sub> Im <sup>Me</sup> ·GeCl <sub>4</sub>	1.976(3)	2.2960(7)	2.3117(8)	2.1604(8)	2.1565(7)	174.53(3)	114.74(3)
octahedral	E–C1	E–Cl1	E–Cl2	E–Cl3	E–Cl4	Cl1–E–Cl2	Cl3–E–Cl4
(4) <i>i</i> Pr <sub>2</sub> Im <sup>Me</sup> ·SnCl <sub>4</sub> ·THF	2.231(4)	2.4131(11)	2.4205(11)	2.4029(12)	2.4166(12)	170.23(4)	165.73(4)



**Figure 4.** The molecular structure of [Dipp<sub>2</sub>Im·GeClMe<sub>3</sub>][Cl] (**5**) in the solid-state. Hydrogen atoms (except the imidazolium protons) and solvent molecules (benzene) are omitted for clarity. Only one of two independent molecules of the asymmetric unit is shown. Atomic displacement ellipsoids are set at 50% probability and Dipp groups are shown as wire-and-stick-model. Selected bond lengths [Å] and angles [°]: **5**: Ge–C1, 1.944(2); Ge–C1, 2.2325(8); Ge–C2, 1.938(3); Ge–C3, 1.922(3); C1–Ge–Cl1, 99.99(8); C1–Ge–C2, 108.48(11); C1–Ge–C3, 120.20(11); Cl1–Ge–C2, 101.67(8); Cl1–Ge–C3, 101.43(9); C2–Ge–C3, 120.48(12)

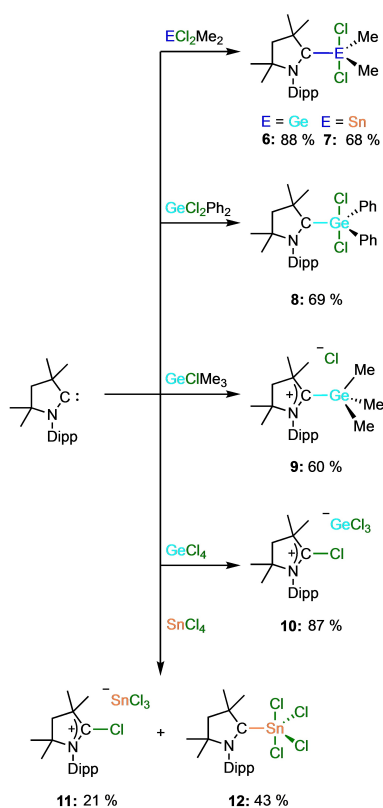
most probably due to steric repulsion of the methyl groups and the Dipp substituents of the backbone-bonded NHC.

Thus, salt formation is preferred and one of the chloride substituents is expelled from the coordination sphere of germanium. It is also interesting to note that the methyl groups at germanium keep intact in the presence of the acidic imidazole hydrogen atoms. The Ge–C1 distance of the covalent Ge–C single bond of **5** (1.944(2) Å) is smaller compared to the Ge–C distance observed for the NHC adduct **1c** (C1–Ge: 1.9987(15) Å), which is most probably due to the better donation properties of <sup>3</sup>NHC compared to the NHC ligand and the lower coordination number of **5** compared to that of **1c**. Compound **5** represents a rare example of an NHC backbone-coordinated to germanium. For the formation of **5** we assume a mechanism similar to that reported previously by Goicoechea *et al.* for the formation of <sup>3</sup>Dipp<sub>2</sub>Im·EBr<sub>3</sub> from Dipp<sub>2</sub>Im·EBr<sub>3</sub> (E=Sb, Bi).<sup>[14]</sup> This isomerization likely proceeds *via* cleavage of the Ge–C bond generating free Dipp<sub>2</sub>Im in solution, which allows deprotonation of another coordinated Dipp<sub>2</sub>Im ligand and isomerization.

In contrast to the NHC adducts of Ge(IV) and Sn(IV), adducts with cAACs are unknown so far. For this reason we also investigated the behavior of various Ge(IV) and Sn(IV) compounds towards cAAC<sup>Me</sup> (1-(2,6-di-*iso*-propylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene) (Scheme 4). Like the syntheses of **1a–2c**, the reactions of cAAC<sup>Me</sup> with GeCl<sub>2</sub>Me<sub>2</sub>, SnCl<sub>2</sub>Me<sub>2</sub> and GeCl<sub>2</sub>Ph<sub>2</sub>, respectively, afforded the corresponding cAAC<sup>Me</sup> adducts cAAC<sup>Me</sup>·GeCl<sub>2</sub>Me<sub>2</sub> (**6**), cAAC<sup>Me</sup>·SnCl<sub>2</sub>Me<sub>2</sub> (**7**) and cAAC<sup>Me</sup>·GeCl<sub>2</sub>Ph<sub>2</sub> (**8**) as benzene-soluble, colorless solids in good to very good yields (68%–88%, Scheme 4). The reaction of cAAC<sup>Me</sup> with GeClMe<sub>3</sub> and GeCl<sub>4</sub>, respectively, afforded colorless precipitates which are poorly soluble in non-polar solvents. Isolation of these precipitates led to the characterization of the salts [cAAC<sup>Me</sup>GeMe<sub>3</sub>][Cl] (**9**) and [cAAC<sup>Me</sup>Cl][GeCl<sub>3</sub>] (**10**) as dichloromethane-soluble, colorless solids in 60% (**9**) and 87% (**10**) yield, respectively. Note that salt formation depends on the halide content of the germane, as the reaction of cAAC<sup>Me</sup> with GeClMe<sub>3</sub> led to chloride elimination to yield the chloride salt [cAAC<sup>Me</sup>GeMe<sub>3</sub>][Cl] (**9**) ([cAAC<sup>Me</sup>GeMe<sub>3</sub>]<sup>+</sup> cation) whereas the reaction of cAAC<sup>Me</sup> with GeCl<sub>4</sub> afforded [cAAC<sup>Me</sup>Cl][GeCl<sub>3</sub>] with chlorine transfer to the cAAC ([GeCl<sub>3</sub>]<sup>−</sup> anion; see below). Evidence for the formation of the compounds **6–10** was obtained by NMR and IR spectroscopy as well as elemental analysis. Due to the strong broadening of the resonances of the methyl groups in C<sub>6</sub>D<sub>6</sub> at room temperature, the NMR spectra of the compounds **6** and **7** were recorded in toluene-*d*<sub>8</sub> at −40 °C. In the <sup>1</sup>H NMR spectra, the characteristic resonances of the backbone CH<sub>2</sub> unit (**6**: 1.28 ppm; **7**: 1.21 ppm) and the methine protons (**6**: 3.23 ppm; **7**: 3.06 ppm) of the Dipp groups are shifted towards higher field compared to free cAAC<sup>Me</sup> (CH<sub>2</sub>: 1.52 ppm; *i*Pr-CH: 3.10 ppm; in toluene-*d*<sub>8</sub>).

The carbene carbon NCE (E=Ge, Sn) resonances in the <sup>13</sup>C {<sup>1</sup>H} NMR spectra are significantly high-field shifted to 214.1 ppm (**6**) and 226.3 ppm (**7**) compared to uncoordinated cAAC<sup>Me</sup> (313.9 ppm; in toluene-*d*<sub>8</sub>). In the <sup>119</sup>Sn{<sup>1</sup>H} NMR spectrum of compound **7** a signal was detected at −214.1 ppm. Similar coordination shifts were observed for the adduct **8** (see Experimental Part). The spectroscopy of the compounds **9** and **10** differ significantly from that of **6–8**. In the <sup>1</sup>H NMR spectrum of **9**, a broad resonance at 0.35 ppm with a relative intensity of **9** was observed for the germanium-bound methyl groups.

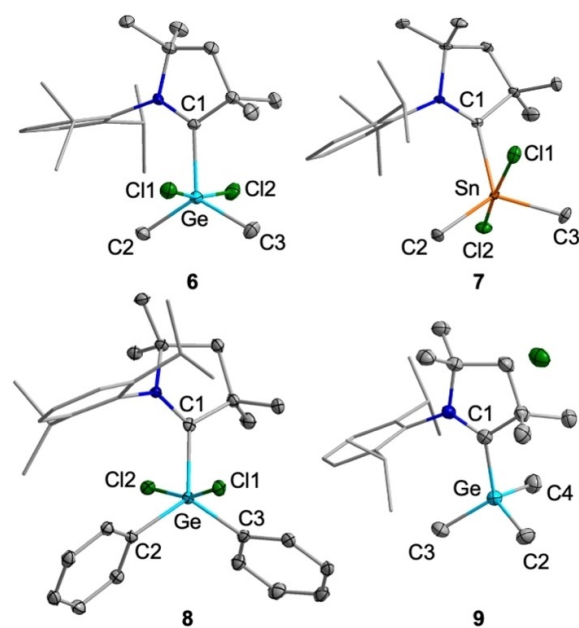
In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, the NCGe resonance was detected at 222.9 ppm, which is slightly up field shifted



**Scheme 4.** Synthesis of the cAAC<sup>Me</sup>-stabilized adducts cAAC<sup>Me</sup>·GeCl<sub>2</sub>Me<sub>2</sub> (**6**), cAAC<sup>Me</sup>·SnCl<sub>2</sub>Me<sub>2</sub> (**7**), cAAC<sup>Me</sup>·GeCl<sub>2</sub>Ph<sub>2</sub> (**8**), and the salts [cAAC<sup>Me</sup>GeMe<sub>3</sub>][Cl] (**9**), [cAAC<sup>Me</sup>Cl][GeCl<sub>3</sub>] (**10**) and [cAAC<sup>Me</sup>Cl][SnCl<sub>3</sub>] (**11**) and cAAC<sup>Me</sup>·SnCl<sub>4</sub> (**12**).

compared to other germanium coordinated cAAC<sup>Me</sup> carbene carbon atoms (NCGe: 226.3–249.8 ppm).<sup>[9d,15]</sup> Formation of the cation [cAAC<sup>Me</sup>Cl]<sup>+</sup> in [cAAC<sup>Me</sup>Cl][GeCl<sub>3</sub>] (**10**) is evident from the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **10**, in which the NCCI resonance was detected at 190.6 ppm which is in range of NCCI signals of literature known [cAAC–Cl]<sup>+</sup> cations (188.5–190.6 ppm).<sup>[16]</sup>

Additional evidence for the formation of the compounds **6–9** was obtained from X-ray crystallography, and the molecular structures of these compounds are depicted in Figure 5. Crystals suitable for X-ray diffraction were obtained by storing a saturated solution in benzene at 6 °C (**6**, **8**), by slow evaporation of a benzene solution at room temperature (**7**) and storing a



**Figure 5.** Molecular structures of cAAC<sup>Me</sup>·GeCl<sub>2</sub>Me<sub>2</sub> (**6**), cAAC<sup>Me</sup>·SnCl<sub>2</sub>Me<sub>2</sub> (**7**), cAAC<sup>Me</sup>·GeCl<sub>2</sub>Ph<sub>2</sub> (**8**) and [cAAC<sup>Me</sup>GeMe<sub>3</sub>][Cl] (**9**) in the solid-state. Hydrogen atoms and solvent molecules (**6** and **8**: benzene) are omitted for clarity. Atomic displacement ellipsoids are set at 50% probability and Dipp groups are shown as wire-and-stick model. Selected bond lengths and angles are given in Table 3.

saturated solution in THF at room temperature (**9**), respectively. The adducts crystallize in the triclinic space group *P* $\bar{1}$  (**7**), in the monoclinic space group *P*2<sub>1</sub>/*n* (**8**), in the orthorhombic space group *Pbca* (**6**), and the tetragonal space group *I*4/*cd* (**9**), respectively, in each case with one molecule in the asymmetric unit. Selected bonding parameters are summarized in Table 3.

The compounds **6–8** adopt – similar to the NHC adducts **1a–3** – trigonal bipyramidal structures. The axial chloride substituents are slightly more tilted towards the cAAC than in the NHC adducts **1a–3** (Cl1–E–Cl2: 172.39(2)°–179.445(17)°) with Cl1–E–Cl2 angles from 166.582(18)° to 170.59(2)°, owing to the better donor properties of the cAAC.<sup>[11,2c,31]</sup> Interestingly, the C1–E bond lengths of **6–8** (**6**: 2.078(18) Å; **8**: 2.0177(19) Å; **7**: 2.231(2) Å; Table 3) are slightly longer as observed in the structures of the NHC supported compounds **1a–c** (1.9803(18)–

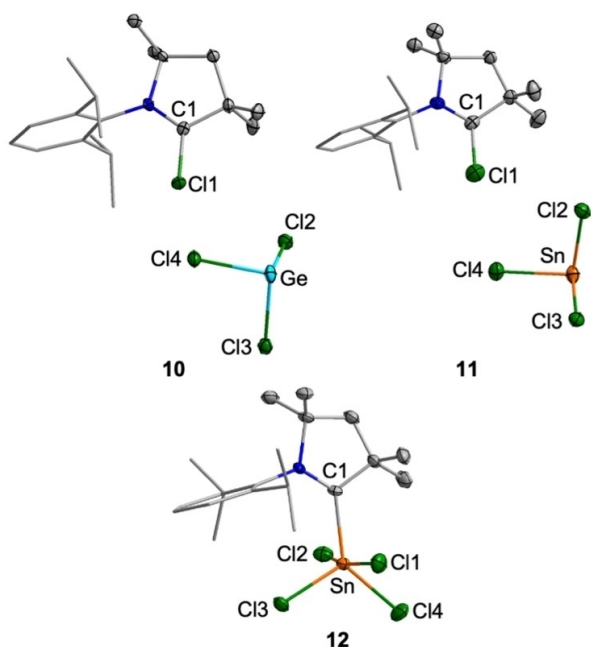
**Table 3.** Selected bond lengths [Å] and angles [°] of the compounds **6–12**.

trigonal bipyramidal	E–C1	E–Cl1	E–Cl2	E–C2/Cl3	E–C3/Cl4	Cl1–E–Cl2	C2–E–C3
( <b>6</b> ) cAAC <sup>Me</sup> ·GeCl <sub>2</sub> Me <sub>2</sub>	2.078(18)	2.4303(4)	2.4325(4)	1.9379(15)	1.9426(16)	169.355(14)	119.72(7)
( <b>7</b> ) cAAC <sup>Me</sup> ·SnCl <sub>2</sub> Me <sub>2</sub>	2.231(2)	2.5502(7)	2.5726(7)	2.122(3)	2.124(3)	170.59(2)	127.95(11)
( <b>8</b> ) cAAC <sup>Me</sup> ·GeCl <sub>2</sub> Ph <sub>2</sub>	2.0177(19)	2.2965(5)	2.5488(5)	1.9485(18)	1.9762(19)	166.582(18)	115.03(8)
( <b>12</b> ) cAAC <sup>Me</sup> ·SnCl <sub>4</sub>	2.214(5)	2.3878(5)	2.4385(13)	2.3181(12)	2.3356(15)	165.83(5)	110.31(5)
tetrahedral	E–C1	E–C2	E–C3	E–C4	C2–E–C3	C3vE–C4	C2–E–C4
( <b>9</b> ) [cAAC <sup>Me</sup> GeMe <sub>3</sub> ][Cl]	2.030(4)	1.947(4)	1.943(4)	1.954(4)	107.86(18)	110.41(19)	111.17(19)
trigonal pyramidal	C1–Cl1	E–Cl2	E–Cl3	E–Cl4	Cl2–E–Cl3	Cl3–E–Cl4	Cl2–E–Cl4
( <b>10</b> ) [cAAC <sup>Me</sup> Cl][GeCl <sub>3</sub> ]	1.691(3)	2.3085(9)	2.2975(9)	2.2914(8)	94.63(3)	97.30(3)	97.79(3)
( <b>11</b> ) [cAAC <sup>Me</sup> Cl][SnCl <sub>3</sub> ]	1.683(7)	2.477(3)	2.462(4)	2.458(3)	92.53(14)	95.97(12)	96.53(12)

1.9987(15) Å; Table 2) and **2b–c** (2.189(3)–2.202(2) Å; Table 2), respectively. The crystal structure of **9** reveals the formation of an ionic structure featuring a chloride anion and the  $[cAAC^{Me}GeMe_3]^+$  cation, which adopts a tetrahedral coordination at germanium with three methyl groups and one  $cAAC^{Me}$  ligand occupying the coordination sites. Similarly, the crystal structure of **10** (Figure 6) does not confirm the formation of an adduct  $cAAC^{Me}\cdot GeCl_4$ , but the formation of the salt  $[cAAC^{Me}Cl][GeCl_3]$  instead, featuring the discrete cation  $[cAAC^{Me}Cl]^+$  and the  $[GeCl_3]^-$  counterion.

In contrast to the synthesis of **10**, the reaction of  $SnCl_4$  with  $cAAC^{Me}$  does not lead to clean formation of the salt  $[cAAC^{Me}Cl][SnCl_3]$  (**11**). In fact, a mixture of **11** and the adduct  $cAAC^{Me}\cdot SnCl_4$  (**12**) (Scheme 4) was obtained. Compound **12** is partially soluble in benzene and can be extracted and isolated in a yield of 43% from the crude product. Subsequent recrystallization of the remaining solid afforded **11** in 21% yield. The formation of the  $[cAAC^{Me}Cl]^+$  cation can be concluded from a resonance at 190.7 ppm of the former carbene carbon atom in the  $^{13}C\{^1H\}$  NMR spectrum of **11**, which was already observed for compound **10**. For compound **12** a characteristic  $NCSn$  signal was detected at 218.9 ppm, in a similar region as observed for compound **7** ( $NCSn$ , 225.3 ppm; in toluene- $d_6$ ). In the  $^{119}Sn\{^1H\}$  NMR spectra, resonances were detected at  $-34.8$  ppm for **11** and at  $-406.3$  ppm for **12**, the latter close to that observed for  $Dipp_2Im\cdot SnCl_4$  ( $-422.6$  ppm, in toluene- $d_6$ ).<sup>[11c]</sup>

Crystals suitable for X-ray diffraction were obtained for **10** by slow evaporation of a dichloromethane solution at room temperature, for **11** by slow diffusion of *n*-hexane into a



**Figure 6.** Molecular structures of  $[cAAC^{Me}Cl][GeCl_3]$  (**10**),  $[cAAC^{Me}Cl][SnCl_3]$  (**11**) and  $cAAC^{Me}\cdot SnCl_4$  (**12**) in the solid-state. Hydrogen atoms are omitted for clarity. The  $[SnCl_3]^-$  anion in compound **11** is disordered and the data corresponds to the part with 86% occupancy. Atomic displacement ellipsoids are set at 50% probability and Dipp groups are shown as wire-and-stick model. Selected bond lengths and angles are given in Table 3.

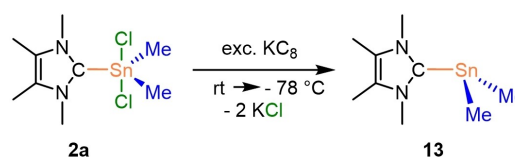
saturated dichloromethane solution and for **12** by slow evaporation of a saturated benzene solution at room temperature, respectively (Figure 6). The compounds **10**, **11** and **12** crystallize in the orthorhombic space group  $P2_12_12_1$  with one molecule in the asymmetric unit. Selected bonding parameters of **10**, **11** and **12** are summarized in Table 3. The germanium and tin salts **10** (Figure 6) and **11** (Figure 6) are isostructural with an  $[ECl_3]^-$  ( $E=Ge$ , **10**;  $Sn$ , **11**) anion and the  $[cAAC^{Me}Cl]^+$  cation, whereas compound **12** (Figure 6) shows a slightly distorted trigonal bipyramidal coordinated tin atom as found for the related dichlorodimethyl compound **7** (Figure 5).

Furthermore, the  $Sn-C1$  distances of **12** ( $Sn-C1$ : 2.214(5) Å) and **7** ( $Sn-C1$ : 2.231(2) Å) are identical within  $3\sigma$ . However, the angles in the coordination sphere of the tin atom are noticeably reduced in **12** ( $Cl1-Sn-Cl2$ : 165.83(5)°,  $Cl3-Sn-Cl4$ : 110.31(5)°) compared to the dimethyl analogue **7** ( $Cl1-Sn-Cl2$ : 170.59(2)°,  $C2-Sn-C3$ : 127.95(11)°), which reflects the lower steric demand of the chlorine atoms in comparison to the methyl groups.

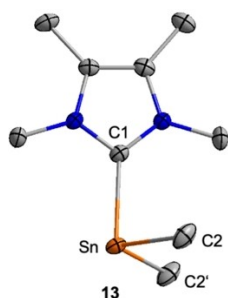
We also performed preliminary experiments concerning the reduction chemistry of the NHC adducts. Reduction of **2a** with  $KC_8$  led to the NHC stabilized stannylenes  $Me_2Im^{Me}\cdot SnMe_2$  (**13**) as a yellow solid in 67% yield. However, analogous experiments with the adducts **2b** and **2c**, respectively, were unsuccessful. The  $^1H$  NMR spectrum of **13** reveals strongly shifted methyl group resonances ( $SnCH_3$ , 0.73 ppm;  $NCCH_3$ , 1.31 ppm;  $NCH_3$ , 3.19 ppm) compared to the adduct **2a** ( $SnCH_3$ , 0.05 ppm;  $NCCH_3$ , 1.59 ppm;  $NCH_3$ , 3.66 ppm), and the  $^{13}C\{^1H\}$  NMR NHC carbene resonance was shifted from 160.0 ppm (**2a**) to 183.4 ppm (**13**), (Scheme 5).

Most significant, a resonance at  $-83.3$  ppm was recorded for **13** in the  $^{119}Sn\{^1H\}$  NMR spectrum, clearly downfield-shifted compared to the signal observed for  $Me_2Im^{Me}\cdot SnCl_2\cdot Me_2$  ( $\delta_{119Sn} = -222.5$  ppm), but also downfield-shifted compared to closely related NHC adducts of diarylsubstituted stannylenes  $Et_2Im^{Me}\cdot SnAr_2$  ( $Ar=Ph$ ,  $\delta_{119Sn} = -121.0$  ppm;  $Ar=Tripp$ ,  $\delta_{119Sn} = -150.7$  ppm) reported previously.<sup>[17]</sup>

The molecular structure of **13** (Figure 7) confirms stannylenes formation. Crystals of **13** suitable for X-ray diffraction were obtained by slow evaporation of a concentrated solution in toluene at room temperature. Stannylene **13** crystallizes in the orthorhombic space group  $Pnma$  with one molecule in the asymmetric unit, and a crystallographically imposed mirror plane runs through the tin atom and NHC plane. The molecular structure clearly reveals a trigonal pyramidal coordination at tin with almost ideal perpendicular angles ( $C1-Sn-C2$ : 93.33(11)° and  $C2-Sn-C2'$ : 95.66(18)°) and is thus isostructural to the literature known stannylenes.<sup>[17,18]</sup> The NHC  $\sigma$ -orbital (occupied  $sp^2$ -hybrid orbital) is donating into the vacant stannylenes  $p$ -orbital and thus stabilizes the stannylene. The  $Sn-C1$  distance 2.316(4) Å lies in the upper



**Scheme 5.** Synthesis of  $Me_2Im^{Me}\cdot SnMe_2$  (**13**).

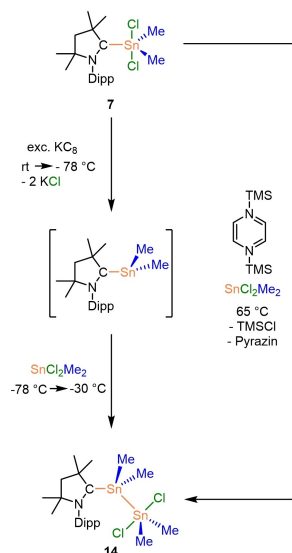


**Figure 7.** Molecular structure of  $\text{Me}_3\text{Im}^{\text{Me}}\cdot\text{SnMe}_2$  (**13**) in the solid-state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50% probability and Dipp groups are shown as wire-and-stick model. Symmetry generated atoms and their associated values are indicated with  $^{\text{sym}}$ . Selected bond lengths [Å] and angles [°]: **13**: Sn–C1, 2.316(4); Sn–C2=Sn–C2', 2.212(3); C1–Sn–C2=C1–Sn–C2', 93.33(11); C2–Sn–C2', 95.66(18).

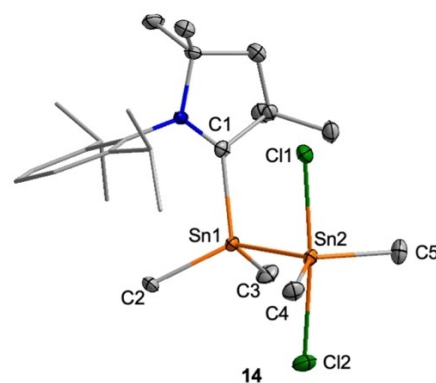
range of other NHC stabilized organo-substituted stannylenes (Sn–C1: 2.230(2)–2.295(2) Å).<sup>[17,18]</sup>

Furthermore, we also attempted to synthesize the stannylene  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2$  via metallic reduction in analogy to **13**. The reduction of **7** with  $\text{KC}_8$  (Scheme 6) quickly led to a red colored reaction mixture, which completely decolorized after a short time and turned pale brown at room temperature. We failed so far to isolate the unstable red intermediate, but obtained a colorless crystal suitable for X-ray diffraction (Figure 8) after cooling a reaction mixture in toluene shortly after the onset of the red coloration to  $-78^\circ\text{C}$ , filtration at this temperature and storage of the resulting solution at  $-30^\circ\text{C}$ .

The molecular structure revealed the formation of a stannylene-stannane adduct  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2\cdot\text{SnMe}_2\text{Cl}_2$  (**14**),



**Scheme 6.** *In situ* formation of  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2$  by reduction of  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2\text{Cl}_2$  (**7**) with excess  $\text{KC}_8$  and subsequent stabilization of the intermediate  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2$  with  $\text{SnMe}_2\text{Cl}_2$  to form  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2\cdot\text{SnMe}_2\text{Cl}_2$  (**14**) (top). Reduction of  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2\text{Cl}_2$  (**7**) with 1,4-bis(trimethylsilyl)-1,4-dihydropyrazin in the presence of  $\text{SnMe}_2\text{Cl}_2$  to form  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2\cdot\text{SnMe}_2\text{Cl}_2$  (**14**) (bottom).



**Figure 8.** Molecular structure of  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2\cdot\text{SnCl}_2\text{Me}_2$  (**14**) in the solid-state. Hydrogen atoms and solvent molecules (benzene) are omitted for clarity. Atomic displacement ellipsoids are set at 50% probability and Dipp groups are shown as wire-and-stick model. Selected bond lengths [Å] and angles [°]: **14**: Sn1–C1, 2.243(3); Sn1–C2, 2.148(3); Sn1–C3, 2.147(3); Sn1–Sn2, 2.7667(3); Sn2–Cl1, 2.5714(7); Sn1–Cl2, 2.6684(8); Sn1–C4, 2.133(3); Sn1–C5, 2.136(3); C1–Sn1–C2, 111.01(12); C2–Sn1–C3, 107.30(13); C1–Sn1–C3, 106.02(7); Cl1–Sn2–Cl2, 173.08(3); C4–Sn2–C5, 114.99(14).

which can also be regarded as a push-pull-stabilized stannylene, i.e., the stannylene  $\text{SnMe}_2$  is stabilized by the donor  $\text{cAAC}^{\text{Me}}$  and the acceptor  $\text{SnMe}_2\text{Cl}_2$ .

Compound **14** crystallizes in the triclinic space group  $P\bar{1}$ , with one molecule in the asymmetric unit. The stannylene center Sn1 is tetrahedrally coordinated by two methyl groups, the  $\text{cAAC}^{\text{Me}}$  ligand and one molecule  $\text{SnMe}_2\text{Cl}_2$ . The Sn1–C1 bond length (2.243(3) Å) is longer than the two single bonds between tin and the methyl substituents (Sn1–C2: 2.148(3) Å, Sn1–C3: 2.147(3) Å). The tin(IV) atom Sn2 is trigonal bipyramidal coordinated, with Sn1 and the methyl substituents in equatorial positions. The Sn1–Sn2 bond length is 2.7667(3) Å, which is similar to Sn–Sn distances observed for other distannanes, for example  $\text{Sn}_2\text{H}_4\text{Tripp}_2$  (Sn1–Sn2: 2.7449(2) Å; Figure 1, C;  $\text{R}^1 = \text{H}$ ).<sup>[17b]</sup>

As metallic reduction failed for the isolation of  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2$  (which most likely causes the red color) compound  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2\cdot\text{SnMe}_2\text{Cl}_2$  (**14**) was prepared by reacting the red solution with another equivalent  $\text{SnCl}_2\text{Me}_2$  (see Experimental Part). Furthermore, we discovered that 1,4-bis(trimethylsilyl)-1,4-dihydropyrazin is a suitable reductant for  $\text{cAAC}^{\text{Me}}\cdot\text{SnMe}_2\text{Cl}_2$  (**7**), which led to isolation of **14** in good yield (Scheme 6) and to characterization of the compound by using NMR and IR spectroscopy, as well as elemental analysis. In the  $^1\text{H}$  NMR spectrum of **14**, two broad resonances were observed for the stannylene methyl substituents at 0.24 ppm and a sharp singlet at 0.96 ppm for the chlorostannane methyl protons. Two sets of tin satellites were detected for the latter, with  $^2J$ -coupling of the methyl protons with  $^{119}\text{Sn}$  ( $^2J_{\text{H}-119\text{Sn}} = 67.8$  Hz) and  $^{117}\text{Sn}$  ( $^2J_{\text{H}-117\text{Sn}} = 64.9$  Hz) to the stannane tin atom and  $^3J$ -coupling to the stannylene tin atom with  $^2J$ -coupling constants of 11.3 Hz ( $^3J_{\text{H}-117\text{Sn}} = ^3J_{\text{H}-119\text{Sn}} = 11.3$  Hz). The  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectrum of **14** (Figures S45 and S46) shows two signals for the two tin atoms, the resonance of the stannylene tin atom was observed at  $-120.6$  ppm and is therefore only slightly down-

field shifted compared to the signal of the stannane tin atom at  $-127.1$  ppm.

Both signals show satellite sets with a  $^1J_{119\text{Sn}-117\text{Sn}}$ -coupling constant of 9492 Hz. Furthermore, an AB system was observed for the  $^{119}\text{Sn}$  satellites, from which a  $^1J_{119\text{Sn}-119\text{Sn}}$  coupling constant of 9910 Hz emerged. To precisely determine the  $^1J_{119\text{Sn}-119\text{Sn}}$  coupling constant, the corresponding  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectrum was simulated based on the experimentally determined coupling constants (Figure S46), which also allowed the identification of the position of the signals of the AB system with very low intensity.

## Conclusion

We present here a study on the synthesis, spectroscopic properties and molecular structures of various NHC-stabilized Ge(IV) and Sn(IV) adducts. The synthesis of NHC·ECl<sub>2</sub>Me<sub>2</sub> (**1a–2c**) was performed by the reaction of ECl<sub>2</sub>Me<sub>2</sub> (E=Ge, Sn), with the NHCs Me<sub>2</sub>Im<sup>Me</sup> (**a**), *i*Pr<sub>2</sub>Im<sup>Me</sup> (**b**) and Dipp<sub>2</sub>Im (**c**), respectively. The reaction of Me<sub>2</sub>Im<sup>Me</sup> with GeCl<sub>4</sub> and *i*Pr<sub>2</sub>Im<sup>Me</sup> with SnCl<sub>4</sub> in THF led to different coordinated adducts (trigonal bipyramidal: Me<sub>2</sub>Im<sup>Me</sup>·GeCl<sub>4</sub> (**3**); octahedral: *i*Pr<sub>2</sub>Im<sup>Me</sup>·SnCl<sub>4</sub>·THF (**4**)). Thermal treatment of the NHC adduct **1c** led to formation of an isomer salt with abnormally coordinated NHC [<sup>3</sup>Dipp<sub>2</sub>Im·GeClMe<sub>2</sub>][Cl] (**5**). The reaction of cAAC<sup>Me</sup> with ECl<sub>2</sub>Me<sub>2</sub> (E=Ge, Sn) and GeCl<sub>2</sub>Ph<sub>2</sub>, respectively, afforded the adducts cAAC<sup>Me</sup>·GeCl<sub>2</sub>Me<sub>2</sub> (**6**), cAAC<sup>Me</sup>·SnCl<sub>2</sub>Me<sub>2</sub> (**7**) and cAAC<sup>Me</sup>·GeCl<sub>2</sub>Ph<sub>2</sub> (**8**). In contrast to similar reactions with NHCs, the reaction of cAAC<sup>Me</sup> with GeClMe<sub>3</sub> and GeCl<sub>4</sub> led to formation of the salts [cAAC<sup>Me</sup>GeMe<sub>3</sub>][Cl] (**9**) and [cAAC<sup>Me</sup>Cl][GeCl<sub>3</sub>] (**10**), respectively. Unlike the synthesis of **10**, both the isostructural salt [cAAC<sup>Me</sup>Cl][SnCl<sub>3</sub>] (**11**) and the adduct cAAC<sup>Me</sup>·SnCl<sub>4</sub> (**12**) were isolated from the reaction of cAAC<sup>Me</sup> with SnCl<sub>4</sub>. Starting from Me<sub>2</sub>Im<sup>Me</sup>·SnCl<sub>2</sub>Me<sub>2</sub> (**2a**), the stannylene Me<sub>2</sub>Im<sup>Me</sup>·SnMe<sub>2</sub> (**13**) was obtained by reduction with KC<sub>8</sub>. Analogous reduction of SnCl<sub>2</sub>Me<sub>2</sub> in the presence of *i*Pr<sub>2</sub>Im<sup>Me</sup> or Dipp<sub>2</sub>Im as well as reduction of the adducts **2b** and **2c**, respectively, was unsuccessful. In contrast, the reduction of **7** resulted in an unstable stannylene, which was stabilized by an additional equivalent of SnCl<sub>2</sub>Me<sub>2</sub> to afford cAAC<sup>Me</sup>·SnMe<sub>2</sub>·SnMe<sub>2</sub>Cl<sub>2</sub> (**14**).

## Experimental Section

### General Considerations

All reactions and subsequent manipulations involving organometallic reagents were performed under an argon atmosphere by using standard Schlenk techniques or in a Glovebox (Innovative Technology Inc. and MBraun Uni Lab as reported previously.<sup>[19]</sup> All reactions were carried out in oven-dried glassware. Toluene, *n*-hexane, Et<sub>2</sub>O and THF were purified and dried using a solvent purification system (Innovative Technology). Benzene was dried over sodium. Deuterated Solvents were purchased from Sigma-Aldrich and stored over molecular sieves (4 Å). The carbenes Me<sub>2</sub>Im<sup>Me</sup>,<sup>[20]</sup> *i*Pr<sub>2</sub>Im<sup>Me</sup>,<sup>[20]</sup> Dipp<sub>2</sub>Im,<sup>[21]</sup> and cAAC<sup>Me</sup><sup>[22]</sup> and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazin<sup>[23]</sup> were synthesized according to literature procedures. All other reagents were purchased from

Sigma-Aldrich or ABCR and used without further purification. Elemental analyses were performed in the micro-analytical laboratory of the University of Würzburg with an Elementar vario micro cube. NMR spectra were recorded at 298 K using Bruker Avance 400 (<sup>1</sup>H: 400.5 MHz; <sup>13</sup>C{<sup>1</sup>H}: 100.7 MHz, <sup>119</sup>Sn: 149.3 MHz) and Bruker Avance 500 (<sup>1</sup>H: 500.1 MHz, <sup>13</sup>C{<sup>1</sup>H}: 125.8 MHz, <sup>119</sup>Sn: 186.5 MHz) spectrometers. Assignment of the NMR data was supported by <sup>1</sup>H-<sup>1</sup>H, <sup>1</sup>H-<sup>13</sup>C, and <sup>1</sup>H-<sup>119</sup>Sn correlation experiments. <sup>13</sup>C NMR spectra were broad-band proton-decoupled (<sup>13</sup>C{<sup>1</sup>H}). Assignment of the <sup>13</sup>C NMR data was supported by <sup>13</sup>C, <sup>1</sup>H correlation experiments. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts are listed in parts per million (ppm). The <sup>1</sup>H NMR shifts were referenced *via* residual proton resonances of the corresponding deuterated solvent C<sub>6</sub>D<sub>6</sub>H (<sup>1</sup>H:  $\delta = 7.16$  ppm, C<sub>6</sub>D<sub>6</sub>), C<sub>7</sub>D<sub>7</sub>H (<sup>1</sup>H:  $\delta = 2.08, 6.97, 7.01, 7.09$  ppm, toluene-*d*<sub>8</sub>) and CDHCl<sub>2</sub> (<sup>1</sup>H:  $\delta = 5.32$  ppm, CD<sub>2</sub>Cl<sub>2</sub>). <sup>13</sup>C NMR spectra are reported relative to TMS using the carbon resonances of the deuterated solvent C<sub>6</sub>D<sub>6</sub> (<sup>13</sup>C:  $\delta = 128.06$  ppm), toluene-*d*<sub>8</sub> (<sup>13</sup>C:  $\delta = 20.43, 125.13, 127.96, 128.87, 137.48$  ppm) and CD<sub>2</sub>Cl<sub>2</sub> (<sup>13</sup>C:  $\delta = 53.84$  ppm).<sup>[24]</sup> <sup>119</sup>Sn NMR spectra are reported relative to SnMe<sub>4</sub> ( $\delta = 0.00$  ppm). Coupling constants are quoted in Hertz. Infrared spectra were recorded on solid samples at room temperature on a Bruker Alpha FT-IR spectrometer using an ATR unit and are reported in cm<sup>-1</sup>. In dependence of the intensity of the vibration bands the following abbreviations were used: very strong (vs), strong (s), middle (m), weak (w) and very weak (vw).

### Experimental Procedures and Characterization of Products

**Me<sub>2</sub>Im<sup>Me</sup>·GeCl<sub>2</sub>Me<sub>2</sub> (1 a).** GeCl<sub>2</sub>Me<sub>2</sub> (140  $\mu\text{L}$ , 210 mg, 1.21 mmol, 1.0 eq) was added dropwise to a solution of Me<sub>2</sub>Im<sup>Me</sup> (150 mg, 1.97 mmol, 1.0 eq) in *n*-hexane (7 mL) and stirred at room temperature for 30 minutes. The resulting precipitate was collected by filtration, washed with *n*-hexane (3  $\times$  5 mL) and dried *in vacuo* to yield **1a** (313 mg, 1.05 mmol, 87%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by storing a solution of **1a** in benzene at 6 °C. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 0.97$  (s, 6 H, CCH<sub>3</sub>), 1.96 (s, 6 H, GeCH<sub>3</sub>), 3.20 (s, 6 H, NCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 7.6$  (CCH<sub>3</sub>), 20.7 (GeCH<sub>3</sub>), 33.3 (NCH<sub>3</sub>), 125.2 (NCCN), 155.8 (NCGe). **Elemental analysis** (%) calcd. for C<sub>9</sub>H<sub>18</sub>Cl<sub>2</sub>GeN<sub>2</sub> [297.79 g/mol]: C, 36.30; H, 6.09; N, 9.41; found: C, 37.65; H, 6.61; N, 10.07. IR (cm<sup>-1</sup>): 3155 (vw), 2979 (w), 2935 (s), 2843 (w), 2790 (w), 1769 (vw), 1650 (m), 1637 (m), 1581 (s), 1486 (m), 1447 (s), 1411 (m), 1401 (m), 1374 (w), 1341 (vw), 1318 (vw), 1244 (m), 1219 (m), 1149 (w), 1114 (vw), 1096 (w), 1045 (w), 994 (w), 890 (m), 852 (vs), 796 (m), 753 (m), 671 (vw), 630 (s), 587 (m), 571 (m), 531 (vw), 508 (vw).

***i*Pr<sub>2</sub>Im<sup>Me</sup>·GeCl<sub>2</sub>Me<sub>2</sub> (1 b).** GeCl<sub>2</sub>Me<sub>2</sub> (91.2  $\mu\text{L}$ , 137 mg, 788  $\mu\text{mol}$ , 1.0 eq) was added dropwise to a solution of *i*Pr<sub>2</sub>Im<sup>Me</sup> (142 mg, 788  $\mu\text{mol}$ , 1.0 eq) in *n*-hexane (7 mL) and stirred at room temperature for 30 minutes. The resulting precipitate was collected by filtration, washed with *n*-hexane (3  $\times$  5 mL) and dried *in vacuo* to yield **1b** (215 mg, 468  $\mu\text{mol}$ , 60%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by storing a solution of **1b** in benzene at 6 °C. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 1.17$  (d, 12 H, <sup>3</sup>J<sub>H-H} = 7.0 Hz, *i*Pr-CH<sub>3</sub>), 1.38 (s, 6 H, CH<sub>3</sub>CCCH<sub>3</sub>), 1.97 (s, 6 H, GeCH<sub>3</sub>), 5.39 (sept, 2 H, <sup>3</sup>J<sub>H-H} = 7.0 Hz, *i*Pr-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 9.9$  (NCCH<sub>3</sub>), 21.0 (*i*Pr-CH<sub>3</sub>), 22.1 (GeCH<sub>3</sub>), 52.3 (*i*Pr-CH), 125.8 (NCCN), 157.5 (NCN). **Elemental analysis** (%) calcd. for C<sub>13</sub>H<sub>26</sub>Cl<sub>2</sub>GeN<sub>2</sub> [353.90 g/mol]: C, 44.12; H, 7.41; N, 7.92; found: C, 44.20; H, 7.51; N, 7.97. IR (cm<sup>-1</sup>): 2996 (vw), 2972 (w), 2938 (w), 2880 (vw), 1629 (w), 1550 (vw), 1464 (m), 1439 (m), 1412 (s), 1391 (m), 1370 (m), 1338 (w), 1309 (vw), 1241 (w), 1219 (s), 1173 (vw), 1139 (vw), 1112 (m), 1083 (m), 1030 (vw), 931 (w), 903 (vw), 885 (vw), 853 (s), 842 (vs), 794 (m), 775 (m), 753 (m), 664 (vw), 628 (m), 590 (m), 543 (m), 437 (vw), 409 (vw).</sub></sub>



**Dipp<sub>2</sub>Im·GeCl<sub>2</sub>Me<sub>2</sub> (1c).** GeCl<sub>2</sub>Me<sub>2</sub> (45.4 μL, 68.4 mg, 394 μmol, 1.0 eq) was added dropwise to a solution of Dipp<sub>2</sub>Im (153 mg, 394 μmol, 1.0 eq) in *n*-hexane (7 mL) and stirred at room temperature for 30 minutes. The resulting precipitate was collected by filtration, washed with *n*-hexane (3×5 mL) and dried *in vacuo* to yield **1c** (171 mg, 373 μmol, 95%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by storing a solution of **1c** in benzene at 6°C. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 0.95 (d, 12 H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 1.03 (s, 6 H, GeCH<sub>3</sub>), 1.57 (d, 12 H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 3.45 (sept, 4 H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, *i*Pr-CH), 6.50 (s, 2 H, CHCH), 7.13 (m, 4 H, Dipp-*m*-CH), 7.19 (m, 2 H, Dipp-*p*-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 20.7 (GeCH<sub>3</sub>), 23.0 (*i*Pr-CH<sub>3</sub>), 26.8 (*i*Pr-CH<sub>3</sub>), 29.2 (*i*Pr-CH), 124.1 (CHCH), 124.7 (Dipp-*m*-CH), 132.0 (Dipp-*p*-CH), 132.9 (Dipp-*i*-C), 147.6 (Dipp-*o*-C), 160.5 (NCN). **Elemental analysis** (%) calcd. for C<sub>29</sub>H<sub>42</sub>Cl<sub>2</sub>GeN<sub>2</sub> [562.20 g/mol]: C, 61.96; H, 7.53; N, 4.98; found: C, 62.08; H, 7.66; N, 5.04. IR (cm<sup>-1</sup>): 3161 (vw), 3111 (vw), 3077 (w), 2965 (m), 2930 (w), 2868 (w), 1644 (vw), 1588 (vw), 1558 (vw), 1535 (w), 1464 (m), 1441 (m), 1418 (m), 1385 (m), 1363 (m), 1330 (m), 1307 (vw), 1269 (vw), 1252 (vw), 1238 (vw), 1210 (m), 1182 (w), 1146 (vw), 1122 (m), 1101 (w), 1059 (m), 948 (w), 932 (m), 848 (vw), 802 (s), 771 (s), 758 (vs), 730 (vw), 709 (w), 636 (m), 582 (w), 548 (vw), 462 (w), 439 (vw).

**Me<sub>2</sub>Im<sup>Me</sup>·SnCl<sub>2</sub>Me<sub>2</sub> (2a).** A solution of SnCl<sub>2</sub>Me<sub>2</sub> (265 mg, 1.21 mmol, 1.0 eq) and Me<sub>2</sub>Im<sup>Me</sup> (150 mg, 1.21 mmol, 1.0 eq) in *n*-hexane (10 mL) was stirred at room temperature overnight. The resulting precipitate was collected by filtration, washed with *n*-hexane (3×5 mL) and dried *in vacuo* yield **2a** (324 mg, 942 μmol, 78%) as a colorless solid. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 0.96 (s, 6 H, CCH<sub>3</sub>), 1.55 (s, 6 H, <sup>3</sup>J<sub>H-1195Sn</sub> = 84.9 Hz, <sup>3</sup>J<sub>H-1195Sn</sub> = 81.0 Hz, SnCH<sub>3</sub>), 3.14 (s, 6 H, NCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 7.7 (CCH<sub>3</sub>), 12.0 (GeCH<sub>3</sub>), 34.0 (NCH<sub>3</sub>), 125.8 (NCCN), 160.0 (NCN). <sup>119</sup>Sn{<sup>1</sup>H} NMR (186.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = -222.5. **Elemental analysis** (%) calcd. for C<sub>9</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>Sn [343.87 g/mol]: C, 31.44; H, 5.28; N, 8.15; found: C, 31.44; H, 5.32; N, 8.09. IR (cm<sup>-1</sup>): 2995 (vw), 2956 (vw), 2922 (vw), 2869 (vw), 1650 (m), 1577 (vw), 1542 (vw), 1483 (w), 1474 (w), 1445 (s), 1408 (m), 1398 (s), 1374 (w), 1230 (w), 1195 (vw), 1142 (vw), 1102 (vw), 1044 (vw), 978 (vw), 849 (s), 795 (vs), 745 (s), 661 (vw), 623 (vw), 561 (s), 528 (m), 459 (vw).

***i*Pr<sub>2</sub>Im<sup>Me</sup>·SnCl<sub>2</sub>Me<sub>2</sub> (2b).** A solution of SnCl<sub>2</sub>Me<sub>2</sub> (183 mg, 832 μmol, 1.0 eq) and *i*Pr<sub>2</sub>Im<sup>Me</sup> (150 mg, 832 μmol, 1.0 eq) in *n*-hexane (10 mL) was stirred at room temperature overnight. The resulting precipitate was collected by filtration, washed with *n*-hexane (3×5 mL) and dried *in vacuo* to yield **2b** (273 mg, 682 μmol, 82%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of a solution of **2b** in benzene at room temperature. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 1.15 (d, 12 H, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, *i*Pr-CH<sub>3</sub>), 1.39 (s, 6 H, CCH<sub>3</sub>), 1.52 (s, 6 H, <sup>3</sup>J<sub>H-1195Sn</sub> = 82.7 Hz, <sup>3</sup>J<sub>H-1195Sn</sub> = 79.0 Hz, SnCH<sub>3</sub>), 5.25 (sept, 2 H, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, *i*Pr-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 9.8 (NCCH<sub>3</sub>), 12.8 (SnCH<sub>3</sub>), 21.3 (*i*Pr-CH<sub>3</sub>), 54.0 (*i*Pr-CH), 126.3 (NCCN), 162.6 (NCN). <sup>119</sup>Sn{<sup>1</sup>H} NMR (186.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = -227.8. **Elemental analysis** (%) calcd. for C<sub>13</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>2</sub>Sn [399.98 g/mol]: C, 39.04; H, 6.55; N, 7.00; found: C, 38.65; H, 6.58; N, 6.83. IR (cm<sup>-1</sup>): 3013 (vw), 2978 (w), 2938 (vw), 2912 (vw), 2879 (vw), 1628 (w), 1557 (vw), 1461 (m), 1440 (m), 1405 (s), 1390 (m), 1373 (s), 1337 (m), 1308 (vw), 1221 (s), 1186 (w), 1171 (vw), 1141 (m), 1111 (m), 1080 (vw), 1026 (vw), 907 (w), 887 (vw), 796 (vs), 766 (s), 693 (vw), 620 (vw), 556 (s), 524 (m), 458 (vw), 424 (w).

**Dipp<sub>2</sub>Im·SnCl<sub>2</sub>Me<sub>2</sub> (2c).** A solution of SnCl<sub>2</sub>Me<sub>2</sub> (113 mg, 515 μmol, 1.0 eq) and Dipp<sub>2</sub>Im (200 mg, 515 μmol, 1.0 eq) in *n*-hexane (10 mL) was stirred at room temperature overnight. The resulting precipitate was collected by filtration, washed with *n*-hexane (3×5 mL) and dried *in vacuo* to yield **2c** (237 mg, 390 μmol, 76%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of a solution of **2c** in benzene

at room temperature. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 0.57 (s, 6 H, <sup>2</sup>J<sub>H-1195Sn</sub> = 84.2 Hz, <sup>2</sup>J<sub>H-1195Sn</sub> = 88.1 Hz, SnCH<sub>3</sub>), 0.95 (d, 12 H, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, *i*Pr-CH<sub>3</sub>), 1.57 (d, 12 H, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, *i*Pr-CH<sub>3</sub>), 3.31 (sept, 4 H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, *i*Pr-CH), 6.54 (s, 2 H, CHCH), 7.14 (m, 4 H, Dipp-*m*-CH), 7.20 (m, 2 H, Dipp-*p*-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 11.9 (GeCH<sub>3</sub>), 23.1 (*i*Pr-CH<sub>3</sub>), 26.8 (*i*Pr-CH<sub>3</sub>), 29.2 (*i*Pr-CH), 124.6 (CHCH), 124.7 (Dipp-*m*-CH), 132.0 (Dipp-*p*-CH), 133.3 (Dipp-*i*-C), 147.4 (Dipp-*o*-C), 165.9 (NCN). <sup>119</sup>Sn{<sup>1</sup>H} NMR (186.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = -217.6. **Elemental analysis** (%) calcd. for C<sub>29</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>2</sub>Sn [608.28 g/mol]: C, 57.26; H, 6.96; N, 4.61; found: C, 56.82; H, 7.03; N, 4.46. IR (cm<sup>-1</sup>): 3160 (vw), 3115 (w), 3082 (w), 2964 (m), 2928 (m), 2868 (w), 1638 (vw), 1529 (vw), 1557 (w), 1537 (vw), 1463 (m), 1441 (m), 1415 (m), 1385 (m), 1363 (m), 1352 (w), 1329 (m), 1305 (w), 1269 (w), 1253 (w), 1211 (m), 1183 (w), 1147 (vw), 1118 (m), 1102 (w), 1059 (m), 949 (w), 932 (w), 902 (vw), 874 (vw), 802 (vs), 768 (s), 757 (vs), 703 (w), 631 (w), 565 (m), 527 (w), 459 (w), 438 (vw).

**Me<sub>2</sub>Im<sup>Me</sup>·GeCl<sub>4</sub> (3).** GeCl<sub>4</sub> (200 μL, 376 mg, 1.76 mmol, 1.0 eq) was added dropwise to a solution of Me<sub>2</sub>Im<sup>Me</sup> (218 mg, 1.76 mmol, 1.0 eq) in *n*-hexane (7 mL) at -78°C. The temperature of the solution was warmed to room temperature and stirred overnight. A precipitate formed during that time was collected by filtration, washed with Et<sub>2</sub>O (5 mL) and *n*-hexane (5 mL) and dried *in vacuo* to yield **3** (473 mg, 1.40 mmol, 80%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of a concentrated toluene solution of **3** at room temperature. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 0.80 (s, 6 H, NCH<sub>3</sub>), 3.28 (s, 6 H, CCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 7.3 (CCH<sub>3</sub>), 33.5 (NCCH<sub>3</sub>), 125.0 (NCCN), 153.6 (NCN)\*. \* The resonance at 153.6 ppm was detected in the corresponding <sup>1</sup>H,<sup>13</sup>C {<sup>1</sup>H} HMBC spectrum. IR (cm<sup>-1</sup>): 3156 (vw), 3082 (vw), 2976 (m), 2930 (m), 2865 (w), 2785 (vw), 1640 (s), 1579 (m), 1537 (vw), 1486 (m), 1446 (vs), 1404 (s), 1372 (m), 1338 (w), 1267 (vw), 1230 (w), 1206 (w), 1110 (w), 1096 (w), 1044 (w), 1007 (vw), 966 (vw), 937 (vw), 847 (vs), 756 (m), 712 (w), 664 (vw), 629 (w), 605 (vw), 569 (m), 539 (vw), 506 (vw), 473 (vw), 415 (vw).

***i*Pr<sub>2</sub>Im<sup>Me</sup>·SnCl<sub>4</sub>·THF (4).** SnCl<sub>4</sub> (130 μL, 289 mg, 1.11 mmol, 1.0 eq) was added dropwise to a solution of *i*Pr<sub>2</sub>Im<sup>Me</sup> (200 mg, 2.63 mmol, 1.0 eq) in THF (10 mL) and stirred at room temperature for one hour. The reaction mixture was filtered, and the filtrate layered with *n*-hexane (10 mL). The product crystallized after one week at -30°C and the micro crystalline solid was isolated by filtration and dried *in vacuo* to yield **4** (1.13 g, 2.26 mmol, 85%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by layering a concentrated solution of **4** in THF with *n*-hexane and storing this solution at -30°C. <sup>1</sup>H NMR (400.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 1.12 (d, 12 H, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, *i*Pr-CH<sub>3</sub>), 1.29 (s, 6 H, CH<sub>2</sub>CCCH<sub>3</sub>), 1.40 (m, 4 H, OCH<sub>2</sub>CH<sub>2</sub>), 3.78 (m, 4 H, OCH<sub>2</sub>), 5.67 (sept, 2 H, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, *i*Pr-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (100.7 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 9.7 (NCCH<sub>3</sub>), 21.2 (*i*Pr-CH<sub>3</sub>), 25.6 (OCH<sub>2</sub>CH<sub>2</sub>), 54.6 (*i*Pr-CH), 68.5 (OCH<sub>2</sub>), 126.8 (NCCN), 160.1 (NCN). <sup>119</sup>Sn{<sup>1</sup>H} NMR (149.3 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = -446.5 (br). **Elemental analysis** (%) calcd. for C<sub>15</sub>H<sub>28</sub>Cl<sub>4</sub>N<sub>2</sub>O + C<sub>4</sub>H<sub>8</sub>O [585.02 g/mol]: C, 39.01; H, 6.20; N, 4.79; found: C, 37.96; H, 5.95; N, 6.90. IR (cm<sup>-1</sup>): 3144 (vw), 2987 (w), 2976 (w), 2938 (w), 2877 (vw), 1636 (w), 1551 (vw), 1444 (m), 1385 (m), 1367 (vs), 1283 (vw), 1204 (s), 1163 (w), 1141 (m), 1114 (m), 1070 (w), 1014 (w), 968 (vw), 932 (vw), 901 (w), 882 (vw), 853 (w), 833 (w), 754 (m), 677 (vw), 650 (vw), 585 (vw), 541 (m), 506 (vw), 464 (vw), 432 (m).

**[<sup>†</sup>Dipp<sub>2</sub>Im·GeClMe<sub>2</sub>][Cl] (5).** GeCl<sub>2</sub>Me<sub>2</sub> (59.6 μL, 89.4 mg, 515 μmol, 1.0 eq) was added to a solution of Dipp<sub>2</sub>Im (200 mg, 515 μmol, 1.0 eq) in benzene (10 mL) and refluxed overnight. The resulting precipitate was collected by filtration, washed with *n*-hexane (3×5 mL) and dried *in vacuo* to yield **5** (205 mg, 365 μmol, 71%) as a colorless solid. Crystals of **5** suitable for X-ray diffraction were obtained by cooling an at reflux saturated benzene solution of this

compound to room temperature.  $^1\text{H NMR}$  (400.5 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  = 0.76 (s, 6 H,  $\text{GeCH}_3$ ), 1.28 (d, 6 H,  $^3J_{\text{H-H}} = 6.9$  Hz,  $i\text{Pr-CH}_3$ ), 1.29 (d, 6 H,  $^3J_{\text{H-H}} = 6.9$  Hz,  $i\text{Pr-CH}_3$ ), 1.30 (d, 6 H,  $^3J_{\text{H-H}} = 6.9$  Hz,  $i\text{Pr-CH}_3$ ), 1.35 (d, 6 H,  $^3J_{\text{H-H}} = 6.9$  Hz,  $i\text{Pr-CH}_3$ ), 2.41 (sept, 2 H,  $^3J_{\text{H-H}} = 6.9$  Hz,  $i\text{Pr-CH}$ ), 2.44 (sept, 2 H,  $^3J_{\text{H-H}} = 6.9$  Hz,  $i\text{Pr-CH}$ ), 7.40 (d, 2 H,  $^3J_{\text{H-H}} = 7.9$  Hz, Dipp- $m$ -CH), 7.43 (d, 2 H,  $^3J_{\text{H-H}} = 7.9$  Hz, Dipp- $m$ -CH), 7.62 (t, 1 H,  $^3J_{\text{H-H}} = 7.9$  Hz, Dipp- $p$ -CH), 7.66 (t, 1 H,  $^3J_{\text{H-H}} = 7.9$  Hz, Dipp- $p$ -CH), 7.68 (s, 1 H, NCHGe), 12.2 (s, 1 H, NCHN).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.7 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  = 5.3 ( $\text{GeCH}_3$ ), 22.3 ( $i\text{Pr-CH}_3$ ), 23.9 ( $i\text{Pr-CH}_3$ ), 24.9 ( $i\text{Pr-CH}_3$ ), 26.6 ( $i\text{Pr-CH}_3$ ), 29.6 ( $i\text{Pr-CH}$ ), 29.7 ( $i\text{Pr-CH}$ ), 125.0 (Dipp- $m$ -CH), 125.1 (Dipp- $m$ -CH), 130.4 (Dipp- $i$ -C), 131.0 (Dipp- $i$ -C), 132.0 (NCHGe), 132.4 (Dipp- $p$ -CH), 132.9 (Dipp- $p$ -CH), 136.8 (NCGe), 145.1 (NCHN), 145.6 (Dipp- $o$ -C), 146.0 (Dipp- $o$ -C). **Elemental analysis** (%) calcd. for  $\text{C}_{29}\text{H}_{42}\text{Cl}_2\text{GeN}_2$  [562.20 g/mol]: C, 61.96; H, 7.53; N, 4.98; found: C, 62.34; H, 7.97; N, 4.74. IR ( $\text{cm}^{-1}$ ): 3151 (vw), 3076 (w), 2962 (s), 2929 (m), 2868 (m), 2827 (m), 2753 (s), 1888 (vw), 1644 (vw), 1588 (vw), 1545 (w), 1531 (m), 1496 (w), 1463 (s), 1443 (w), 1419 (w), 1386 (m), 1365 (m), 1330 (m), 1301 (w), 1259 (w), 1204 (m), 1183 (m), 1106 (w), 1059 (s), 951 (m), 935 (m), 853 (m), 810 (vs), 773 (s), 759 (vs), 739 (vs), 709 (w), 698 (m), 685 (m), 637 (m), 582 (vw), 538 (vs), 522 (w), 466 (vs), 443 (m).

**cAAC<sup>Me</sup>·GeCl<sub>2</sub>Me<sub>2</sub> (6).**  $\text{GeCl}_2\text{Me}_2$  (250  $\mu\text{L}$ , 563 mg, 1.97 mmol, 1.0 eq) was added dropwise to a solution of cAAC<sup>Me</sup> (342 mg, 1.97 mmol, 1.0 eq) in *n*-hexane (7 mL) and the resulting solution was stirred at room temperature for 30 minutes. A precipitate formed during that time was collected by filtration, washed with *n*-hexane (3 x 5 mL) and dried *in vacuo* to yield **6** (798 mg, 1.74 mmol, 88%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by storing a solution of **6** in benzene at 6 °C.  $^1\text{H NMR}$  (500.1 MHz, toluene- $d_8$ , 233 K):  $\delta$  = 0.81 (s, 3 H,  $\text{GeCH}_3$ ), 0.94 (s, 6 H,  $\text{NC}(\text{CH}_3)_2$ ), 1.04 (d, 6 H,  $^3J_{\text{H-H}} = 6.7$  Hz,  $i\text{Pr-CH}_3$ ), 1.28 (s, 2 H,  $\text{CH}_2$ ), 1.64 (d, 6 H,  $^3J_{\text{H-H}} = 6.7$  Hz,  $i\text{Pr-CH}_3$ ), 1.75 (s, 6 H,  $\text{NCC}(\text{CH}_3)_2$ ), 1.97 (s, 3 H,  $\text{GeCH}_3$ ), 3.23 (sept, 2 H,  $^3J_{\text{H-H}} = 6.7$  Hz,  $i\text{Pr-CH}$ ), 6.94 (m, 2 H, Dipp- $m$ -CH), 6.98 (m, 1 H, Dipp- $p$ -CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, toluene- $d_8$ , 233 K):  $\delta$  = 15.0 ( $\text{GeCH}_3$ ), 25.2 ( $\text{GeCH}_3$ ), 27.0 ( $i\text{Pr-CH}_3$ ), 28.2 ( $\text{NC}(\text{CH}_3)_2$ ), 28.3 ( $i\text{Pr-CH}_3$ ), 29.2 ( $i\text{Pr-CH}$ ), 32.1 ( $\text{NCC}(\text{CH}_3)_2$ ), 51.5 ( $\text{CH}_2$ ), 54.4 ( $\text{NCC}(\text{CH}_3)_2$ ), 82.1 ( $\text{NC}(\text{CH}_3)_2$ ), 126.5 (Dipp- $m$ -CH), 130.7 (Dipp- $p$ -CH), 132.5 (Dipp- $i$ -C), 147.0 (Dipp- $o$ -C), 214.1 (NCGe). **Elemental analysis** (%) calcd. for  $\text{C}_{22}\text{H}_{37}\text{Cl}_2\text{GeN}$  [459.08 g/mol]: C, 57.56; H, 8.12; N, 3.05; found: C, 58.21; H, 8.47; N, 3.15. IR ( $\text{cm}^{-1}$ ): 3079 (vw), 2986 (m), 2970 (m), 2933 (m), 2868 (m), 2823 (m), 1638 (m), 1592 (vw), 1525 (vw), 1465 (s), 1390 (w), 1377 (m), 1369 (m), 1359 (w), 1343 (m), 1270 (w), 1257 (w), 1246 (w), 1205 (w), 1171 (vw), 1135 (w), 1110 (w), 1053 (m), 950 (w), 933 (vw), 901 (m), 883 (m), 844 (s), 811 (vs), 788 (s), 768 (s), 717 (vw), 676 (w), 652 (m), 630 (w), 607 (w), 592 (w), 559 (w), 517 (vw), 489 (w), 425 (vw).

**cAAC<sup>Me</sup>·SnCl<sub>2</sub>Me<sub>2</sub> (7).** A solution of  $\text{SnCl}_2\text{Me}_2$  (154 mg, 701  $\mu\text{mol}$ , 1.0 eq) and cAAC<sup>Me</sup> (200 mg, 701  $\mu\text{mol}$ , 1.0 eq) in *n*-hexane (10 mL) was stirred at room temperature overnight. A precipitate formed during that time was collected by filtration, washed with *n*-hexane (3 x 5 mL) and dried *in vacuo* to yield **7** (240 mg, 475  $\mu\text{mol}$ , 68%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of a solution of **7** in benzene at room temperature.  $^1\text{H NMR}$  (500.1 MHz, toluene- $d_8$ , 233 K):  $\delta$  = 0.42 (s, 3 H, overlapping broad satellites,  $\text{SnCH}_3$ ), 0.82 (s, 6 H,  $\text{NC}(\text{CH}_3)_2$ ), 1.04 (d, 6 H,  $^3J_{\text{H-H}} = 6.7$  Hz,  $i\text{Pr-CH}_3$ ), 1.21 (s, 2 H,  $\text{CH}_2$ ), 1.60 (d, 6 H,  $^3J_{\text{H-H}} = 6.7$  Hz,  $i\text{Pr-CH}_3$ ), 1.66 (s, 3 H, overlapping broad satellites,  $\text{SnCH}_3$ ), 1.70 (s, 6 H,  $\text{NCC}(\text{CH}_3)_2$ ), 3.06 (sept, 2 H,  $^3J_{\text{H-H}} = 6.7$  Hz,  $i\text{Pr-CH}$ ), 6.91 (m, 2 H, Dipp- $m$ -CH), 6.97 (m, 1 H, Dipp- $p$ -CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, toluene- $d_8$ , 233 K):  $\delta$  = 5.9 ( $\text{SnCH}_3$ ), 18.6 ( $\text{SnCH}_3$ ), 26.2 ( $i\text{Pr-CH}_3$ ), 28.6 ( $\text{NC}(\text{CH}_3)_2$ ), 29.0 ( $i\text{Pr-CH}$ ), 29.1 ( $i\text{Pr-CH}_3$ ), 31.0 ( $\text{NCC}(\text{CH}_3)_2$ ), 50.0 ( $\text{CH}_2$ ), 55.7 ( $\text{NCC}(\text{CH}_3)_2$ ), 83.4 ( $\text{NC}(\text{CH}_3)_2$ ), 126.4 (Dipp- $m$ -CH), 130.7 (Dipp- $p$ -CH), 132.6 (Dipp- $i$ -C), 146.6 (Dipp- $o$ -C), 226.3 (NCSn).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (186.5 MHz, toluene- $d_8$ , 233 K):  $\delta$  = -214.1. **Elemental analysis** (%) calcd. for  $\text{C}_{22}\text{H}_{37}\text{Cl}_2\text{N}_2\text{Sn}$  [505.16 g/

mol]: C, 52.31; H, 7.38; N, 2.77; found: C, 52.22; H, 7.45; N, 2.61. IR ( $\text{cm}^{-1}$ ): 2964 (m), 2930 (m), 2872 (w), 1643 (vw), 1587 (vw), 1529 (m), 1458 (m), 1390 (m), 1375 (m), 1346 (w), 1324 (w), 1265 (w), 1207 (w), 1188 (m), 1181 (m), 1160 (vw), 1128 (w), 1107 (w), 1053 (w), 1015 (vw), 997 (vw), 973 (vw), 930 (vw), 879 (vw), 809 (vs), 775 (vs), 610 (w), 556 (s), 521 (m), 492 (vw), 433 (vw), 412 (vw).

**cAAC<sup>Me</sup>·GeCl<sub>2</sub>Ph<sub>2</sub> (8).** A solution of  $\text{GeCl}_2\text{Ph}_2$  (147  $\mu\text{L}$ , 209 mg, 0.70 mmol, 1.0 eq) in *n*-hexane (5 mL) was added to a solution of cAAC<sup>Me</sup> (200 mg, 0.70 mmol, 1.0 eq) in *n*-hexane (5 mL) at -78 °C and allowed to warm to room temperature overnight under stirring. A precipitate formed during that time was collected by filtration, washed with *n*-hexane (2 x 5 mL) and dried *in vacuo* to yield **8** (281 mg, 482  $\mu\text{mol}$ , 69%) as a colorless solid. Partial decomposition of the compound in solution was observed. Crystals suitable for single crystal X-ray diffraction were obtained by storing a solution of **8** in benzene at 6 °C.  $^1\text{H NMR}$  (500.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  = 0.99 (d, 6 H,  $^3J_{\text{H-H}} = 6.5$  Hz,  $i\text{Pr-CH}_3$ ), 1.18 (s, 6 H,  $\text{NC}(\text{CH}_3)_2$ ), 1.30 (d, 6 H,  $^3J_{\text{H-H}} = 6.5$  Hz,  $i\text{Pr-CH}_3$ ), 1.45 (s, 2 H,  $\text{CH}_2$ ), 1.70 (s, 6 H,  $\text{NCC}(\text{CH}_3)_2$ ), 3.31 (sept, 2 H,  $^3J_{\text{H-H}} = 6.5$  Hz,  $i\text{Pr-CH}$ ), 6.88 (br, 3 H, Ph-CH), 7.00 (d, 2 H,  $^3J_{\text{H-H}} = 7.7$  Hz, Dipp- $m$ -CH), 7.13 (t, 1 H,  $^3J_{\text{H-H}} = 7.7$  Hz, Dipp- $p$ -CH), 7.31 (br, 2 H, Ph-CH), 7.42 (br, 2 H, Ph-CH), 7.55 (m, 1 H, Ph-CH), 9.37 (br, 2 H, Ph-CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  = 25.7 ( $i\text{Pr-CH}_3$ ), 28.0 ( $\text{NC}(\text{CH}_3)_2$ ), 28.2 ( $i\text{Pr-CH}_3$ ), 29.2 ( $i\text{Pr-CH}$ ), 32.9 ( $\text{NCC}(\text{CH}_3)_2$ ), 52.4 ( $\text{CH}_2$ ), 55.1 ( $\text{NCC}(\text{CH}_3)_2$ ), 82.7 ( $\text{NC}(\text{CH}_3)_2$ ), 126.9 (Dipp- $m$ -CH), 127.0 (Ph-CH), 128.2 (Ph-CH), 129.2 (Ph-CH), 130.8 (Dipp- $p$ -CH), 131.8 (Ph-CH), 133.0 (Ph-CH), 134.5 (Dipp- $i$ -C), 135.4 (Ph-CH), 138.0 (Ph-CH), 141.0 (Ph- $i$ -C), 145.0 (Ph- $i$ -C), 147.9 (Dipp- $o$ -C), 213.0 (NCGe). **Elemental analysis** (%) calcd. for  $\text{C}_{22}\text{H}_{37}\text{Cl}_2\text{GeN}$  [459.08 g/mol]: C, 65.90; H, 7.09; N, 2.40; found: C, 65.44; H, 7.34; N, 2.34. IR ( $\text{cm}^{-1}$ ): 3050 (vw), 2970 (m), 2931 (m), 2870 (w), 1683 (vw), 1639 (vw), 1584 (vw), 1513 (m), 1471 (m), 1456 (m), 1431 (m), 1391 (m), 1376 (w), 1367 (w), 1346 (vw), 1322 (w), 1302 (w), 1265 (w), 1205 (vw), 1182 (m), 1158 (vw), 1127 (w), 1097 (w), 1082 (w), 1072 (m), 1054 (w), 1026 (w), 999 (w), 932 (vw), 911 (vw), 874 (vw), 810 (m), 778 (w), 747 (s), 736 (vs), 692 (vs), 674 (m), 610 (vw), 564 (w), 519 (vw), 503 (vs), 475 (s), 461 (s), 437 (vw), 416 (vw).

**[cAAC<sup>Me</sup>·GeMe<sub>3</sub>][Cl] (9).**  $\text{GeClMe}_3$  (100  $\mu\text{L}$ , 124 mg, 809  $\mu\text{mol}$ , 1.5 eq) was added dropwise to a solution of cAAC<sup>Me</sup> (154 mg, 515  $\mu\text{mol}$ , 1.0 eq) in THF (3 mL) and stirred at room temperature for 2 h. The reaction mixture was left standing at room temperature overnight to crystallize **9**. The solvent was decanted, and the solid material dried *in vacuo* to yield **9** (215 mg, 468  $\mu\text{mol}$ , 60%) as a colorless microcrystalline solid. Partial decomposition of the compound in solution was observed. Crystals suitable for single crystal X-ray diffraction were obtained by storing a concentrated solution of **9** in THF at room temperature.  $^1\text{H NMR}$  (400.5 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  = 0.35 ( $s_{\text{br}}$ , 9 H,  $\text{Ge}(\text{CH}_3)_3$ ), 1.20 (d, 6 H,  $^3J_{\text{H-H}} = 6.7$  Hz,  $i\text{Pr-CH}_3$ ), 1.35 (d, 6 H,  $^3J_{\text{H-H}} = 6.7$  Hz,  $i\text{Pr-CH}_3$ ), 1.59 (s, 6 H,  $\text{NCC}(\text{CH}_3)_2$ ), 1.67 (s, 6 H,  $\text{NC}(\text{CH}_3)_2$ ), 2.48 (s, 2 H,  $\text{CH}_2$ ), 2.74 (sept, 2 H,  $^3J_{\text{H-H}} = 6.7$  Hz,  $i\text{Pr-CH}$ ), 7.41 (d, 2 H,  $^3J_{\text{H-H}} = 7.8$  Hz, Dipp- $m$ -CH), 7.59 (t, 2 H,  $^3J_{\text{H-H}} = 7.8$  Hz, Dipp- $p$ -CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.7 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  = 2.4 ( $\text{Ge}(\text{CH}_3)_3$ ), 24.8 ( $i\text{Pr-CH}_3$ ), 25.8 ( $i\text{Pr-CH}_3$ ), 28.6 ( $\text{NC}(\text{CH}_3)_2$ ), 29.2 ( $\text{NCC}(\text{CH}_3)_2$ ), 29.4 ( $i\text{Pr-CH}$ ), 50.0 ( $\text{CH}_2$ ), 56.7 ( $\text{NCC}(\text{CH}_3)_2$ ), 86.4 ( $\text{NC}(\text{CH}_3)_2$ ), 126.9 (Dipp- $m$ -CH), 131.9 (Dipp- $i$ -C), 132.3 (Dipp- $p$ -CH), 145.1 (Dipp- $o$ -C), 222.9 (NCGe). **Elemental analysis** (%) calcd. for  $\text{C}_{23}\text{H}_{40}\text{ClGeN}$  [438.66 g/mol]: C, 62.98; H, 9.19; N, 3.19; found: C, 62.53; H, 9.35; N, 3.28. IR ( $\text{cm}^{-1}$ ): 2967 (s), 2930 (m), 2867 (m), 2823 (m), 1638 (m), 1590 (vw), 1561 (vw), 1465 (s), 1440 (m), 1391 (w), 1378 (m), 1368 (m), 1359 (m), 1342 (m), 1325 (w), 1256 (w), 1239 (w), 1205 (m), 1174 (vw), 1135 (m), 1110 (vw), 1053 (m), 1000 (vw), 972 (vw), 949 (m), 901 (w), 841 (m), 811 (vs), 797 (s), 767 (m), 754 (w), 676 (w), 652 (vw), 608 (s), 559 (m), 517 (vw), 489 (w), 469 (vw), 446 (vw), 426 (vw), 409 (vw).

**[cAAC<sup>Me</sup>Cl][GeCl<sub>4</sub>] (10).** A solution of cAAC<sup>Me</sup> (1.00 g, 3.50 mmol, 1.0 eq) in  $\text{Et}_2\text{O}$  (15 mL) was added to a solution of  $\text{GeCl}_4$  (400  $\mu\text{L}$ ,

751 mg, 3.50 mmol, 1.0 eq) in Et<sub>2</sub>O (15 mL) at  $-78^{\circ}\text{C}$ . The reaction mixture was allowed to warm to room temperature over a period of 2 h. The resulting precipitate was collected by filtration, washed with Et<sub>2</sub>O (5 mL) and *n*-hexane (2 x 5 mL) and dried *in vacuo* to yield **10** (1.53 g, 3.06 mmol, 87%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of a dichloromethane solution of **10** at room temperature. <sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 1.20$  (d, 6 H, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, *iPr-CH<sub>3</sub>*), 1.39 (s, 6 H, NC(CH<sub>3</sub>)<sub>2</sub>), 1.64 (s, 2 H, CH<sub>2</sub>), 1.77 (s, 6 H, NCC(CH<sub>3</sub>)<sub>2</sub>), 2.48 (sept, 2 H, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, *iPr-CH*), 2.76 (d, 6 H, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, *iPr-CH<sub>3</sub>*), 7.47 (d, 2 H, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, Dipp-*m-CH*), 7.66 (t, 1 H, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, Dipp-*p-CH*). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 23.4$  (*iPr-CH<sub>3</sub>*), 26.3 (*iPr-CH<sub>3</sub>*), 28.4, (NCC(CH<sub>3</sub>)<sub>2</sub>), 29.0 (NC(CH<sub>3</sub>)<sub>2</sub>), 30.4 (*iPr-CH*), 48.2 (CH<sub>2</sub>), 51.7 (NC(CH<sub>3</sub>)<sub>2</sub>), 84.5 (NCC(CH<sub>3</sub>)<sub>2</sub>), 126.9 (Dipp-*m-CH*), 127.6 (Dipp-*i-C*), 133.2 (Dipp-*p-CH*), 144.7 (Dipp-*o-C*), 190.6 (NCCl). **Elemental analysis** (%) calcd. for C<sub>20</sub>H<sub>31</sub>Cl<sub>4</sub>GeN [499.91 g/mol]: C, 48.05; H, 6.25; N, 2.80; found: C, 48.07; H, 6.21; N, 2.70. IR (cm<sup>-1</sup>): 3003 (vw), 2974 (m), 2932 (w), 2872 (w), 1606 (vs), 1596 (w), 1460 (m), 1440 (m), 1379 (m), 1366 (m), 1335 (w), 1315 (vw), 1266 (w), 1206 (vw), 1183 (w), 1169 (w), 1134 (s), 1114 (m), 1061 (m), 1053 (m), 1014 (vw), 972 (vw), 955 (vw), 929 (w), 870 (w), 818 (vs), 795 (vw), 743 (m), 711 (vw), 700 (vw), 633 (vw), 610 (m), 567 (m), 506 (w), 494 (m), 426 (w).

**Synthesis of [cAAC<sup>Me</sup>Cl][SnCl<sub>3</sub>] (11) and cAAC<sup>Me</sup>·SnCl<sub>4</sub> (12).** A solution of cAAC<sup>Me</sup> (1.00 g, 3.50 mmol, 1.0 eq) in Et<sub>2</sub>O (15 mL) was added to a solution of SnCl<sub>4</sub> (409  $\mu\text{L}$ , 913 mg, 3.50 mmol, 1.0 eq) in Et<sub>2</sub>O (15 mL) at  $-78^{\circ}\text{C}$ . The reaction mixture was allowed to warm to room temperature overnight. All volatile material of the resulting suspension was removed *in vacuo* and the remaining solid was washed with benzene (3 x 8 mL). The solid was dried *in vacuo* to yield **11** (729 mg, 1.34 mmol, 38%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by slow diffusion of *n*-hexane into a saturated dichloromethane solution of **11** at room temperature. Removing all volatile material of the filtrate *in vacuo* afforded **12** (841 mg, 1.54 mmol, 44%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of **12** in benzene at room temperature. **11**: <sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 1.20$  (d, 6 H, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, *iPr-CH<sub>3</sub>*), 1.39 (d, 6 H, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, *iPr-CH<sub>3</sub>*), 1.64 (s, 6 H, NC(CH<sub>3</sub>)<sub>2</sub>), 1.77 (s, 6 H, NCC(CH<sub>3</sub>)<sub>2</sub>), 2.48 (sept, 2 H, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, *iPr-CH*), 2.79 (s, 2 H, CH<sub>2</sub>), 7.46 (d, 2 H, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, Dipp-*m-CH*), 7.66 (t, 1 H, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, Dipp-*p-CH*). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 23.5$  (*iPr-CH<sub>3</sub>*), 26.3 (*iPr-CH<sub>3</sub>*), 28.4 (NCC(CH<sub>3</sub>)<sub>2</sub>), 29.1 (NC(CH<sub>3</sub>)<sub>2</sub>), 30.4 (*iPr-CH*), 48.2 (CH<sub>2</sub>), 51.8 (NCC(CH<sub>3</sub>)<sub>2</sub>), 84.6 (NC(CH<sub>3</sub>)<sub>2</sub>), 126.9 (Dipp-*m-CH*), 127.7 (Dipp-*i-C*), 133.2 (Dipp-*p-CH*), 144.7 (Dipp-*o-C*), 190.6 (NCCl). **Elemental analysis** (%) calcd. for C<sub>20</sub>H<sub>31</sub>Cl<sub>4</sub>NSn [545.99 g/mol]: C, 44.00; H, 5.72; N, 2.57; found: C, 44.20; H, 6.05; N, 2.31. IR (cm<sup>-1</sup>): 2969 (s), 2930 (m), 2871 (w), 1643 (vw), 1605 (vs), 1584 (w), 1458 (s), 1440 (m), 1378 (m), 1366 (m), 1335 (w), 1265 (w), 1205 (w), 1183 (w), 1168 (w), 1129 (s), 1113 (m), 1059 (m), 973 (vw), 955 (vw), 928 (w), 896 (vw), 869 (vw), 815 (vs), 768 (vw), 743 (w), 710 (vw), 675 (vw), 652 (vw), 632 (vw), 609 (w), 566 (w), 507 (vw), 493 (w), 425 (w). **12**: <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 1.32$  (d, 6 H, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, *iPr-CH<sub>3</sub>*), 1.41 (d, 6 H, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, *iPr-CH<sub>3</sub>*), 1.53 (s, 6 H, <sup>4</sup>J<sub>H-117Sn</sub> = 7.7 Hz overlapped by <sup>4</sup>J<sub>H-119Sn</sub> = 7.7 Hz, NCC(CH<sub>3</sub>)<sub>2</sub>), 1.99 (s, 6 H, NC(CH<sub>3</sub>)<sub>2</sub>), 2.28 (s, 2 H, CH<sub>2</sub>), 2.85 (sept, 2 H, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, *iPr-CH*), 7.40 (d, 2 H, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, Dipp-*m-CH*), 7.55 (t, 1 H, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, Dipp-*p-CH*). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 26.4$  (*iPr-CH<sub>3</sub>*), 28.3 (*iPr-CH<sub>3</sub>*), 29.6 (*iPr-CH*), 29.8 (NCC(CH<sub>3</sub>)<sub>2</sub>), 31.0 (NC(CH<sub>3</sub>)<sub>2</sub>), 51.1 (CH<sub>2</sub>), 55.1 (NCC(CH<sub>3</sub>)<sub>2</sub>), 87.1 (NC(CH<sub>3</sub>)<sub>2</sub>), 127.0 (Dipp-*m-CH*), 131.5 (Dipp-*i-C*), 131.8 (Dipp-*p-CH*), 146.7 (Dipp-*o-C*), 218.9 (NCSn). <sup>119</sup>Sn{<sup>1</sup>H} NMR (186.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = -406.3$ . **Elemental analysis** (%) calcd. for C<sub>20</sub>H<sub>31</sub>Cl<sub>4</sub>NSn [545.99 g/mol]: C, 44.00; H, 5.72; N, 2.57; found: C, 43.76; H, 5.72; N, 2.43. IR (cm<sup>-1</sup>): 2971 (m), 2932 (m), 2871 (w), 1644 (vw), 1604 (m), 1583 (vw), 1550 (w), 1456 (s), 1390 (m), 1374 (m),

1342 (w), 1329 (w), 1266 (w), 1197 (w), 1179 (w), 1126 (m), 1105 (m), 1053 (m), 1013 (vw), 970 (vw), 930 (w), 873 (vw), 809 (vs), 773 (m), 738 (vw), 712 (vw), 677 (vw), 649 (vw), 631 (vw), 608 (w), 558 (w), 493 (w), 426 (vw), 412 (vw).

**Me<sub>2</sub>Im<sup>Me</sup>·SnMe<sub>2</sub> (13).** A suspension of Me<sub>2</sub>Im<sup>Me</sup>·SnCl<sub>2</sub>Me<sub>2</sub> (**2a**) (15.0 mg, 43.6  $\mu\text{mol}$ , 1.0 eq) and KC<sub>8</sub> (24.0 mg, 175  $\mu\text{mol}$ , 4.0 eq) in C<sub>6</sub>D<sub>6</sub> (0.6 mL) was stirred for 2 d. Afterwards, insoluble material was filtered off all volatile material of the filtrate was removed *in vacuo* to yield **13** (8.00 mg, 29.3  $\mu\text{mol}$ , 67%) as a colorless solid. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of a concentrated toluene solution of **13** at room temperature. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 0.73$  (s, 6 H, overlapping broad satellites, SnCH<sub>3</sub>), 1.31 (s, 6 H, NCC(CH<sub>3</sub>)<sub>2</sub>), 3.19 (s, 6 H, NCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 0.5$  (SnCH<sub>3</sub>), 8.3 (CCH<sub>3</sub>), 34.4 (NCH<sub>3</sub>), 124.2 (NCC(CH<sub>3</sub>)<sub>2</sub>), 183.4 (NCN). <sup>119</sup>Sn{<sup>1</sup>H} NMR (186.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = -83.3$ . **Elemental analysis** (%) calcd. for C<sub>9</sub>H<sub>18</sub>SnN<sub>2</sub> [272.97 g/mol]: C, 39.60; H, 6.65; N, 10.26; found: C, 36.93; H, 6.40; N, 8.91. After several attempts, this is the best result so far. This may be due to the high air sensitivity of **13**. IR (cm<sup>-1</sup>): 2977 (w), 2947 (m), 2919 (m), 1897 (m), 1855 (w), 1784 (vw), 1688 (w), 1662 (m), 1649 (m), 1598 (w), 1574 (w), 1455 (m), 1431 (s), 1396 (m), 1374 (s), 1366 (s), 1309 (w), 1226 (w), 1194 (w), 1122 (vw), 1095 (vw), 965 (m), 844 (m), 754 (s), 732 (s), 712 (m), 664 (w), 569 (s), 549 (s), 515 (w), 475 (vw), 449 (vs).

**cAAC<sup>Me</sup>·SnMe<sub>2</sub>·SnCl<sub>2</sub>Me<sub>2</sub> (14).** **Route A:** A suspension of **7** (200 mg, 396  $\mu\text{mol}$ , 1.0 eq) and KC<sub>8</sub> (401 mg, 2.97 mmol, 7.5 eq) in toluene (15 mL) was sonicated for 7 min (until the color of the solution was deep red). The suspension was further stirred at 0  $^{\circ}\text{C}$  for 15 min. After cooling to  $-78^{\circ}\text{C}$ , the dark red suspension was filtrated at  $-78^{\circ}\text{C}$  through a pad of celite to precooled ( $-78^{\circ}\text{C}$ ) SnCl<sub>2</sub>Me<sub>2</sub> (87.0 mg, 396  $\mu\text{mol}$ , 1.0 eq). The red solution was allowed to warm to 0  $^{\circ}\text{C}$  and stirred for 2 h. The color changed to pale yellow. Removing all volatiles *in vacuo* afforded a pale-yellow oil. Washing with *n*-hexane (3 x 10 mL) and subsequent removal of all volatile material *in vacuo* yielded **14** (188 mg, 287  $\mu\text{mol}$ , 73%) as a colorless solid. In some instances, the product had to be recrystallized for further purification by storing a saturated dichloromethane solution of **14** at  $-30^{\circ}\text{C}$  for several days. Crystals suitable for single crystal X-ray diffraction were obtained by storing a concentrated toluene solution of **14** at  $-30^{\circ}\text{C}$ . **Route B:** A solution of **7** (20 mg, 39.6  $\mu\text{mol}$ , 1.0 eq), SnCl<sub>2</sub>Me<sub>2</sub> (8.70 mg, 39.6  $\mu\text{mol}$ , 1.0 eq), and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazin (8.70 mg, 39.6  $\mu\text{mol}$ , 1.0 eq) in C<sub>6</sub>D<sub>6</sub> (0.6 mL) was heated to 65  $^{\circ}\text{C}$  for 1 d. Cooling the reaction mixture to room temperature and storage of the solution for several hours led to colorless crystals, which were separated from the solution, washed with *n*-hexane (2 x 1 mL) and dried *in vacuo* to yield **14** (21.0 mg, 32.1  $\mu\text{mol}$ , 81%) as a colorless crystalline solid. Partial decomposition of the compound in solution was observed. <sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 0.24$  (br, 6 H, SnCH<sub>3</sub>), 0.96 (s, 6 H, satellites overlapping: <sup>3</sup>J<sub>H-117Sn} = <sup>3</sup>J<sub>H-119Sn} = 11.3 Hz, <sup>2</sup>J<sub>H-117Sn} = 64.9 Hz, <sup>2</sup>J<sub>H-119Sn} = 67.8 Hz, Sn-CH<sub>3</sub>), 1.24 (d, 6 H, <sup>3</sup>J<sub>H-H} = 6.6 Hz, *iPr-CH<sub>3</sub>*), 1.32 (d, 6 H, <sup>3</sup>J<sub>H-H} = 6.6 Hz, *iPr-CH<sub>3</sub>*), 1.49 (s, 6 H, NC(CH<sub>3</sub>)<sub>2</sub>), 1.78 (s<sub>br</sub>, 6 H, NCC(CH<sub>3</sub>)<sub>2</sub>), 2.22 (s, 2 H, CH<sub>2</sub>), 3.05 (br, 2 H, *iPr-CH*), 7.40 (d, 2 H, <sup>3</sup>J<sub>H-H} = 7.9 Hz, Dipp-*m-CH*), 7.54 (d, 1 H, <sup>3</sup>J<sub>H-H} = 7.9 Hz, Dipp-*p-CH*). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = -9.5$  (SnCH<sub>3</sub>), 24.3 (*iPr-CH<sub>3</sub>*), 27.4 (*iPr-CH<sub>3</sub>*), 28.8 (NCC(CH<sub>3</sub>)<sub>2</sub>), 29.1 (NC(CH<sub>3</sub>)<sub>2</sub> overlapped by *iPr-CH*), 49.5 (CH<sub>2</sub>), 57.7 (NCC(CH<sub>3</sub>)<sub>2</sub>), 85.2 (NC(CH<sub>3</sub>)<sub>2</sub>), 126.7 (Dipp-*m-CH*), 131.6 (Dipp-*p-CH*), 133.2 (Dipp-*i-C*), 146.1 (Dipp-*o-C*), 237.9 (NCSn). One of the SnCH<sub>3</sub>-resonances could not be observed due to the broadening. <sup>119</sup>Sn{<sup>1</sup>H} NMR (186.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = -120.6$  (s, <sup>1</sup>J<sub>119Sn-117Sn} = 9492 Hz, <sup>1</sup>J<sub>119Sn-119Sn} = 9910 Hz, CSnMe<sub>2</sub>),  $-127.1$  (<sup>1</sup>J<sub>119Sn-117Sn} = 9492 Hz, <sup>1</sup>J<sub>119Sn-119Sn} = 9910 Hz, SnCl<sub>2</sub>Me<sub>2</sub>). **Elemental analysis** (%) calcd. for C<sub>24</sub>H<sub>43</sub>Cl<sub>2</sub>NSn<sub>2</sub> + C<sub>6</sub>H<sub>6</sub> [732.05 g/mol]: C, 49.22; H, 6.75; N, 1.91; found: C, 49.16; H, 6.70; N, 1.92. IR (cm<sup>-1</sup>): 3008 (vw), 2966 (m), 2926 (w), 2868 (w), 2280 (vw), 1589 (vw) 1541 (w), 1457 (w), 1385 (w), 1366 (vw), 1345 (w), 1326 (vw), 1269 (vw),</sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub>

1250 (w), 1196 (w), 1181 (w), 1125 (vw), 1110 (vw), 1053 (vw), 1008 (vw), 993 (vw), 932 (vw), 876 (m), 818 (s), 778 (s), 761 (vw), 671 (vw), 608 (vw), 590 (vw), 566 (vw), 541 (m), 525 (m), 505 (vs), 431 (vw).

### Crystallographic Details

Crystal data were collected on a Bruker X8 Apex-2 diffractometer with a CCD area detector and graphite monochromated Mo-K $\alpha$  radiation or a Rigaku XtaLAB Synergy-DW diffractometer with an Hy-Pix-6000HE detector and monochromated CuK $\alpha$  radiation equipped with an Oxford Cryo 800 cooling unit or a Rigaku XtaLAB Synergy-R diffractometer with a HPA area detector and multi-layer mirror monochromated Cu-K $\alpha$  radiation. The crystals were immersed in a film of perfluoropoly-ether oil on a glass fiber MicroMount<sup>TM</sup> (MiTeGen) and data were collected at 100 K. The images were processed with the Bruker or CrysAlis software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. The structures were solved by using the ShelXTL software package.<sup>[25]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factors calculations.

**Crystal Data for Me<sub>2</sub>Im<sup>Me</sup>·GeCl<sub>2</sub>Me<sub>2</sub> (1 a):** C<sub>9</sub>H<sub>18</sub>Cl<sub>2</sub>GeN<sub>2</sub>, M<sub>r</sub> = 297.74, T = 100(2) K,  $\lambda$  = 1.54184 Å, colorless block, 0.286 × 0.060 × 0.041 mm<sup>3</sup>, orthorhombic space group *Pbca*, a = 13.5365(2) Å, b = 10.58890(10) Å, c = 17.7540(2) Å,  $\alpha$  = 90°,  $\beta$  = 90°,  $\gamma$  = 90°, V = 2544.80(5) Å<sup>3</sup>, Z = 8,  $\rho_{\text{calcd}}$  = 1.554 mg/m<sup>3</sup>,  $\mu$  = 6.865 mm<sup>-1</sup>, F(000) = 1216, 64069 reflections, -16 ≤ h ≤ 17, -13 ≤ k ≤ 13, -22 ≤ l ≤ 19, 4.982° <  $\theta$  < 77.481°, completeness 99.6%, 2692 independent reflections, 2571 reflections observed with [I > 2 $\sigma$ (I)], 133 parameters, 2 restraints, R indices (all data) R<sub>1</sub> = 0.0305, wR<sub>2</sub> = 0.0768, final R indices [I > 2 $\sigma$ (I)] R<sub>1</sub> = 0.0293, wR<sub>2</sub> = 0.0758, largest difference peak and hole 0.501 and -0.507 e Å<sup>-3</sup>, Goof = 1.077.

**Crystal Data for iPr<sub>2</sub>Im<sup>Me</sup>·GeCl<sub>2</sub>Me<sub>2</sub> (1 b):** C<sub>13</sub>H<sub>26</sub>Cl<sub>2</sub>GeN<sub>2</sub>, M<sub>r</sub> = 353.85, T = 100(2) K,  $\lambda$  = 1.54184 Å, colorless block, 0.648 × 0.357 × 0.276 mm<sup>3</sup>, orthorhombic space group *Pca*2<sub>1</sub>, a = 9.67890(10) Å, b = 12.9637(2) Å, c = 13.56800(10) Å,  $\alpha$  = 90°,  $\beta$  = 90°,  $\gamma$  = 90°, V = 1702.44(3) Å<sup>3</sup>, Z = 4,  $\rho_{\text{calcd}}$  = 1.381 mg/m<sup>3</sup>,  $\mu$  = 5.216 mm<sup>-1</sup>, F(000) = 736, 9359 reflections, -12 ≤ h ≤ 11, -15 ≤ k ≤ 16, -16 ≤ l ≤ 13, 3.409° <  $\theta$  < 73.700°, completeness 1.39/0.72, 2499 independent reflections, 2488 reflections observed with [I > 2 $\sigma$ (I)], 171 parameters, 1 restraints, R indices (all data) R<sub>1</sub> = 0.0277, wR<sub>2</sub> = 0.0764, final R indices [I > 2 $\sigma$ (I)] R<sub>1</sub> = 0.0276, wR<sub>2</sub> = 0.0763, largest difference peak and hole 0.395 and -0.564 e Å<sup>-3</sup>, Goof = 1.058.

**Crystal Data for Dipp<sub>2</sub>Im·GeCl<sub>2</sub>Me<sub>2</sub> (1 c):** C<sub>29</sub>H<sub>42</sub>Cl<sub>2</sub>GeN<sub>2</sub>, M<sub>r</sub> = 562.13, T = 100(2) K,  $\lambda$  = 1.54184 Å, colorless block, 0.235 × 0.155 × 0.108 mm<sup>3</sup>, monoclinic space group *P2<sub>1</sub>/c*, a = 11.12230(10) Å, b = 13.83290(10) Å, c = 19.6171(2) Å,  $\alpha$  = 90°,  $\beta$  = 105.0720(10)°,  $\gamma$  = 90°, V = 2914.34(5) Å<sup>3</sup>, Z = 4,  $\rho_{\text{calcd}}$  = 1.281 mg/m<sup>3</sup>,  $\mu$  = 3.246 mm<sup>-1</sup>, F(000) = 1184, 103834 reflections, -14 ≤ h ≤ 13, -17 ≤ k ≤ 17, -24 ≤ l ≤ 24, 3.957° <  $\theta$  < 76.974°, completeness 99.0%, 6099 independent reflections, 5814 reflections observed with [I > 2 $\sigma$ (I)], 317 parameters, 1 restraints, R indices (all data) R<sub>1</sub> = 0.0301, wR<sub>2</sub> = 0.0785, final R indices [I > 2 $\sigma$ (I)] R<sub>1</sub> = 0.0286, wR<sub>2</sub> = 0.0775, largest difference peak and hole 0.435 and -0.407 e Å<sup>-3</sup>, Goof = 1.055.

**Crystal Data for iPr<sub>2</sub>Im<sup>Me</sup>·SnCl<sub>2</sub>Me<sub>2</sub> (2 b):** (C<sub>13</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>2</sub>Sn), M<sub>r</sub> = 399.95, T = 100(2) K,  $\lambda$  = 1.54184 Å, colorless block, 0.475 × 0.373 × 0.191 mm<sup>3</sup>, monoclinic space group *P2<sub>1</sub>/n*, a = 12.16210(10) Å, b = 9.98220(10) Å, c = 15.3491(2) Å,  $\alpha$  = 90°,  $\beta$  = 110.0280(10)°,  $\gamma$  = 90°, V = 1750.76(3) Å<sup>3</sup>, Z = 4,  $\rho_{\text{calcd}}$  = 1.517 mg/m<sup>3</sup>,  $\mu$  = 14.305 mm<sup>-1</sup>, F(000) = 808, 17734 reflections, -15 ≤ h ≤ 14, -12 ≤ k ≤ 9, -19 ≤ l ≤ 18, 4.030° <  $\theta$  < 73.950°, completeness 98.8%, 3509 independent

reflections, 3463 reflections observed with [I > 2 $\sigma$ (I)], 171 parameters, 0 restraints, R indices (all data) R<sub>1</sub> = 0.0310, wR<sub>2</sub> = 0.0859, final R indices [I > 2 $\sigma$ (I)] R<sub>1</sub> = 0.0306, wR<sub>2</sub> = 0.0855, largest difference peak and hole 1.099 and -0.611 e Å<sup>-3</sup>, Goof = 1.071.

**Crystal Data for Dipp<sub>2</sub>Im·SnMe<sub>2</sub>Cl<sub>2</sub> (2 c):** C<sub>29</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>2</sub>Sn, M<sub>r</sub> = 608.26, T = 100(2) K,  $\lambda$  = 1.54184 Å, colorless block, 0.624 × 0.221 × 0.149 mm<sup>3</sup>, monoclinic space group *P2<sub>1</sub>/n*, a = 11.32100(10) Å, b = 13.92150(10) Å, c = 19.75810(10) Å,  $\alpha$  = 90°,  $\beta$  = 105.8100(10)°,  $\gamma$  = 90°, V = 2996.18(4) Å<sup>3</sup>, Z = 4,  $\rho_{\text{calcd}}$  = 1.348 mg/m<sup>3</sup>,  $\mu$  = 8.552 mm<sup>-1</sup>, F(000) = 1256, 62097 reflections, -14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -25 ≤ l ≤ 21, 3.936° <  $\theta$  < 80.679°, completeness 99.1%, 6516 independent reflections, 6325 reflections observed with [I > 2 $\sigma$ (I)], 317 parameters, 0 restraints, R indices (all data) R<sub>1</sub> = 0.0396, wR<sub>2</sub> = 0.1090, final R indices [I > 2 $\sigma$ (I)] R<sub>1</sub> = 0.0391, wR<sub>2</sub> = 0.1084, largest difference peak and hole 2.078 and -1.103 e Å<sup>-3</sup>, Goof = 1.053.

**Crystal Data for Me<sub>2</sub>Im<sup>Me</sup>·GeCl<sub>4</sub> (3):** C<sub>7</sub>H<sub>12</sub>Cl<sub>4</sub>GeN<sub>2</sub>, M<sub>r</sub> = 338.58, T = 100(2) K,  $\lambda$  = 1.54184 Å, colorless block, 0.178 × 0.102 × 0.076 mm<sup>3</sup>, orthorhombic space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*, a = 8.17960(10) Å, b = 9.94560(10) Å, c = 15.39610(10) Å,  $\alpha$  = 90°,  $\beta$  = 90°,  $\gamma$  = 90°, V = 1252.49(2) Å<sup>3</sup>, Z = 4,  $\rho_{\text{calcd}}$  = 1.796 mg/m<sup>3</sup>,  $\mu$  = 10.901 mm<sup>-1</sup>, F(000) = 672, 45523 reflections, -9 ≤ h ≤ 10, -12 ≤ k ≤ 12, -19 ≤ l ≤ 19, 5.295° <  $\theta$  < 76.775°, completeness 1.70/0.99, 2626 independent reflections, 2596 reflections observed with [I > 2 $\sigma$ (I)], 131 parameters, 0 restraints, R indices (all data) R<sub>1</sub> = 0.0179, wR<sub>2</sub> = 0.0437, final R indices [I > 2 $\sigma$ (I)] R<sub>1</sub> = 0.0177, wR<sub>2</sub> = 0.0435, largest difference peak and hole 0.370 and -0.440 e Å<sup>-3</sup>, Goof = 1.093.

**Crystal Data for [iPr<sub>2</sub>Im<sup>Me</sup>·SnCl<sub>4</sub>·THF] (4):** (C<sub>15</sub>H<sub>28</sub>Cl<sub>4</sub>N<sub>2</sub>OSn) + (C<sub>4</sub>H<sub>8</sub>O), M<sub>r</sub> = 584.99, T = 100(2) K,  $\lambda$  = 1.54184 Å, colorless block, 0.372 × 0.283 × 0.224 mm<sup>3</sup>, triclinic space group *P* $\bar{1}$ , a = 9.47310(10) Å, b = 11.3568(2) Å, c = 13.4858(2) Å,  $\alpha$  = 108.3300(10)°,  $\beta$  = 104.3500(10)°,  $\gamma$  = 105.6170(10)°, V = 1235.56(3) Å<sup>3</sup>, Z = 2,  $\rho_{\text{calcd}}$  = 1.572 mg/m<sup>3</sup>,  $\mu$  = 12.342 mm<sup>-1</sup>, F(000) = 596, 24727 reflections, -11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16, 3.707° <  $\theta$  < 69.244°, completeness 100%, 4627 independent reflections, 4571 reflections observed with [I > 2 $\sigma$ (I)], 225 parameters, 24 restraints, R indices (all data) R<sub>1</sub> = 0.0507, wR<sub>2</sub> = 0.1309, final R indices [I > 2 $\sigma$ (I)] R<sub>1</sub> = 0.0504, wR<sub>2</sub> = 0.1306, largest difference peak and hole 1.559 and -1.934 e Å<sup>-3</sup>, Goof = 1.039.

**Crystal Data for [Dipp<sub>2</sub>Im·GeMe<sub>2</sub>Cl][Cl] (5):** 2(C<sub>29</sub>H<sub>42</sub>Cl<sub>2</sub>GeN<sub>2</sub>) + 0.5(C<sub>6</sub>H<sub>6</sub>), M<sub>r</sub> = 1163.32, T = 100(2) K,  $\lambda$  = 1.54184 Å, colorless block, 0.150 × 0.068 × 0.042 mm<sup>3</sup>, triclinic space group *P* $\bar{1}$ , a = 13.0263(2) Å, b = 13.4049(2) Å, c = 18.8752(3) Å,  $\beta$  = 79.2360(10)°,  $\alpha$  = 82.1360(10)°,  $\gamma$  = 75.6850(10)°, V = 3123.13(9) Å<sup>3</sup>, Z = 2,  $\rho_{\text{calcd}}$  = 1.237 mg/m<sup>3</sup>,  $\mu$  = 3.046 mm<sup>-1</sup>, F(000) = 1226, 33512 reflections, -15 ≤ h ≤ 16, -16 ≤ k ≤ 16, -23 ≤ l ≤ 23, 2.394° <  $\theta$  < 76.770°, completeness 97.6%, 12850 independent reflections, 11411 reflections observed with [I > 2 $\sigma$ (I)], 699 parameters, 93 restraints, R indices (all data) R<sub>1</sub> = 0.0548, wR<sub>2</sub> = 0.1269, final R indices [I > 2 $\sigma$ (I)] R<sub>1</sub> = 0.0479, wR<sub>2</sub> = 0.1226, largest difference peak and hole 0.880 and -0.570 e Å<sup>-3</sup>, Goof = 1.042.

**Crystal Data for cAAC<sup>Me</sup>·GeCl<sub>2</sub>Me<sub>2</sub> (6):** (C<sub>22</sub>H<sub>37</sub>Cl<sub>2</sub>GeN) + (C<sub>6</sub>H<sub>6</sub>), M<sub>r</sub> = 537.12, T = 100(2) K,  $\lambda$  = 1.54184 Å, colorless block, 0.068 × 0.067 × 0.053 mm<sup>3</sup>, orthorhombic space group *Pbca*, a = 16.99880(10) Å, b = 18.01200(10) Å, c = 18.15720(10) Å,  $\alpha$  = 90°,  $\beta$  = 90°,  $\gamma$  = 90°, V = 5559.41(5) Å<sup>3</sup>, Z = 8,  $\rho_{\text{calcd}}$  = 1.283 mg/m<sup>3</sup>,  $\mu$  = 3.366 mm<sup>-1</sup>, F(000) = 2272, 59327 reflections, -17 ≤ h ≤ 21, -22 ≤ k ≤ 22, -22 ≤ l ≤ 22, 4.327° <  $\theta$  < 77.556°, completeness 99.5%, 5886 independent reflections, 5491 reflections observed with [I > 2 $\sigma$ (I)], 385 parameters, 420 restraints, R indices (all data) R<sub>1</sub> = 0.0312, wR<sub>2</sub> = 0.0752, final R indices [I > 2 $\sigma$ (I)] R<sub>1</sub> = 0.0289, wR<sub>2</sub> = 0.0738, largest difference peak and hole 0.652 and -0.656 e Å<sup>-3</sup>, Goof = 1.049.

**Crystal Data for cAAC<sup>Me</sup>·SnMe<sub>2</sub>Cl<sub>2</sub> (7):** C<sub>22</sub>H<sub>37</sub>Cl<sub>2</sub>N<sub>2</sub>Sn, M<sub>r</sub> = 505.11, T = 100(2) K,  $\lambda$  = 1.54184 Å, colorless block, 0.330 × 0.290 ×

0.211 mm<sup>3</sup>, triclinic space group  $P\bar{1}$ ,  $a = 9.4684(2) \text{ \AA}$ ,  $b = 9.6068(2) \text{ \AA}$ ,  $c = 14.1265(2) \text{ \AA}$ ,  $\alpha = 91.8280(10)^\circ$ ,  $\beta = 96.2570(10)^\circ$ ,  $\gamma = 113.620(2)^\circ$ ,  $V = 1166.26(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.438 \text{ mg/m}^3$ ,  $\mu = 10.847 \text{ mm}^{-1}$ ,  $F(000) = 520$ , 24004 reflections,  $-11 \leq h \leq 11$ ,  $-11 \leq k \leq 12$ ,  $-17 \leq l \leq 16$ ,  $3.158^\circ < \theta < 74.505^\circ$ , completeness 99.9%, 4739 independent reflections, 4699 reflections observed with  $[I > 2\sigma(I)]$ , 245 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0353$ ,  $wR_2 = 0.0959$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0351$ ,  $wR_2 = 0.0957$ , largest difference peak and hole 2.566 and  $-1.288 \text{ e \AA}^{-3}$ , Goof = 1.062.

**Crystal Data for cAAC<sup>Me</sup>·GeCl<sub>2</sub>Ph<sub>2</sub> (8):** (C<sub>32</sub>H<sub>41</sub>Cl<sub>2</sub>GeN) + (C<sub>6</sub>H<sub>6</sub>),  $M_r = 661.25$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.220 \times 0.098 \times 0.077 \text{ mm}^3$ , monoclinic space group  $P2_1/n$ ,  $a = 9.68380(10) \text{ \AA}$ ,  $b = 17.0286(2) \text{ \AA}$ ,  $c = 20.6365(2) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 97.6300(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 5559.41(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.302 \text{ mg/m}^3$ ,  $\mu = 2.881 \text{ mm}^{-1}$ ,  $F(000) = 1392$ , 31242 reflections,  $-12 \leq h \leq 12$ ,  $-16 \leq k \leq 21$ ,  $-25 \leq l \leq 26$ ,  $3.377^\circ < \theta < 76.970^\circ$ , completeness 98.7%, 7043 independent reflections, 6696 reflections observed with  $[I > 2\sigma(I)]$ , 387 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0342$ ,  $wR_2 = 0.0803$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0328$ ,  $wR_2 = 0.0797$ , largest difference peak and hole 0.760 and  $-0.496 \text{ e \AA}^{-3}$ , Goof = 1.073.

**Crystal Data for [cAAC<sup>Me</sup>·GeMe<sub>3</sub>][Cl] (9):** C<sub>23</sub>H<sub>40</sub>ClGeN,  $M_r = 438.60$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.158 \times 0.122 \times 0.096 \text{ mm}^3$ , tetragonal space group  $I4_1cd$ ,  $a = 17.36620(10) \text{ \AA}$ ,  $b = 17.36620(10) \text{ \AA}$ ,  $c = 30.9499(2) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 9334.02(12) \text{ \AA}^3$ ,  $Z = 16$ ,  $\rho_{\text{calcd}} = 1.248 \text{ mg/m}^3$ ,  $\mu = 2.862 \text{ mm}^{-1}$ ,  $F(000) = 3744$ , 162287 reflections,  $-21 \leq h \leq 21$ ,  $-21 \leq k \leq 21$ ,  $-39 \leq l \leq 39$ ,  $4.597^\circ < \theta < 77.231^\circ$ , completeness 1.96/1.00, 4928 independent reflections, 4904 reflections observed with  $[I > 2\sigma(I)]$ , 246 parameters, 1 restraints, R indices (all data)  $R_1 = 0.0342$ ,  $wR_2 = 0.0945$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0341$ ,  $wR_2 = 0.0944$ , largest difference peak and hole 0.352 and  $-0.552 \text{ e \AA}^{-3}$ , Goof = 1.111.

**Crystal Data for [cAAC<sup>Me</sup>·GeCl<sub>3</sub>][Cl] (10):** C<sub>20</sub>H<sub>31</sub>Cl<sub>4</sub>GeN,  $M_r = 499.85$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.068 \times 0.067 \times 0.053 \text{ mm}^3$ , orthorhombic space group  $P2_12_12_1$ ,  $a = 10.69660(10) \text{ \AA}$ ,  $b = 11.64060(10) \text{ \AA}$ ,  $c = 18.8687(2) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2349.43(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.413 \text{ mg/m}^3$ ,  $\mu = 5.983 \text{ mm}^{-1}$ ,  $F(000) = 1032$ , 14411 reflections,  $-13 \leq h \leq 13$ ,  $-14 \leq k \leq 14$ ,  $-18 \leq l \leq 23$ ,  $4.463^\circ < \theta < 77.270^\circ$ , completeness 1.65/0.94, 4650 independent reflections, 4445 reflections observed with  $[I > 2\sigma(I)]$ , 243 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0301$ ,  $wR_2 = 0.0670$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0271$ ,  $wR_2 = 0.0660$ , largest difference peak and hole 0.425 and  $-0.362 \text{ e \AA}^{-3}$ , Goof = 1.010.

**Crystal Data for [cAAC<sup>Me</sup>·SnCl<sub>3</sub>][Cl] (11):** C<sub>20</sub>H<sub>31</sub>Cl<sub>4</sub>NSn,  $M_r = 545.95$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.086 \times 0.073 \times 0.032 \text{ mm}^3$ , orthorhombic space group  $P2_12_12_1$ ,  $a = 10.7542(2) \text{ \AA}$ ,  $b = 11.5957(3) \text{ \AA}$ ,  $c = 19.1588(4) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2389.15(9) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.518 \text{ mg/m}^3$ ,  $\mu = 12.649 \text{ mm}^{-1}$ ,  $F(000) = 1104$ , 14413 reflections,  $-9 \leq h \leq 13$ ,  $-9 \leq k \leq 14$ ,  $-24 \leq l \leq 23$ ,  $4.457^\circ < \theta < 77.631^\circ$ , completeness 1.58/0.89, 4551 independent reflections, 4246 reflections observed with  $[I > 2\sigma(I)]$ , 268 parameters, 4 restraints, R indices (all data)  $R_1 = 0.0464$ ,  $wR_2 = 0.1119$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0428$ ,  $wR_2 = 0.1094$ , largest difference peak and hole 0.768 and  $-0.864 \text{ e \AA}^{-3}$ , Goof = 1.061.

**Crystal Data for cAAC<sup>Me</sup>·SnCl<sub>4</sub> (12):** C<sub>20</sub>H<sub>31</sub>Cl<sub>4</sub>NSn,  $M_r = 545.95$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.137 \times 0.082 \times 0.044 \text{ mm}^3$ , orthorhombic space group  $P2_12_12_1$ ,  $a = 10.1159(2) \text{ \AA}$ ,  $b = 15.0495(2) \text{ \AA}$ ,  $c = 15.1458(2) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2305.79(6) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.573 \text{ mg/m}^3$ ,  $\mu = 13.106 \text{ mm}^{-1}$ ,  $F(000) = 1104$ , 14518 reflections,  $-11 \leq h \leq 12$ ,  $-19 \leq k \leq 17$ ,  $-17 \leq l \leq 19$ ,  $4.141^\circ < \theta < 77.492^\circ$ , completeness 1.66/0.94, 4568 independent reflections, 4387 reflections observed with  $[I > 2\sigma(I)]$ , 243 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0325$ ,  $wR_2 = 0.0779$ , final R

indices  $[I > 2\sigma(I)]$   $R_1 = 0.0309$ ,  $wR_2 = 0.0770$ , largest difference peak and hole 1.589 and  $-0.549 \text{ e \AA}^{-3}$ , Goof = 1.020.

**Crystal Data for Me<sub>2</sub>Im<sup>Me</sup>·SnMe<sub>2</sub> (13):** C<sub>9</sub>H<sub>18</sub>N<sub>2</sub>Sn,  $M_r = 272.94$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , yellow block,  $0.200 \times 0.108 \times 0.088 \text{ mm}^3$ , orthorhombic space group  $Pnma$ ,  $a = 8.3559(2) \text{ \AA}$ ,  $b = 7.1898(2) \text{ \AA}$ ,  $c = 19.0230(3) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1142.85(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.586 \text{ mg/m}^3$ ,  $\mu = 17.419 \text{ mm}^{-1}$ ,  $F(000) = 544$ , 6427 reflections,  $-10 \leq h \leq 10$ ,  $-7 \leq k \leq 8$ ,  $-14 \leq l \leq 23$ ,  $4.649^\circ < \theta < 68.848^\circ$ , completeness 100%, 1148 independent reflections, 1073 reflections observed with  $[I > 2\sigma(I)]$ , 75 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0328$ ,  $wR_2 = 0.0809$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0313$ ,  $wR_2 = 0.0795$ , largest difference peak and hole 1.097 and  $-0.952 \text{ e \AA}^{-3}$ , Goof = 1.046.

**Crystal Data for cAAC<sup>Me</sup>·SnMe<sub>2</sub>·SnMe<sub>2</sub>Cl<sub>2</sub> (14):** (C<sub>24</sub>H<sub>43</sub>Cl<sub>2</sub>NSn<sub>2</sub>) + (C<sub>6</sub>H<sub>6</sub>),  $M_r = 731.98$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , yellow block,  $0.360 \times 0.234 \times 0.179 \text{ mm}^3$ , triclinic space group  $P\bar{1}$ ,  $a = 10.4925(2) \text{ \AA}$ ,  $b = 12.3831(2) \text{ \AA}$ ,  $c = 15.0195(2) \text{ \AA}$ ,  $\alpha = 66.391(2)^\circ$ ,  $\beta = 88.034(2)^\circ$ ,  $\gamma = 67.155(2)^\circ$ ,  $V = 1630.82(6) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.491 \text{ mg/m}^3$ ,  $\mu = 13.807 \text{ mm}^{-1}$ ,  $F(000) = 740$ , 31522 reflections,  $-12 \leq h \leq 12$ ,  $-15 \leq k \leq 15$ ,  $-16 \leq l \leq 18$ ,  $3.245^\circ < \theta < 69.253^\circ$ , completeness 100%, 6086 independent reflections, 5771 reflections observed with  $[I > 2\sigma(I)]$ , 383 parameters, 258 restraints, R indices (all data)  $R_1 = 0.0382$ ,  $wR_2 = 0.0999$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0370$ ,  $wR_2 = 0.0985$ , largest difference peak and hole 1.627 and  $-1.71 \text{ e \AA}^{-3}$ , Goof = 1.028.

Deposition Numbers 2184111 (2b), 21841112 (2c), 2184113 (1a), 2184114 (4), 2184115 (1b), 2184116 (1c), 2184117 (7), 2184118 (10), 2184119 (9), 2184120 (5), 2184121 (3), 2184122 (13), 2184123 (14), 2184124 (8), 2184125 (12), 2184126 (11), and 2184127 (6) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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## Conflict of Interest

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.

- [1] a) W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed.* **1997**, *36*, 2162–2187; *Angew. Chem.* **1997**, *109*, 2256–2282; b) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3504; c) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92; d) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; *Angew. Chem.* **2008**, *120*, 3166–3216; e) T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* **2010**, *49*, 6940–6952; *Angew. Chem.* **2010**, *122*, 7094–7107; f) Y. Wang, G. H. Robinson,

- Inorg. Chem.* **2011**, *53*, 12326–12337; g) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nat. Chem.* **2014**, *510*, 485–496; h) Y. Wang, G. H. Robinson, *Inorg. Chem.* **2014**, *53*, 11815–11832; i) S. Würtemberger-Pietsch, U. Radius, T. B. Marder, *Dalton Trans.* **2016**, *45*, 5880–5895; j) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, *Chem. Rev.* **2018**, *118*, 9678–9842; k) A. Doddi, M. Peters, M. Tamm, *Chem. Rev.* **2019**, *119*, 6994–7112.
- [2] a) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849; *Angew. Chem.* **2010**, *122*, 8992–9032; b) M. Soleilhavoup, G. Bertrand, *Acc. Chem. Res.* **2015**, *48*, 256–266; c) M. Melaimi, R. Jazzar, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2017**, *56*, 10046–10068; *Angew. Chem.* **2017**, *129*, 10180–10203; d) U. S. Paul, U. Radius, *Chem. Eur. J.* **2017**, *23*, 3993–4009; e) U. S. D. Paul, M. J. Krahfuß, U. Radius, *Chem. Unserer Zeit* **2019**, *53*, 212–223.
- [3] a) R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 2485–2495; b) S. Diez-Gonzalez, S. P. Nolan, *Coord. Chem. Rev.* **2007**, *251*, 874–883; c) A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* **2009**, 1759–1766; d) H. Clavier, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 841–861; e) C. Lujan, S. P. Nolan, *J. Organomet. Chem.* **2011**, *696*, 3935–3938; f) O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 2939–2943; *Angew. Chem.* **2013**, *125*, 3011–3015; g) A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Ganter, *Organometallics* **2013**, *32*, 5269–5272; h) D. J. Nelson, S. P. Nolan, *Chem. Soc. Rev.* **2013**, *42*, 6723–6753; i) K. Verlinden, H. Buhl, W. Frank, C. Ganter, *Eur. J. Inorg. Chem.* **2015**, 2416–2425; j) S. V. C. Vummaleti, D. J. Nelson, A. Poater, A. Gomez-Suarez, D. B. Cordes, A. M. Z. Slawin, S. P. Nolan, L. Cavallo, *Chem. Sci.* **2015**, *6*, 1895–1904; k) K. C. Mondal, S. Roy, B. Maity, D. Koley, H. W. Roesky, *Inorg. Chem.* **2016**, *55*, 163–169; l) U. S. D. Paul, U. Radius, *Eur. J. Inorg. Chem.* **2017**, 3362–3375; m) H. V. Huynh, *Chem. Rev.* **2018**, *118*, 9457–9492; n) D. Munz, *Organometallics* **2018**, *37*, 275–289.
- [4] a) D. Schmidt, J. H. J. Berthel, S. Pietsch, U. Radius, *Angew. Chem. Int. Ed.* **2012**, *51*, 8881–8885; *Angew. Chem.* **2012**, *124*, 9011–9015; b) P. Hemberger, A. Bodi, J. H. Berthel, U. Radius, *Chem. Eur. J.* **2015**, *21*, 1434–1438; c) H. Schneider, D. Schmidt, U. Radius, *Chem. Eur. J.* **2015**, *21*, 2793–2797.
- [5] H. Schneider, M. J. Krahfuß, U. Radius, *Z. Anorg. Allg. Chem.* **2016**, *642*, 1282–1286.
- [6] a) C. J. Carmalt, A. H. Cowley, *Adv. Inorg. Chem.* **2000**, *50*, 1–32; b) N. Kuhn, A. Al-Sheikh, *Coord. Chem. Rev.* **2005**, *249*, 829–857; c) C. E. Willans, *Organomet. Chem.* **2010**, *36*, 1–28; d) G. Prabusankar, A. Sathyanarayana, P. Suresh, C. N. Babu, K. Srinivas, B. P. R. Metla, *Coord. Chem. Rev.* **2014**, *269*, 96–133; e) K. C. Mondal, S. Roy, H. W. Roesky, *Chem. Soc. Rev.* **2016**, *45*, 1080–1111.
- [7] a) N. Kuhn, T. Kratz, D. Bläser, R. Boese, *Chem. Ber.* **1995**, *128*, 245–250; b) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, R. P. v. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069–1071; c) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem. Int. Ed.* **2009**, *48*, 5683–5686; *Angew. Chem.* **2009**, *121*, 5793–5796; d) Y. Wang, G. H. Robinson, *Inorg. Chem.* **2011**, *50*, 12326–12337; e) T. Böttcher, B. S. Bassil, L. Zhechkov, T. Heine, G.-V. Rösenthaller, *Chem. Sci.* **2013**, *4*, 77–83; f) T. Böttcher, S. Steinhauer, B. Neumann, H. G. Stammer, G. V. Rösenthaller, B. Hoge, *Chem. Commun.* **2014**, *50*, 6204–6206; g) F. Uhlemann, R. Köppe, A. Schnepf, *Z. Anorg. Allg. Chem.* **2014**, *640*, 1658–1664; h) F. Uhlemann, A. Schnepf, *Chem. Eur. J.* **2016**, *22*, 10748–10753.
- [8] K. C. Mondal, H. W. Roesky, A. C. Stückl, F. Ehret, W. Kaim, B. Dittrich, B. Maity, D. Koley, *Angew. Chem. Int. Ed.* **2013**, *52*, 11804–11807; *Angew. Chem.* **2013**, *125*, 12020–12023.
- [9] a) P. A. Rugar, V. N. Staroverov, P. J. Ragona, K. M. Baines, *J. Am. Chem. Soc.* **2007**, *129*, 15138–15139; b) K. C. Thimer, S. M. Al-Rafia, M. J. Ferguson, R. McDonald, E. Rivard, *Chem. Commun.* **2009**, 7119–7121; c) A. C. Filippou, O. Chernov, B. Blom, K. W. Stumpf, G. Schnakenburg, *Chem. Eur. J.* **2010**, *16*, 2866–2872; d) A. J. Ruddy, P. A. Rugar, K. J. Bladec, C. J. Allan, J. C. Avery, K. M. Baines, *Organometallics* **2010**, *29*, 1362–1367; e) N. Katir, D. Matioszek, S. Ladeira, J. Escudie, A. Castel, *Angew. Chem. Int. Ed.* **2011**, *50*, 5352–5355; *Angew. Chem.* **2011**, *123*, 5464–5467; f) Y. Li, K. C. Mondal, H. W. Roesky, H. Zhu, P. Stollberg, R. Herbst-Irmer, D. Stalke, D. M. Andrada, *J. Am. Chem. Soc.* **2013**, *135*, 12422–12428; g) B. Lyhs, D. Bläser, C. Wölper, S. Schulz, R. Haack, G. Jansen, *Inorg. Chem.* **2013**, *52*, 7236–7241.
- [10] a) B. Bantu, G. M. Pawar, U. Decker, K. Wurst, A. M. Schmidt, M. R. Buchmeiser, *Chem. Eur. J.* **2009**, *15*, 3103–3109; b) A. P. Singh, P. P. Samuel, K. C. Mondal, H. W. Roesky, N. S. Sidhu, B. Dittrich, *Organometallics* **2013**, *32*, 354–357.
- [11] a) P. A. Rugar, V. N. Staroverov, K. M. Baines, *Organometallics* **2010**, *29*, 4871–4881; b) T. Böttcher, B. S. Bassil, G. V. Rösenthaller, *Inorg. Chem.* **2012**, *51*, 763–765; c) I. S. M. Al-Rafia, P. A. Lummis, A. K. Swarnakar, K. C. Deutsch, M. J. Ferguson, R. McDonald, E. Rivard, *Aust. J. Chem.* **2013**, *66*, 1235–1245; d) J. Sinclair, G. Dai, R. McDonald, M. J. Ferguson, A. Brown, E. Rivard, *Inorg. Chem.* **2020**, *59*, 10996–11008.
- [12] N. Kuhn, C. Maichle-Mößmer, E. Niquet, I. Walker, *Z. Naturforsch. B* **2002**, *57*, 47–52.
- [13] a) G. Horrer, M. J. Krahfuß, K. Lubitz, I. Krummenacher, H. Braunschweig, U. Radius, *Eur. J. Inorg. Chem.* **2020**, 281–291; b) G. Horrer, I. Krummenacher, S. Mann, H. Braunschweig, U. Radius, *Dalton Trans.* **2022**, *51*, 11054–11071.
- [14] J. B. Waters, Q. Chen, T. A. Everitt, J. M. Goicoechea, *Dalton Trans.* **2017**, *46*, 12053–12066.
- [15] C. Gendy, J. M. Rautiainen, A. Mailman, H. M. Tuononen, *Chem. Eur. J.* **2021**, *27*, 14405–14409.
- [16] a) A. S. Romanov, M. Bochmann, *Organometallics* **2015**, *34*, 2439–2454; b) M. S. M. Philipp, U. Radius, *Z. Anorg. Allg. Chem.* **2022**, e202200085..
- [17] a) A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, *J. Chem. Soc. Chem. Commun.* **1995**, 1157–1158; b) C. P. Sindlinger, L. Wesemann, *Chem. Sci.* **2014**, *5*, 2739–2746.
- [18] a) T. G. Kocsor, D. Matioszek, G. Nemes, A. Castel, J. Escudie, P. M. Petrar, N. Saffon, I. Haiduc, *Inorg. Chem.* **2012**, *51*, 7782–7787; b) C. P. Sindlinger, W. Grahneis, F. S. Aicher, L. Wesemann, *Chem. Eur. J.* **2016**, *22*, 7554–7566.
- [19] J. H. J. Berthel, L. Tendra, M. W. Kuntze-Fechner, L. Kuehn, U. Radius, *Eur. J. Inorg. Chem.* **2019**, 3061–3072.
- [20] a) N. Kuhn, T. Kratz, *Synthesis* **1993**, 561–562; b) T. Schaub, M. Backes, U. Radius, *Organometallics* **2006**, *25*, 4196–4206; c) T. Schaub, U. Radius, A. Brucks, M. P. Choules, M. T. Olsen, T. B. Rauchfuss, *Inorg. Synth.* **2010**, *35*, 78–83.
- [21] L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.* **2000**, *606*, 49–54.
- [22] V. Lavallo, Y. Canac, C. Prasang, B. Donnadiu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709; *Angew. Chem.* **2005**, *117*, 5851–5855.
- [23] R. A. Sulzbach, A. F. M. Iqbal, *Angew. Chem. Int. Ed.* **1971**, *10*, 127; *Angew. Chem.* **1971**, *4*, 145.
- [24] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
- [25] G. M. Sheldrick, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **2015**, *71*, 3–8.

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