

# N-Heterocyclic Carbene and Cyclic (Alkyl)(amino)carbene Adducts of Antimony(III)

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A systematic study on Lewis-acid/base adducts of *N*-heterocyclic carbenes (NHCs) and the cyclic (alkyl)(amino)carbene cAAC<sup>Me</sup> (1-(2,6-di-*iso*-propylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene) with antimony(III) chlorides of the general formula SbCl<sub>2</sub>R (R=Cl, Ph, Mes) is presented. The reaction of the NHCs Me<sub>2</sub>Im<sup>Me</sup> (1,3,4,5-tetra-methyl-imidazolin-2-ylidene), *i*Pr<sub>2</sub>Im<sup>Me</sup> (1,3-di-*isopropyl*-4,5-dimethyl-imidazolin-2-ylidene), Mes<sub>2</sub>Im, Dipp<sub>2</sub>Im (R<sub>2</sub>Im = 1,3-di-organyl-imidazolin-2-ylidene; Mes = 2,4,6-trimethylphenyl, Dipp = 2,6-di-*isopropylphenyl*) and cAAC<sup>Me</sup> with antimony(III) compounds SbCl<sub>2</sub>R (R=Cl (1), Ph (2) and Mes

(3)) yields the adducts NHC·SbCl<sub>2</sub>R (R=Cl (4), Ph (5) and Mes (6); 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) and Mes<sub>2</sub>Im (d)) and cAAC<sup>Me</sup>·SbCl<sub>2</sub>R (R=Cl (4e) and Ph (5e)). Thermal treatment of (Dipp<sub>2</sub>Im)·SbCl<sub>2</sub>Ar (Ar=Ph (5c) and Mes (6c)) in benzene leads to isomerization to the backbone coordinated <sup>a</sup>NHC-adduct <sup>a</sup>(Dipp<sub>2</sub>Im)·SbCl<sub>2</sub>Ar (Ar=Mes (7) and Ph (8)) ("<sup>a</sup>" denotes "abnormal" coordination mode of the NHC) in high yields. One of the chloride substituents at antimony of 7 can be abstracted by GaCl<sub>3</sub> or Ag[BF<sub>4</sub>] to obtain the imidazolium salts [<sup>a</sup>Dipp<sub>2</sub>Im·SbClMes][BF<sub>4</sub>] (9) and [<sup>a</sup>Dipp<sub>2</sub>Im·SbClMes][GaCl<sub>4</sub>] (10).

## Introduction

*N*-heterocyclic carbenes (NHCs) and related molecules play currently an important role in main-group chemistry,<sup>[1]</sup> mainly due to their tuneable ambiphilicity and steric properties.<sup>[1e,2]</sup> Over the last few years we and others reported on the reactivity of NHCs and related molecules towards compounds of group 13,<sup>[1d,j,m,3]</sup> 14<sup>[1d,j,m,4]</sup> and 15<sup>[1m,j,5]</sup> elements. A plethora of NHC ligated phosphorus compounds is known,<sup>[6]</sup> including phosphorus in low oxidation states as in phosphinidenes (NHC·PR)<sup>[5b,7]</sup> and molecules with uncommon binding modes such as carbene stabilized P<sub>2</sub>, P<sub>4</sub> and P<sub>12</sub>.<sup>[6l,8]</sup> In contrast, reports on carbene stabilized compounds of the heavier homologues arsenic<sup>[6h,9]</sup> and bismuth<sup>[9b,10]</sup> are rather scarce, whereas some antimony compounds are known. Most of them are based on antimony(III) halides (L·SbX<sub>3</sub>) (Figure 1).

To date, only a number of Lewis-acid/base adducts of the type L·SbX<sub>3</sub> of NHCs and related molecules were isolated, (Figure 1, top), i.e. 6-Dipp·SbCl<sub>3</sub><sup>[11]</sup> (6-Dipp = 1,3-bis(2,6-di-*isopropylphenyl*)-4,5,6-hexahydropyrimidine-2-ylidene) cAAC<sup>Cy</sup>·SbCl<sub>3</sub><sup>[12]</sup> (cAAC<sup>Cy</sup> = 2-azaspiro[4.5]dec-2-(2,6-diisopropylphenyl)-3,3-dimethyl-1-ylidene) and Dipp<sub>2</sub>Im·SbX<sub>3</sub> (X=F, Br)<sup>[10b-c]</sup> (Dipp<sub>2</sub>Im = 1,3-bis(2,6-di-*isopropylphenyl*)-imidazolin-2-ylidene). For the latter thermal induced isomerization processes from carbene carbon ligated Dipp<sub>2</sub>Im·SbX<sub>3</sub> to the backbone position

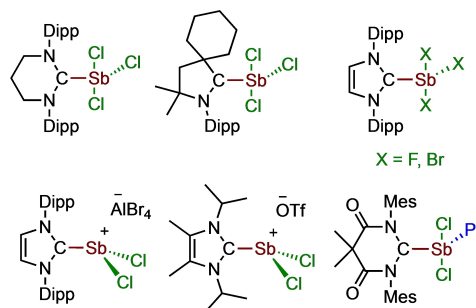


Figure 1. NHC stabilized Sb(III) compounds.

ligated compounds [(<sup>a</sup>Dipp<sub>2</sub>Im)(Dipp<sub>2</sub>Im)SbF<sub>2</sub>][SbF<sub>4</sub>] and <sup>a</sup>-Dipp<sub>2</sub>Im·SbBr<sub>3</sub> (<sup>a</sup> denotes "abnormal coordination"), respectively, were observed.<sup>[10b-c]</sup> Halide abstraction of Dipp<sub>2</sub>Im·SbBr<sub>3</sub> and <sup>a</sup>Dipp<sub>2</sub>Im·SbBr<sub>3</sub> by using AlBr<sub>3</sub> and Na[B(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>] (Na[BAR<sup>F</sup><sub>4</sub>]) as halide acceptor afforded [Dipp<sub>2</sub>Im·SbBr<sub>2</sub>][AlBr<sub>4</sub>] (Figure 1, bottom left) and [<sup>a</sup>Dipp<sub>2</sub>Im·SbBr<sub>2</sub>][BAR<sup>F</sup><sub>4</sub>], respectively.<sup>[10c]</sup> Recently the number of substances with [NHC-SbX<sub>2</sub>]<sup>+</sup> moieties was extended as the reaction of SbCl<sub>3</sub> with [*i*Pr<sub>2</sub>Im<sup>Me</sup>·SiMe<sub>3</sub>][OTf] led to the isolation of [*i*Pr<sub>2</sub>Im<sup>Me</sup>·SbCl<sub>2</sub>][OTf] (Figure 1, bottom middle; *i*Pr<sub>2</sub>Im<sup>Me</sup> = 1,3-di-*isopropyl*-4,5-dimethylimidazolin-2-ylidene; OTf = trifluoromethane-sulfonate).<sup>[6h]</sup> Related ionic compounds were synthesized by the group of Tamm who reported recently the zwitterionic adduct ((B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>)-Dipp<sub>2</sub>Im)·SbCl<sub>2</sub> and by Benjamin and co-workers who isolated the η<sup>3</sup>-cp\* coordinated compound [Mes<sub>2</sub>Im·SbCp\*F][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].<sup>[13]</sup>

It has been demonstrated over the last few years for selected examples, that Lewis-acid/base adducts of antimony(III) halides are interesting entry-points into the chemistry of subvalent antimony compounds, including antimony radicals, stibinidenes and multiply bonded antimony dimers.<sup>[10g,12-14]</sup> However, the examples for the stabilization of these species are

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Supporting information for this article is available on the WWW under  
https://doi.org/10.1002/ejic.202100632

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scarce in the literature and the carbenes involved in the stabilization process of each different compound seems to be rather specific. So far, different cAACs, DACs (=4-6-diketo-1,3-diorgananyl-5,5-dimethyl-pyrimidine-2-ylidenes) and NHCs have been involved in this type of chemistry. A systematic study is currently missing, even on synthesis and characterization of *Lewis*-acid/base adducts of antimony halides with NHCs. We thus provide herein a detailed report on *Lewis*-acid/base adducts of NHCs and the cyclic (alkyl)(amino)carbene cAAC<sup>Me</sup> (1-(2,6-di-*iso*-propylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene) with antimony(III) chlorides of the general formula SbCl<sub>2</sub>R (R = Cl, Ph, Mes).

## Results and Discussion

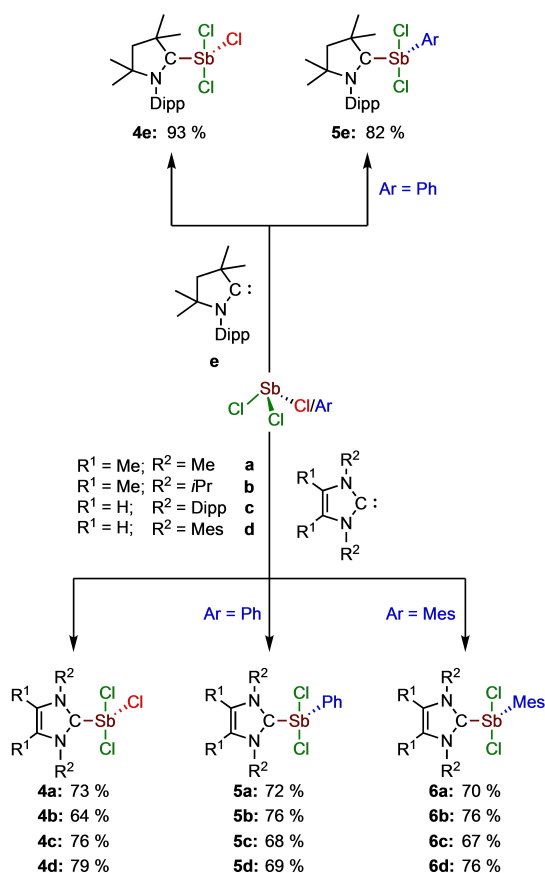
### Synthesis of NHC·SbCl<sub>3</sub> and NHC·SbCl<sub>2</sub>Ar (Ar = Ph, Mes)

We started our investigations with the reaction of *Lewis*-acidic antimony compounds and selected NHCs. Reaction of SbCl<sub>3</sub> (in Et<sub>2</sub>O), SbCl<sub>2</sub>Ph<sup>[15]</sup> (in toluene) and SbCl<sub>2</sub>Mes<sup>[15–16]</sup> (in Et<sub>2</sub>O) with the corresponding 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), Mes<sub>2</sub>Im (d) and cAAC<sup>Me</sup> (e)) led to formation of NHC·SbCl<sub>3</sub> (4a–e), NHC·SbCl<sub>2</sub>Ph (5a–e) and NHC·SbCl<sub>2</sub>Mes (6a–d) in high yields (64–93%; Scheme 1).

A solution of SbCl<sub>2</sub>R was added at –78 °C to a solution or suspension (depending on the carbene) of the respective carbene and the reaction mixture was allowed to warm to room temperature overnight. In all cases the reaction led to a colorless precipitate, which was isolated by filtration. As an unknown impurity was formed for the Me<sub>2</sub>Im<sup>Me</sup> antimony compounds in course of the reaction, the adducts, 4a, 5a and 6a, had to be recrystallized by slow diffusion of *n*-hexane into a dichloromethane solution of the crude product. Furthermore, adduct 6d is very unstable in solution and decomposes within several minutes.

Adduct formation is evident from <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy as well as elemental analysis. The resonances of the carbene carbon atoms (C2) in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of 4a–6d show a strong upfield shift compared to the corresponding free carbene (see Table 1). Additionally, the <sup>1</sup>H NMR methine proton resonances of the *iso*-propyl substituents of 4b, 5b, 6b and 4c, 5c, 6c are considerably shifted compared to the signals of the free carbenes (4b 5.45 ppm, 5b 5.08 ppm and 5.57 ppm, 6b 5.55 ppm; *i*Pr<sub>2</sub>Im<sup>Me</sup> 3.95 ppm; 4c 3.25 ppm, 5c 3.30 ppm and 6c 2.92 ppm; Dipp<sub>2</sub>Im 2.96 ppm; see Table 1). The <sup>13</sup>C{<sup>1</sup>H} NMR resonance of the carbenic carbon atom is shifted to higher field depending on the substitution pattern at antimony starting from the adducts of SbCl<sub>3</sub>, via SbCl<sub>2</sub>Ph to SbCl<sub>2</sub>Mes (see Table 1). The adducts 6c and 6d are quite unstable and show decomposition in solution already at ambient conditions.

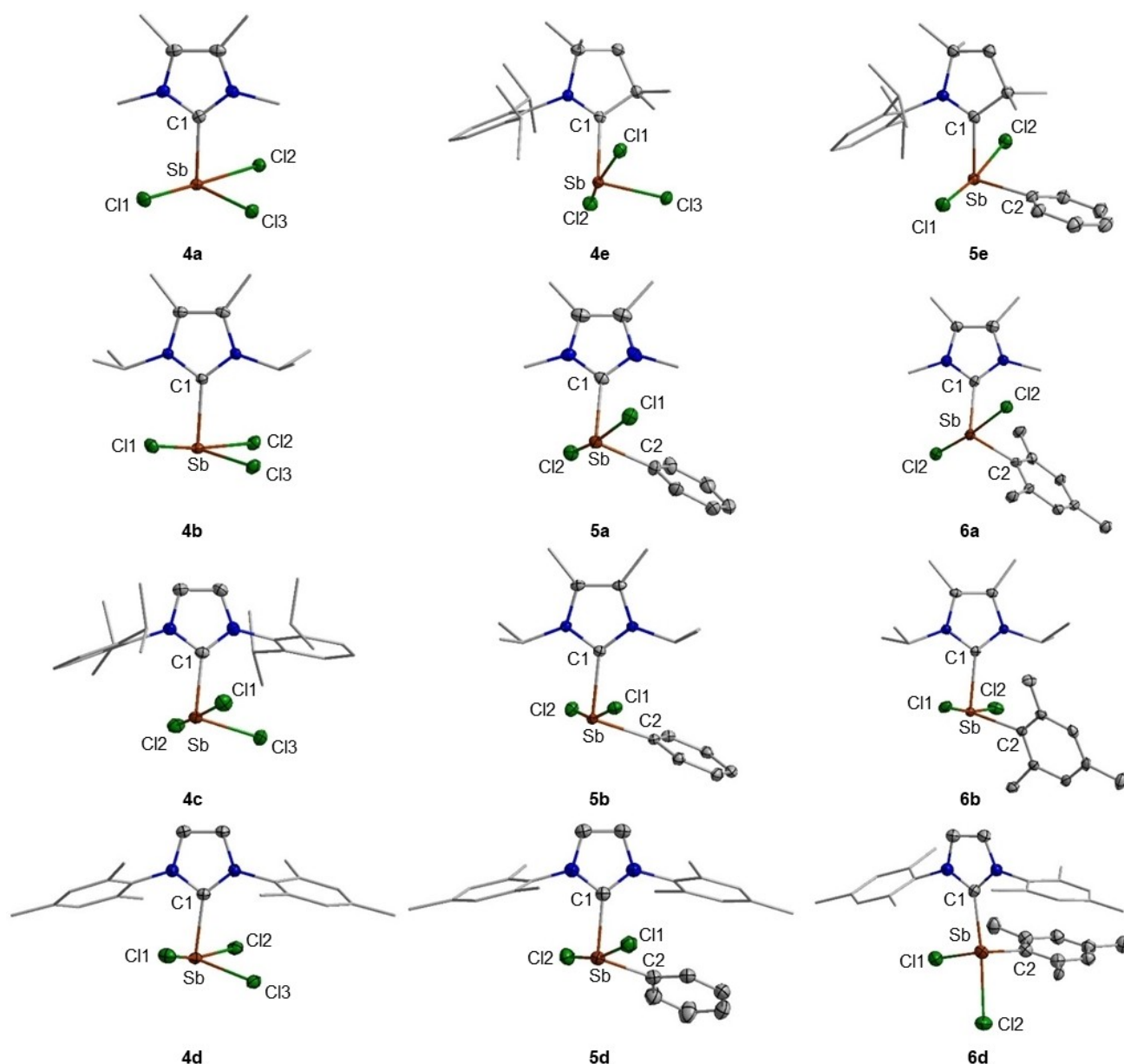
Crystals suitable for X-ray diffraction were obtained for the compounds 4a–4e, 5a, 5b, 5d, 5e, 6a, 6b and 6d (Figure 2). The adducts crystallize in the monoclinic space groups C2/c (4a and 4b), P2<sub>1</sub>/n (4c, 4d, 5d, 5e and 6d), P2<sub>1</sub>/c (4e) and Cc (6a) and in the triclinic space group P $\bar{1}$  (5a, 5b and 6b), respectively, with one molecule in the asymmetric unit. The most important bonding parameters of the adducts 4a–5b, 5d–6b and 6d are summarized in Table 2. The solid-state



Scheme 1. Synthesis of cAAC<sup>Me</sup>- (top) and NHC- (bottom) stabilized SbCl<sub>3</sub> (4a–e), SbCl<sub>2</sub>Ph (5a–e) and SbCl<sub>2</sub>Mes (6a–d) adducts.

	NHC·SbCl <sub>3</sub> 4a–e		NHC·SbCl <sub>2</sub> Ph 5a–e		NHC·SbCl <sub>2</sub> Mes 6a–e		Free NHC	
	δ <sup>13</sup> C (NCN)	δ <sup>1</sup> H ( <i>i</i> Pr–CH)	δ <sup>13</sup> C (NCN)	δ <sup>1</sup> H ( <i>i</i> Pr–CH)	δ <sup>13</sup> C (NCN)	δ <sup>1</sup> H ( <i>i</i> Pr–CH)	δ <sup>13</sup> C (NCN)	δ <sup>1</sup> H ( <i>i</i> Pr–CH)
Me <sub>2</sub> Im <sup>Me</sup>	162.5 <sup>[a]</sup>	/	157.7 <sup>[a]</sup>	/	155.7 <sup>[b]</sup>	/	212.4	/
<i>i</i> Pr <sub>2</sub> Im <sup>Me</sup>	164.3	5.45	161.3	5.08, 5.57	158.4	5.55	207.6	3.95
Dipp <sub>2</sub> Im	165.7	3.25	162.1	3.30	/	2.92	220.1	2.96
Mes <sub>2</sub> Im	164.1	/	161.0	/	174.0 <sup>[c]</sup>	/	215.8 <sup>[a]</sup>	/
cAAC <sup>Me</sup>	231.0	3.11	225.8	3.25	/	/	313.6	3.13

[a] Recorded in THF-d<sub>8</sub>. [b] Recorded in CDCl<sub>3</sub>. [c] Recorded in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure 2.** Molecular structures of  $\text{Me}_2\text{Im}^{\text{Me}} \cdot \text{SbCl}_3$  (**4a**),  $i\text{Pr}_2\text{Im}^{\text{Me}} \cdot \text{SbCl}_3$  (**4b**),  $\text{Dipp}_2\text{Im} \cdot \text{SbCl}_3$  (**4c**),  $\text{Mes}_2\text{Im} \cdot \text{SbCl}_3$  (**4d**),  $\text{cAAC}^{\text{Me}} \cdot \text{SbCl}_3$  (**4e**),  $\text{Me}_2\text{Im}^{\text{Me}} \cdot \text{SbCl}_2\text{Ph}$  (**5a**),  $i\text{Pr}_2\text{Im}^{\text{Me}} \cdot \text{SbCl}_2\text{Ph}$  (**5b**),  $\text{Mes}_2\text{Im} \cdot \text{SbCl}_2\text{Ph}$  (**5d**),  $\text{cAAC}^{\text{Me}} \cdot \text{SbCl}_2\text{Ph}$  (**5e**),  $\text{Me}_2\text{Im}^{\text{Me}} \cdot \text{SbCl}_2\text{Mes}$  (**6a**),  $i\text{Pr}_2\text{Im}^{\text{Me}} \cdot \text{SbCl}_2\text{Mes}$  (**6b**) and  $\text{Mes}_2\text{Im} \cdot \text{SbCl}_2\text{Mes}$  (**6d**) in the solid-state. Hydrogen atoms and solvent molecules (**4a**, **4d**, **5a** and **6b**: benzene; **4b**: THF) are omitted for clarity. Atomic displacement ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: **4a**: Sb–C1, 2.2031(18); Sb–C1, 2.6351(5); Sb–Cl2, 2.5598(5); Sb–Cl3, 2.3858(5); C1–Sb–Cl3, 96.70(5); Cl1–Sb–Cl2, 171.202(17); **4b**: Sb–C1, 2.229(2); Sb–C1, 2.5682(5); Sb–Cl2, 2.5795(5); Sb–Cl3, 2.4012(5); C1–Sb–Cl3, 98.46(5); Cl1–Sb–Cl2, 169.362(18); **4c**: Sb–C1, 2.2192(2); Sb–C1, 2.5734(8); Sb–Cl2, 2.5084(7); Sb–Cl3, 2.3506(6); C1–Sb–Cl3, 97.99(6); Cl1–Sb–Cl2, 171.26(2); **4d**: Sb–C1, 2.220(2); Sb–C1, 2.5107(6); Sb–Cl2, 2.5915(6); Sb–Cl3, 2.3692(6); C1–Sb–Cl3, 100.72(6); Cl1–Sb–Cl2, 166.38(2); **4e**: Sb–C1, 2.239(2); Sb–Cl1, 2.4990(6); Sb–Cl2, 2.5968(5); Sb–Cl3, 2.3616(6); C1–Sb–Cl3, 99.28(6); Cl1–Sb–Cl2, 166.68(2); **5a**: Sb–C1, 2.1942(2); Sb–C2, 2.159(3); Sb–Cl1, 2.6251(6); Sb–Cl2, 2.5777(6); C1–Sb–C2, 101.85(9); Cl1–Sb–Cl2, 165.87(2); **5b**: Sb–C1, 2.210(2); Sb–C2, 2.170(2); Sb–Cl1, 2.6184(5); Sb–Cl2, 2.5785(5); C1–Sb–C2, 101.55(8); Cl1–Sb–Cl2, 164.772(19); **5d**: Sb–C1, 2.220(3); Sb–C2, 2.173(3); Sb–Cl1, 2.6183(8); Sb–Cl2, 2.5747(8); C1–Sb–C2, 100.75(11); Cl1–Sb–Cl2, 168.41(3); **5e**: Sb–C1, 2.243(3); Sb–C2, 2.184(3); Sb–Cl1, 2.6229(8); Sb–Cl2, 2.5425(8); C1–Sb–C2, 99.03(12); Cl1–Sb–Cl2, 170.73(3); **6a**: Sb–C1, 2.193(6); Sb–C2, 2.170(6); Sb–Cl1, 2.5912(19); Sb–Cl2, 2.6136(16); C1–Sb–C2, 104.5(2); Cl1–Sb–Cl2, 171.42(6); **6b**: Sb–C1, 2.2255(17); Sb–C2, 2.1748(18); Sb–Cl1, 2.6017(5); Sb–Cl2, 2.6097(5); C1–Sb–C2, 104.65(7); Cl1–Sb–Cl2, 173.064(15); **6d**: Sb–C1, 2.367(6); Sb–C2, 2.142(9); Sb–Cl1, 2.353(2); Sb–Cl2, 2.737(2); C1–Sb–C2, 92.73(3); Cl1–Sb–Cl2, 83.77(8).

structures, with the exception of **6d**, were found to be essentially isostructural and adopt a disphenoidal geometry at antimony with the angles C1–Sb–C2/Cl3 and Cl1–Sb–Cl2 varying from 96.70(5) to 104.5(2)° and 164.772(19) to 173.064(15)°, respectively. The axial positions are occupied by

the two chlorine atoms Cl1 and Cl2 while C1 and Cl3/C2 are bound in equatorial positions. This geometry was also found in carbene stabilized Sb(III) compounds reported previously.<sup>[10b-c,11–12]</sup> The bond lengths from antimony to the substituents are by and large unaffected by the substitution

**Table 2.** Selected bond lengths [Å] and angles [°] of the NHC-adducts **4a–4e**, **5a**, **5b**, **5d**, **5e**, **6a** and **6b** as well as the <sup>a</sup>NHC adducts **7** and **8**.

	Sb–C1	Sb–C2/Cl3	Sb–Cl1	Sb–Cl2	C1–Sb–Cl3/C2	Cl1–Sb–Cl2
(4a) Me <sub>2</sub> Im <sup>Me</sup> ·SbCl <sub>3</sub>	2.2031(18)	2.3858(5)	2.6351(5)	2.5598(5)	96.70(5)	171.202(17)
(4b) <i>i</i> Pr <sub>2</sub> Im <sup>Me</sup> ·SbCl <sub>3</sub>	2.229(2)	2.4012(5)	2.5682(5)	2.5795(5)	98.46(5)	169.362(18)
(4c) Dipp <sub>2</sub> Im·SbCl <sub>3</sub>	2.2192(2)	2.3506(6)	2.5734(8)	2.5084(7)	97.99(6)	171.26(2)
(4d) Mes <sub>2</sub> Im·SbCl <sub>3</sub>	2.220(2)	2.3692(6)	2.5107(6)	2.5915(6)	100.72(6)	166.38(2)
(4e) cAAC <sup>Me</sup> ·SbCl <sub>3</sub>	2.239(2)	2.3616(6)	2.4990(6)	2.5968(5)	99.28(6)	166.68(2)
(5a) Me <sub>2</sub> Im <sup>Me</sup> ·SbCl <sub>2</sub> Ph	2.1942(2)	2.159(3)	2.6251(6)	2.5777(6)	101.85(9)	165.87(2)
(5b) <i>i</i> Pr <sub>2</sub> Im <sup>Me</sup> ·SbCl <sub>2</sub> Ph	2.210(2)	2.170(2)	2.6184(5)	2.5785(5)	101.55(8)	164.772(19)
(5d) Mes <sub>2</sub> Im·SbCl <sub>2</sub> Ph	2.220(3)	2.173(3)	2.6183(8)	2.5747(8)	100.75(11)	168.41(3)
(5e) cAAC <sup>Me</sup> ·SbCl <sub>2</sub> Ph	2.243(3)	2.184(3)	2.6229(8)	2.5425(8)	99.03(12)	170.73(3)
(6a) Me <sub>2</sub> Im <sup>Me</sup> ·SbCl <sub>2</sub> Mes	2.193(6)	2.170(6)	2.5912(19)	2.6136(16)	104.5(2)	171.42(6)
(6b) <i>i</i> Pr <sub>2</sub> Im <sup>Me</sup> ·SbCl <sub>2</sub> Mes	2.2255(17)	2.1748(18)	2.6017(5)	2.6097(5)	104.65(7)	173.064(15)
(6d) Mes <sub>2</sub> Im·SbCl <sub>2</sub> Mes <sup>[a]</sup>	2.367(6)	2.142(9)	2.353(2)	2.737(2)	92.73(3)	83.77(8)
	Sb–C3	Sb–C2	Sb–Cl1	Sb–Cl2	C2–Sb–C3	Cl1–Sb–Cl2
(7) <sup>a</sup> Dipp <sub>2</sub> Im·SbCl <sub>2</sub> Mes	2.1639(18)	2.1716(19)	2.6578(5)	2.5752(5)	100.80(7)	169.969(15)
(8) <sup>a</sup> Dipp <sub>2</sub> Im·SbCl <sub>2</sub> Ph <sup>[b]</sup>	2.1582(18)	2.163(2)	2.6093(5)	2.5641(5)	93.16(7)	170.303(17)
	2.1545(18)	2.1656(19)	2.6627(5)	2.5388(5)	95.39(7)	180.233(17)

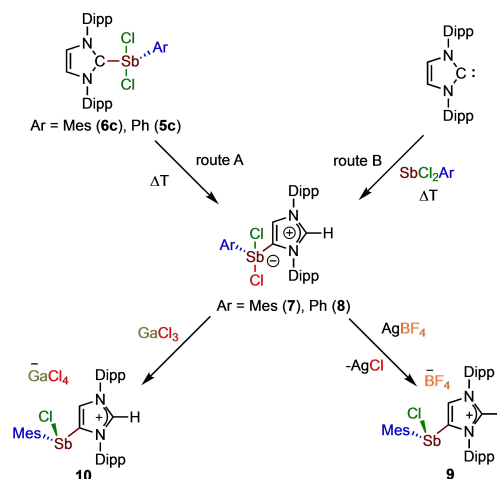
[a] The molecule is disordered and the data reported corresponds to the part with 84% occupancy. [b] Two independent molecules were found in the unit cell.

pattern of the carbene. The distances Sb–C1 in the SbCl<sub>3</sub> adducts **4a–e** range from 2.2031(18) to 2.239(2) Å, which is consistent with those observed in cAAC<sup>Me</sup>·SbCl<sub>3</sub> (Sb–C1: 2.223(3) Å)<sup>[12]</sup> and 6-Dipp<sub>2</sub>Im·SbCl<sub>3</sub> (Sb–C1: 2.288(2) Å).<sup>[11]</sup> The bond lengths Sb–C1 and Sb–Cl2 for the chlorine atoms in axial positions (2.4990(6) to 2.6351(5) Å) are notably longer than the Sb–Cl distances of the chlorines in equatorial position (Sb–Cl3: 2.3506(6) to 2.3858(5) Å) in the compounds **4a–e**. This is in line with the understanding of a three-center, four electron bond of the axial moiety X–Sb–X (X=Cl, Br), as reported previously for Dipp<sub>2</sub>Im·SbBr<sub>3</sub>. Furthermore, some electron donation of the NHC into an anti-bonding σ\*-orbital of Sb–X<sub>axial</sub> may weaken and thus further elongates these bonds.<sup>[10c,17]</sup> For the SbCl<sub>2</sub>Ar (Ar=Ph, Mes) adducts **5a**, **5b** and **5d–6b** the distances Sb–C1 to the carbene carbon atom are in the same range as determined for **4a–e** and are slightly longer than those observed for the bond to the aryl substituent (Sb–C2: 2.159(3) to 2.184(3) Å).

Compared to DAC<sup>Mes</sup>·SbCl<sub>2</sub>Ph (Sb–C1: 2.330(4) Å, Sb–C2: 2.364(4) Å; average of two independent molecules in the asymmetric unit) the difference between Sb–C1 and Sb–C2 is slightly smaller. In contrast to DAC·SbCl<sub>2</sub>Ph (Sb–C1: 2.6550(12) Å, Sb–Cl2: 2.5157(13) Å; average)<sup>[14a]</sup> *d*(Sb–Cl1) and *d*(Sb–Cl2) of **5a**, **5b**, **5d**, **6a** and **6b** are in the small range from 2.5777(6) Å to 2.6251(6) Å. However, the corresponding distances of **5e** (Sb–Cl1: 2.6229(8) Å, Sb–Cl2: 2.5425(8) Å) differ remarkably. In contrast to the aforementioned adducts, compound **6d** shows an anomaly in its molecular structure. The chlorine atom Cl1 is in *cis*-position to Cl2 which is caused by the approaching and repulsive *ortho*-methyl groups of the mesityl substituent. To get some deeper insight into this situation, quantum-mechanical DFT calculations on the B3LYP/def2-SV(P) level of theory were performed.<sup>[18,19]</sup> According to these calculations this geometry is energetically favored by 15.8 kJ/mol compared to the disphenoidal geometry found for the other adducts.

### Thermal induced isomerization of **5c** and **6c**

It has been reported previously that sterically demanding NHCs may switch coordination mode from „normal“ (coordination *via* the C2 carbon atom) to „abnormal“ (coordination *via* the backbone C4 carbon atom). Two examples were presented earlier for antimony chemistry with thermally induced isomerization of Dipp<sub>2</sub>Im·SbX<sub>3</sub> to [(<sup>a</sup>Dipp<sub>2</sub>Im)(Dipp<sub>2</sub>Im)SbF<sub>2</sub>][SbF<sub>4</sub>] and <sup>a</sup>Dipp<sub>2</sub>Im·SbBr<sub>3</sub>, respectively.<sup>[10b–c]</sup> Similarly, heating solutions of **5c** and **6c** in benzene to 80 °C overnight and removal of all volatiles *in vacuo* afforded the zwitterionic <sup>a</sup>NHC adducts <sup>a</sup>Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Mes (**7**) and <sup>a</sup>Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Ph (**8**) in nearly quantitative yields (route A: **7**, 98%; **8**, 95%; Scheme 2, top). Another synthetic approach towards the <sup>a</sup>NHC adducts **7** and **8** was the reaction of SbCl<sub>2</sub>Mes and SbCl<sub>2</sub>Ph, respectively, with Dipp<sub>2</sub>Im in benzene at elevated temperatures. Heating these



**Scheme 2.** Synthesis of <sup>a</sup>Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Mes (**7**) and <sup>a</sup>Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Ph (**8**) (top) and chloride abstraction from **7** by GaCl<sub>3</sub> and Ag[BF<sub>4</sub>] to form the salts [<sup>a</sup>Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Mes]BF<sub>4</sub> (**9**) and [<sup>a</sup>Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Mes]GaCl<sub>4</sub> (**10**) (bottom).

reaction mixtures to 80 °C overnight led in both cases to a colorless precipitate, which was collected by filtration and afforded **7** and **8** in very good yields (route B: **7**, 89%; **8**, 86%). For other adducts, similar rearrangements were detected in traces or minor amounts after prolonged heating.

Both compounds show two characteristic resonances in their  $^1\text{H}$  NMR spectra (see Table 3), i.e., one doublet for the remaining backbone proton C4–H (7.87 ppm, **7**; 7.22 ppm, **8**) and a second doublet for the imidazolium proton C2–H (8.08 ppm, **7**; 8.13 ppm, **8**). Both hydrogen atoms show coupling with one another ( $^4J_{\text{HH}} = 1.5$  Hz). Additional prove of the asymmetry in **7** and **8** are the resonances of the substituents at the nitrogen atoms, which show two separate sets of signals in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra. The characteristic resonances of the methine protons of the *iso*-propyl groups were observed at 2.54 ppm and 2.80 ppm (**7**) and at 2.45 ppm and 2.94 ppm (**8**). The  $^{13}\text{C}\{^1\text{H}\}$  NMR resonances for the NHC C2 carbon atom were shifted to 135.2 ppm (**7**) and 135.7 ppm (**8**), whereas the antimony bound carbon atom (C4) was observed at 146.5 ppm (**7**) and 151.1 ppm (**8**), respectively (see Table 3).

Furthermore, crystals suitable for X-ray diffraction of **7** and **8** were obtained by diffusion of *n*-pentane into a saturated

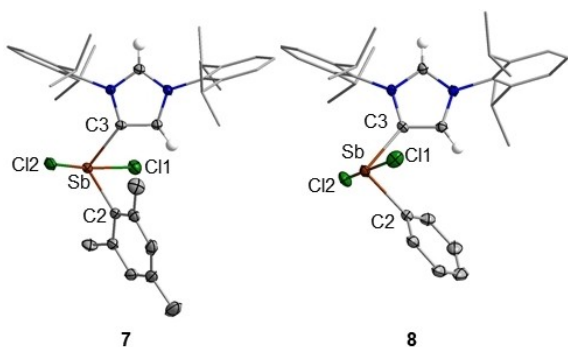
solution of the corresponding adduct in dichloromethane at 12 °C (Figure 3).

The compounds **7** and **8** crystallize in the monoclinic space groups  $P2_1/c$  (**7**) and  $C2/c$  (**8**). In analogy to the normal coordinated adducts **4a–6d**, the peripheries of the antimony centers of **7** and **8** adopt disphenoidal geometries. The  $\text{SbCl}_2\text{Ar}$  moiety is coordinated to the backbone carbon atom C4 with bond lengths of 2.1639(18) Å (**7**) and 2.1582(18) Å/2.1545(18) Å (**8**).

Compared to the  $\text{Sb}-\text{C}_{\text{carbene}}$  (C1) bond lengths found in the NHC-adducts, the distances  $\text{Sb}-\text{C}3$  of the abnormal coordinated NHCs in **7** and **8** are notably shorter, which underscores an increased  $\text{Sb}-\text{C}$  bond strength and thus higher thermodynamic stability of these adducts. In contrast, the  $\text{Sb}-\text{C}2$  distances of **7** (2.1716(19) Å) and **8** (2.163(2) Å; 2.1656(19) Å) are similar to the corresponding bond lengths of the normal coordinated adducts (see Table 2). The angles about the antimony center of **7** ( $\text{C}2-\text{Sb}-\text{C}3$ : 100.80(7)°;  $\text{Cl}1-\text{Sb}-\text{Cl}2$ : 169.969(15)°) and **8** ( $\text{C}2-\text{Sb}-\text{C}3$ : molecule 1, 93.16(7)°; molecule 2, 95.39(7)°;  $\text{Cl}1-\text{Sb}-\text{Cl}2$ : molecule 1, 170.303(17)°; molecule 2, 180.233(17)°) are only marginally affected by the coordination mode.

**Table 3.** Selected  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR chemical shifts (ppm) of the  $^{\text{a}}\text{NHC}$ -adducts **7–10** recorded in  $\text{CD}_2\text{Cl}_2$

	$\delta^1\text{H}$ ( <i>i</i> Pr–CH)	$\delta^1\text{H}$ (SbCCH)	$\delta^1\text{H}$ (NCHN)	$\delta^{13}\text{C}$ (NCHN)	$\delta^{13}\text{C}$ (NCSb)	$\delta^{13}\text{C}$ (NCCN)
<b>7</b>	2.54 2.80	7.87	8.08	135.2	146.5	136.4
<b>8</b>	2.45 2.94	7.22	8.13	135.7	151.1	132.8
<b>9</b>	2.33 2.43	7.65	9.13	141.2	139.2	133.1
<b>10</b>	2.45 2.51	7.72	8.68	139.9	139.4	133.1

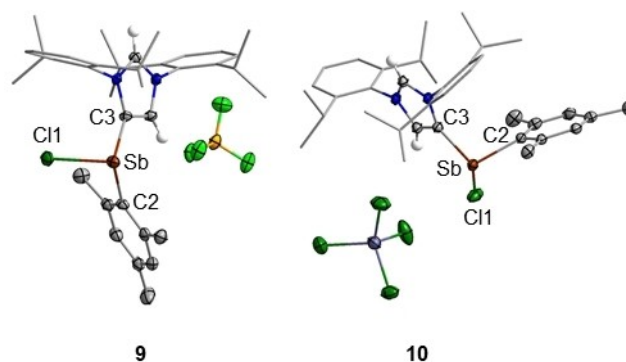


**Figure 3.** Molecular structures of  $^{\text{a}}\text{Dipp}_2\text{Im}\cdot\text{SbCl}_2\text{Mes}$  (**7**) and  $^{\text{a}}\text{Dipp}_2\text{Im}\cdot\text{SbCl}_2\text{Ph}$  (**8**) in the solid-state. Hydrogen atoms (except the imidazolium protons) and solvent molecules (**7**: benzene, **8**: toluene) are omitted for clarity. For compound **8**, only one of two independent molecules of the asymmetric unit is shown. Atomic displacement ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: **7**:  $\text{Sb}-\text{C}3$ , 2.1639(18);  $\text{Sb}-\text{C}2$ , 2.1716(19);  $\text{Sb}-\text{Cl}1$ , 2.6578(5);  $\text{Sb}-\text{Cl}2$ , 2.5752(5);  $\text{C}2-\text{Sb}-\text{C}3$ , 100.80(7);  $\text{Cl}1-\text{Sb}-\text{Cl}2$ , 169.969(15); **8** (molecule 1):  $\text{Sb}-\text{C}3$ , 2.1582(18);  $\text{Sb}-\text{C}2$ , 2.163(2);  $\text{Sb}-\text{Cl}1$ , 2.6093(5);  $\text{Sb}-\text{Cl}2$ , 2.5641(5);  $\text{C}2-\text{Sb}-\text{C}3$ , 93.16(7);  $\text{Cl}1-\text{Sb}-\text{Cl}2$ , 170.303(17); **8** (molecule 2):  $\text{Sb}-\text{C}3$ , 2.1545(18);  $\text{Sb}-\text{C}2$ , 2.1656(19);  $\text{Sb}-\text{Cl}1$ , 2.6627(5);  $\text{Sb}-\text{Cl}2$ , 2.5388(5);  $\text{C}2-\text{Sb}-\text{C}3$ , 95.39(7);  $\text{Cl}1-\text{Sb}-\text{Cl}2$ , 180.233(17).

### Chloride Abstraction from **7** and **8** by $\text{AgBF}_4$ and $\text{GaCl}_3$

For the synthesis of three-coordinate antimony cations we reacted **7** with the chloride abstracting agents  $\text{Ag}[\text{BF}_4]$  and  $\text{GaCl}_3$ . Driven by the precipitation of  $\text{AgCl}$  and the formation of  $[\text{GaCl}_4]$  as counterion, the reactions afforded the imidazolium salts  $[\text{Dipp}_2\text{Im}\cdot\text{SbClAr}][\text{BF}_4]$  (**9**) and  $[\text{Dipp}_2\text{Im}\cdot\text{SbClAr}][\text{GaCl}_4]$  (**10**) in very good yields (**9**, 83%; **10**, 91%) (Scheme 2, bottom). The formation is evident from  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data. Compared to the starting material **7** all resonances of **9** and **10** (see Table 3) are shifted.

Single crystals suitable for X-Ray diffraction (see Figure 4) were obtained for **9** and **10** by storing a concentrated dichloro-



**Figure 4.** Molecular structures of  $[\text{Dipp}_2\text{Im}\cdot\text{SbClMes}][\text{BF}_4]$  (**9**) and  $[\text{Dipp}_2\text{Im}\cdot\text{SbClMes}][\text{GaCl}_4]$  (**10**) in the solid-state. Hydrogen atoms (except the imidazolium protons) and solvent molecules (**10**:  $\text{CH}_2\text{Cl}_2$ ) are omitted for clarity. Atomic displacement ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: **9**:  $\text{Sb}-\text{C}3$ , 2.151(2);  $\text{Sb}-\text{C}2$ , 2.166(2);  $\text{Sb}-\text{Cl}1$ , 2.3971(6);  $\text{C}3-\text{Sb}-\text{C}2$ , 94.71(8);  $\text{C}3-\text{Sb}-\text{Cl}1$ , 96.59(6);  $\text{C}2-\text{Sb}-\text{Cl}1$ , 97.37(6); **10**:  $\text{Sb}-\text{C}3$ , 2.158(2);  $\text{Sb}-\text{C}2$ , 2.149(2);  $\text{Sb}-\text{Cl}1$ , 2.3563(6);  $\text{C}3-\text{Sb}-\text{C}2$ , 100.99(9);  $\text{C}3-\text{Sb}-\text{Cl}1$ , 91.26(7);  $\text{C}2-\text{Sb}-\text{Cl}1$ , 98.07(7).

methane solution at 6 °C. The compounds **9** and **10** crystallize in the monoclinic space group  $P2_1/c$ , with one molecule in the asymmetric unit. In both structures the central atom Sb is surrounded by three substituents and adopts a pseudo tetrahedral geometry. The angles C2–Sb–C3, C2–Sb–Cl1 and C3–Sb–Cl1 range from 94.71(8)° to 100.99(9)°. There are no significant changes of the carbon antimony distances Sb–C2 (**9**, 2.166(2) Å; **10**, 2.149(2) Å; **7**, 2.1639(18) Å) and Sb–C3 (**9**, 2.151(2) Å; **10**, 2.158(2) Å; **7**, 2.1716(19) Å) upon chloride abstraction. However, the bond from Sb to chlorine Sb–Cl1 (**9**, 2.3971(6) Å; **10**, 2.3563(6) Å) is significantly shortened in comparison to parent **7** (Sb1–Cl1, 2.6578(5) Å; Sb–Cl2, 2.5752(5) Å).

## Conclusion

We present here a comprehensive study on synthesis, spectroscopy and molecular structures of NHC-stabilized antimony(III) adducts, which have been prepared by the reaction of different carbenes with the antimony compounds  $\text{SbCl}_2\text{R}$  (R=Cl, Ph, Mes). The results obtained for the adducts NHC· $\text{SbCl}_2\text{R}$  (R=Cl, Ph, Mes) (**4a–6d**) give further insight into the bonding situation at antimony as well as the influence of different carbenes and NHC substitution pattern as well as different substituents at antimony on these adducts. Heating of the NHC adducts **6c** and **5c** or their precursors, respectively, led to isolation of the abnormally coordinated adducts  $^{\text{a}}\text{Dipp}_2\text{Im}\cdot\text{SbCl}_2\text{Ar}$  (Ar=Mes (**7**), Ph (**8**)). Chloride abstraction from **7** by the Lewis-acids  $\text{GaCl}_3$  and  $\text{Ag}[\text{BF}_4]$  afforded the ionic compounds  $[\text{Dipp}_2\text{Im}\cdot\text{SbClAr}][\text{X}]$  (X=[ $\text{BF}_4$ ] (**9**); [ $\text{GaCl}_4$ ] (**10**)), which might be useful as precursors for the synthesis of other antimony (III) compounds with abnormally coordinated NHCs or novel, backbone Sb-substituted NHCs. The variety of the NHC-stabilized antimony(III) compounds reported herein is a promising starting point for a further development of NHC antimony chemistry.

## Experimental Section

### General Procedure

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>[20]</sup> All reactions were carried out in oven-dried glassware. Toluene, *n*-hexane,  $\text{Et}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$  and THF were obtained from 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  $\text{Me}_2\text{Im}^{\text{Me}}$ ,<sup>[21]</sup>  $i\text{Pr}_2\text{Im}^{\text{Me}}$ ,<sup>[21]</sup>  $\text{Mes}_2\text{Im}$ ,<sup>[22]</sup>  $\text{Dipp}_2\text{Im}$ ,<sup>[23]</sup> and  $\text{cAAC}^{\text{Me}}$ <sup>[24]</sup> were prepared according to published procedures. The antimony compounds  $\text{SbMes}_3$ ,<sup>[15–16]</sup>  $\text{SbCl}_2\text{Mes}$ ,<sup>[15–16]</sup> and  $\text{SbCl}_2\text{Ph}$ ,<sup>[15]</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 ( $^1\text{H}$ : 400.4 MHz;  $^{13}\text{C}\{^1\text{H}\}$ : 100.7 MHz) or

Bruker Avance 500 ( $^1\text{H}$ : 500.1 MHz;  $^{13}\text{C}\{^1\text{H}\}$ : 125.8 MHz) NMR spectrometers. Assignment of the  $^1\text{H}$  NMR spectra was supported by  $^1\text{H},^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\},^1\text{H}$  correlation experiments.  $^{13}\text{C}$  NMR spectra were broad-band proton-decoupled ( $^{13}\text{C}\{^1\text{H}\}$ ). Assignment of the  $^{13}\text{C}$  NMR data was supported by  $^{13}\text{C}\{^1\text{H}\},^1\text{H}$  correlation experiments.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR chemical shifts are listed in parts per million (ppm), and were referenced via residual proton resonances of the corresponding deuterated solvent  $\text{C}_6\text{D}_6$  ( $^1\text{H}$ :  $\delta=7.16$ ,  $\text{C}_6\text{D}_6$ ),  $\text{C}_7\text{D}_8$  ( $^1\text{H}$ :  $\delta=2.08$ , 6.97, 7.01, 7.09,  $\text{d}_8$ -toluene),  $\text{CDHCl}_2$  ( $^1\text{H}$ :  $\delta=5.32$ ,  $\text{CD}_2\text{Cl}_2$ ),  $\text{CHCl}_3$  ( $^1\text{H}$ :  $\delta=7.26$ ,  $\text{CDCl}_3$ ),  $\text{d}_7$ -THF ( $^1\text{H}$ :  $\delta=3.58$ , 1.72,  $\text{d}_8$ -THF).  $^{13}\text{C}$  NMR spectra are reported relative to TMS using the carbon resonances of the deuterated solvent  $\text{C}_6\text{D}_6$  ( $^{13}\text{C}$ :  $\delta=128.06$ ),  $\text{d}_8$ -toluene ( $^{13}\text{C}$ :  $\delta=20.43$ , 125.13, 127.96, 128.87, 137.48),  $\text{CD}_2\text{Cl}_2$  ( $^{13}\text{C}$ :  $\delta=53.84$ ),  $\text{CDCl}_3$  ( $^{13}\text{C}$ :  $\delta=77.16$ ),  $\text{d}_8$ -THF ( $^{13}\text{C}$ :  $\delta=67.21$ , 65.31).<sup>[25]</sup> 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  $\text{cm}^{-1}$ . 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).

### Synthesis

#### General procedure for the adducts NHC· $\text{SbCl}_3$ (**4a–6d**)

A solution of  $\text{SbCl}_2\text{R}$  (R=Cl, Ph, Mes) in 5 mL  $\text{Et}_2\text{O}$  (**4a–e**, **6a–d**) or 5 mL toluene (**5a–e**) was added at  $-78^\circ\text{C}$  via a cannula to a suspension of the corresponding NHC (1.0 eq) in 5 mL of the same solvent. The reaction mixture was allowed to warm to room temperature overnight. The resulting colorless precipitate was collected by filtration, washed with *n*-hexane (2×5 mL) and dried *in vacuo*.

#### $\text{Me}_2\text{Im}^{\text{Me}}\cdot\text{SbCl}_3$ (**4a**)

$\text{SbCl}_3$  (100 mg, 371  $\mu\text{mol}$ ) was reacted with  $\text{Me}_2\text{Im}^{\text{Me}}$  (46.0 mg, 371  $\mu\text{mol}$ ). Recrystallization via diffusion of *n*-hexane into a solution of the crude product in THF yielded **4a** (107 mg, 272  $\mu\text{mol}$ , 73%) as colorless crystals. Crystals of **4a** suitable for single crystal X-ray diffraction were grown by layering a THF solution with *n*-hexane and storing at room temperature.

$^1\text{H}$  NMR (400.5 MHz, THF- $\text{d}_6$ , 298 K):  $\delta=2.24$  (s, 6 H,  $\text{CCH}_3$ ), 4.03 (s, 6 H,  $\text{NCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.7 MHz, THF- $\text{d}_6$ , 298 K):  $\delta=8.5$  ( $\text{NCCCH}_3$ ), 35.3 ( $\text{NCH}_3$ ), 128.7 ( $\text{NCCN}$ ), 162.5 ( $\text{NCN}$ ). Elemental analysis (%) calcd. for  $\text{C}_7\text{H}_{12}\text{Cl}_3\text{N}_2\text{Sb}$  [352.30 g/mol]: C, 23.87; H, 3.43; N, 7.95 found: C, 23.94; H, 3.39; N, 7.68. IR ( $[\text{cm}^{-1}]$ ): 3146 (vw), 3067 (w), 2984 (vw), 2957 (w), 2925 (w), 2863 (vw), 1682 (vw), 1642 (m), 1573 (m), 1472 (s), 1442 (vs), 1391 (s), 1368 (s), 1261 (m), 1229 (m), 1205 (m), 1127 (m), 1095 (m), 1056 (m), 1032 (m), 867 (vw), 841 (vs), 801 (m), 745 (vs), 701 (m), 621 (w), 591 (vw), 567 (m), 505 (vw), 464 (vw).

#### $i\text{Pr}_2\text{Im}^{\text{Me}}\cdot\text{SbCl}_3$ (**4b**)

$\text{SbCl}_3$  (127 mg, 555  $\mu\text{mol}$ ) was reacted with  $i\text{Pr}_2\text{Im}^{\text{Me}}$  (100 mg, 555  $\mu\text{mol}$ ) to yield **4b** (145 mg, 354  $\mu\text{mol}$ , 64%) as a colorless solid. Crystals of **4b** suitable for single crystal X-ray diffraction were grown by storing a saturated benzene solution at 6 °C.

$^1\text{H}$  NMR (500.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=1.13$  (d, 12 H,  $^3J_{\text{HH}}=6.9$  Hz,  $i\text{Pr}-\text{CH}_2$ ), 1.32 (s, 6 H,  $\text{CH}_3\text{CCCH}_3$ ), 5.45 (sept, 2 H,  $^3J_{\text{HH}}=6.9$  Hz,  $i\text{Pr}-\text{CH}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=9.8$  ( $\text{NCCCH}_3$ ), 21.3 ( $i\text{Pr}-\text{CH}_2$ ), 53.5 ( $i\text{Pr}-\text{CH}$ ), 127.1 ( $\text{NCCN}$ ), 164.3 ( $\text{NCN}$ ). Elemental analysis (%) calcd. for  $\text{C}_{11}\text{H}_{20}\text{Cl}_3\text{N}_2\text{Sb}$  [408.41 g/mol]: C, 32.35; H, 4.94; N, 6.86; found: C, 33.19; H, 5.23; N, 7.05. IR ( $[\text{cm}^{-1}]$ ): 3010 (vw),

2979 (w), 2944 (w), 2926 (w), 2876 (w), 1623 (w), 1595 (w), 1552 (w), 1448 (s), 1438 (s), 1381 (vs), 1372 (vs), 1344 (m), 1315 (w), 1291 (w), 1228 (vw), 1204 (m), 1167 (w), 1138 (w), 1110 (m), 1073 (vw), 1027 (m), 1004 (vw), 974 (vw), 952 (vw), 936 (vw), 898 (w), 886 (vw), 858 (s), 760 (w), 747 (m), 706 (w), 688 (vw), 648 (vw), 580 (w), 548 (m), 540 (w), 497 (vw), 431 (w), 412 (vw).

#### Dipp<sub>2</sub>Im·SbCl<sub>3</sub> (4c)

SbCl<sub>3</sub> (766 mg, 1.97 mmol) was reacted with Dipp<sub>2</sub>Im (450 mg, 1.97 mmol) to give **4c** (930 mg, 1.51 mmol, 76%) as a colorless solid. Crystals of **4c** suitable for single crystal X-ray diffraction were grown by storing a saturated benzene solution at 6 °C.

<sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 0.93 (d, 12 H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *i*Pr-CH<sub>3</sub>), 1.55 (d, 12 H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *i*Pr-CH<sub>3</sub>), 3.25 (sept, 4 H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *i*Pr-CH), 6.47 (s, 2 H, CHCH), 7.11 (d, 4 H, Dipp-*m*-CH), 7.19 (d, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, Dipp-*p*-CH), 7.21 (d, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.1 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): δ = 23.1 (*i*Pr-CH<sub>3</sub>), 26.7 (*i*Pr-CH<sub>3</sub>), 29.3 (*i*Pr-CH), 124.7 (Dipp-*m*-CH), 125.4 (CHCH) 132.1 (Dipp-*i*-C), 132.2 (Dipp-*p*-CH), 147.0 (Dipp-*o*-C), 165.7 (NCN). **Elemental analysis** (%) calcd. for C<sub>27</sub>H<sub>36</sub>Cl<sub>3</sub>N<sub>2</sub>Sb [616.71 g/mol]: C, 52.59; H, 5.88; N, 4.54; found: C, 52.69; H, 5.89; N, 4.38. **IR** ([cm<sup>-1</sup>): 3159 (w), 3124 (w), 3083 (w), 3032 (vw), 2964 (s), 2929 (m), 2869 (m), 1632 (vw), 2586 (vw), 1555 (w), 1538 (w), 1462 (s), 1439 (s), 1418 (m), 1384 (m), 1362 (m), 1328 (m), 1309 (w), 1268 (w), 1254 (w), 1208 (m), 1182 (m), 1146 (w), 1116 (m), 1100 (w), 1060 (m), 1043 (w), 948 (w), 933 (w), 903 (vw), 884 (vw), 867 (vw), 802 (vs), 769 (s), 756 (vs), 698 (m), 681 (w), 630 (w), 581 (vw), 544 (vw), 518 (vw), 459 (w), 436 (w), 416 (vw).

#### Mes<sub>2</sub>Im·SbCl<sub>3</sub> (4d)

SbCl<sub>3</sub> (100 mg, 438 μmol) was reacted with Mes<sub>2</sub>Im (133 mg, 438 μmol) to yield **4d** (184.6 mg, 345 μmol, 79%) as a colorless solid. Crystals of **4d** suitable for single crystal X-ray diffraction were grown by storing a saturated toluene solution at -30 °C.

<sup>1</sup>H NMR (400.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 2.04 (s, 6 H, Mes-*p*-CH<sub>3</sub>), 2.32 (s, 12 H, Mes-*o*-CH<sub>3</sub>), 5.95 (s, 2 H, CHCH), 6.68 (s, 4 H, Mes-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (100.7 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 19.1 (Mes-*o*-CH<sub>3</sub>), 21.1 (Mes-*p*-CH<sub>3</sub>), 124.2 (CHCH), 129.9 (Mes-*m*-CH), 131.8 (Mes-*i*-C), 136.3 (Mes-*o*-C), 141.2 (Mes-*p*-C), 164.1 (NCN). **Elemental analysis** (%) calcd. for C<sub>21</sub>H<sub>24</sub>Cl<sub>3</sub>N<sub>2</sub>Sb [532.55 g/mol]: C, 47.36; H, 4.54; N, 5.26; found: C, 47.51; H, 4.96; N, 5.45. **IR** ([cm<sup>-1</sup>): 3170 (vw), 3147 (w), 3108 (w), 3079 (w), 3022 (m), 2971 (m), 2950 (m), 2916 (m), 1860 (m), 2786 (w), 2761 (w), 1607 (m), 1538 (s), 1481 (s), 1456 (m), 1446 (m), 1411 (w), 1380 (m), 1335 (vw), 1318 (vw), 1296 (vw), 1254 (vw), 1229 (vs), 1163 (w), 1117 (w), 1097 (w), 1076 (w), 1059 (m), 1036 (m), 966 (vw), 932 (m), 902 (vw), 854 (vs), 812 (vw), 756 (s), 736 (w), 726 (m), 698 (s), 678 (s), 589 (w), 570 (s), 551 (w), 502 (w), 453 (vw), 423 (vw).

#### cAAC<sup>Me</sup>·SbCl<sub>3</sub> (4e)

SbCl<sub>3</sub> (200 mg, 1.61 mmol) was reacted with cAAC<sup>Me</sup> (367 mg, 1.61 mmol) to yield **4e** (386 mg, 1.10 mmol, 68%) as a colorless solid. Crystals of **4e** suitable for single crystal X-ray diffraction were grown by storing a saturated benzene solution at room temperature.

<sup>1</sup>H NMR (400.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 1.06 (s, 6 H, NC(CH<sub>3</sub>)<sub>2</sub>), 1.14 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *i*Pr-CH<sub>3</sub>), 1.32 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *i*Pr-CH<sub>3</sub>), 1.50 (s, 2 H, CH<sub>2</sub>), 1.60 (s, 6 H, NCC(CH<sub>3</sub>)<sub>2</sub>), 3.11 (sept, 2 H, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, *i*Pr-CH), 7.08 (m, 2 H, Dipp-*m*-CH), 7.16 (m, 1 H, Dipp-*p*-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (100.7 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 23.7 (*i*Pr-CH<sub>3</sub>), 26.3 (*i*Pr-CH<sub>3</sub>),

28.6 (NC(CH<sub>3</sub>)<sub>2</sub>), 29.2 (NCC(CH<sub>3</sub>)<sub>2</sub>), 29.3 (*i*Pr-CH), 51.1 (CH<sub>2</sub>), 58.5 (NCC(CH<sub>3</sub>)<sub>2</sub>), 82.7 NC(CH<sub>3</sub>)<sub>2</sub>, 124.8 (Dipp-*m*-CH), 129.3 (Dipp-*p*-CH), 135.9 (Dipp-*i*-C), 146.3 (Dipp-*o*-C), 231.0 (NCSb). The resonance at 231.0 ppm could not be observed in the <sup>13</sup>C{<sup>1</sup>H} NMR Spektrum but *via* <sup>13</sup>C{<sup>1</sup>H} HMBC NMR. **Elemental analysis** (%) calcd. for C<sub>20</sub>H<sub>31</sub>Cl<sub>3</sub>NSb [513.59 g/mol]: C, 46.77; H, 6.08; N, 2.73; found: C, 47.47; H, 6.06; N, 2.31. **IR** ([cm<sup>-1</sup>): 3073 (vw), 2971 (m), 2931 (m), 2871 (w), 1639 (vw), 1587 (vw), 1522 (m), 1457 (s), 1388 (m), 1372 (m), 1347 (m), 1324 (w), 1317 (w), 1271 (w), 1206 (w), 1183 (m), 1160 (w), 1127 (m), 1105 (m), 1054 (m), 1016 (vw), 993 (w), 971 (w), 953 (w), 932 (m), 876 (w), 837 (vw), 813 (vs), 773 (s), 697 (m), 675 (w), 652 (vw), 630 (vw), 609 (m), 560 (m), 492 (m), 432 (vw), 408 (vw).

#### Me<sub>2</sub>Im<sup>Me</sup>·SbCl<sub>2</sub>Ph (5a)

SbCl<sub>2</sub>Ph (150 mg, 438 μmol) was reacted with Me<sub>2</sub>Im<sup>Me</sup> (69.0 mg, 438 μmol). Recrystallization by diffusion of *n*-hexane into a dichloromethane solution of the crude product yielded **5a** (158 mg, 401 μmol, 72%) as colorless crystals. Crystals of **5a** suitable for single crystal X-ray diffraction were grown by layering a THF solution with *n*-hexane and storing at room temperature.

<sup>1</sup>H NMR (400.5 MHz, THF-*d*<sub>8</sub>, 298 K): δ = 2.18 (s<sub>br</sub>, 6 H, CCH<sub>3</sub>) 3.28 (br, 3 H, NCH<sub>3</sub>), 4.00 (br, 3 H, NCH<sub>3</sub>), 7.33 (m, 1 H, Ph-*p*-CH), 7.39 (m, 2 H, Ph-*m*-CH), 8.54 (m, 2 H, Ph-*o*-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (100.7 MHz, THF-*d*<sub>8</sub>, 298 K): δ = 8.5 (NCCCH<sub>3</sub>), 35.5 (NCH<sub>3</sub>), 128.0 (NCCN), 129.0 (Ph-*m*-CH), 129.8 (Ph-*p*-CH), 137.9 (Ph-*o*-CH), 144.2 (Ph-*i*-C), 157.7 (NCN). **Elemental analysis** (%) calcd. for C<sub>13</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>2</sub>Sb [393.95 g/mol]: C, 39.63; H, 4.35; N, 7.11; found: C, 40.23; H, 4.47; N, 6.43. **IR** ([cm<sup>-1</sup>): 3064 (vw), 3047 (vw), 3035 (vw), 2986 (vw), 2953 (w), 2919 (vw), 1647 (m), 1575 (w), 1474 (m), 1433 (s), 1397 (m), 1373 (m), 1330 (vw), 1303 (vw), 1264 (vw), 1229 (w), 1205 (vw), 1184 (vw), 1160 (vw), 1105 (vw), 1061 (m), 1018 (vw), 997 (m), 977 (vw), 912 (vw), 847 (m), 763 (vs), 692 (s), 654 (w), 623 (vw), 595 (vw), 569 (w), 562 (w), 455 (s).

#### *i*Pr<sub>2</sub>Im<sup>Me</sup>·SbCl<sub>2</sub>Ph (5b)

SbCl<sub>2</sub>Ph (80.0 mg, 297 μmol) was reacted with *i*Pr<sub>2</sub>Im<sup>Me</sup> (53.5 mg, 297 μmol) to yield **5b** (101 mg, 224 μmol, 76%) as a colorless solid. Crystals of **5b** suitable for single crystal X-ray diffraction were grown by storing a saturated benzene solution at room temperature.

<sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 0.86 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, *i*Pr-CH<sub>3</sub>), 1.21 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, *i*Pr-CH<sub>3</sub>), 1.33 (s, 3 H, CH<sub>3</sub>), 1.37 (s, 3 H, CH<sub>3</sub>), 5.08 (sept<sub>br</sub>, 1 H, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, *i*Pr-CH), 5.57 (sept<sub>br</sub>, 1 H, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, *i*Pr-CH), 7.17 (m, 1 H, Ph-*p*-CH), 7.34 (m, 2 H, Ph-*m*-CH), 9.19 (m, 2 H, Ph-*o*-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 9.6 (NC(CH<sub>3</sub>)C(CH<sub>3</sub>)), 9.9 (NC(CH<sub>3</sub>)C(CH<sub>3</sub>)), 20.9 (*i*Pr-CH<sub>3</sub>), 21.2 (*i*Pr-CH<sub>3</sub>), 52.8 (*i*Pr-CH), 55.2 (*i*Pr-CH), 126.3 (NCCN), 126.8 (NCCN), 129.1 (Ph-*m*-CH), 129.7 (Ph-*p*-CH), 137.2 (Ph-*o*-CH), 143.8 (Ph-*i*-CH), 161.3 (NCN). **Elemental analysis** (%) calcd. for C<sub>17</sub>H<sub>25</sub>Cl<sub>2</sub>N<sub>2</sub>Sb [450.06 g/mol]: C, 45.37; H, 5.60; N, 6.22; found: C, 45.50; H, 5.63; N, 6.15. **IR** ([cm<sup>-1</sup>): 3044 (vw), 2999 (w), 2970 (w), 2934 (w), 2875 (vw), 1627 (w), 1477 (w), 1460 (w), 1428 (m), 1400 (m), 1369 (m), 1335 (w), 1305 (vw), 1218 (m), 1186 (w), 1171 (w), 1139 (m), 1109 (m), 1076 (w), 1059 (m), 1018 (w), 998 (w), 905 (w), 885 (vw), 854 (vw), 764 (w), 742 (vs), 696 (s), 648 (w), 540 (w), 452 (m), 427 (w)

#### Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Ph (5c)

SbCl<sub>2</sub>Ph (50.0 mg, 185 μmol) was reacted with Dipp<sub>2</sub>Im (72.0 mg, 185 μmol) to yield **5c** (83.5 mg, 127 μmol, 68%) as a colorless solid.

<sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 0.92 (s<sub>br</sub>, 12 H, *iPr-CH<sub>3</sub>*), 1.50 (s<sub>br</sub>, 12 H, *iPr-CH<sub>3</sub>*), 3.30 (sept, 4 H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *iPr-CH*), 6.49 (s, 2 H, *CHCH*), 6.91 (m, 3 H, *Ph-p/m-CH*), 7.05 (br, 6 H, *Dipp-p/m-CH*), 8.32 (m, 2 H, *Dipp-o-CH*). <sup>13</sup>C {<sup>1</sup>H} NMR (125.8 MHz, toluene-d<sub>8</sub>, 258 K): δ = 0.86 (br, 6 H, *iPr-CH<sub>3</sub>*), 0.95 (br, 6 H, *iPr-CH<sub>3</sub>*), 1.32 (br, 6 H, *iPr-CH<sub>3</sub>*), 1.63 (br, 6 H, *iPr-CH<sub>3</sub>*), 3.21 (br, 2 H, *iPr-CH*), 3.28 (br, 2 H, *iPr-CH*), 6.34 (br, 2 H, *CHCH*), 6.74 (br, 2 H, *Dipp-p-CH*), 6.89 (m, 3 H, overlap of *Ph-m-CH* and *Ph-p-CH*), 6.95 (br, 1 H, *Dipp-p-CH*), 7.07 (br, 2 H, *Dipp-m-CH*), 7.16 (br, 1 H, *Dipp-p-CH*), 8.29 (m, 2 H, *Ph-o-CH*). <sup>13</sup>C {<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 23.0 (*iPr-CH<sub>3</sub>*), 26.6 (*iPr-CH<sub>3</sub>*), 29.1 (*iPr-CH*), 124.5 (*Dipp-m-CH*), 125.5 (*NCCN*), 127.5, (*Ph-p-CH*), 128.3 (*Ph-m-CH*), 131.8 (*Dipp-p-CH*), 133.3 (*Dipp-i-C*), 137.4 (*Ph-o-CH*), 142.6 (*Ph-i-C*), 146.7 (*Dipp-o-C*), 162.0 (*NCN*). <sup>13</sup>C {<sup>1</sup>H} NMR (125.8 MHz, toluene-d<sub>8</sub>, 258 K): δ = 22.9 (*iPr-CH<sub>3</sub>*), 26.1 (*iPr-CH<sub>3</sub>*), 26.8 (*iPr-CH<sub>3</sub>*), 28.7 (*iPr-CH*), 29.2 (*iPr-CH*), 124.1 (*NCCN*), 124.4 (*Dipp-m-CH*), 125.8 (*NCCN*), 127.5 (*Ph-p/m-CH*), 128.2 (*Ph-p/m-CH*), 131.3 (*Dipp-p-CH*), 132.0 (*Dipp-p-CH*), 132.5 (*Dipp-i-C*), 133.3 (*Dipp-i-C*), 137.2 (*Ph-o-CH*), 141.7 (*Ph-i-C*), 145.6 (*Dipp-o-C*), 146.8 (*Dipp-o-C*), 162.1 (*NCN*). **Elemental analysis** (%) calcd. for C<sub>33</sub>H<sub>41</sub>Cl<sub>2</sub>N<sub>2</sub>Sb [658.37 g/mol]: C, 60.20; H, 6.28; N, 4.26; found: C, 61.73; H, 6.53; N, 3.86. **IR** ([cm<sup>-1</sup>]): 3243 (vw), 3159 (vw), 3123 (w), 3080 (w), 3031 (vw), 2965 (s), 2929 (m), 2870 (w), 1714 (vw), 1588 (m), 1538 (m), 1463 (m), 1440 (w), 1417 (m), 1385 (m), 1363 (m), 1328 (w), 1309 (w), 1256 (m), 1205 (w), 1182 (vw), 1146 (w), 1116 (m), 1101 (m), 1060 (m), 1043 (w), 1022 (w), 949 (w), 934 (w), 884 (vw), 864 (vw), 828 (vw), 802 (s), 769 (m), 756 (vs), 705 (s), 682 (w), 630 (w), 580 (vw), 570 (vw), 543 (vw), 518 (vw), 507 (vw), 483 (vw), 459 (w), 438 (w), 415 (vw).

#### Mes<sub>2</sub>Im · SbCl<sub>2</sub>Ph (5d)

SbCl<sub>2</sub>Ph (300 mg, 1.11 mmol) was reacted with Mes<sub>2</sub>Im (339 mg, 1.11 mmol) to yield **5d** (439 mg, 0.76 mmol, 69%) as a colorless solid. Crystals of **5d** suitable for single crystal X-ray diffraction were grown by storing a saturated benzene solution at 6 °C.

<sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 1.92 (s<sub>br</sub>, 3 H, *Mes-p-CH<sub>3</sub>*), 2.02 (s<sub>br</sub>, 3 H, *Mes-p-CH<sub>3</sub>*), 2.15 (s<sub>br</sub>, 6 H, *Mes-o-CH<sub>3</sub>*), 2.42 (s<sub>br</sub>, 6 H, *Mes-o-CH<sub>3</sub>*), 5.84 (d<sub>br</sub>, 2 H, *CHCH*), 6.23 (s<sub>br</sub>, 2 H, *Mes-CH*), 6.74 (s<sub>br</sub>, 2 H, *Mes-CH*), 6.97 (m, 3 H, overlap of *Ph-p-CH* and *Ph-m-CH*), 8.66 (m, 2 H, *Ph-o-CH*). <sup>13</sup>C {<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 18.8 (*Mes-p-CH<sub>3</sub>*), 19.7 (*Mes-o-CH<sub>3</sub>*), 21.0 (*Mes-o-CH<sub>3</sub>*), 123.2 (*NCCN*), 124.1 (*NCCN*), 127.6 (*Ph-p/m-CH*), 129.1 (*Mes-m-CH*), 129.9 (*Mes-m-CH*), 132.9 (*Mes-o-C*), 135.7 (*Mes-p-C*), 136.4 (*Mes-p-C*), 137.0 (*Ph-o-CH*), 140.1 (*Mes-o-C*), 141.0 (*Ph-i-C*), 161.0 (*NCN*). **Elemental analysis** (%) calcd. for C<sub>27</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>2</sub>Sb [574.20 g/mol]: C, 56.48; H, 5.09; N, 4.88; found: C, 55.96; H, 5.05; N, 4.83. **IR** ([cm<sup>-1</sup>]): 3153 (w), 3128 (w), 3087 (vw), 3055 (w), 3045 (w), 2976 (w), 2919 (w), 2861 (w), 2736 (vw), 1820 (vw), 1765 (vw), 1727 (vw), 1698 (vw), 1608 (m), 1576 (w), 1556 (w), 1478 (s), 1464 (m), 1429 (m), 1413 (m), 1378 (m), 1299 (m), 1230 (s), 1195 (w), 1168 (w), 1157 (vw), 1120 (m), 1095 (w), 1056 (m), 1038 (m), 998 (w), 976 (vw), 931 (m), 901 (w), 880 (vw), 863 (m), 847 (s), 759 (s), 728 (vs), 697 (m), 690 (s), 670 (vw), 641 (w), 593 (w), 577 (w), 565 (w), 500 (vw), 480 (w), 449 (m), 421 (vw).

#### cAAC<sup>Me</sup> · SbCl<sub>2</sub>Ph (5e)

SbCl<sub>2</sub>Ph (100 mg, 371 μmol) was reacted with cAAC<sup>Me</sup> (106 mg, 371 μmol) to give **5e** (169 mg, 304 μmol, 82%) as a colorless solid. Crystals of **5e** suitable for single crystal X-ray diffraction were grown by storing a saturated benzene solution at room temperature.

<sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 1.04 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, *iPr-CH<sub>3</sub>*), 1.12 (s, 6 H, *NC(CH<sub>3</sub>)<sub>2</sub>*), 1.32 (s, 2 H, *CH<sub>2</sub>*), 1.45 (s, 6 H *NCC*

(*CH<sub>3</sub>)<sub>2</sub>*), 1.72 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, *iPr-CH<sub>3</sub>*), 3.25 (sept, 2 H, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, *iPr-CH*), 7.10 (m, 3 H, overlap of *Dipp-m-CH* and *Ph-p-CH*), 7.15 (t<sub>br</sub>, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, *Ph-p-CH*), 7.32 (t<sub>br</sub>, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, *Ph-m-CH*), 9.27 (br, 2 H, *Ph-o-CH*). <sup>13</sup>C {<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 26.1 (*iPr-CH<sub>3</sub>*), 27.3 (*iPr-CH<sub>3</sub>*), 27.7 (*NC(CH<sub>3</sub>)<sub>2</sub>*), 29.2 (*iPr-CH*), 31.0 (*NCC(CH<sub>3</sub>)<sub>2</sub>*), 51.2 (*CH<sub>2</sub>*), 59.9 (*NC(CH<sub>3</sub>)<sub>2</sub>*), 82.4 (*NCC(CH<sub>3</sub>)<sub>2</sub>*), 126.4 (*Dipp-m-CH*), 128.8 (*Ph-m-CH*), 129.6 (*Dipp-p-CH*), 131.3 (*Ph-p-CH*), 133.7 (*Dipp-i-C*), 138.1 (*Ph-o-CH*), 144.2 (*Ph-i-C*), 146.8 (*Dipp-o-C*), 225.8 (*NCSb*). **Elemental analysis** (%) calcd. for C<sub>26</sub>H<sub>36</sub>Cl<sub>2</sub>NSb [555.24 g/mol]: C, 56.24; H, 6.54; N, 2.77; found: C, 55.13; H, 6.63; N, 2.59. **IR** ([cm<sup>-1</sup>]): 3148 (vw), 2971 (m), 2930 (w), 2869 (vw), 1644 (vw), 1587 (vw), 1513 (m), 1468 (m), 1456 (m), 1431 (m), 1392 (m), 1378 (w), 1366 (m), 1347 (w), 1318 (w), 1266 (w), 1222 (vw), 1205 (w), 1183 (m), 1158 (w), 1129 (m), 1105 (w), 1057 (m), 1019 (vw), 999 (w), 973 (vw), 927 (w), 877 (vw), 861 (vw), 826 (vw), 808 (s), 771 (s), 743 (vs), 696 (s), 648 (vw), 608 (w), 591 (vw), 562 (w), 549 (vw), 492 (w), 456 (m), 433 (vw).

#### Me<sub>2</sub>Im<sup>Me</sup> · SbCl<sub>2</sub>Mes (6a)

SbCl<sub>2</sub>Mes (225 mg, 722 μmol) was reacted with Me<sub>2</sub>Im<sup>Me</sup> (89.6 mg, 722 μmol). Recrystallization by diffusion of *n*-hexane into a dichloromethane solution of the crude product yielded **6a** (249 mg, 506 μmol, 70%) as colorless crystals. Crystals of **6a** suitable for single crystal X-ray diffraction were grown by layering a THF solution with *n*-hexane and storing at room temperature.

<sup>1</sup>H NMR (400.5 MHz, CDCl<sub>3</sub>, 298 K): δ = 2.23 (s, 6 H, *Mes-o-CH<sub>3</sub>*), 2.27 (s, 3 H, *Mes-p-CH<sub>3</sub>*), 2.65 (s<sub>br</sub>, 6 H, *NCCH<sub>3</sub>*), 3.90 (s<sub>br</sub>, 6 H, *NCH<sub>3</sub>*), 6.94 (s, 2 H, *Mes-CH*). <sup>13</sup>C {<sup>1</sup>H} NMR (100.7 MHz, CDCl<sub>3</sub>, 298 K): δ = 9.3 (*Mes-o-CH<sub>3</sub>*), 21.1 (*Mes-p-CH<sub>3</sub>*), 24.8 (*NCCH<sub>3</sub>*), 36.5 (*NCH<sub>3</sub>*), 128.2 (*Mes-p-C*), 130.0 (*Mes-m-CH*), 139.9 (*Mes-o-C*), 143.2 (*Mes-i-C*), 144.2 (*NCCN*), 155.7 (*NCN*). **Elemental analysis** (%) calcd. for C<sub>16</sub>H<sub>23</sub>Cl<sub>2</sub>N<sub>2</sub>Sb [436.03 g/mol]: C, 44.07; H, 5.32; N, 6.42; found: C, 43.70; H, 5.33; N, 6.35. **IR** ([cm<sup>-1</sup>]): 3047 (vw), 2986 (vw), 2955 (w), 2919 (m), 2860 (vw), 2736 (vw), 1770 (vw), 1644 (m), 1596 (w), 1555 (w), 1473 (s), 1436 (vs), 1402 (m), 1393 (m), 1385 (m), 1371 (s), 1291 (m), 1262 (w), 1228 (m), 1112 (w), 1057 (w), 1033 (m), 924 (vw), 906 (w), 870 (s), 845 (s), 802 (w), 743 (m), 708 (m), 660 (vw), 623 (vw), 583 (w), 569 (m), 552 (m), 541 (w), 498 (vw).

#### *iPr*<sub>2</sub>Im<sup>Me</sup> · SbCl<sub>2</sub>Mes (6b)

SbCl<sub>2</sub>Mes (800 mg, 2.57 mmol) was reacted with *iPr*<sub>2</sub>Im<sup>Me</sup> (463 mg, 2.57 mmol) to yield **6b** (960 mg, 1.95 mmol, 76%) as a colorless solid. Crystals of **6b** suitable for single crystal X-ray diffraction were grown by storing a saturated benzene solution at room temperature.

<sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 1.22 (d, 12 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr-CH<sub>3</sub>*), 1.44 (s, 6 H, *Mes-o-CH<sub>3</sub>*), 2.13 (s, 3 H, *Mes-p-CH<sub>3</sub>*), 2.92 (s<sub>br</sub>, 6 H, *Mes-o-CH<sub>3</sub>*), 5.55 (br, 2 H, *iPr-CH*), 6.84 (s<sub>br</sub>, 2 H, *Mes-CH*). <sup>13</sup>C {<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 10.1 (*NCCH<sub>3</sub>*), 21.0 (*Mes-p-CH<sub>3</sub>*), 22.0 (*iPr-CH<sub>3</sub>*), 27.1 (*Mes-o-CH<sub>3</sub>*), 54.7 (*iPr-CH*), 128.4 (*NCCN*), 130.1 (*Mes-m-CH*), 139.4 (*Mes-p-C*), 144.6 (*Mes-i-C*), 145.3 (*Mes-o-C*), 158.4 (*NCN*). **Elemental analysis** (%) calcd. for C<sub>20</sub>H<sub>31</sub>Cl<sub>2</sub>N<sub>2</sub>Sb [492.14 g/mol]: C, 48.81; H, 6.35; N, 5.69; found: C, 48.46; H, 6.28; N, 5.54. **IR** ([cm<sup>-1</sup>]): 3010 (w), 2979 (m), 2945 (m), 2926 (m), 2882 (w), 2732 (vw), 1623 (w), 1595 (w), 1552 (w), 1448 (s), 1438 (s), 1381 (vs), 1372 (vs), 1345 (m), 1290 (w), 1237 (w), 1205 (m), 1167 (w), 1138 (w), 1110 (m), 1073 (vw), 1026 (m), 1004 (vw), 974 (vw), 952 (vw), 937 (vw), 898 (w), 886 (vw), 858 (m), 760 (w), 747 (m), 706 (w), 688 (w), 648 (vw), 579 (w), 548 (m), 540 (w), 497 (vw), 466 (vw), 430 (w), 411 (vw).



**Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Mes (6c)**

SbCl<sub>2</sub>Mes (666 mg, 2.57 mmol) was reacted with Dipp<sub>2</sub>Im (830 mg, 2.57 mmol) to yield **6c** (1.10 g, 1.43 mmol, 67%) as a colorless solid.

<sup>1</sup>H NMR (400.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 0.94 (d, 12 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *i*Pr-CH<sub>3</sub>), 1.26 (d, 12 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *i*Pr-CH<sub>3</sub>), 1.98 (s, 3 H, Mes-*p*-CH<sub>3</sub>), 2.37 (s, 6 H, Mes-*o*-CH<sub>3</sub>), 2.92 (sept, 4 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *i*Pr-CH), 6.54 (s, 2 H, CHCH), 6.56 (s, 2 H, Mes-*m*-CH), 7.04 (d, 4 H, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, Dipp-*m*-CH), 7.20 (t, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, Dipp-*p*-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (100.7 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 21.0 (Mes-*p*-CH<sub>3</sub>), 22.8 (*i*Pr-CH<sub>3</sub>), 23.1 (Mes-*o*-CH<sub>3</sub>), 26.3 (*i*Pr-CH<sub>3</sub>), 29.1 (*i*Pr-CH), 124.6 (Dipp-*m*-CH), 124.9 (CHCH), 130.3 (Mes-*m*-CH), 131.2 (Dipp-*p*-CH), 135.0 (Dipp-*i*-C)\*, 138.9 (Mes-*p*-C)\*, 143.6 (Mes-*o*-C), 146.4 (Dipp-*o*-C), 150.5 (Mes-*i*-C)\*. The resonances at 135.0 ppm, 138.9 ppm and 150.5 ppm could not be observed in the <sup>13</sup>C{<sup>1</sup>H} NMR Spektrum but via <sup>13</sup>C{<sup>1</sup>H} HMBC NMR. No Signal was detected for (NCN). **Elemental analysis** (%) calcd. for C<sub>36</sub>H<sub>47</sub>Cl<sub>2</sub>N<sub>2</sub>Sb [700.45 g/mol]: C, 61.73; H, 6.76; N, 4.00; found: C, 61.31; H, 6.71; N, 3.82. IR ([cm<sup>-1</sup>]): 3163 (vw), 3059 (vw), 2961 (m), 2925 (w), 2864 (w), 1596 (w), 1556 (w), 1538 (w), 1462 (m), 1456 (m), 1442 (m), 1386 (m), 1361 (w), 1323 (w), 1291 (w), 1275 (w), 1256 (w), 1202 (w), 1179 (w), 1148 (vw), 1114 (w), 1088 (m), 1058 (m), 1036 (m), 935 (w), 884 (vw), 845 (w), 808 (m), 756 (s), 702 (vw), 682 (vs), 636 (w), 580 (w), 540 (w), 519 (vw), 456 (w), 441 (w), 416 (w).

**Mes<sub>2</sub>Im·SbCl<sub>2</sub>Mes (6d)**

SbCl<sub>2</sub>Mes (100 mg, 321 μmol) was reacted with Mes<sub>2</sub>Im (97.6 mg, 321 μmol) to yield **6d** (151 mg, 245 μmol, 76%) as a colorless solid. Crystals of **6d** suitable for single crystal X-ray diffraction were grown by storing a saturated benzene solution at room temperature.

<sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 2.00 (s<sub>br</sub>, 12 H, Mes-*o*-CH<sub>3</sub>), 2.21 (br, 9 H, overlap of Sb-Mes-*p*-CH<sub>3</sub> and Mes-*p*-CH<sub>3</sub>), 2.36 (s<sub>br</sub>, 6 H, Mes-*o*-CH<sub>3</sub>), 6.55 (s<sub>br</sub>, 2 H, Sb-Mes-CH), 6.88 (s<sub>br</sub>, 4 H, Mes-CH), 7.13 (s<sub>br</sub>, 2 H, CHCH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 18.1 (Mes-*o*-CH<sub>3</sub>), 21.1 (Sb-Mes-*o*-CH<sub>3</sub>), 21.3 (Mes-*p*-CH<sub>3</sub>), 23.0, (Sb-Mes-*p*-CH<sub>3</sub>), 124.4 (NCCN), 129.7 (Mes-CH), 129.8 (Sb-Mes-*o*-C), 130.1 (Sb-Mes-CH), 133.9 (Mes-*o*-C), 135.2 (Mes-*i*-C), 138.8 (Sb-Mes-*i*-C), 140.4 (Mes-*p*-C), 145.7 (Sb-Mes-*p*-C), 174.0 (NCN). **Elemental analysis** (%) calcd. for C<sub>30</sub>H<sub>35</sub>Cl<sub>2</sub>N<sub>2</sub>Sb [616.28 g/mol]: C, 58.47; H, 5.72; N, 4.55; found: C, 57.09; H, 5.92; N, 4.47. After several attempts this is the best result so far. IR ([cm<sup>-1</sup>]): 3109 (vw), 3067 (vw) 3013 (w), 2947 (m), 2915 (m), 2858 (m), 2736 (vw), 1597 (w) 1538 (s) 1480 (s), 1444 (s), 1405 (m), 1377 (m), 1336 (vw), 1319 (vw), 1288 (w), 1258 (vw), 1227 (s), 1161 (w), 1092 (w), 1058 (m), 1032 (m), 966 (vw), 930 (w), 840 (vs), 754 (m), 724 (m), 702 (s), 674 (vs), 569 (vs), 550 (m), 542 (m), 498 (vw), 453 (vw).

**<sup>o</sup>Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Mes (7)**

Procedure A: A solution of **6c** (100 mg, 143 μmol) in benzene (5 mL) was refluxed for 24 h. After cooling to room temperature all volatiles were removed *in vacuo* to yield **7** (98.3 mg, 140 μmol, 98%) as a colorless solid. Procedure B: A solution of SbCl<sub>2</sub>Mes (225 mg, 722 μmol) and Dipp<sub>2</sub>Im (280 mg, 722 μmol, 1.0 eq) in benzene (5 mL) was refluxed for 24 hours. After cooling to room temperature *n*-hexane (7 mL) was added. The resulting precipitate was collected by filtration, washed with *n*-hexane (2×4 mL) and dried *in vacuo* to give **7** (451 mg, 644 μmol, 89%) as a colorless solid. Crystals of **7** suitable for single crystal X-ray diffraction were grown by diffusion of *n*-pentane into a dichloromethane solution and storing at 12 °C.

<sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 1.14 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 1.22 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 1.26 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 1.50 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 2.24 (s, 3 H, Mes-*p*-CH<sub>3</sub>), 2.54 (sept, 2 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH), 2.69 (s, 6 H, Mes-*o*-CH<sub>3</sub>), 2.80 (sept, 2 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH), 6.89 (s<sub>br</sub>, 1 H, Mes-CH), 7.37 (d, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2 H, Dipp-*m*-CH), 7.41 (d, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, Dipp-*m*-CH), 7.58 (t, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, Dipp-*p*-CH), 7.61 (t, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, Dipp-*p*-CH), 7.87 (m, 1 H, SbCCH), 8.08 (m, 1 H, NCHN). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 21.0 (Mes-*p*-CH<sub>3</sub>), 22.5 (*i*Pr-CH<sub>3</sub>), 24.4 (*i*Pr-CH<sub>3</sub>), 24.5 (*i*Pr-CH<sub>3</sub>), 24.8 (Mes-*o*-CH<sub>3</sub>), 26.9 (*i*Pr-CH<sub>3</sub>), 29.3 (*i*Pr-CH), 29.6 (*i*Pr-CH), 124.9 (Dipp-*m*-CH), 125.1 (Dipp-*m*-CH), 129.8 (Mes-CH), 130.0 (Dipp-*i*-C), 131.5 (Dipp-*i*-C), 132.1 (Dipp-*p*-CH), 132.3 (Dipp-*p*-CH), 135.2 (NCHN), 136.4 (SbCCHN), 139.1, (Mes-*o*-C), 143.4 (Mes-*p*-C), 145.8 (Dipp-*p*-CH), 146.3 (Dipp-*o*-C), 146.5 (NCSb), 147.6 (Mes-*i*-C). **Elemental analysis** (%) calcd. for C<sub>36</sub>H<sub>47</sub>Cl<sub>2</sub>N<sub>2</sub>Sb [700.45 g/mol]: C, 61.73; H, 6.76; N, 4.00; found: C, 61.74; H, 6.52; N, 4.00. IR ([cm<sup>-1</sup>]): 3148 (vw), 3090 (w), 3060 (w), 3015 (vw), 2959 (s), 2925 (m), 2867 (m), 1707 (vw), 1660 (vw), 1597 (w), 1540 (m), 1488 (m), 1462 (s), 1442 (m), 1385 (m), 1364 (m), 1350 (w), 1327 (m), 1289 (w), 1275 (w), 1255 (w), 1199 (w), 1183 (m), 1147 (m), 1108 (s), 1058 (m), 1042 (m), 978 (w), 957 (vw), 935 (w), 922 (vw), 908 (vw), 858 (w), 841 (m), 802 (vs), 754 (vs), 703 (vw), 688 (w), 672 (m), 637 (vw), 580 (w), 540 (w), 518 (vw), 472 (vw), 451 (w), 438 (w), 420 (w).

**<sup>o</sup>Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Ph (8)**

Procedure A: A solution of **5c** (60 mg, 143 μmol) in benzene (5 mL) was refluxed for 24 h. After cooling to room temperature all volatiles were removed *in vacuo* to yield **8** (57.1 mg, 140 μmol, 95%) as a colorless solid. Procedure B: A solution of SbCl<sub>2</sub>Ph (70.0 mg, 259 μmol) and Dipp<sub>2</sub>Im (101 mg, 259 μmol, 1.0 eq) in benzene (5 mL) was refluxed for 24 h. After cooling to room temperature *n*-hexane (7 mL) was added. The resulting precipitate was collected by filtration, washed with *n*-hexane (2×4 mL) and dried *in vacuo* to yield **8** (147 mg, 223 μmol, 86%) as a colorless solid. Crystals of **8** suitable for single crystal X-ray diffraction were grown by diffusion of *n*-pentane into a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution at 12 °C.

<sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 1.11 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 1.20 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 1.21 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 1.49 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 2.45 (sept, 2 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH), 2.94 (sept, 2 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *i*Pr-CH), 7.22 (d, 1 H, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, SbCCH), 7.31 (m, 1 H, Ph-*p*-CH), 7.33 (d, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, Dipp-*m*-CH), 7.38 (m, 2 H, Ph-*m*-CH), 7.44 (d, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, Dipp-*m*-CH), 7.55 (t, 1 H, Dipp-*p*-CH), 7.64 (t, 1 H, Dipp-*p*-CH), 8.13 (d, 1 H, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, NCHN), 8.27 (m, 2 H, Ph-*o*-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 22.9 (*i*Pr-CH<sub>3</sub>), 24.3 (*i*Pr-CH<sub>3</sub>), 24.5 (*i*Pr-CH<sub>3</sub>), 26.9 (*i*Pr-CH<sub>3</sub>), 29.3 (*i*Pr-CH), 29.4 (*i*Pr-CH), 125.0 (Dipp-*m*-CH), 125.1 (Dipp-*m*-CH), 128.5 (Ph-*m*-CH), 129.1 (Ph-*p*-CH), 130.2 (Dipp-*i*-C), 131.5 (Dipp-*i*-C), 132.3 (Dipp-*p*-CH), 132.4 (Dipp-*p*-CH), 132.8 (NCHCSb), 135.7 (NCHN), 137.0 (Ph-*m*-CH), 145.7 (Dipp-*o*-C), 146.5 (Dipp-*o*-C), 148.1 (Ph-*i*-C), 151.1 (NCSb). **Elemental analysis** (%) calcd. for C<sub>33</sub>H<sub>41</sub>Cl<sub>2</sub>N<sub>2</sub>Sb [658.37 g/mol]: C, 60.20; H, 6.28; N, 4.26; found: C, 61.08; H, 7.02; N, 4.71. IR ([cm<sup>-1</sup>]): 3148 (vw), 3091 (w), 3062 (w), 3014 (vw), 2959 (s), 2925 (m), 2867 (m), 1714 (vw), 1661 (vw), 1598 (w), 1540 (m), 1488 (m), 1462 (s), 1442 (m), 1385 (m), 1364 (m), 1350 (w), 1327 (m), 1289 (w), 1275 (w), 1255 (w), 1199 (m), 1183 (m), 1147 (vw), 1108 (m), 1059 (s), 1042 (m), 978 (w), 957 (vw), 935 (w), 923 (vw), 908 (vw), 858 (w), 841 (m), 802 (vs), 754 (vs), 703 (vw), 688 (vw), 672 (m), 637 (vw), 581 (w), 540 (w), 517 (vw), 472 (vw), 452 (w), 437 (w), 420 (vw).

**[<sup>o</sup>Dipp]<sub>2</sub>Im·SbClMes][BF<sub>4</sub>] (9)**

A solution of **7** (225 mg, 321 μmol) and AgBF<sub>4</sub> (63.5 mg, 321 μmol, 1.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was stirred for 15 min. The resulting precipitate was collected by filtration and washed with dichloromethane (2×3 mL). All Volatiles were removed *in vacuo* to yield **9** (177 mg, 267 μmol, 83%) as a colorless solid. Crystals suitable for single crystal X-Ray diffraction were obtained by storing a concentrated dichloromethane solution at 6 °C.

<sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 1.03 (b, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *iPr*-CH<sub>3</sub>), 1.13 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *iPr*-CH<sub>3</sub>), 1.24 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *iPr*-CH<sub>3</sub>), 1.28 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *iPr*-CH<sub>3</sub>), 2.25 (s, 3 H, Mes-*p*-CH<sub>3</sub>), 2.33 (m, 8 H, overlap of Mes-*o*-CH<sub>3</sub> and *iPr*-CH), 2.43 (sept, 2 H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, *iPr*-CH), 6.92 (s, 2 H, Mes-CH), 7.36 (d, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, Dipp-*m*-CH), 7.40 (d, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, Dipp-*m*-CH), 7.64 (t, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, Dipp-*p*-CH), 7.65 (d, 1 H, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, NCHN), 7.66 (t, 1 H, Dipp-*p*-CH), 9.13 (d, 1 H, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, NCHCSb). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 21.3 (Mes-*p*-CH<sub>3</sub>), 21.7 (*iPr*-CH<sub>3</sub>), 23.9 (Mes-*o*-CH<sub>3</sub>), 24.27 (*iPr*-CH<sub>3</sub>), 24.32 (*iPr*-CH<sub>3</sub>), 26.3 (*iPr*-CH<sub>3</sub>), 29.6 (*iPr*-CH), 29.9 (*iPr*-CH), 125.2 (Dipp-*m*-CH), 125.6 (Dipp-*m*-CH), 129.9 (Dipp-*i*-C), 130.2 (Dipp-*i*-C), 130.8 (Mes-*m*-CH), 132.7 (Dipp-*p*-CH), 133.1 (NCHCSb), 133.5 (Dipp-*p*-CH), 138.0 (Mes-*i*-C), 139.2 (NCSb), 141.2 (NCHN), 143.1 (Mes-*o*-C), 145.4 (Dipp-*o*-C), 145.5 (Dipp-*o*-C), 145.9 (Mes-*p*-C). **Elemental analysis** (%) calcd. for C<sub>36</sub>H<sub>47</sub>ClBF<sub>4</sub>N<sub>2</sub>Sb [751.80 g/mol]: C, 57.51; H, 6.30; N, 4.72; found: C, 57.16; H, 6.69; N, 3.91. **IR** ([cm<sup>-1</sup>]): 3116 (w), 3067 (vw), 3024 (vw), 2965 (m), 2928 (m), 2870 (w), 1597 (w), 1540 (m), 1496 (w), 1462 (m), 1387 (w), 1366 (m), 1330 (m), 1288 (w), 1256 (w), 1207 (m), 1185 (m), 1082 (s), 1057 (s), 1037 (s), 1008 (vs), 978 (m), 958 (m), 937 (m), 884 (w), 847 (m), 802 (s), 756 (s), 732 (w), 703 (w), 671 (m), 636 (vw), 580 (w), 542 (w), 518 (m), 451 (w), 431 (w).

**[<sup>o</sup>Dipp]<sub>2</sub>Im·SbClMes][GaCl<sub>4</sub>] (10)**

A solution of **7** (100 mg, 143 μmol) and GaCl<sub>3</sub> (25.1 mg, 143 μmol, 1.0 eq) in dichloromethane (5 mL) was stirred for 24 h. All volatiles were removed *in vacuo* to yield **10** (114 mg, 130 μmol, 91%) as an off-white solid. Crystals suitable for single crystal X-Ray diffraction were obtained by storing a concentrated dichloromethane solution at 6 °C.

<sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 0.50 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH<sub>3</sub>), 1.05 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH<sub>3</sub>), 1.19 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH<sub>3</sub>), 1.25 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH<sub>3</sub>), 1.26 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH<sub>3</sub>), 1.28 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH<sub>3</sub>), 1.34 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH<sub>3</sub>), 1.49 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH<sub>3</sub>), 2.04 (sept, 1 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH), 2.26 (s, 3 H, Mes-*p*-CH<sub>3</sub>), 2.30 (s, 6 H, Mes-*o*-CH<sub>3</sub>), 2.31 (sept, 1 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH), 2.45 (sept, 1 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH), 2.51 (sept, 1 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, *iPr*-CH), 6.94 (s, 2 H, Mes-CH), 7.27 (dd, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, Dipp-*m*-CH), 7.45 (m, 2 H, Dipp-*m*-CH), 7.51 (dd, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, Dipp-*m*-CH), 7.67 (t, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, Dipp-*p*-CH), 7.70 (t, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, Dipp-*p*-CH), 7.72 (d, 1 H, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, NCHCSb), 8.68 (d, 1 H, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, NCHN). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 20.6 (*iPr*-CH<sub>3</sub>), 21.3 (Mes-*p*-CH<sub>3</sub>), 22.6 (*iPr*-CH<sub>3</sub>), 23.7 (Mes-*o*-CH<sub>3</sub>), 24.2 (*iPr*-CH<sub>3</sub>), 24.2 (*iPr*-CH<sub>3</sub>), 24.5 (*iPr*-CH<sub>3</sub>), 24.9 (*iPr*-CH<sub>3</sub>), 26.5 (*iPr*-CH<sub>3</sub>), 26.9 (*iPr*-CH<sub>3</sub>), 29.7 (*iPr*-CH), 29.9 (*iPr*-CH), 30.1 (*iPr*-CH), 125.5 (Dipp-*m*-CH), 125.6 (Dipp-*m*-CH), 125.9 (Dipp-*m*-CH), 126.1 (Dipp-*m*-CH), 129.5 (Dipp-*i*-C), 129.7 (Dipp-*i*-C), 131.0 (Mes-*m*-CH), 133.1 (NCHCSb), 133.2 (Dipp-*p*-CH), 134.0 (Dipp-*p*-CH), 136.8 (Mes-*i*-C), 139.4 (NCSb), 139.9 (NCHN), 143.7 (Mes-*o*-C), 145.2 (Dipp-*o*-C), 145.3 (Dipp-*o*-C), 145.5 (Dipp-*o*-C), 145.8 (Dipp-*o*-C), 146.0 (Mes-*p*-C). **Elemental analysis** (%) calcd. for C<sub>36</sub>H<sub>47</sub>Cl<sub>3</sub>GaN<sub>2</sub>Sb [876.52 g/mol]: C, 49.33; H, 5.41; N, 3.20; found: C, 48.63; H, 5.64; N, 3.34. **IR** ([cm<sup>-1</sup>]): 3148 (vw), 3111 (m), 3069 (vw), 3028 (vw), 2964 (s), 2928 (m), 2871 (m), 1715 (vw), 1660 (vw), 1596 (w), 1541 (m), 1501

(w), 1477 (w), 1463 (s), 1442 (s), 1389 (m), 1367 (m), 1351 (w), 1329 (m), 1289 (w), 1276 (w), 1256 (w), 1202 (m), 1182 (m), 1149 (vw), 1093 (m), 1070 (m), 1061 (m), 1034 (w), 959 (vw), 937 (w), 860 (s), 803 (vs), 755 (s), 705 (vw), 681 (vw), 670 (m), 638 (vw), 579 (w), 542 (m), 519 (vw), 493 (vw), 451 (vw), 435 (vw), 420 (w).

**Crystallographic Details**

Crystal data were collected on a Bruker X8 Apex-2 diffractometer with a CCD area detector and graphite monochromated Mo-Kα radiation or a Rigaku XtaLAB Synergy-DW diffractometer with an Hy-Pix-6000HE detector and monochromated CuKα radiation equipped with an Oxford Cryo 800 cooling unit. The Crystals were immersed in a film of perfluoropoly-ether oil on a glass fiber MicroMount™ (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>[26]</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>·SbCl<sub>3</sub> (4a):** C<sub>7</sub>H<sub>12</sub>Cl<sub>3</sub>N<sub>2</sub>Sb + (C<sub>6</sub>H<sub>6</sub>), M<sub>r</sub> = 430.39, T = 100(2) K, λ = 0.71073 Å, colorless block, 0.520 × 0.297 × 0.240 mm<sup>3</sup>, monoclinic space group C2/c, a = 15.0334(3) Å, b = 9.5157(2) Å, c = 23.6362(4) Å, α = 90°, β = 92.244(2)°, γ = 90°, V = 3378.64(11) Å<sup>3</sup>, Z = 8, ρ<sub>calcd</sub> = 1.692 Mg/m<sup>3</sup>, μ = 2.096 mm<sup>-1</sup>, F(000) = 1696, 33512 reflections, -18 ≤ h ≤ 18, -11 ≤ k ≤ 11, -29 ≤ l ≤ 29, 2.534° < θ < 26.020°, completeness 100.0%, 3311 independent reflections, 3248 reflections observed with [I > 2σ(I)], 176 parameters, 0 restraints, R indices (all data) R<sub>1</sub> = 0.0267, wR<sub>2</sub> = 0.0698, final R indices [I > 2σ(I)] R<sub>1</sub> = 0.0262, wR<sub>2</sub> = 0.0695, largest difference peak and hole 1.316 and -0.746 e Å<sup>-3</sup>, Goof = 1.178.

**Crystal Data for *iPr*<sub>2</sub>Im<sup>Me</sup>·SbCl<sub>3</sub> (4b):** 2(C<sub>11</sub>H<sub>20</sub>Cl<sub>3</sub>N<sub>2</sub>Sb<sub>2</sub>) + (C<sub>4</sub>H<sub>8</sub>O), M<sub>r</sub> = 888.90, T = 100(2) K, λ = 0.71073 Å, colorless block, 0.244 × 0.060 × 0.050 mm<sup>3</sup>, monoclinic space group C2/c, a = 16.0658(2) Å, b = 9.37880(10) Å, c = 24.9781(3) Å, α = 90°, β = 110.6610(10)°, γ = 90°, V = 3521.59(7) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.677 Mg/m<sup>3</sup>, μ = 16.561 mm<sup>-1</sup>, F(000) = 1776, 35265 reflections, -20 ≤ h ≤ 20, -11 ≤ k ≤ 10, -31 ≤ l ≤ 31, 3.783° < θ < 77.641°, completeness 99.5%, 3727 independent reflections, 3652 reflections observed with [I > 2σ(I)], 183 parameters, 0 restraints, R indices (all data) R<sub>1</sub> = 0.0221, wR<sub>2</sub> = 0.0565, final R indices [I > 2σ(I)] R<sub>1</sub> = 0.0216, wR<sub>2</sub> = 0.0562, largest difference peak and hole 0.663 and -0.457 e Å<sup>-3</sup>, Goof = 1.089.

**Crystal Data for Dipp<sub>2</sub>Im·SbCl<sub>3</sub> (4c):** C<sub>27</sub>H<sub>36</sub>Cl<sub>3</sub>N<sub>2</sub>Sb, M<sub>r</sub> = 616.68, T = 100(2) K, λ = 1.54184 Å, colorless block, 0.383 × 0.348 × 0.231 mm<sup>3</sup>, monoclinic space group P2<sub>1</sub>/n, a = 11.19460(10) Å, b = 13.80210(10) Å, c = 18.87190(10) Å, α = 90°, β = 104.7520(10)°, γ = 90°, V = 2819.76(4) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.453 Mg/m<sup>3</sup>, μ = 10.500 mm<sup>-1</sup>, F(000) = 1256, 47791 reflections, -13 ≤ h ≤ 14, -17 ≤ k ≤ 16, -23 ≤ l ≤ 23, 4.016° < θ < 77.029°, completeness 99.1%, 5922 independent reflections, 5881 reflections observed with [I > 2σ(I)], 331 parameters, 60 restraints, R indices (all data) R<sub>1</sub> = 0.0314, wR<sub>2</sub> = 0.0814, final R indices [I > 2σ(I)] R<sub>1</sub> = 0.0313, wR<sub>2</sub> = 0.0813, largest difference peak and hole 1.607 and -1.292 e Å<sup>-3</sup>, Goof = 0.991.

**Crystal Data for Mes<sub>2</sub>Im·SbCl<sub>3</sub> (4d):** C<sub>21</sub>H<sub>24</sub>Cl<sub>3</sub>N<sub>2</sub>Sb + 2(C<sub>6</sub>H<sub>6</sub>), M<sub>r</sub> = 688.75, T = 100(2) K, λ = 1.54184 Å, colorless block, 0.231 × 0.146 × 0.112 mm<sup>3</sup>, monoclinic space group P2<sub>1</sub>/n, a = 13.92890(10) Å, b = 18.03170(10) Å, c = 26.14180(10) Å, α = 90°, β = 101.7570(10)°, γ = 90°, V = 6428.07(7) Å<sup>3</sup>, Z = 8, ρ<sub>calcd</sub> = 1.423 Mg/m<sup>3</sup>, μ = 9.279 mm<sup>-1</sup>, F(000) = 2800, 133948 reflections, -17 ≤ h ≤ 17, -20 ≤ k ≤ 22, -33 ≤ l ≤ 31, 2.998° < θ < 77.643°, completeness 99.5%, 13614 in-

dependent reflections, 12862 reflections observed with  $[I > 2\sigma(I)]$ , 711 parameters, 362 restraints, R indices (all data)  $R_1 = 0.0349$ ,  $wR_2 = 0.0857$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0332$ ,  $wR_2 = 0.0847$ , largest difference peak and hole 1.483 and  $-0.683 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof} = 1.075$ .

**Crystal Data for cAAC<sup>Me</sup>·SbCl<sub>3</sub> (4e):** C<sub>20</sub>H<sub>31</sub>Cl<sub>3</sub>NSb,  $M_r = 513.56$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.152 \times 0.119 \times 0.057 \text{ mm}^3$ , monoclinic space group  $P2_1/c$ ,  $a = 10.30910(10) \text{ \AA}$ ,  $b = 14.01190(10) \text{ \AA}$ ,  $c = 15.36990(10) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 95.1610(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2211.18(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.543 \text{ Mg/m}^3$ ,  $\mu = 13.244 \text{ mm}^{-1}$ ,  $F(000) = 1040$ , 23699 reflections,  $-12 \leq h \leq 13$ ,  $-12 \leq k \leq 17$ ,  $-19 \leq l \leq 19$ ,  $4.278^\circ < \theta < 77.619^\circ$ , completeness 98.9%, 4650 independent reflections, 4415 reflections observed with  $[I > 2\sigma(I)]$ , 234 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0276$ ,  $wR_2 = 0.0690$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0263$ ,  $wR_2 = 0.0681$ , largest difference peak and hole 0.915 and  $-0.651 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof} = 1.077$ .

**Crystal Data for Me<sub>2</sub>Im<sup>Me</sup>·SbCl<sub>2</sub>Ph (5a):** C<sub>13</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>2</sub>Sb + 0.5(C<sub>6</sub>H<sub>6</sub>),  $M_r = 436.01$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.329 \times 0.252 \times 0.115 \text{ mm}^3$ , monoclinic space group  $P\bar{1} = 9.0918(2) \text{ \AA}$ ,  $b = 13.9305(2) \text{ \AA}$ ,  $c = 13.8844(2) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 94.4570(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1753.19(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.652 \text{ Mg/m}^3$ ,  $\mu = 15.236 \text{ mm}^{-1}$ ,  $F(000) = 872$ , 10037 reflections,  $-11 \leq h \leq 11$ ,  $-17 \leq k \leq 17$ ,  $-17 \leq l \leq 15$ ,  $5.824^\circ < \theta < 77.346^\circ$ , completeness 1.59/0.80, 2965 independent reflections, 2961 reflections observed with  $[I > 2\sigma(I)]$ , 197 parameters, 2 restraints, R indices (all data)  $R_1 = 0.0357$ ,  $wR_2 = 0.0947$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0357$ ,  $wR_2 = 0.0946$ , largest difference peak and hole 0.805 and  $-1.813 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof} = 1.068$ .

**Crystal Data for iPr<sub>2</sub>Im<sup>Me</sup>·SbCl<sub>2</sub>Ph (5b):** C<sub>17</sub>H<sub>25</sub>Cl<sub>2</sub>N<sub>2</sub>Sb,  $M_r = 450.04$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.178 \times 0.251 \times 0.054 \text{ mm}^3$ , Triclinic space group  $P\bar{1} = 9.49120(10) \text{ \AA}$ ,  $b = 10.31550(10) \text{ \AA}$ ,  $c = 11.26580(10) \text{ \AA}$ ,  $\alpha = 105.5560(10)^\circ$ ,  $\beta = 105.5400(10)^\circ$ ,  $\gamma = 105.2660(10)^\circ$ ,  $V = 954.673(18) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.566 \text{ Mg/m}^3$ ,  $\mu = 14.009 \text{ mm}^{-1}$ ,  $F(000) = 452$ , 20063 reflections,  $-11 \leq h \leq 12$ ,  $-13 \leq k \leq 11$ ,  $-14 \leq l \leq 13$ ,  $4.374^\circ < \theta < 77.558^\circ$ , completeness 98.8%, 3995 independent reflections, 3947 reflections observed with  $[I > 2\sigma(I)]$ , 205 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0240$ ,  $wR_2 = 0.0618$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0238$ ,  $wR_2 = 0.0617$ , largest difference peak and hole 1.051 and  $-1.058 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof} = 1.059$ .

**Crystal Data for Mes<sub>2</sub>Im·SbCl<sub>2</sub>Ph (5d):** C<sub>27</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>2</sub>Sb,  $M_r = 574.17$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.190 \times 0.246 \times 0.372 \text{ mm}^3$ , monoclinic space group  $P2_1/n$ ,  $a = 7.52380(10) \text{ \AA}$ ,  $b = 26.9401(4) \text{ \AA}$ ,  $c = 12.8135(2) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 100.0930(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2557.00(7) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.491 \text{ Mg/m}^3$ ,  $\mu = 10.602 \text{ mm}^{-1}$ ,  $F(000) = 1160$ , 27180 reflections,  $-9 \leq h \leq 9$ ,  $-34 \leq k \leq 31$ ,  $-16 \leq l \leq 16$ ,  $3.281^\circ < \theta < 77.541^\circ$ , completeness 98.5%, 5361 independent reflections, 5016 reflections observed with  $[I > 2\sigma(I)]$ , 295 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0439$ ,  $wR_2 = 0.1156$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0419$ ,  $wR_2 = 0.1134$ , largest difference peak and hole 1.415 and  $-0.961 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof} = 1.076$ .

**Crystal Data for cAAC<sup>Me</sup>·SbCl<sub>2</sub>Ph (5e):** C<sub>26</sub>H<sub>36</sub>Cl<sub>2</sub>NSb,  $M_r = 555.21$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.118 \times 0.097 \times 0.037 \text{ mm}^3$ , monoclinic space group  $P2_1/n$ ,  $a = 10.12050(10) \text{ \AA}$ ,  $b = 18.1587(2) \text{ \AA}$ ,  $c = 13.7546(2) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 94.1680(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2521.07(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.463 \text{ Mg/m}^3$ ,  $\mu = 10.712 \text{ mm}^{-1}$ ,  $F(000) = 1136$ , 28215 reflections,  $-12 \leq h \leq 12$ ,  $-22 \leq k \leq 16$ ,  $-17 \leq l \leq 17$ ,  $4.039^\circ < \theta < 77.358^\circ$ , completeness 99.0%, 5296 independent reflections, 4814 reflections observed with  $[I > 2\sigma(I)]$ , 279 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0447$ ,  $wR_2 = 0.1122$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0400$ ,  $wR_2 = 0.1069$ , largest difference peak and hole 1.564 and  $-1.492 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof} = 1.076$ .

**Crystal Data for Me<sub>2</sub>Im<sup>Me</sup>·SbCl<sub>2</sub>Mes (6a):** C<sub>16</sub>H<sub>23</sub>Cl<sub>2</sub>N<sub>2</sub>Sb,  $M_r = 436.01$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.329 \times 0.252 \times$

$0.115 \text{ mm}^3$ , monoclinic space group  $Cc = 9.0918(2) \text{ \AA}$ ,  $b = 13.9305(2) \text{ \AA}$ ,  $c = 13.8844(2) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 94.4570(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1753.19(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.652 \text{ Mg/m}^3$ ,  $\mu = 15.236 \text{ mm}^{-1}$ ,  $F(000) = 872$ , 10037 reflections,  $-11 \leq h \leq 11$ ,  $-17 \leq k \leq 17$ ,  $-17 \leq l \leq 15$ ,  $5.824^\circ < \theta < 77.346^\circ$ , completeness 1.59/0.80, 2965 independent reflections, 2961 reflections observed with  $[I > 2\sigma(I)]$ , 197 parameters, 2 restraints, R indices (all data)  $R_1 = 0.0357$ ,  $wR_2 = 0.0947$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0357$ ,  $wR_2 = 0.0946$ , largest difference peak and hole 0.805 and  $-1.813 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof} = 1.068$ .

**Crystal Data for iPr<sub>2</sub>Im<sup>Me</sup>·SbCl<sub>2</sub>Mes (6b):** C<sub>20</sub>H<sub>31</sub>Cl<sub>2</sub>N<sub>2</sub>Sb + 1.5(C<sub>6</sub>H<sub>6</sub>),  $M_r = 609.28$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.309 \times 0.165 \times 0.127 \text{ mm}^3$ , triclinic space group  $P\bar{1} = 9.44150(10) \text{ \AA}$ ,  $b = 12.3204(2) \text{ \AA}$ ,  $c = 13.19960(10) \text{ \AA}$ ,  $\alpha = 90.5420(10)^\circ$ ,  $\beta = 108.3490(10)^\circ$ ,  $\gamma = 101.8630(10)^\circ$ ,  $V = 1421.67(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.423 \text{ Mg/m}^3$ ,  $\mu = 9.560 \text{ mm}^{-1}$ ,  $F(000) = 626$ , 28857 reflections,  $-11 \leq h \leq 11$ ,  $-15 \leq k \leq 15$ ,  $-13 \leq l \leq 16$ ,  $3.539^\circ < \theta < 72.088^\circ$ , completeness 99.8%, 5588 independent reflections, 5480 reflections observed with  $[I > 2\sigma(I)]$ , 316 parameters, 2 restraints, R indices (all data)  $R_1 = 0.0224$ ,  $wR_2 = 0.0550$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0220$ ,  $wR_2 = 0.0547$ , largest difference peak and hole 0.419 and  $-0.581 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof} = 1.052$ .

**Crystal Data for Mes<sub>2</sub>Im·SbCl<sub>2</sub>Mes (6d):** C<sub>30</sub>H<sub>35</sub>Cl<sub>2</sub>N<sub>2</sub>Sb,  $M_r = 616.25$ ,  $T = 99.9(3) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.062 \times 0.028 \times 0.019 \text{ mm}^3$ , monoclinic space group  $P2_1/n$ ,  $a = 9.8157(3) \text{ \AA}$ ,  $b = 16.4193(6) \text{ \AA}$ ,  $c = 17.4309(5) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 98.206(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2780.52(16) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.472 \text{ Mg/m}^3$ ,  $\mu = 9.789 \text{ mm}^{-1}$ ,  $F(000) = 1256$ , 55045 reflections,  $-12 \leq h \leq 12$ ,  $-20 \leq k \leq 20$ ,  $-17 \leq l \leq 22$ ,  $3.716^\circ < \theta < 78.943^\circ$ , completeness 98.2%, 5897 independent reflections, 4893 reflections observed with  $[I > 2\sigma(I)]$ , 379 parameters, 1382 restraints, R indices (all data)  $R_1 = 0.1049$ ,  $wR_2 = 0.1999$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0894$ ,  $wR_2 = 0.1908$ , largest difference peak and hole 1.741 and  $-2.090 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof} = 1.078$ .

**Crystal Data for <sup>a</sup>Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Ph (7):** C<sub>36</sub>H<sub>47</sub>Cl<sub>2</sub>N<sub>2</sub>Sb + 1.5(C<sub>6</sub>H<sub>6</sub>),  $M_r = 2725.44$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.190 \times 0.246 \times 0.372 \text{ mm}^3$ , monoclinic space group  $C2/c$ ,  $a = 43.4925(2) \text{ \AA}$ ,  $b = 12.27340(10) \text{ \AA}$ ,  $c = 26.36400(10) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 106.8230(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 13470.84(15) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.344 \text{ Mg/m}^3$ ,  $\mu = 8.134 \text{ mm}^{-1}$ ,  $F(000) = 5608$ , 70498 reflections,  $-54 \leq h \leq 53$ ,  $-15 \leq k \leq 15$ ,  $-33 \leq l \leq 27$ ,  $2.122^\circ < \theta < 77.490^\circ$ , completeness 98.0%, 14058 independent reflections, 13750 reflections observed with  $[I > 2\sigma(I)]$ , 735 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0300$ ,  $wR_2 = 0.0773$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0294$ ,  $wR_2 = 0.0768$ , largest difference peak and hole 1.244 and  $-1.137 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof} = 1.055$ .

**Crystal Data for <sup>a</sup>Dipp<sub>2</sub>Im·SbCl<sub>2</sub>Mes (8):** 4(C<sub>33</sub>H<sub>41</sub>Cl<sub>2</sub>N<sub>2</sub>Sb) + (C<sub>7</sub>H<sub>9</sub>),  $M_r = 817.56$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.285 \times 0.139 \times 0.119 \text{ mm}^3$ , monoclinic space group  $P2_1/n$ ,  $a = 11.50670(10) \text{ \AA}$ ,  $b = 26.9756(2) \text{ \AA}$ ,  $c = 13.92100(10) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 100.7870(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 4244.73(6) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.279 \text{ Mg/m}^3$ ,  $\mu = 6.541 \text{ mm}^{-1}$ ,  $F(000) = 1700$ , 45286 reflections,  $-10 \leq h \leq 14$ ,  $-33 \leq k \leq 33$ ,  $-17 \leq l \leq 17$ ,  $3.277^\circ < \theta < 77.531^\circ$ , completeness 98.3%, 8882 independent reflections, 8244 reflections observed with  $[I > 2\sigma(I)]$ , 462 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0295$ ,  $wR_2 = 0.0706$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0273$ ,  $wR_2 = 0.0693$ , largest difference peak and hole 0.603 and  $-0.611 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof} = 1.073$ .

**Crystal Data for [<sup>a</sup>Dipp<sub>2</sub>Im·SbClMes][BF<sub>4</sub>] (9):** C<sub>36</sub>H<sub>47</sub>BClF<sub>4</sub>N<sub>2</sub>Sb,  $M_r = 751.76$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.327 \times 0.163 \times 0.110 \text{ mm}^3$ , monoclinic space group  $P2_1/c$ ,  $a = 12.61250(10) \text{ \AA}$ ,  $b = 15.55780(10) \text{ \AA}$ ,  $c = 18.8160(2) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 94.4600(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 3680.95(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.357 \text{ Mg/m}^3$ ,  $\mu = 6.997 \text{ mm}^{-1}$ ,  $F(000) = 1544$ , 38793 reflections,  $-15 \leq h \leq 15$ ,  $-17 \leq k \leq 19$ ,  $-23 \leq l \leq 21$ ,  $3.515^\circ < \theta < 77.496^\circ$ , completeness 98.2%,

7680 independent reflections, 7235 reflections observed with  $[I > 2\sigma(I)]$ , 417 parameters, 0 restraints, R indices (all data)  $R_1=0.0306$ ,  $wR_2=0.0812$ , final R indices  $[I > 2\sigma(I)]$   $R_1=0.0322$ ,  $wR_2=0.0823$ , largest difference peak and hole 0.770 and  $-0.738 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof}=1.069$ .

**Crystal Data for  $[\text{Dipp}_2\text{Im} \cdot \text{SbClMes}][\text{GaCl}_4]$  (10):**  $2(\text{C}_{36}\text{GaH}_{47}\text{Cl}_5\text{N}_2\text{Sb}) + (\text{CH}_2\text{Cl}_2)$ ,  $M_r=1837.90$ ,  $T=100(2) \text{ K}$ ,  $\lambda=1.54184 \text{ \AA}$ , colorless block,  $0.265 \times 0.149 \times 0.115 \text{ mm}^3$ , monoclinic space group  $P2_1/n$ ,  $a=11.06630(10) \text{ \AA}$ ,  $b=21.20200(10) \text{ \AA}$ ,  $c=17.98420(10) \text{ \AA}$ ,  $\alpha=90^\circ$ ,  $\beta=98.1800(10)^\circ$ ,  $\gamma=90^\circ$ ,  $V=4176.66(5) \text{ \AA}^3$ ,  $Z=2$ ,  $\rho_{\text{calcd}}=1.461 \text{ Mg/m}^3$ ,  $\mu=9.653 \text{ mm}^{-1}$ ,  $F(000)=1860$ , 85587 reflections,  $-14 \leq h \leq 13$ ,  $-26 \leq k \leq 20$ ,  $-22 \leq l \leq 22$ ,  $3.242^\circ < \theta < 77.625^\circ$ , completeness 99.3%, 8827 independent reflections, 8403 reflections observed with  $[I > 2\sigma(I)]$ , 445 parameters, 0 restraints, R indices (all data)  $R_1=0.0341$ ,  $wR_2=0.0854$ , final R indices  $[I > 2\sigma(I)]$   $R_1=0.0327$ ,  $wR_2=0.0844$ , largest difference peak and hole 1.079 and  $-0.882 \text{ e } \text{\AA}^{-3}$ ,  $\text{Goof}=1.062$ .

Deposition Numbers 2098205 (for 5a), 2098206 (for 4e), 2098207 (for 4a), 2098208 (for 5b), 2098209 (for 6a), 2098210 (for 4b), 2098211 (for 4c), 2098212 (for 4d), 2098213 (for 6b), 2098214 (for 5d), 2098215 (for 5e), 2098216 (for 7), 2098217 (for 6d), 2098218 (for 10), 2098219 (for 9), and 2098220 (for 8) 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).

## Acknowledgements

This work was supported by the Julius-Maximilians-Universität Würzburg and the Deutsche Forschungsgemeinschaft (RA720/13). Open Access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** Antimony · Cyclic (alkyl)(amino)carbenes · Lewis acid/base adducts · Main group element halides · N-Heterocyclic carbenes

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Manuscript received: July 21, 2021  
Revised manuscript received: August 12, 2021  
Accepted manuscript online: August 17, 2021