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Synthesis and Characterization of 1,3-Dihalogeno-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-*cyclo*-1,3-distiba-2,4-diazanes, $[X–Sb(\mu\text{-}NR)]_2$ (X = F, Cl, Br, and I)

Mathias Lehmann,[a] Axel Schulz,*[a,b] and Alexander Villinger[a]

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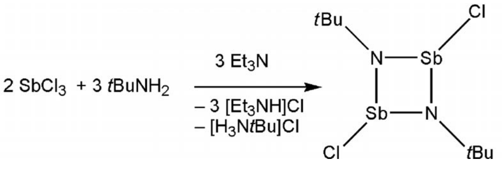
The whole series of four-membered rings of the type $[X–Sb(\mu\text{-}NR)]_2$, containing alternating antimony(III) and nitrogen centers, have been synthesized and fully characterized (X = halogen, R = supermesityl = 2,4,6-tri-*tert*-butylphenyl = Mes*) and represent rare examples of *cyclo*-distiba-diazanes. The synthesis was carried out starting from the triflate species $[TfO–Sb(\mu\text{-}NR)]_2$, which has been generated by utilizing a new synthetic route. By $Me_3Si–OTf$ elimination, reactions of $[TfO–Sb(\mu\text{-}NR)]_2$ with $Me_3Si–X$ yielded the halogen compounds $[X–Sb(\mu\text{-}NR)]_2$ with the exception of the fluorine species for which an iodine/fluorine exchange reaction with AgF was successfully applied. The structures of all starting materials, along the reaction pathway, and of all halogen species were determined by single-crystal X-ray diffraction. While for the compounds $[X–Sb(\mu\text{-}NR)]_2$ (X = OTf, Cl, Br, and I), a molecular structure with no significant intermolecular interactions was observed, the analogous fluorine species $[F–Sb(\mu\text{-}NR)]_2$ displays Sb···F van der Waals interactions between the centrosymmetric dimers, which leads to a chain-like structure in the crystal.

Introduction

Four-membered rings of the type $[X–Sb(\mu\text{-}NR)]_2$, containing alternating antimony(III) and nitrogen centers, are known as *cyclo*-1,3-distiba(III)-2,4-diazanes (X = halogen, R = organic group). Current interest in these ring systems has increased in the recent past, mainly because such species are good starting materials for polycyclic inorganic and organometallic compounds.[1–3] The *cyclo*-distiba(III)-diazane $[Cl–Sb(\mu\text{-}N\mathit{t}Bu)]_2$ was first generated by the reaction of $SbCl_3$ with $LiN(SiMe_3)\mathit{t}Bu$.[4] However, Stahl has shown that $[Cl–Sb(\mu\text{-}N\mathit{t}Bu)]_2$ can be prepared in a simple one-pot synthesis, as displayed in Scheme 1, and the structure was later determined by Chivers et al.[5,6] No other antimony compounds of the type $[X–Sb(\mu\text{-}NR)]_2$ (X = halogen) have been isolated to date.



Scheme 1. One-pot synthesis of $[Cl–Sb(\mu\text{-}N\mathit{t}Bu)]_2$.

Burford and co-workers have studied the stabilities of the monomeric species $R–N{=}E^{(III)}–X$ (E = P, As, Sb) with respect to the corresponding dimers by using Mes* groups (Mes* = 2,4,6-tri-*t*Bu-phenyl) at the N atom and a chloro or triflate (triflate = $CF_3SO_3^-$ = –OTf) substituent at the pnictogen atom.[7] Monomeric Mes*–N=P–Cl was first reported by Niecke et al.[8] While for the triflate derivative both the monomer and the dimer were isolated, it was shown that for the heavier arsenic and antimony analogs only the dimers were obtained in the solid state.[7b] In contrast to the antimony species, it has been proven by NMR studies that the arsenic dimer dissociates in solution, and a 1:1.7 equilibrium between the dimer and the monomer is observed at ambient temperature.[9]

We are interested in heterocycles of the type $[X–E(\mu\text{-}NR)]_2$ with a central E_2N_2 ring (E = element of group 15) as building blocks for cyclic cations.[10] Particularly useful for this purpose are dihalogeno-substituted species, since reaction with AgX (X = weakly coordinating anion)[11] or halogen abstraction by means of strong Lewis acids result in the formation of salts containing *cyclo*-dipnictadiazenium cations.[10] Here, we report on the synthesis and full characterization of 1,3-dihalogeno-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-*cyclo*-1,3-distiba-2,4-diazanes $[X–Sb(\mu\text{-}NMes^*)]_2$. Structural data of the full halogen series (X = F, Cl, Br, and I) are presented for the first time.

Results and Discussion

Depending on the reaction conditions and stoichiometry, the reaction of $Mes^*–NH_2$ and $SbCl_3$ in the presence of a base such as Et_3N, DBU (1,8-diazabicyclo[5.4.0]undec-7-

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[a] Universität Rostock, Institut für Chemie, Abteilung Anorganische Chemie,
Albert-Einstein-Strasse 3a, 18059 Rostock, Germany
E-mail: axel.schulz@uni-rostock.de
[b] Leibniz-Institut für Katalyse e.V. an der Universität Rostock,
Albert-Einstein-Strasse 29a, 18059 Rostock, Germany

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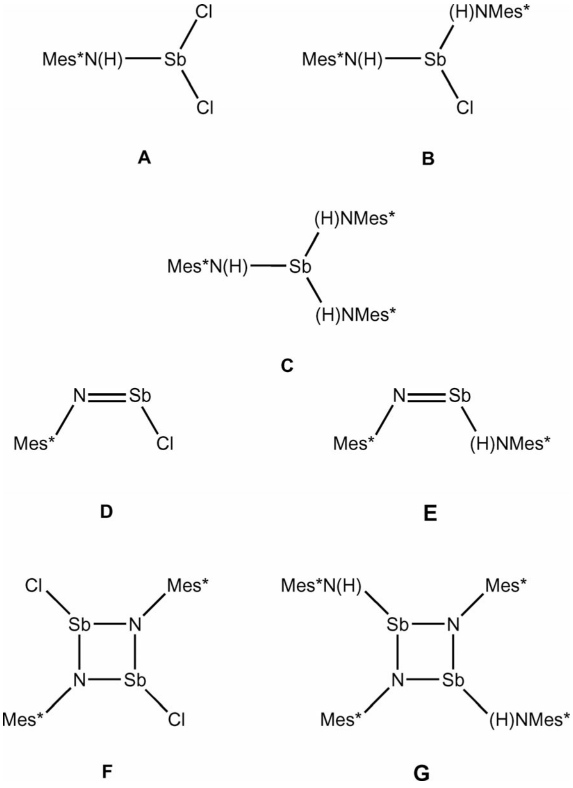
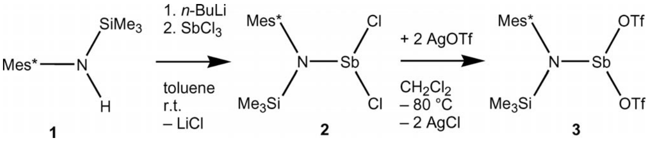
ene), and Mes*–NH_2 etc. does not result in the exclusive generation of a *cyclo*-distiba(III)-diazane, [Cl–Sb(μ-NMes*)]$_2$ (**F**), but instead mixtures of mono- and disubstituted products (**A** and **B**) along with traces of the desired *cyclo*-distiba(III)-diazanes (**F**) were observed as illustrated in Scheme 2.[7b,12] With a large excess of Mes*–NH_2, the triply substituted species **C** is formed. Hence, a new straightforward synthetic route to *cyclo*-distiba(III)-diazanes had to be found. The idea was to use the elimination of trimethylsilyl trifluoromethanesulfonate, Me_3Si–OTf, as driving force to introduce a halogen (X) according to R_2Sb–OTf + Me_3Si–X → Me_3Si–OTf + R_2Sb–X. For this reason [TfO–Sb(μ-NMes*)]$_2$ had to be isolated in good yields. However, the synthesis [addition of AgOTf to a mixture of $SbCl_3$ and LiN(H)Mes*], published by the Burford group,[7b] results in the formation of a complex mixture, from which [TfO–Sb(μ-NMes*)]$_2$ was isolated in small yields (14%), and thus is not suitable to for the development of this chemistry.



Scheme 2. Possible reaction products in the reaction of Mes*–NH_2 and $SbCl_3$ in the presence of a base.

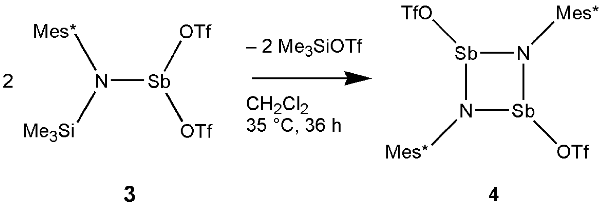
Synthesis of [TfO–Sb(μ-NMes*)]$_2$

Our new three-step synthesis of [TfO–Sb(μ-NMes*)]$_2$ starts from *N*-(2,4,6-tri-*tert*-butyl-phenyl)-*N*-(trimethylsilyl)-amine [Mes*N(H)$SiMe_3$, **1**], which is easily obtained from Mes*–NH_2, *n*BuLi, and Me_3Si–Cl.[13] Treatment of a toluene solution of **1** with *n*BuLi and $SbCl_3$ resulted in the formation of a brownish suspension. Filtration and removal of the solvent followed by re-crystallization from *n*-hexane led to the deposition of colorless crystals of Mes*N($SiMe_3$)-$SbCl_2$ (**2**) in good yields (86%) (Scheme 3). Compound **2** is thermally stable up to 116 °C (melting point) and then decomposes at this temperature. For this reason, it was not possible to generate [Cl–Sb(μ-NMes*)]$_2$ by means of base or thermally induced Me_3Si–Cl elimination.



Scheme 3. Synthesis of **2** and **3**.

The second reaction step involves the addition of Mes*N($SiMe_3$)$SbCl_2$ (**2**) to a stirred suspension of silver triflate AgOTf in CH_2Cl_2 at low temperature (–80 °C). By allowing this mixture to warm up to 0 °C for 30 min and to crystallize at –25 °C after concentration, crystalline **3** (95%, Scheme 3) was afforded. While **3** is thermally stable as a solid up to 90 °C (dec.), it slowly eliminates Me_3Si–OTf at slightly elevated temperatures (35 °C) in CH_2Cl_2, which results in the formation of dimeric [TfO–Sb(μ-NMes*)]$_2$ (**4**) in very good yields (94%) (Scheme 4). The intramolecular elimination of Me_3Si–OTf is easily followed by ^1H or ^{19}F NMR spectroscopy.

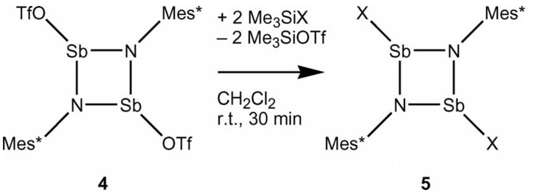


Scheme 4. Synthesis of **4**.

The major advantage of this three-step procedure is that all three reaction products (**2**, **3**, and **4**) along the reaction sequence can be purified easily and isolated in bulk as well as in good yields. All compounds have been fully characterized. Compounds **2** and **3** are stable for long periods when stored in a sealed tube and kept at low temperatures. As a consequence, [TfO–Sb(μ-NMes*)]$_2$ (**4**) can also be prepared in bulk and as a very pure crystalline orange solid, which allows follow-up chemistry. Interestingly, triflate-substituted *cyclo*-distiba(III)-diazane **4** was found to decompose at 187 °C, which is in contrast to the published decomposition temperature, $T_{dec} > 360$ °C.[7b]

Synthesis of [X–Sb(μ-NMes*)]$_2$ (X = F, Cl, Br, and I)

The halogen compounds [X–Sb(μ-NMes*)]$_2$ (X = Cl, Br, I) are prepared in high yields (Cl: 86, Br: 91, I: 95%) by reaction of **4** with Me_3Si–X in CH_2Cl_2 at ambient temperature for 30 min. Removal of the solvent and Me_3Si–OTf, followed by washing with *n*-hexane, afforded crystalline solids (Scheme 5). The fluorine-substituted species was prepared by an I/F exchange reaction by means of AgF, since the analogous reaction with Me$_3$Si–F could not be applied because of the very large Si–F bond dissociation energy. To a stirred suspension of [I–Sb(μ-NMes*)]$_2$ in THF was added finely powdered AgF at ambient temperature. Removal of the solvent and washing with *n*-hexane, followed by extraction with THF, afforded [F–Sb(μ-NMes*)]$_2$ in good yields (78 %).



4 **5**

Scheme 5. Synthesis of **5**Cl (X = Cl), **5**Br (X = Br) and **5**I (X = I).

All halogen compounds [X–Sb(μ-NMes*)]$_2$ (**5**F: X = F, **5**Cl: X = Cl, **5**Br: X = Br, **5**I: X = I) are moisture sensitive but can be handled in air for a short period. They are easily prepared in bulk and are stable under argon atmosphere over a long period when stored in a sealed tube at ambient temperature or in common organic solvents. All species are thermally stable up to over 170 °C ($T_{dec.}$ **5**F: 240, **5**Cl: 172, **5**Br: 173, **5**I: 173 °C). It should be noted that the color changes from pale yellow for **5**F through to yellow for **5**Cl to orange for **5**Br and **5**I.

The Raman data of all species considered show sharp bands in the expected region **5**F: 549/490, **5**Cl: 308/297, **5**Br: 252/234/211, **5**I: 169/148/122 cm^{-1}, which can be assigned to the stretching frequencies $\nu_{s,Sb-X}$ and $\nu_{as,Sb-X}$, respectively. Especially in the case of **5**Br and **5**I, the asymmetric stretching mode combines strongly with Sb–N deformation modes. Only very small deviations are observed in the ^{1}H and ^{13}C NMR spectra.

X-ray Structure Analysis

The solid-state structures of the starting materials **2**, **3**, and **4** are displayed in Figures 1, 2, and 4, respectively, along with selected bond lengths and angles. The structure of **4** is already known,[7b] but for comparison, we would like to include our structural data into the discussion. The molecular structures of halogen compounds [X–Sb(μ-NMes*)] are shown in Figure 5. Selected bond lengths and angles for **4** and **5**X are summarized in Table 1. Crystallographic details for all compounds are given in Tables 2 and 3. X-ray quality crystals of all species considered were selected in Kel-F-oil (Riedel deHaen) or Fomblin YR-1800 (Alfa Aesar) at ambient temperatures. All samples were cooled to 173(2) K during the measurement.

*Mes*N(SiMe$_3$)–SbCl$_2$ (2)*

Compound **2** (Figure 1) crystallizes in the monoclinic space group $P2_1/n$ with four formula units per cell. The structure consists of separated Mes*N(SiMe$_3$)–SbCl$_2$ molecules with no significant intermolecular contacts. Only weak Cl···HC interactions are found. The positions of the SbCl$_2$ and SiMe$_3$ moieties are disordered. In contrast to the trigonal-pyramidal antimony atom, the central nitrogen atom sits in a trigonal-planar environment (Σ<N = 359.2°) with an Si–N single bond of 1.737(3) and N–Sb bond of 2.056(3) Å [Σr_{cov}(Si–N) = 1.87 and Σr_{cov}(Sb–N) = 2.11 Å].[14] Since the phenyl ring of the Mes* group lies orthogonal to the plane composed of Si, N, and Sb atoms, there is no interaction between the nitrogen lone pair (which is localized on a p atomic orbital) and the π system of the phenyl ring (Figure 1). A look along the Sb–Si axis displays a staggered conformation for the SbCl$_2$/SiMe$_3$ groups. The Sb–Cl bond lengths between 2.359–2.369 Å are in the range expected for a typical Sb–Cl single bond [Σr_{cov}(Sb–Cl) = 2.4 Å].[14]

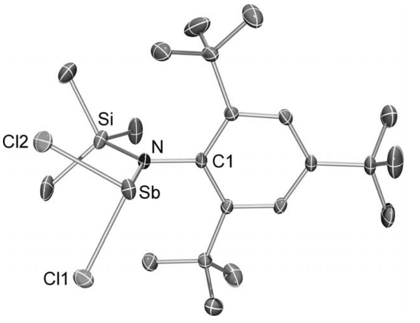


Figure 1. ORTEP drawing of the molecular structure of **2** in the crystal. Thermal ellipsoids with 50 % probability at 173 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Sb1–N 2.056(3), Sb1–Cl2 2.359(2), Sb1–Cl1 2.369(2), Si1–N 1.737(3), N–C1 1.476(4); N–Sb1–Cl2 99.18(7), N–Sb1–Cl1 103.58(7), Cl2–Sb1–Cl1 90.92(5), C1–N–Sb 105.3(2), C1–N–Si 127.2(2), Si–N–Sb 127.42(1).

*Mes*N(SiMe$_3$)–Sb(OTf)$_2$ (3)*

Compound **3** crystallizes in the space group $P2_1/n$ with four molecules per unit cell and one independent molecule per asymmetric unit (Figure 2). Upon exchanging Cl by OTf, the major structural features do not change much. The primary coordination sphere consists again of a trigonal-planar nitrogen atom and a pyramidal (O2,N)Sb core, how-

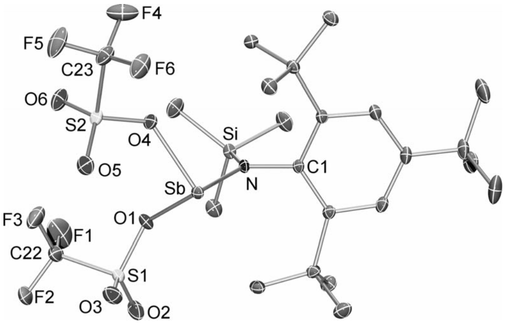


Figure 2. ORTEP drawing of the molecular structure of **3** in the crystal. Thermal ellipsoids with 50 % probability at 173 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Sb–N1 1.966(1), Sb–O1 2.089(1), Sb–O4 2.098(1), N1–C1 1.473(2), N1–Si 1.798(1), N1–Sb–O1 92.42(6); N1–Sb–O4 94.22(4), O1–Sb–O4 83.50(4), C1–N1–Si1 117.43(7), C1–N1–Sb1 113.42(8), Si1–N1–Sb1 128.76(6), S1–O1–Sb1 124.93(6), S2–O4–Sb1 123.41(6).

ever, with two secondary intermolecular interactions between the antimony and O3′ and O5′ atoms of an adjacent molecule, which forms a centrosymmetric dimer. The distances Sb···O3′ and Sb···O5′ of 3.314 and 3.379 Å, respectively, lie within the range of weak Sb···O van der Waals interactions [cf. Σr_{vdW}(Sb–O) = 3.7 Å].[14] Moreover, intramolecular Sb···O interactions are also found between Sb···O3 [3.295(2) Å] and Sb···O5 [3.200(2) Å], which finally lead to a distorted Sb_2O_4 octahedron (Figure 3). The Sb–O bond lengths are 2.089(1) (Sb–O1) and 2.098(1) Å (Sb–O4). While the Si–N bond length of 1.798(1) Å is slightly longer than that in **2**, the Sb–N distance decreases considerably [1.966(1) vs. 2.056(3) Å].

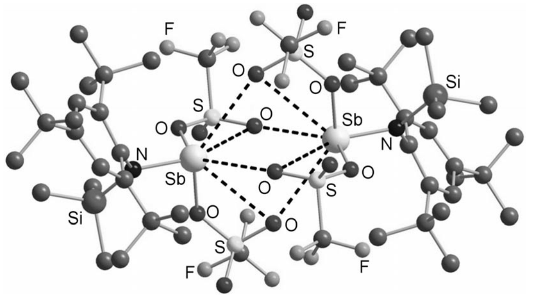


Figure 3. View of the centrosymmetric dimer **3** formed by intermolecular Sb···O contacts. Together with intramolecular Sb···O interactions, a distorted Sb_2O_4 octahedron is observed.

[X–Sb(μ-NMes)]$_2$ (X = OTf, F, Cl, Br, and I)*

While compounds **4**, **5**F and **5**Cl crystallize in the monoclinic space groups $P2_1/n$ and $P2_1/c$, with four molecules per unit cell, the triclinic space group $P\bar{1}$ is found for **5**Br and **5**I with two molecules in the unit cell. Noteworthy, only **5**Br crystallizes with one (disordered) solvent molecule, CH_2Cl_2, per unit cell.

The molecular structures of the triflate derivative of [X–Sb(μ-NMes*)] (Figure 4) and all the halogen derivatives (Figure 5) display *trans*-substituted centrosymmetric dimers with a planar Sb_2N_2 core protected by two bulky Mes* groups. Astonishingly, the metrical parameters of the Sb_2N_2 core such as the Sb···Sb and Sb–N distances or the N–Sb–N′ and Sb–N–Sb′ angles (Table 1) do not change along the series **5**F, **5**Cl, **5**Br, and **5**I and are in the same range found for the triflate species **4**. Two slightly different Sb–N bond lengths between 2.016 and 2.055 Å are found in the expected range for a typical single bond {cf. Σr_{cov}(Sb–N) = 2.11 Å, Table 1, 2.009(7)–2.022(7) Å in [Cl–Sb(μ-N*t*Bu)]$_2$}.[6,14] The Sb···Sb distances between 3.11–3.16 Å are only slightly longer than the sum of the covalent radii (2.82 Å) but significantly shorter than the sum of the van der Waals radii (4.4 Å).[14] Thus, strong van der Waals inter-

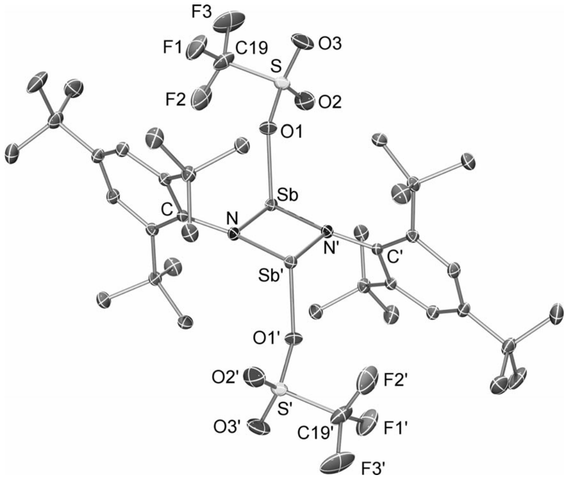


Figure 4. ORTEP drawing of the molecular structure of **4** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity). See the text for values of selected metrical parameters.

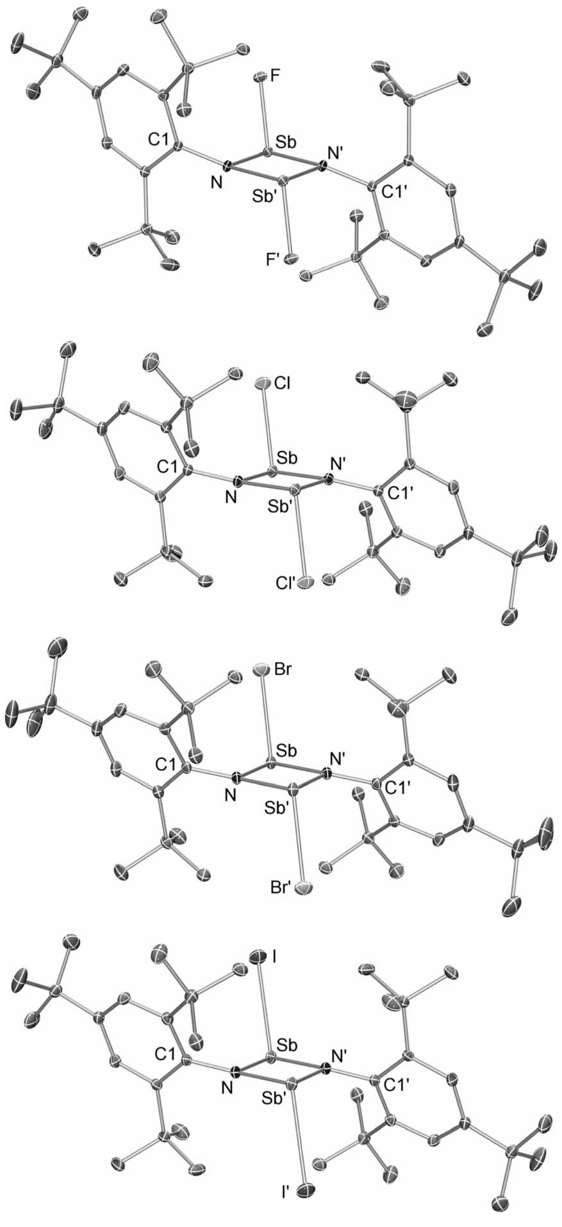


Figure 5. ORTEP drawing of the molecular structures of **5**F, **5**Cl, **5**Br, and **5**I in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity). See Table 1 for values of selected metrical parameters.

Table 1. Selected structural data of **4** and **5**X (X = F, Cl, Br, I); distances in Å, angles in °.

	4	**5**F	**5**Cl	**5**Br	**5**I
Sb–X	2.139(2)	1.974(1)	2.4143(6)	2.565(1)	2.797(1)
Sb–N	2.016(3)	2.038(2)	2.038(1)	2.034(2)	2.039(2)
Sb–N′	2.022(3)	2.055(2)	2.052(1)	2.052(2)	2.054(2)
C–N	1.449(4)	1.436(2)	1.442(1)	1.441(2)	1.432(2)
Sb···Sb	3.113(1)	3.154(1)	3.148(5)	3.148(1)	3.157(1)
N–Sb–N′	79.1(1)	79.18(7)	79.36(4)	79.18(5)	79.08(7)
Sb–N–Sb′	100.9(1)	100.82(7)	100.64(4)	100.82(5)	100.92(7)
X–Sb–N	90.3(1)	91.31(7)	95.85(3)	99.78(4)	101.59(4)
X–Sb–N′	96.8(1)	100.31(7)	102.11(3)	104.04(5)	107.83(4)
C–N–Sb	114.6(2)	113.29(1)	114.59(7)	116.6(1)	117.1(1)
C–N–Sb′	141.1(2)	140.64(1)	142.58(8)	140.6(1)	139.4(1)

actions across the ring can be assumed. Similar structural features are found in $[X–Sb(\mu\text{-}N\mathit{t}Bu)]_2$ (X = OTf, N_3, Cl).[5,6]

As expected the halogen–antimony bond lengths increase in the order, **5**F [1.974(1), cf. Σr_{cov}(Sb–F) = 2.05 Å] < **5**Cl [2.4143(6), cf. Σr_{cov}(Sb–Cl) = 2.40] < **5**Br [2.565(1), cf. Σr_{cov}(Sb–Br) = 2.55 Å] and **5I** [2.797(1), cf. Σr_{cov}(Sb–I) = 2.74 Å],[14] as well as the X–Sb–N angles, in accord with the VSEPR model. The two antimony atoms adopt a trigonal-pyramidal geometry with very small N–Sb–N angles of ca. 79° and Sb–N–Sb angles of ca. 100.1°. In contrast to species **2** and **3**, the nitrogen atoms also sit in a slightly trigonal-pyramidal environment with the two Mes* groups in a *trans* position.

Only weak CH···X and CH···Sb interactions are found between the [X–Sb(μ-NMes*)] dimers with one exception. In **5**F, these dimers interact further through a weak symmetric interaction involving both fluorine atoms [d(Sb′···F′′) = 2.706(2) Å; cf. Σr_{vdW}(Sb···F) = 3.7 Å],[14] as shown in Figure 6; if these interactions are considered, the overall Sb coordination geometry is strongly distorted tetragonal. Hence, the crystal structure of **5**F can be described as a weakly bound polymer of strongly bound centrosymmetric dimers. Such intermolecular interactions can be assumed to be responsible for the observed trend of the thermal stability, **5**F (240) >> **4** (187) > **5**Cl (172) ≈ **5**Br (173) ≈ **5I** (173 °C). The largest decomposition temperature is seen for **5**F, the species with the strongest intermolecular interactions.

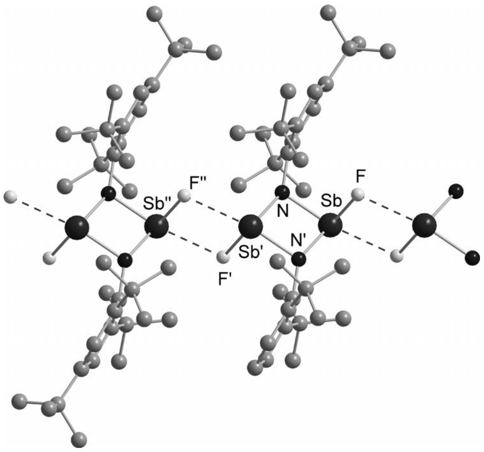


Figure 6. View of the molecular structure of **5**F showing the chains of dimers.

Conclusions

The reaction of Mes*N(H)$SiMe_3$ with $SbCl_3$ in the presence of 1 equiv. nBuLi has been studied, which results in the formation of Mes*N($SiMe_3$)$SbCl_2$ in high yields. Hitherto unknown Mes*N($SiMe_3$)$SbCl_2$ represents a very good precursor for further synthesis. For example, reaction of Mes*N($SiMe_3$)$SbCl_2$ with 2 equiv. AgOTf gave Mes*N($SiMe_3$)Sb$(OTf)_2$, which eliminates thermally Me_3Si–OTf to form $[TfO–Sb(\mu\text{-}NMes^*)]_2$. This synthetic route represents a novel pathway to $[TfO–Sb(\mu\text{-}NMes^*)]_2$ and the hitherto unknown halogen species, $[X–Sb(\mu\text{-}NMes^*)]_2$, which can easily be obtained by treatment of $[TfO–Sb(\mu\text{-}NMes^*)]_2$ with Me_3Si–X (X = Cl, Br, I) where Me_3Si–OTf is eliminated . The fluorine-substituted species $[F–Sb(\mu\text{-}NMes^*)]_2$ is generated by the reaction of $[I–Sb(\mu\text{-}NMes^*)]_2$ with AgF. Thus, it was possible for the first time to discuss the chemical and physical properties, as well as structural trends, for the whole halogen series.

Experimental Section

General Information: All manipulations were carried out under oxygen- and moisture-free conditions under argon by using standard Schlenk or drybox techniques. Dichloromethane was purified according to a literature procedure,[15] dried with P_4O_{10}, and freshly distilled prior to use. Tetrahydrofuran (THF), benzene, toluene, and ethyl ether were dried with Na/benzophenone and freshly distilled prior to use. N-hexane was dried with Na/benzophenone/tetraglyme and freshly distilled prior to use. Mes*N(H)$SiMe_3$ was prepared as described in a literature procedure.[13]

NMR: $^{13}C\{^1H\}$, ^{13}C DEPT, ^1H, $^{19}F\{^1H\}$, and ^{29}Si INEPT NMR spectra were obtained on a Bruker AVANCE 300 spectrometer and were referenced internally to the deuterated solvent (^{13}C, CD_2Cl_2: $\delta_{reference}$ = 54 ppm, C_6D_6: $\delta_{reference}$ = 128.0 ppm) or to protic impurities in the deuterated solvent (^1H, $CDHCl_2$: $\delta_{reference}$ = 5.31 ppm, C_6D_5H: $\delta_{reference}$ = 7.16 ppm). CD_2Cl_2 was dried with P_4O_{10}, and C_6D_6 was dried with Na/benzophenone. IR: A Nicolet 380 FTIR with a Smart Orbit ATR device was used. Raman: A Bruker VERTEX 70 FTIR with RAM II FT-Raman module, equipped with a

Nd:YAG laser (1064 nm) was used. CHN Analyses: An Analysator Flash EA 1112 from Thermo Quest or C/H/N/S-Mikronalysator TruSpec-932 from Leco was used. Melting Points: These are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate 20 °C/min (clearing-points are reported). MS: A Finnigan MAT 95-XP from Thermo Electron was used.

X-ray Structure Determination: X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) K during measurement. The data were collected on a Bruker Apex Kappa-II CCD diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073). The structures were solved by direct methods

Table 2. Crystallographic details of **2**, **3**, and **4**.

	2	**3**	**4**
Formula	$C_{21}H_{38}Cl_2NSbSi$	$C_{23}H_{38}F_6NO_6S_2SbSi$	$C_{36}H_{58}F_6N_2O_6S_2Sb_2$
F_w [g mol^{-1}]	525.26	752.5	1060.48
Color	colorless	colorless	yellow
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [Å]	12.767(6)	14.090(8)	11.453(6)
b [Å]	12.816(7)	16.142(9)	16.477(8)
c [Å]	15.170(7)	14.472(8)	11.961(6)
α [°]	90	90	90
β [°]	92.413(13)	90.318(11)	90.36(2)
γ [°]	90	90	90
V [Å^3]	2480(2)	3292(3)	2257(2)
Z	4	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.407	1.518	1.560
μ [mm^{-1}]	1.382	1.070	1.358
T [K]	173(2)	173(2)	173(2)
Measured reflections	24981	83570	39701
Independent reflections	6963	11713	5969
Reflections with $I > 2\sigma(I)$	5600	9679	5214
R_{int}	0.0238	0.0302	0.0341
$F(000)$	1080	1528	1072
R_1 $\{R[I > 2\sigma(I)]\}$	0.0457	0.0225	0.0330
wR_2 (F^2)	0.1109	0.0564	0.0746
GooF	1.093	1.018	1.123
No. parameters	313	373	263
CCDC	794567	794568	794569

Table 3. Crystallographic details of **5**X (X = F, Cl, Br, I).

	5F	**5**Cl	**5**Br	**5**I
Formula	$C_{36}H_{58}F_2N_2Sb_2$	$C_{36}H_{58}Cl_2N_2Sb_2$	$C_{36}H_{58}Br_2N_2Sb_2$, $C_2H_4Cl_4$	$C_{36}H_{58}I_2N_2Sb_2$
F_w [g mol^{-1}]	800.34	833.24	1092.02	1016.14
Color	colorless	yellow	orange	orange
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	6.150(3)	15.325(3)	10.079(5)	8.138(3)
b [Å]	29.67(2)	10.702(2)	10.588(6)	11.003(4)
c [Å]	10.034(5)	12.134(2)	13.116(6)	11.334(4)
α [°]	90	90	77.51(2)	76.70(1)
β [°]	100.67(2)	100.03(3)	69.55(2)	85.64(2)
γ [°]	90	90	61.62(2)	89.27(2)
V [Å^3]	1800(2)	1959.7(7)	1152(1)	984.8(7)
Z	2	2	1	1
$\rho_{calcd.}$ [g cm^{-3}]	1.477	1.412	1.574	1.713
μ [mm^{-1}]	1.537	1.540	3.166	2.964
T [K]	173(2)	173(2)	173(2)	173(2)
Measured reflections	24836	40560	29271	26036
Independent reflections	6423	8585	8289	7081
Reflections with $I > 2\sigma(I)$	4766	7068	6932	5668
R_{int}	0.0356	0.0266	0.0275	0.0323
$F(000)$	816	848	544	496
R_1 ($R[I > 2\sigma(I)]$)	0.0319	0.0235	0.0252	0.0260
wR_2 (F^2)	0.0602	0.0503	0.0583	0.0540
GooF	1.020	1.010	1.043	1.018
No. parameters	199	199	248	199
CCDC	794573	794570	794571	794572

(SHELXS-97)[16] and refined by full-matrix least-squares procedures (SHELXL-97)[17] Semiempirical absorption corrections were applied (SADABS).[18] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions by using a riding model. The crystallographic details of the compounds are presented in Tables 2 and 3. The CCDC numbers refer to the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[TfO–Sb(μ-NMes*)]$_2$ (4): A solution of Mes*N(SiMe$_3$)–Sb(OTf)$_2$ (**2**) (1.51 g, 2 mmol) in CH_2Cl_2 (25 mL) was warmed at 35 °C for 36 h, which resulted in the deposition of orange crystals. The dark orange supernatant was transferred by syringe, concentrated to approximately 5 mL, and stored at –25 °C for several hours, which again resulted in the deposition of orange crystals. Drying of the combined crystalline fractions in vacuo yielded 1.01 g (0.94 mmol, 94%) of **4** as orange crystals. Mp. 187 °C (dec.). $C_{36}H_{58}F_6N_2O_6S_2Sb_2$ (1060.48): calcd. C 43.04, H 5.51, N 2.64; found C 43.31, H 5.91, N 2.48. ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): 1.29 (s, 18 H, *p*-*t*Bu), 1.64 (s, 36 H, *o*-*t*Bu), 7.41 (s, 4 H, C*H*) ppm. ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.48 MHz): 31.57 [*p*-C(*C*H$_3$)$_3$], 34.94 [*p*-*C*(CH$_3$)$_3$], 35.49 [*o*-C(*C*H$_3$)$_3$], 37.39 [*o*-*C*(CH$_3$)$_3$], 118.97 (q, *C*F$_3$), 124.68 (*C*H), 140.59 (Ar-*C*), 146.34 (Ar-*C*), 147.39 (Ar-*C*) ppm. ^{19}F {^{1}H} NMR (25 °C, CD_2Cl_2, 282.38 MHz): –78.03 ppm. IR (ATR, 25 °C, 32 scans): $\tilde{\nu}$ = 3024 (vw), 2964 (m), 2944 (m), 2914 (m), 2872 (m), 1593 (w), 1479 (w), 1462 (w), 1435 (vw), 1414 (w), 1394 (m), 1360 (s), 1297 (w), 1281 (w), 1265 (w), 1232 (m), 1188 (s), 1149 (s), 1100 (m), 1026 (m), 933 (s), 884 (m), 878 (m), 841 (s), 818 (w), 779 (s), 766 (w), 751 (m), 701 (m), 667 (vw), 650 (w), 625 (s), 587 (s), 572 (m), 543 (m), 532 (s) cm^{-1}. Raman [100 mW, 25 °C, 800 scans]: 3027 (2), 2968 (9), 2940 (8), 2908 (10), 2782 (2), 2755 (2), 2710 (2), 1594 (8), 1463 (4), 1416 (6), 1393 (3), 1364 (3), 1287 (4), 1268 (2), 1236 (5), 1215 (10), 1203 (8), 1185 (7), 1145 (8), 1113 (3), 1013 (1), 944 (3), 922 (2), 867 (3), 820 (4), 779 (2), 766 (3), 619 (2), 593 (1), 564 (3), 547 (2), 538 (2), 509 (2), 475 (2), 410 (3), 364 (2), 344 (2), 317 (2), 301 (2), 245 (8), 214 (2), 160 (2), 148 (2), 130 (2) cm^{-1}.

[F–Sb(μ-NMes*)]$_2$ (5F): To a stirred suspension of [I–Sb(μ-NMes*)]$_2$ (**5I**) (1.02 g, 1 mmol) in THF (25 mL), finely powdered AgF (0.26 g, 2 mmol) was added in one portion, and the resulting red supension was stirred for 8 h at ambient temperatures. The solvent was removed, and the residue was dried in vacuo for 30 min. The resulting grey residue was washed three times with *n*-hexane (5 mL) and was then extracted four times with THF (30 mL), which resulted in a pale yellow suspension. The solvent was removed, and the pale yellow residue was dried in vacuo for 6 h, which yielded 0.62 g (0.78 mmol, 78%) of **5**F as a pale yellow crystalline solid. Mp. 240 °C (dec.). $C_{36}H_{58}F_2N_2Sb_2$ (800.34): calcd. C 54.02, H 7.30, N 3.50; found C 53.48, H 7.46, N 3.42. ^{1}H NMR (25 °C, C_6D_6, 300.13 MHz): 1.32 (s, 18 H, *p*-*t*Bu), 1.79 (s, 36 H, *o*-*t*Bu), 7.59 (s, 4 H, C*H*) ppm. ^{13}C{^{1}H} NMR (25 °C, C_6D_6, 75.48 MHz): 31.63 [C(*C*H$_3$)$_3$], 34.48 [*C*(CH$_3$)$_3$], 35.21 [C(*C*H$_3$)$_3$], 37.62 [*C*(CH$_3$)$_3$], 123.67 (*C*H), 144.81 (Ar-*C*), 148.05 (Ar-*C*) ppm. ^{19}F {^{1}H} NMR (25 °C, C_6D_6, 282.38 MHz): –84.25 ppm. IR [ATR, 25 °C, 32 scans]: $\tilde{\nu}$ = 3085 (vw), 3017 (w), 2947 (s), 2918 (m), 2866 (m), 1597 (w), 1477 (w), 1454 (w), 1447 (w), 1402 (m), 1389 (m), 1358 (m), 1289 (w), 1261 (w), 1239 (m), 1204 (s), 1180 (s), 1175 (s), 1140 (m), 1105 (s), 1022 (vw), 984 (vw), 932 (vw), 910 (w), 875 (m), 839 (s), 819 (w), 784 (s), 750 (m), 681 (s), 647 (w), 627 (s), 592 (m), 563 (w), 538 (m) cm^{-1}. Raman [100 mW, 25 °C, 800 scans] 3082 (2), 3019 (2), 2971 (9), 2951 (10), 2922 (10), 2907 (9), 2775 (2), 2706 (2), 1601 (7), 1449 (4), 1414 (3), 1362 (2), 1293 (3), 1220 (6), 1191 (7), 1146 (5), 1116 (2), 1025 (2), 922 (2), 884 (1), 863 (2), 823 (5), 788 (2), 761 (2), 616 (1), 591 (2), 566 (3), 549 (2), 490 (3), 299 (2), 257 (4), 224 (3), 163 (3), 147 (6), 125 (4), 110 (4) cm^{-1}. MS (CI positiv): *m*/*z* (%) = 206 (18) [Mes*NH$_3$ – *t*Bu]$^+$, 262 (100) [Mes*NH$_3$]$^+$, 382 (7) [Mes*NSb]$^+$, 395 (6) [Mes*N(H)SbN]$^+$, 642 (<1) [M –SbF$_2$]$^+$, 781 (3) [M –F]$^+$, 800 (< 1) [M]$^+$.

[Cl–Sb(μ-NMes*)]$_2$ (5Cl): To a stirred suspension of **4** (1.06 g, 1 mmol) in CH_2Cl_2 (10 mL) was added Me$_3$SiCl (0.24 g, 2.2 mmol) in CH_2Cl_2 (5 mL) over a period of 5 min at ambient temperature. After stirring for 30 min, the solvent was removed from the clear yellow solution, the yellow residue was dried for 2 h in vacuo and washed three times with *n*-hexane (2 mL). Drying of the residue in vacuo yielded 0.72 g (0.86 mmol, 86%) of **5**Cl as a yellow crystalline solid. Mp. 172 °C (dec.). $C_{36}H_{58}Cl_2N_2Sb_2$ (833.24): calcd. C 51.89, H 7.02, N 3.36; found C 51.93, H 7.03, N 3.11. ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): 1.29 (s, 18 H, *p*-*t*Bu), 1.63 (s, 36 H, *o*-*t*Bu), 7.33 (s, 4 H, C*H*) ppm. ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.48 MHz): 31.80 [C(*C*H$_3$)$_3$], 35.79 [C(*C*H$_3$)$_3$], 36.32 [*C*(CH$_3$)$_3$], 38.75 [*C*(CH$_3$)$_3$], 124.13 (*C*H), 143.14 (Ar-*C*), 144.88 (Ar-*C*), 146.64 (Ar-*C*) ppm. IR [ATR, 25 °C, 32 scans]: $\tilde{\nu}$ = 3079 (vw), 3008 (w), 2960 (s), 2949 (s), 2937 (s), 2902 (m), 2867 (m), 1596 (w), 1472 (w), 1463 (w), 1457 (w), 1434 (w), 1409 (m), 1394 (m), 1360 (s), 1289 (w), 1261 (w), 1241 (m), 1208 (s), 1198 (s), 1174 (s), 1140 (w), 1102 (s), 1026 (w), 921 (w), 912 (w), 877 (m), 836 (s), 818 (w), 781 (s), 749 (m), 690 (s), 646 (w), 624 (s), 585 (m), 563 (w), 535 (m) cm^{-1}. Raman [250 mW, 25 °C, 552 scans]: 3078 (1), 2965 (10), 2920 (8), 2903 (9), 2776 (1), 2707 (2), 1597 (7), 1465 (3), 1450 (3), 1412 (3), 1392 (2), 1361 (1), 1293 (3), 1246 (2), 1215 (6), 1203 (5), 1188 (7), 1142 (6), 1113 (2), 1026 (1), 923 (2), 860 (2), 823 (4), 782 (1), 758 (4), 618 (1), 563 (2), 538 (1), 477 (1), 390 (1), 308 (5), 297 (9), 235 (8), 159 (2), 142 (3), 132 (3), 110 (3) cm^{-1}.

[Br–Sb(μ-NMes*)]$_2$ (5Br): To a stirred suspension of **4** (1.06 g, 1 mmol) in CH_2Cl_2 (10 mL) Me$_3$SiBr was added (0.34 g, 2.2 mmol) in CH_2Cl_2 (5 mL) over a period of 5 min at ambient temperature. After stirring for 30 min, the solvent was removed from the orange solution and the orange residue was dried for 2 h in vacuo and washed three times with *n*-hexane (2 mL). Drying of the residue in vacuo yielded 0.84 g (0.91 mmol, 91%) of **5**Br as an orange crystalline solid. Mp. 173 °C (dec.). $C_{36}H_{58}Br_2N_2Sb_2$ (922.19): calcd. C 46.89, H 6.34, N 3.04; found C 46.86, H 6.45, N 2.65. ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): 1.28 (s, 18 H, *p*-*t*Bu), 1.61 (s, 36 H, *o*-*t*Bu), 7.31 (s, 4 H, C*H*) ppm. ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.48 MHz): 31.74 [C(*C*H$_3$)$_3$], 34.80 [*C*(CH$_3$)$_3$], 35.79 [C(*C*H$_3$)$_3$], 37.39 [*C*(CH$_3$)$_3$], 124.15 (*C*H), 143.17 (Ar-*C*), 144.88 (Ar-*C*), 146.35 (Ar-*C*) ppm. IR (ATR, 25 °C, 32 scans): $\tilde{\nu}$ = 3006 (w), 2950 (s), 2936 (s), 2903 (m), 2868 (m), 1594 (w), 1470 (w), 1463 (w), 1455 (w), 1436 (w), 1408 (m), 1404 (m), 1391 (m), 1360 (s), 1283 (w), 1257 (m), 1238 (m), 1208 (m), 1196 (m), 1172 (s), 1140 (w), 1103 (s), 1021 (m), 982 (w), 945 (vw), 934 (vw), 919 (w), 910 (w), 879 (m), 836 (s), 817 (m), 783 (s), 749 (m), 686 (s), 648 (w), 623 (s), 589 (m), 564 (w), 536 (m) cm^{-1}. Raman [100 mW, 25 °C, 544 scans]: 3112 (5), 2963 (7), 2915 (7), 2777 (1), 2707 (1), 1596 (7), 1447 (2), 1412 (3), 1392 (2), 1361 (2), 1285 (3), 1215 (6), 1186 (7), 1143 (5), 1113 (2), 923 (1), 861 (2), 822 (3), 783 (1), 759 (2), 618 (1), 586 (1), 564 (2), 541 (2), 289 (1), 252 (2), 234 (5), 211 (10), 163 (1), 138 (2) cm^{-1}.

[I–Sb(μ-NMes*)]$_2$ (5I): To a stirred suspension of **4** (1.06 g, 1 mmol) in CH_2Cl_2 (10 mL) was added Me$_3$SiI (0.44 g, 2.2 mmol) in CH_2Cl_2 (5 mL) over a period of 5 min at ambient temperature. After stirring for 30 min, the solvent was removed from the orange suspension and the orange residue was dried for 2 h in vacuo and washed three times with *n*-hexane (2 mL). Drying in vacuo yielded

0.97 g (0.95 mmol, 95%) of **5I** as an orange crystalline solid. Mp. 173 °C (dec.). $C_{36}H_{58}I_2N_2Sb_2$ (1016.14): calcd. C 42.55, H 5.75, N 2.76; found C 42.18, H 5.63, N 2.53. ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): 1.27 (s, 18 H, *p-t*Bu), 1.58 (s, 36 H, *o-t*Bu), 7.29 (s, 4 H, C*H*) ppm. $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.48 MHz): 31.74 [$C(CH_3)_3$], 34.79 [$C(CH_3)_3$], 35.72 [$C(CH_3)_3$], 37.45 [$C(CH_3)_3$], 124.20 (*C*H), 143.56 (Ar-*C*), 144.69 (Ar-*C*), 145.98 (Ar-*C*) ppm. IR (ATR, 25 °C, 32 scans): $\tilde{\nu}$ = 2999 (w), 2954 (m), 2935 (m), 2901 (m), 2867 (m), 1596 (w), 1558 (vw), 1539 (vw), 1506 (vw), 1472 (w), 1456 (m), 1435 (w), 1409 (m), 1401 (m), 1398 (m), 1388 (m), 1359 (s), 1287 (w), 1261 (w), 1247 (w), 1240 (m), 1207 (m), 1196 (m), 1171 (s), 1140 (w), 1102 (s), 1022 (w), 994 (vw), 944 (vw), 933 (vw), 921 (w), 909 (w), 878 (m), 835 (s), 816 (m), 780 (s), 748 (m), 683 (s), 649 (w), 621 (s), 587 (s), 563 (w), 535 (s) cm^{-1}. Raman [200 mW, 25 °C, 117 scans]: 3000 (1), 2967 (4), 2957 (3), 2918 (4), 2904 (4), 2775 (1), 2707 (1), 1598 (4), 1448 (2), 1412 (2), 1391 (2), 1361 (1), 1289 (2), 1242 (1), 1213 (4), 1184 (5), 1142 (4), 1112 (1), 1025 (1), 924 (1), 880 (2), 860 (2), 821 (1), 780 (1), 759 (1), 564 (1), 540 (1), 301 (1), 231 (3), 169 (10), 148 (2), 122 (2) cm^{-1}.

Supporting Information (see footnote on the first page of this article): Details for the preparation and characterization of all compounds is presented.

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