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Chlorine/Methyl Exchange Reactions in Silylated Aminostibanes: A New Route To Stibinostibonium Cations

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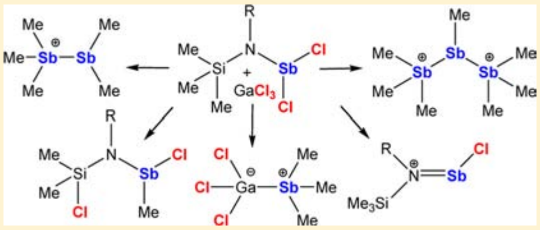
Ⓢ *Supporting Information*

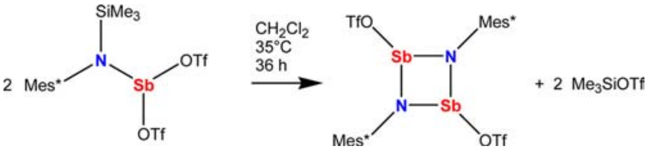
ABSTRACT: The Lewis acid assisted triflate/methyl, azide/methyl, and chlorine/methyl exchange reactions between silicon and antimony have been studied in the reaction of $R(Me_3Si)N{-}SbCl_2$ (R = Ter) with AgOTf, AgN_3, KO*t*Bu, $GaCl_3$, and $Me_3SiN_3/GaCl_3$, resulting in the formation of different methylantimony compounds. Furthermore, $R(Me_3Si)N{-}SbCl_2$ (R = $SiMe_3$) was reacted with $GaCl_3$ at low temperatures to yield a hitherto unreported amino(chloro)stibenium cation, the proposed intermediate in methyl exchange reactions. Tetrachloridogallate salts bearing different stibinostibonium cations such as $[(Me_3Sb)SbMe_2]^+$ and $[(Me_3Sb)_2SbMe]^{2+}$ along with the $GaCl_3$ adduct of $SbMe_3$ were isolated from such $R(Me_3Si)N{-}SbCl_2/GaCl_3$ mixtures (R = $SiMe_3$) at ambient temperatures, depending on the reaction parameters.



■ INTRODUCTION

Following our interest in low-coordinated nitrogen compounds of group 15 elements, we deal with the synthesis of binary four- and five-membered rings, especially of the heavier pnictogens (Pn) arsenic, antimony, and bismuth.[1] Silylated amino-pnictogen compounds $R(Me_3Si)N{-}PnX_2$ (R = Me_3Si, $(Me_3Si)_2N$, Mes* = supermesityl = 2,4,6-tri*tert*-butylphenyl, Ter = terphenyl = 2,6-bis(2,4,6-trimethyl-phenyl)phenyl; Pn = P, As, Sb; X = Cl, OTf = SO_3CF_3 = trifluoromethylsulfonyl) were shown to be unique starting materials for cycloaddition reactions as hidden imino-pnictogen building blocks (Schemes 1–3).[2–5] In these compounds elimination of trimethylsilyl-chloride $Me_3Si{-}Cl$ and -triflate $Me_3Si{-}OTf$ can occur thermally or triggered by the action of a Lewis-acid. Recently, a new synthesis of *cyclo*-distibadiazanes starting from Mes*-$(Me_3Si)N{-}Sb(OTf)_2$, which eliminates $Me_3Si{-}OTf$ at ambient temperatures (Scheme 1), was reported.[5]

Scheme 1. Synthesis of *cyclo*-Distibadiazanes via $Me_3Si{-}OTf$ Elimination[5]



Furthermore, amino-pnictogen compounds were used as hidden dipolarophiles, i.e., $R(Me_3Si)N{-}PnCl_2$ (R = Ter, Mes*; Pn = P, As), in [3 + 2] cycloaddition reactions (Scheme 2).[2–4,6] The dipolarophile, such as the reactive imino species $R{-}N{=}Pn{-}Cl$ (Pn = P, As), is generated *in situ* via elimination of $Me_3Si{-}Cl$ triggered by the action of the Lewis-acid $GaCl_3$. Subsequent reaction with a 1,3-dipole-molecule such as $Me_3Si{-}N_3$ generates the neutral tetrazapnictole as $GaCl_3$ adduct (Scheme 2, eqs 1 and 2). The analogous tetrazastibole, stabilized as $B(C_6F_5)_3$ adduct, was obtained in an unusual isomerization reaction of diazido-*cyclo*-distibadiazane with $B(C_6F_5)_3$ (Scheme 2, eq 3).[7]

Also, triazadiphospholes, another class of five-membered pnictogen-nitrogen heterocycles, were prepared in a $GaCl_3$ assisted [3 + 2] cycloaddition reaction starting from *N,N′,N′*-[tris(trimethylsilyl)]hydrazino(dichloro)phosphane (Scheme 3, eq 1).[2] In this reaction 4 equiv of $Me_3Si{-}Cl$ are eliminated prior to cyclization, and the triazadiphosphole is obtained as $GaCl_3$ mono- or diadduct, which stabilizes the ring system with respect to N_2-elimination.

Astonishingly, the analogous arsenic species *N,N′,N′*-[tris(trimethylsilyl)]hydrazino(dichloro)arsane $(Me_3Si)_2NN(SiMe_3)AsCl_2$ did not react with $GaCl_3$ to give the expected triazadiarsole, but instead both chlorine atoms attached to the arsenic atom were exchanged by a methyl group from one of the trimethylsilyl groups at the terminal nitrogen. The exchange product $[Me_2(Cl)Si]_2NN(SiMe_3)AsMe_2$ was obtained as a $GaCl_3$ adduct (Scheme 3, eq 2).[8] Removal of the Lewis acid is easily achieved by the addition of a stronger base such as 4-(dimethylamino)pyridine (DMAP).

This unusual Cl/methyl exchange reaction was further investigated and could be generalized and applied to different silylated amino(dichloro)arsane species $R(Me_3Si)N{-}AsCl_2$ (R = Me_3Si, $(Me_3Si)_2N$, Ter).[9] An initial chloride abstraction from the arsenic center by $GaCl_3$ and the intermediate formation of an cationic arsenic center triggers the exchange reaction. Due to

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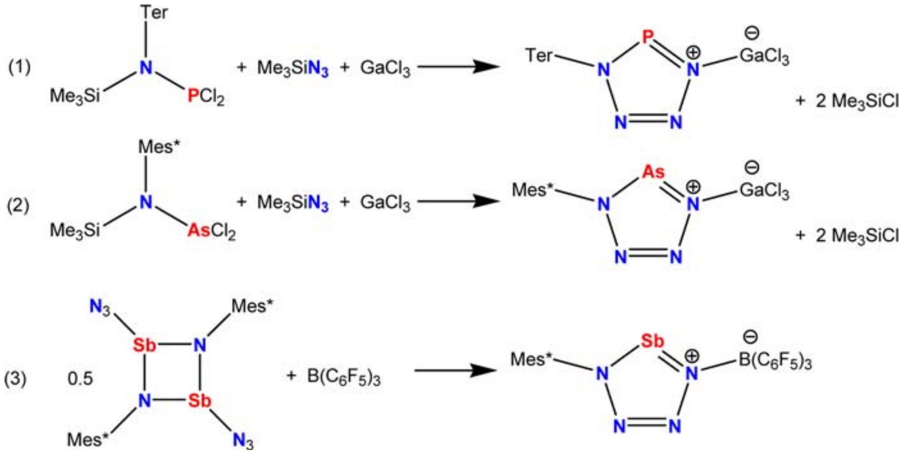
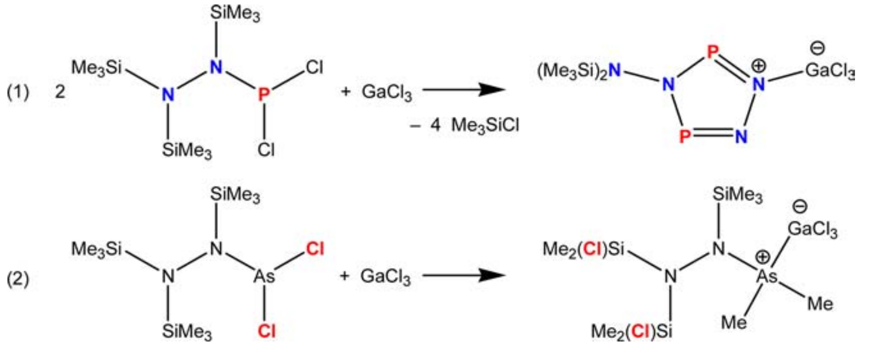
Scheme 2. Synthesis of Tetrazapnictoles via [3 + 2] Cycloaddition Starting from Disguised Dipolarophiles R(Me_3Si)N−$PnCl_2$ (Pn = P, As; R = Ter, Mes*)

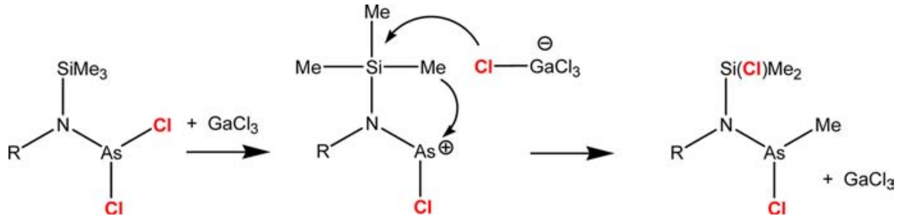


Scheme 3. Different Reaction Channels Observed for the Reaction of $GaCl_3$ and Silylated Hydrazinopnictanes [($Me_3Si)_2N$](Me_3Si)N−$PnCl_2$ (Pn = P, As)[a]



[a] Top: [3 + 2]-cycloaddition to triazadiphosphole. Bottom: methyl/chlorine-exchange.

Scheme 4. Proposed Mechanism for a Methyl/Chlorine-Exchange in Silylated Aminoarsanes



its high Lewis acidity the arsenium center stabilizes itself by abstraction of a methyl group from the Me_3Si moiety, whereas the [$Me_2Si{=}N$]$^+$ fragment finally abstracts a chloride from [$GaCl_4$]$^-$ to form the exchange product (Scheme 4).

The observation of different reaction channels for ($Me_3Si)_2N$−N($SiMe_3$)−PCl_2 and ($Me_3Si)_2N$−N($SiMe_3$)−$AsCl_2$ upon addition of a Lewis acid as well as our interest in the chemistry of the homologous silylated dichlorostibanes prompted us to study the reactions of R(Me_3Si)N−$SbCl_2$ (R = Ter, Mes*, Me_3Si) with the Lewis acids $GaCl_3$, AgOTf, AgN_3, and a mixture of Me_3SiN_3/$GaCl_3$.

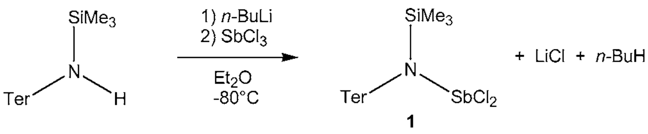
■ RESULTS AND DISCUSSION

In a first series of experiments the synthesis and functionalization of Ter(Me_3Si)N−$SbCl_2$ was studied, followed by the reactions of R(Me_3Si)N−$SbCl_2$ (R = Ter, Mes*, Me_3Si) with $GaCl_3$.

Synthesis and Reactivity of Ter(Me_3Si)N−$SbCl_2$. Ter(Me_3Si)N−$SbCl_2$ (**1**) was prepared according to a procedure already used for the preparation of Mes*(Me_3Si)N−$SbCl_2$ (Scheme 5).[5] The reaction of Ter(Me_3Si)NLi with $SbCl_3$ in Et_2O at −78 °C afforded (after separation of LiCl) a gray crude product which was purified by sublimation at 165 °C (10^{-3} mbar), yielding 68% of pure **1**.

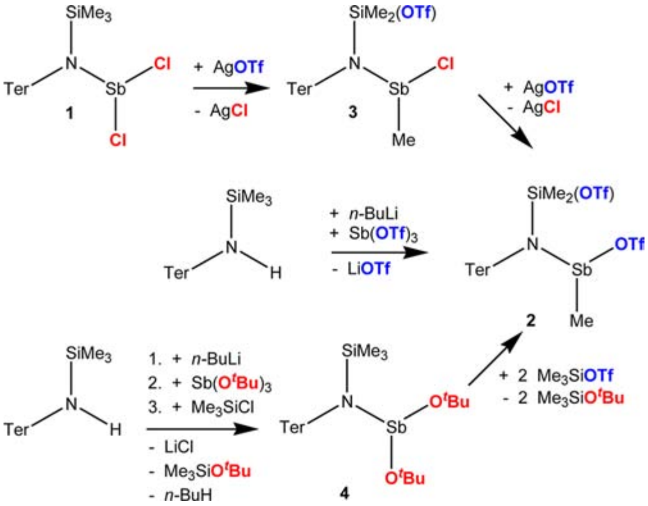
Starting from **1** the synthesis of the triflate derivative Ter(Me_3Si)N−$Sb(OTf)_2$ was attempted to investigate a

Scheme 5. Synthesis of Ter(Me_3Si)N−$SbCl_2$ (1)



possible $Me_3Si-OTf$ elimination accompanied by dimerization of the *in situ* formed imino-stibane, similar to the reaction described for $Mes^*(Me_3Si)N-Sb(OTf)_2$ (Scheme 1).[5] However, the reaction of **1** with 2 equiv of AgOTf in CH_2Cl_2 gave the triflate/methyl exchange product, $Ter[Me_2Si(OTf)]N-Sb(OTf)Me$ (**2**), in 86% yield (Scheme 6). The analogous arsenic product was already observed in the reaction of $Ter(Me_3Si)N-AsCl_2$ with a 2-fold excess of AgOTf.[9] Presumably, the first reaction step is a triflate/methyl exchange, which was shown by reacting equimolar amounts of AgOTf with **1** in toluene, leading to the isolation of $Ter[Me_2Si(OTf)]N-Sb(Cl)Me$ (**3**), in 78% yield (Scheme 6). In the second step the remaining chlorine atom at the antimony atom is substituted by a second triflate group, and **2** is obtained. Unfortunately, **2** is not suitable for thermal elimination of $Me_3Si-OTf$ or $Me_2Si(OTf)_2$.

Scheme 6. Attempted Synthesis of $Ter(Me_3Si)N-Sb(OTf)_2$ Resulting in the Formation of Different Triflate/Methyl Exchange Products 2 and 3 and in *Ot*Bu-Substituted Aminostibane 4

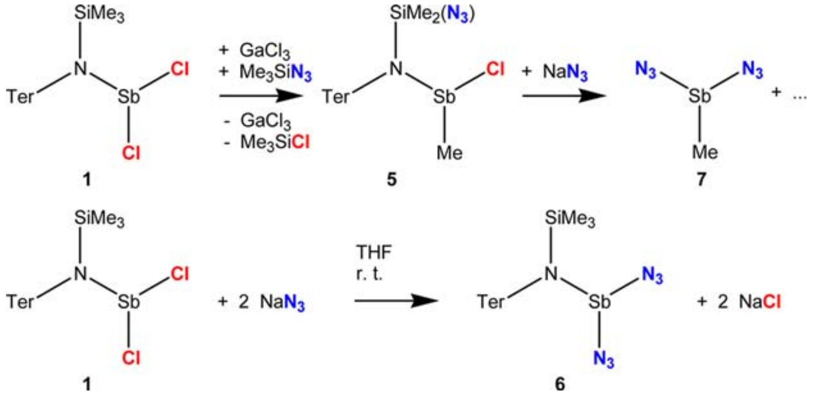


Since the reaction with AgOTf did not lead to the desired *cyclo*-distibadiazane, the *tert*-butoxy derivative of **1**, $Ter(Me_3Si)-N-Sb(OtBu)_2$ (**4**), was prepared from $Ter(Me_3Si)NLi$, $Sb(OtBu)_3$, and Me_3SiCl in Et_2O in an overall yield of 57% (Scheme 6). Surprisingly, also this compound showed no intrinsic thermal elimination of the silylether $Me_3SiOtBu$. By addition of Me_3SiOTf to **4**, a substitution of *Ot*Bu against OTf is observed, which again resulted in the formation of **2** (Scheme 6). Compound **2** was also obtained, when $Ter(Me_3Si)NLi$ was reacted with $Sb(OTf)_3$ in an Et_2O solution at −80 °C. Conclusively these results underline the different chemistry observed for supermesityl and terphenyl substituted aminopnictanes. In contrast to the analogous silylated (supermesityl)-aminostibanes that allow substitution of chlorine atoms in $Mes^*(Me_3Si)N-SbCl_2$ to form $Mes^*(Me_3Si)N-Sb(OTf)_2$, which can then undergo a thermal elimination of Me_3SiOTf, in the case of the terphenyl system **1** no such direct chlorine/triflate substitution is observed and thus cannot not be applied for terphenyl substituted aminopnictanes to generate the desired terphenyl substituted *cyclo*-distibadiazane. These findings are in good agreement with the observations made for the corresponding arsenic compounds, where addition of AgOTf resulted in a triflate/methyl exchange on the arsenic center as well.

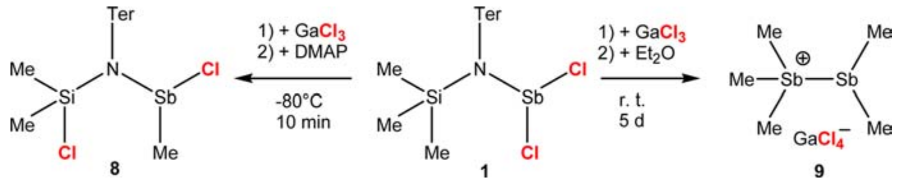
Despite the exchange reactions, we studied the reaction of **1** with $GaCl_3$ in the presence of Me_3SiN_3 (Scheme 7) to determine whether tetrazastibole formation can be observed. Interestingly, after removal of $GaCl_3$ by addition of DMAP (DMAP = 4-(dimethylamino)pyridine), $Ter[Me_2(N_3)Si]N-Sb(Cl)Me$ (**5**) was isolated in 32% yield (Scheme 7), which is analogous to the formal azide/methyl exchange reaction observed for $Ter(Me_3Si)N-AsCl_2$ under the same reaction conditions. We also synthesized the diazide $Ter(Me_3Si)N-Sb(N_3)_2$ (**6a**) starting from **1** and 2 equiv of NaN_3, in 54% yield (Scheme 7). The stoichiometry can be varied, but nevertheless only the formation of **6a** is observed, indicating a favored double over a single substitution. The same result is found when **1** is treated with 1 or 2 equiv of AgN_3. It should be noted that recrystallization of **6a** from CH_2Cl_2 always resulted in a partial Cl/N_3 back-substitution depending on the crystallization time. Thus, it is recommended to use either Cl-free solvents or carry out the crystallization process very quickly. Structural data for such partial chlorine-substituted azide compounds (**6b**−**c**) are found in the Supporting Information.

In contrast to the reaction of **1** with AgOTf no azide/methyl exchange was detected. Moreover, compound **6a** showed no elimination of Me_3Si-N_3 and subsequent dimerization to the desired azido-substituted *cyclo*-distibadiazane, which would be a reasonable starting material for the synthesis of the corresponding tetrazastibole.[7] Following our interest in azidopnictanes and to see whether a chlorine substitution in **5** could give a silicon−antimony azide, **5** was reacted with

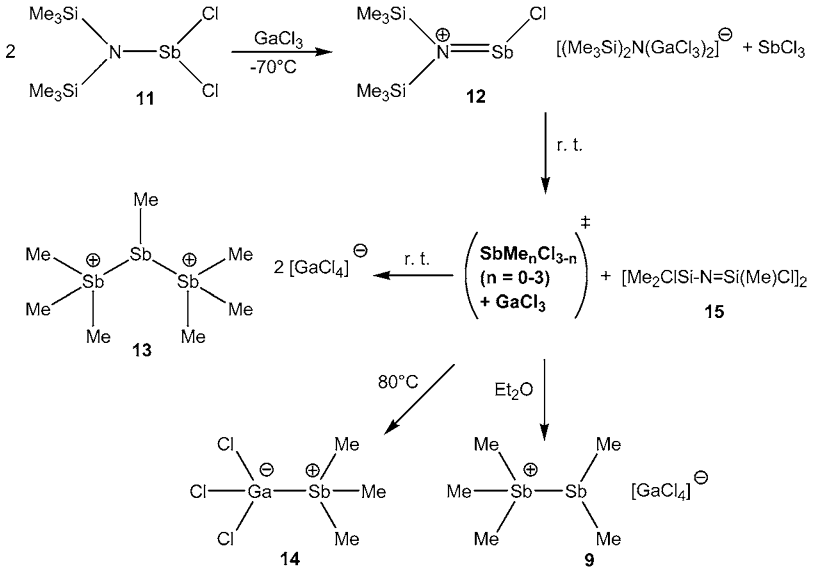
Scheme 7. Synthesis of Azido Species 5−7



Scheme 8. Chlorine/Methyl Exchange Reactions in Silylated Aminostibane 1



Scheme 9. Reaction of 11 with $GaCl_3$: Formation of Salts Containing Different Reactive Antimony Cations Depending on the Reaction Conditions



NaN_3. After workup and crystallization from toluene, among other unidentified products, only a few colorless crystals of the hitherto unreported diazido(methyl)stibane, $MeSb(N_3)_2$ (**7**), could be isolated and structurally characterized by X-ray and IR. Hence, it can be assumed that substitution can be achieved, but is immediately followed by a nitrogen antimony bond cleavage which finally results in the formation of **7** (Scheme 7).

In conclusion the reactivity of terphenyl-substituted aminopnictanes is different compared to the analogous supermesityl compounds. Neither the formation of *cyclo*-distibadiazanes nor a tetrazastibole could be observed, while similar reactions have previously been established for the lighter pnictogens phosphorus and arsenic.[5,7] However, interesting triflate- and azide/methyl exchange reactions have been found to be the main reaction in **1** in analogy to the corresponding arsenic compounds.[9] The hitherto unknown compounds **2**, **3**, **4**, **5**, and **6**, along with decomposition product **7**, could be isolated and characterized. These findings encouraged us to gain further insight in the reactivity of **1** in the presence of the Lewis acid $GaCl_3$, and to further investigate a possible extension of the $GaCl_3$ assisted chlorine/methyl exchange previously reported for hydrazinophosphanes and -arsanes, as well as for the analogous $Ter(Me_3Si)N{-}AsCl_2$.[9]

Reactivity of $R(Me_3Si)N{-}SbCl_2$ (R= Ter, Mes*, Me_3Si) toward $GaCl_3$. Different aminostibanes of the type $R(Me_3Si)$-$N{-}SbCl_2$ (R= Ter, Mes*, Me_3Si) have been prepared and studied in the reaction with the Lewis acid $GaCl_3$. In these reactions different methyl exchange reactions were observed, and a series of products resulting from a chlorine/methyl exchange could be isolated.

When $GaCl_3$ was added to a CH_2Cl_2 solution of **1** at −80 °C and then allowed to stir for 10 min at that temperature, the product of a single chlorine/methyl exchange $Ter[Me_2(Cl)Si]$-$N{-}Sb(Me)Cl$ (**8**) could be isolated after removal of $GaCl_3$ by adduct formation after addition of DMAP and extraction of the product with *n*-hexane (Scheme 8, left). It should be noted that, in contrast to the analogous arsenic compound for which a double chlorine/methyl exchange was observed, stirring of **1** in the presence of $GaCl_3$ at ambient temperatures led to a complex mixture of products. After five days of stirring, and addition of Et_2O, colorless crystals of $[Me_3Sb{-}SbMe_2][GaCl_4]$ (**9**) were isolated and structurally characterized (Scheme 8, right). Obviously, further methylation on the antimony center resulted in the formation of $Sb(Me)_2Cl$ and $SbMe_3$. In the presence of the chloride abstracting agent $GaCl_3$, a salt bearing the stibinostibonium cation (**9**) was formed. The stibinostibonium ion in **9** with a $[MeSbBr_3]^-$ counterion was described before by Breunig et al. in an attempt to crystallize Me_2SbBr from its melt at −28 °C.[10]

The formation of a salt containing a stibinostibonium ion prompted us to take a closer look at the analogous reaction of the supermesityl substituted species. In a previous work, the formation of $Mes^*[Me_2(N_3)Si]N{-}SbCl_2$ was reported in the reaction of $Mes^*(Me_3Si)N{-}SbCl_2$ with $GaCl_3$ and an excess of Me_3SiN_3.[7] However, when $Mes^*(Me_3Si)N{-}SbCl_2$ was reacted exclusively with $GaCl_3$ the complex reaction mixture could not be separated and only small amounts of the single chlorine/methyl exchange product $Mes^*[Me_2(Cl)Si]N{-}Sb(Me)Cl$ (**10**) in analogy to **8a** (Scheme 8, left) were obtained as a side product among other unidentified species. This shows that in the case of the supermesityl derivative such exchange reactions are not favored anymore, contrary to the observations made for terphenyl species **1**.

In a next series of experiments we explored the reactivity of the *N,N*-bis(trimethylsilyl)amino species $(Me_3Si)_2N{-}SbCl_2$ toward Lewis acids. For this reason $(Me_3Si)_2N{-}SbCl_2$ (**11**) was prepared starting from $SbCl_3$ and $(Me_3Si)_2NLi$ in a salt elimination reaction in toluene at −50 °C. The crude product was purified by distillation *in vacuo* at 65 °C (10^{-3} mbar) affording colorless liquid **11** at ambient temperatures. Addition of $GaCl_3$ to a CH_2Cl_2 solution of **11** at −70 °C and subsequent concentration, followed by storage of the reaction mixture at −80 °C for 24 h, led to the deposition of colorless crystals, which were identified as $[(Me_3Si)_2NSbCl][(Me_3Si)_2N(GaCl_3)_2]$ (**12**) bearing a highly reactive aminostibenium cation (Scheme 9). Aminopnictenium cations have already been proposed as intermediate for chlorine/methyl exchange reaction by Schulz et al.[8,9] Compound **12** can be stored in the freezer under an argon atmosphere, but it decomposes within weeks even at −34 °C. Interestingly, $SbCl_3$ is obviously eliminated in the course of this reaction leading to the generation of the hitherto unknown complex amide anion $[(Me_3Si)_2N(GaCl_3)_2]^-$ stabilized by double $GaCl_3$ adduct formation.

Warming a mixture of **11** and $GaCl_3$ from −70 °C to ambient temperatures followed by concentration led to the formation of a black oily layer besides a reddish supernatant. After removal of the supernatant and addition of toluene to the black residue, crystals of the hitherto unknown salt $[(Me_3Sb)_2SbMe][GaCl_4]_2$ (tetragonal polymorph) (**13**) slowly grew from the oil within one week (Scheme 9). The tetragonal polymorph was studied by X-ray analysis, but the data is not sufficient to allow a detailed discussion. However, from the supernatant a monoclinic polymorph of **13** could be isolated and fully characterized. The supernatant was further concentrated, and 1,3-bis(chlorodimethylsilyl)-2,2,4,4-tetramethylchloro-*cyclo*-disilazane (**15**) was also isolated as crystals, which could be characterized by X-ray structure determination. In the crystal structure a partial occupancy of chlorine atoms in place of methyl groups suggests an overall molecular formula that includes about three chlorine atoms.[12] Furthermore, ^1H NMR experiments of the reaction mixture also indicate the presence of several differently substituted methyl/chloro *cyclo*-silazanes. A similar compound was already observed in the reaction of $(Me_3Si)_2N{-}AsCl_2$ with $GaCl_3$.[9] Such a *cyclo*-disiladiazane was first reported in the condensation reaction of dichloromethylsilane Me_2SiCl_2 with either 2,2,4,4,6,6-hexamethylcyclotrisilazane $[Me_2SiNH]_3$ or 2,2,4,4,6,6,8,8-octamethylcyclotetrasilazane $[Me_2SiNH]_4$.[13] The monoclinic polymorph of **13** was also obtained when freshly prepared **12** was stirred at ambient temperatures for 48 h.

Interestingly, when the reaction conditions were changed with respect to the thermal treatment, different products were observed. For instance, from the reaction mixture of **11** and $GaCl_3$ at 80 °C a $SbMe_3$ adduct of $GaCl_3$, $[Me_3Sb{\cdot}GaCl_3]$ (**14**), was obtained upon concentration. Compound **9** could also be prepared, when Et_2O was added to the black oily layer formed when **11** was reacted with $GaCl_3$, in an isolated yield of 5%. The crystal structure of **9** was unequivocally proven by X-ray analysis, and suitable crystals were obtained from both reaction pathways.

The formation of **12** together with the formation of the *cyclo*-disiladiazane finally proves the idea that the chlorine/methyl exchange in silylated aminostibanes is triggered by chloride abstraction upon addition of a Lewis acid such as $GaCl_3$. As a consequence, intermediate formation of an aminostibenium cation is observed, which in turn is able to abstract one methyl group from the Me_3Si moiety inducing the Cl/Me exchange reaction (Scheme 9). Conclusively, a mixture of **11** and $GaCl_3$ leads to the formation of different methylchlorostibanes of the type $SbMe_nCl_{3-n}$ ($n = 0{-}3$), which can be envisioned as a reaction medium for the generation of *catena*-antimony cations, whereas different cations are obtained depending on the temperature, concentration, or solvent.[14]

The catalytic properties of Lewis acids in reactions with Si−C bond cleavage are well described in the literature.[15] For example, in the reaction of $GaCl_3$ and $SiMe_4$, a methyl migration from silicon to gallium was found, for which an intermediate with bridging Cl and Me between Si and Ga was assumed, finally leading to the formation of Me_3SiCl and $(MeGaCl_2)_2$. Another similar reaction was reported by Carmalt et al.: The reaction of $GaCl_3$ with $(Me_3Si)_3N$ yielded, among other products, dimeric $(MeGaCl_2)_2$.[16] In that case, the product $(MeGaCl_2)_2$ is the result of monochloride substitution and transfer of a methyl ligand from the silyl group of the amine to the Ga center. A chlorine/methyl exchange is also assumed in the formation of the $GaCl_3$ diadduct of the six-membered oxadisilathiadiazine heterocycle $O(SiMe_2)(NSN)(SiMe_2)$ as hydrolysis product of the reaction of bis(trimethylsilyl)sulfur diimide and $GaCl_3$.[17] However, in these examples of chlorine/methyl exchange reactions, $GaCl_3$ is part of an intermolecular exchange reaction and stoichiometric amounts are needed, whereas in conversions of $R(Me_3Si)N{-}SbCl_2$ (R = Ter, Mes*, Me_3Si), the Lewis acid $GaCl_3$ only plays a catalytic role in an intramolecular Me/Cl exchange reaction.

Examples of compounds that exhibit a Pn−Pn′ backbone are rare. Burford et al. established the homoatomic coordination chemistry between neutral and cationic phosphorus centers as a high yielding and versatile synthetic route toward *catena*-phosphorus cations.[18] Only recently this concept has been successfully adapted to interpnictogen *catena*-cations displaying heteroatomic coordination chemistry between phosphorus and arsenic as well as antimony. These interpnictogen frameworks are obtained in a one pot reaction of chlorophosphane or dichlorophosphanes with arsanes (R_3As, R = Me, Et, Ph) and Ph_3Sb in the presence of a chloride ion abstracting agent ($AlCl_3$, $GaCl_3$, $Me_3SiOSO_2CF_3$) and therefore provide access to frameworks containing two, three, or four pnictogen centers. The bonding in these compounds can be viewed as interpnictogen coordination with direct As→P and Sb→P bonding.[14]

Over the past decade only a very small number of *catena*-antimony cations containing only antimony in the backbone have been isolated and fully characterized. Only three classes are known: (i) $[R_3Sb{-}(SbR)_n{-}SbR_2]^+$, (ii) $[R_2Sb{-}(SbR)_n{-}SbR_2{-}(SbR)_n{-}SbR_2]^+$, and one dicationic series (iii) $[R_3Sb{-}(SbR)_n{-}SbR_3]^{2+}$ (n = 0, 1, 2, etc.). $[Me_3Sb{-}SbMe_2]^+$ as $[GaCl_4]^-$ (**9**) and $[MeSbBr_3]^{-10}$ salt belong to the $[R_3Sb{-}(SbR)_n{-}SbR_2]^+$ series with $n = 0$, while dication **13** $[R_3Sb{-}Sb(R){-}SbR_3]^{2+}$ ($n = 1$) represents the next example of the series $[R_3Sb{-}(SbR)_n{-}SbR_3]^{2+}$ for which the parent species $[Me_3Sb{-}SbMe_3]^{2+}$ ($n = 0$) was isolated as $[SbF_6]^-$ salt from the reaction of Me_3Sb in the super acidic medium HF/SbF_5 by Minkwitz.[19] Furthermore, only the parent species ($n = 0$) of the monocationic series $[R_2Sb{-}(SbR)_n{-}SbR_2{-}(SbR)_n{-}SbR_2]^+$ has been reported which was characterized as $[Me_2Sb{-}SbMe_2{-}SbMe_2][Me_2SbBr_2]$.[20]

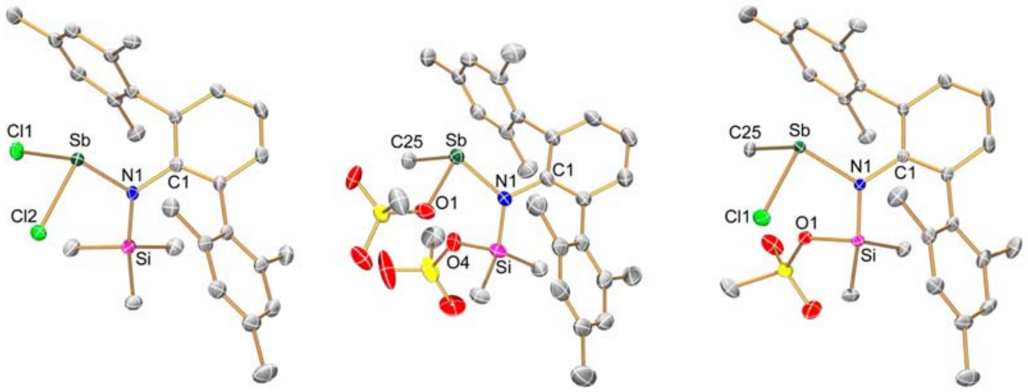


Figure 1. ORTEP drawing[11] **1** (left), **2** (middle), and **3** (right). Thermal ellipsoids with 30% probability at 173 K (hydrogen and fluorine atoms omitted for clarity). Selected bond lengths and angles are given in Table 1.

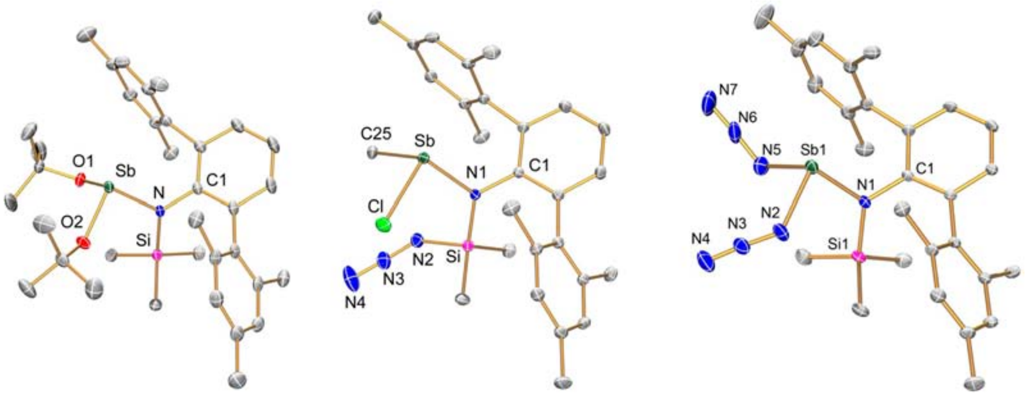


Figure 2. ORTEP drawing[11] of **4** (left), **5** (middle), and **6a** (right). Thermal ellipsoids with 30% probability at 173 K (hydrogen atoms omitted for clarity). Selected bond lengths and angles are given in Table 1.

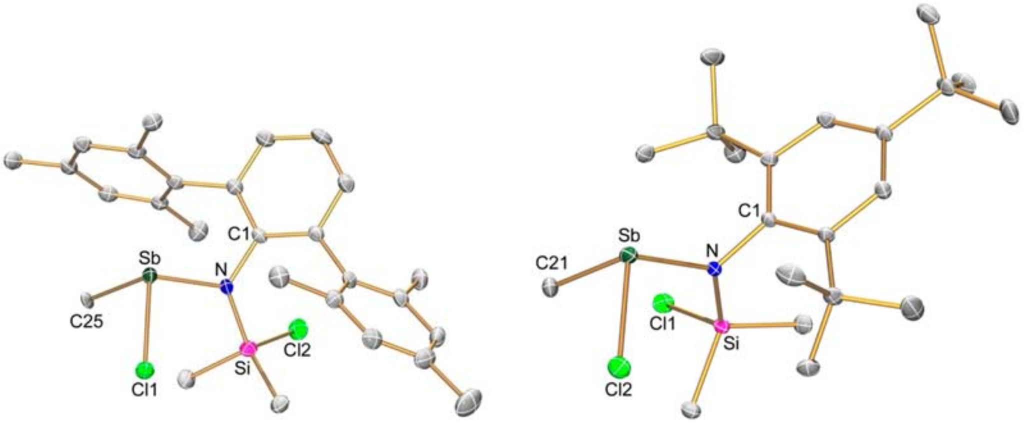


Figure 3. ORTEP drawing[11] of **8a** (left) and **10** (right). Thermal ellipsoids with 30% probability at 173 K (hydrogen atoms omitted for clarity). Selected bond lengths and angles are given in Table 1.

Spectroscopic Characterization. Compounds **2**–**6**, **8**, **11**, and **13** have been characterized by elemental analysis, differential scanning calorimetry (DSC), and vibrational and NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si). For **9** and **12** as well as for adduct **14** only limited analytical data could be collected, because **9** and **14** where obtained in very small amounts and not as pure substances. Compound **12** is thermally labile and very reactive and could therefore not be characterized by Raman and NMR spectroscopy because of fast decomposition.

Terphenyl compounds **1**–**6a** and **8a**,**b** are thermally stable, indicated by high decomposition points ranging from 134 °C for **3** to 217 °C for **2**. Azides **5** and **6a** are neither heat nor shock sensitive, but should be handled with care. In contrast to azides **5** and **6a**, azide **7** detonates, e.g., when acetone is added to a small amount of **7**. $GaCl_3$ adduct **14** decomposes at 130 °C presumably initiated by dissociation of the donor–acceptor bond. Compounds **1**–**6a**, **8**, and **10** are air and moisture sensitive, but can be stored under inert gas conditions for a long period of time at ambient temperatures. They show a good solubility in aromatic solvents like benzene and toluene as well as in polar solvents such as dichloromethane.

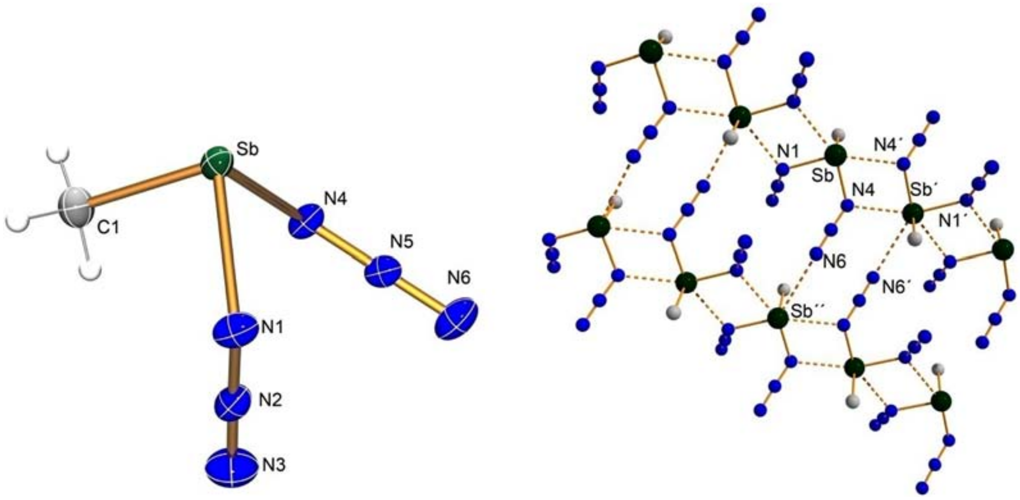


Figure 4. Left: ORTEP drawing[11] of **7**. Thermal ellipsoids with 30% probability at 173 K. Selected bond lengths (Å), and angles (deg): Sb−C1 2.128(3), Sb−N1 2.198(2), Sb−N4 2.183(2), N1−N2 1.223(3), N2−N3 1.140(3), N4−N5 1.238(3), N4−N5 1.136(4), C1−Sb−N1 91.62(11), C1−Sb−N4 91.35(11), N4−Sb−N1 85.84(9), N2−N1−Sb 117.8(2), N5−N4−Sb 118.0(2), N1−N2−N3 177.6(3), N4−N5−N6 177.7(3). Right: intermolecular interactions Sb···N1′ 2.639(2), Sb···N4′ 2.723(2), Sb″···N6 3.16 Å.

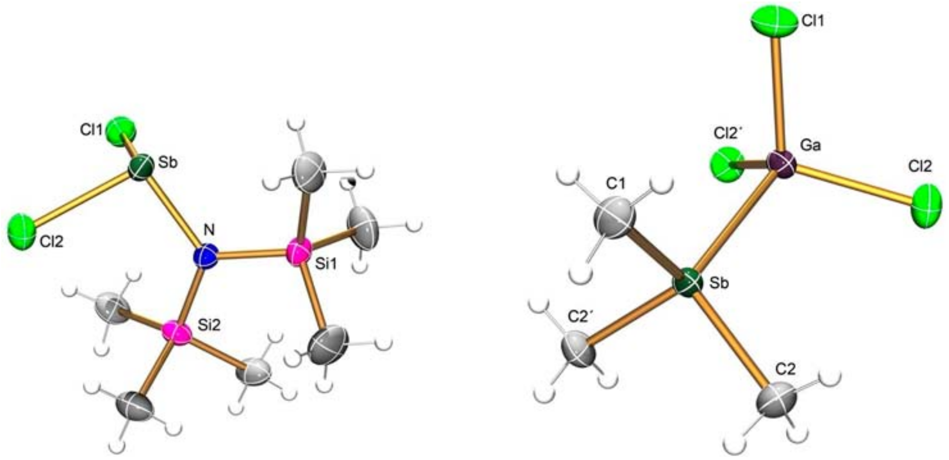


Figure 5. ORTEP drawing[11] of **11** (left) and **14** (right). Thermal ellipsoids with 50% probability at 173 K. Selected bond distances (Å) and angles (deg). **11**: Sb−N1 2.002(2), Sb−Cl1 2.3942(10), Sb−Cl2 2.3822(9), N1−Si1 1.767(3), N1−Si2 1.776(3), Cl1−Sb−N1 99.37(8), Cl2−Sb−N1 98.40(7), Cl1−Sb−Cl2 95.22(3), Si1−N1−Sb1 113.59(13), Si2−N1−Sb1 124.91(14), Si1−N1−Si2 121.37(14). **14**: Sb1−Ga1 2.6119(4), Ga(1)−Cl(1) 2.1649(8), Ga(1)−Cl(2i) 2.1791(7), Ga(1)−Cl(2) 2.1791(7), Sb(1)−C(2) 2.104(3), Sb(1)−C(2i) 2.104(3), Sb(1)−C(1) 2.111(3), C(1)−Sb(1)−Ga(1) 114.2(1), C−Sb1−C 103.7(2), 105.2(1), Cl(1)−Ga(1)−Sb(1) 111.44(3), Cl(1)−Ga(1)−Cl(2i) 110.38 (2), 108.26 (4), C1−Sb1−Ga1−Cl1 0.0.

For the chemical shifts in the ^{1}H NMR data only small differences are detected for the proton signals in the terphenyl-moieties (cf. ^{1}H NMR data for *p*-C*H*$_3$(Mes), $\delta(^1\text{H})$ = 1.99−2.09; *o*-C*H*$_3$(Mes), $\delta(^1\text{H})$ = 2.23 - 2.36; C$_{\text{Aryl}}$*H*, $\delta(^1\text{H})$ = 6.80−7.27). To assign the chemical shifts in the ^{1}H NMR spectra for the protons in the methyl groups attached to the antimony atom in exchange products **2**, **3**, **5**, and **8**, COSY (^{1}H^{13}C) experiments were carried out. The chemical shifts of these protons lie between 0.7 and 0.8 ppm in the ^{1}H NMR spectra depending on the second substituent on the antimony center. It is interesting to note that in the exchange products **2**, **3**, and **5** all carbon atoms are chemically and magnetically non-equivalent, and therefore, 24 (**5**), 27 (**8**), 28 (**3**), and 29 (**2**) different signals are found in the ^{13}C NMR spectra.

The IR spectra of azide species **5**−**7** feature the presence of a covalently bound azido group as shown by the asymmetrical stretching mode in the range 2050−2150 cm^{-1} (**5**, $\nu_{\text{as}}(\text{N}_3)$ = 2134; **6**, 2092/2078; **7**, 2067 cm^{-1}). The splitting of this mode in **6a** into two components indicates the presence of more than one azido group, displaying an in-phase and out-of-phase coupled mode. This splitting was not observed for diazide **7** since only a broad vibrational band is observed.

Compound **13** was fully characterized in the course of this study. In the ^{1}H NMR and ^{13}C NMR spectra two different signals for the protons and carbon atoms of the stibino- and stibonium-methyl groups are detected at 2.00 ppm and 1.57 ppm, respectively, which is in good agreement for the values detected for MeSbCl$_2$ (^{1}H (CDCl$_3$) 1.90 ppm).[21]

Structural Characterization. The structures of all considered amino-stibanes (species **1**-**6**, **8**, **10**); stibanes **7**, **11**, and **14**; and the salts bearing Sb cations (**9**, **12**, and **13**) have been determined. Tables S1−S5 (see Supporting Information) present the X-ray crystallographic data. Molecular structures are shown in Figures 1−7. Table 1 summarizes selected structural parameters of the aminostibanes while for all other species selected structural data are listed along with the

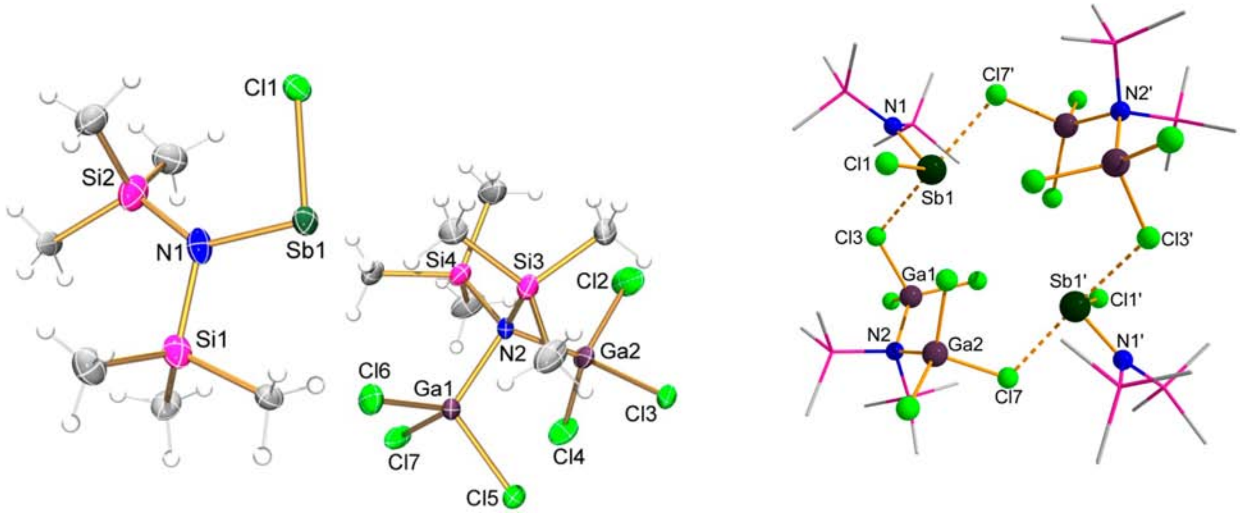


Figure 6. Left: ORTEP drawing[11] of **12**. Thermal ellipsoids with 30% probability at 173 K. Right: Ball and stick drawing of intermolecular interactions in **12**. Selected bond lengths (Å) and angles (deg): Sb−N1 1.953(5), Sb−Cl1 2.351(9), N1−Si1 1.868(7), N1−Si2 1.715(7), N2−Ga1 1.989(5), N2−Ga2 1.979(5); Cl1−Sb−N1 94.6(2), Si1−N1−Sb1 109.7(3), Si2−N1−Sb1 132.3(4), Si1−N1−Si2 118.0(3), Ga1−N2−Ga2 106.7(2); Sb1···Cl3 2.875(2), Sb1···Cl5 3.418(3), Sb1···Cl5′ 3.667(3), Sb1···Cl7′ 2.826(2).

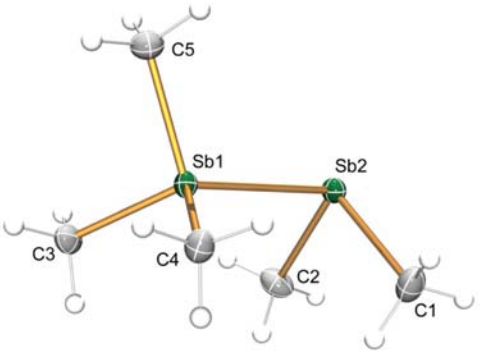


Figure 7. ORTEP drawing[11] of the stibinostibonium cation in **9** ($GaCl_4^-$ anion omitted for clarity). Thermal ellipsoids with 30% probability at 173 K. Selected bond distances (Å) and angles (deg) for **9**: Sb1−C5 2.111(4), Sb1−C3 2.113(4), Sb1−C4 2.114(3), Sb1−Sb2 2.8273(3), Sb2−C2 2.149(4), Sb2−C1 2.151(4).

figures of the molecular structure (Figures 4−7). More details are found in the Supporting Information.

In the solid state structure of compounds bearing bulky terphenyl moieties, the crystal lattice often exhibits large cavities that are accessible by solvent molecules. For example **8** could be crystallized from *n*-hexane, diethylether, benzene (**8b**), and toluene (**8a**) resulting always in solvent containing crystals. It is interesting to note that all solvate structures crystallize isotypically with exception of the different solvent molecules in the cavities. These solvent molecules are highly disordered on their positions in the crystal. The best structure could be determined for the toluene or benzene solvate. To illustrate the crystallographic problem of disordered solvent molecules in cavities of **1** and **8**, the structure refinement was carried out in two different ways: (i) refinement of solvent molecules with an appropriate disorder model (benzene, toluene) or (ii) treatment of solvent molecules as diffuse contribution to the structural factor (benzene, toluene, dichloromethane, diethyl

Table 1. Selected Bond Lengths (Å) and Bond and Torsion Angles (deg) of All Considered Aminostibanes[a]

	1[b]	**2**	**3**	**4**	**5**	**6a**	**8a**[b]	**10**
Sb1−N1	2.033(3)	2.023(3)	2.104(2)	2.033(1)	2.068(1)	2.013(2)	2.065(3)	2.059(2)
Sb1−X1	2.362(2)	2.179(6)	2.400(2)	1.964(1)	2.4103(4)	2.095(2)	2.4079(7)	2.3983(4)
Sb1−X2	2.396(2)	2.111(5)	2.135(3)	1.952(1)	2.181(2)	2.101(2)	2.159(5)	2.152(2)
N1−Si1	1.783(4)	1.761(7)	1.722(2)	1.770(1)	1.739(2)	1.782(2)	1.741(3)	1.732(2)
C1−N1	1.451(5)	1.441(5)	1.436(3)	1.434(2)	1.441(2)	1.445(3)	1.438(4)	1.470(2)
Si1−X3		1.733(7)	1.749(2)		1.776(1)		2.056(2)	2.110(7)
N1−Sb1−X1	106.05(1)	87.6(4)	96.42(5)	93.67(5)	97.03(3)	92.59(8)	105.5(3)	102.47(4)
N1−Sb1−X2	96.72(1)	107.6(2)	103.03(9)	94.18(5)	104.22(5)	101.80(9)	96.36(8)	101.58(6)
X1−Sb1−X2	90.34(5)	90.6(4)	93.38(8)	93.30(6)	91.63(4)	89.5(1)	90.0(2)	89.89(5)
C1−N1−Sb1	110.4(2)	111.2(2)	111.5(2)	114.91(9)	112.43(8)	112.4(1)	111.6(2)	114.84(9)
C1−N1−Si1	123.5(3)	121.0(3)	123.1(2)	123.30(9)	122.36(9)	122.5(2)	124.1(2)	119.0(1)
Sb1−N1−Si1	126.1(2)	127.5(2)	125.4(1)	121.78(6)	125.21(6)	125.1(1)	124.2(1)	126.04(7)
$\sum\angle$(N1)	360.0	359.7	360.0	360.0	360.0	360.0	359.9	359.9
C2−C1−N1−Sb1	123.0(4)	−129.5(3)	−124.9(2)	57.8(2)	54.5(2)	122.4(2)	124.6	−88.8

[a] X2 represents a carbon atom of a methyl group at antimony, and X3-, Cl-, O-, or N-atom of OTf/N_3-groups attached to the silicon atom. [b] Only one data set of the four independent molecules is listed; however, all structural parameters are within the 3σ range.

ether, n-hexane) using Platon/SQUEEZE. The latter data are listed in the Supporting Information.

The compounds **1**−**6**, **8**, and **10** show only weak intermolecular van der Waals interactions which lead to nearly isolated molecules in **1**, **4**, **5**, **8**, and **10**. However, for **2** and **6**, oxygen or nitrogen bridged dimers can be considered. An oxygen bridged chainlike structure is found for **3**. The Sb···X (X = N, O) distances vary between 3.35 and 3.96 Å indicating weak interactions (see Figures S1−S2 in the Supporting Information) comparing these distances with the sum of the van der Waals radii (Σr_{vdw}(Sb···N) = 3.8 and Σr_{vdw}(Sb···O) = 3.7 Å).

In all compounds the trivalent antimony center sits in a trigonal pyramidal environment with bond angles between 88° and 108°. Differences from the ideal pyramidal environment can be attributed to sterical effects from different substituents at the antimony atom. The amino nitrogen atom is nearly planar coordinated in all compounds, as indicated by the sum of the angles around nitrogen (Table 1). The Sb−N−Si moiety sits in a pocket formed by the bulky terphenyl group. To fit in this pocket the Si−N−Sb moiety is always twisted with respect to the central phenyl ring of the terphenyl ligand, exhibiting a torsion angle between 50° and 60°. Supermesityl species **10** shows the typical torsion angle near 90°.[5]

The Sb−N_{amino} bond lengths vary between 2.017(2) and 2.033(3) Å which are in the typical range found for Sb−N single bonds, for example d(Sb−N_{amino}) = 2.056(3) in Mes*N($SiMe_3$)−$SbCl_2$,[5] d(Sb−N_{amino}) = 2.092(2) and d(Sb−N_{azide}) = 2.104(2) in [*t*BuC(*i*PrN)$_2$]Sb(N_3)$_2$,[22] and d(Sb−N_{azide}) = 2.119(4) Å in Sb(N_3)$_3$[23] (cf. Σr_{cov}(Sb−N) = 2.11 Å).[24] The two Sb−N_{azide} bonds in **6a** (2.125(2)/2.166(2) Å) are slightly elongated compared to the Sb−N_{amino} bonds in accord with those found for [*t*BuC(*i*PrN)$_2$]Sb(N_3)$_2$ and Sb(N_3)$_3$ (vide supra).[22,23] The azide group in **5** is covalently bound to the silicon center with a Si−N_{azide} bond length of 1.776(2) Å (cf. Σr_{cov}(Si−N) = 1.87 Å) in good agreement with the analogous arsenic compound (d(Si−N_{azide}) = 1.780(1) Å).[9,24] The Sb−Cl distances in **1** (2.362(2)/2.396(2) Å) and in **3**, **5**, **8**, and **10** (ca. 2.40 Å) are nearly identical and can be regarded as typical single bonds (cf. Σr_{cov}(Sb−Cl) = 2.39 Å).[24] The Sb−C distances are in the range 2.181(2)−2.135(3) Å) (cf. Σr_{cov}(Sb−C) = 2.15 Å).[24]

For both azide species **5** and **6a** the typical *trans*-bent structure with NNN angles of about 173−176° is observed.[25] The N_α−N_β (**5**, 1.217(2); **6a**, 1.221(3)/1.225(4) Å) and also the N_β−N_γ bond lengths (**5**, 1.130(2); **6a**, 1.126(3) /1.125(4) Å) are in the expected range of covalently bound azides.

Diazidomethylstibane **7** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit. The Sb−N_{azide} distances of 2.183(2) and 2.198(2) Å are slightly elongated and in good agreement with previously reported antimony azides (cf. d(Sb−N_{azide}) = 2.125(2)/2.166(2) Å in **6**),[26,27] whereas the Sb−C distance of 2.128(3) Å is shorter than the sum of the covalent radii (cf. Σr_{cov}(Sb−C) = 2.15 Å).[24] Both azide groups are slightly *trans* bent with NNN-angles of 177.6°. In the crystal, significant intermolecular interactions are observed, as the antimony atoms are linked by the N_α atom of the azide groups, resulting in the formation of infinite zigzag chains of centrosymmetric dimers (Figure 4, right). The Sb−Sb′−Sb″angle amounts to 160°, so that the zigzag chain motif is not as obvious as in Sb(N_3)$_2$Cl.[26] The chain in **7** is formed due to interactions between discrete molecules with Sb···N_α distances of 2.639 and 2.723 Å. Between these chains loose interactions via the N_γ atom from an azide group of one chain and an antimony center of a neighboring chain (Sb···N_γ = 3.16 Å) are observed. This structural motif has often been observed in azidopnictanes.[27a] The overall coordination environment around antimony can be described as 3 + 3 coordination leading to a distorted pentagonal pyramide.

Compound **11** crystallizes in the trigonal space group $P3_2$ with nine molecules in the unit cell. The molecular structure is depicted Figure 5 (left). Hyperconjugative effects between σ^* orbitals of the Sb−Cl bond and the p-type lone pair at the nitrogen atom can be discussed, resulting in a shortened Sb−N distance of 2.002(2) Å (cf. Σr_{cov}(Sb−N) = 2.11 Å).[28] The Sb−Cl distances are in the typical range (Sb−Cl 2.3942(10)/2.3822(9) Å) of a single bond (cf. Σr_{cov}(Sb−Cl) = 2.39 Å). The shortest distances between the antimony center and chlorine atoms of a neighboring molecule are in the range of 3.7 Å, which can be regarded as loose electrostatic interactions, resulting in nearly isolated molecules.

Furthermore, a $GaCl_3$ adduct of $SbMe_3$ (**14**) was structurally characterized (Figure 5, right), which crystallizes in the orthorhombic space group *Pnma* with four molecules in the unit cell. Compound **14** lies on a mirror plane, and the Sb−Ga bond in this adduct can be regarded as a dative bond between the donor $SbMe_3$ and the acceptor acid $GaCl_3$ with a Sb−Ga distance of 2.6119(4) Å (cf. Σr_{cov}(Sb−Ga) = 2.64 Å, cf. Sb−Ga 2.662(2)/2.659(2) Å in [Cl_2GaSb(*t*Bu)$_2$]$_3$).[24,29] Molecule **14** shows an eclipsed conformation with Sb−C bonds in the range 2.104(3)-2.111(3) Å. A similar situation is found for the $GaCl_3$ unit with two slightly different bonds (2.1791(7) Å and 2.1649(8) Å).

Upon addition of $GaCl_3$ to **11** at low temperatures a salt bearing an aminostibenium cation is formed. Compound **12** crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in the asymmetric unit. The whole amino(chloro)stibenium cation is disordered with the main part being populated by 51.2%. The Sb−N distances in the cation differ slightly in the two parts and are rather short with 1.953(5)/1.990(5) Å (Figure 6, cf. Σr_{cov}(Sb—N) = 2.11, Σr_{cov}(Sb═N) = 1.93 Å; Sb—N 1.966(1) Å in Mes*(Me_3Si)N—Sb(OTf)$_2$, 1.958(4) Å in (2-MeC_6H_4)$_3$Sb═NSO_2CF_3)[5,24,30] indicating partial SbN double bond character. Also, the Sb—Cl1 distance of 2.351(9) Å is relatively short compared to that of **11**.

The Ga−N distances of 1.978(5) and 1.989(5) Å in the anion are in the range of an elongated single bond (cf. Σr_{cov}(Ga−N) = 1.95 Å),[24] which supports the idea that the anion is a $GaCl_3$ adduct of a *N*,*N*-bis(trimethylsilyl)amide, with a tetrahedrally coordinated nitrogen center. In the solid state two close contacts between chlorine atoms Cl3 and Cl7 of the $GaCl_3$ moieties in the anion and the dicoordinated antimony are found (2.875(2) and 2.826(2) Å). In addition, two larger distances to Cl5 (3.418(3)/3.667(3) Å) are observed. The main structural motif might be regarded as a centrosymmetric dimeric ion pair with two strongly distorted octahedral coordinated antimony centers as depicted in Figure 6 (left). There are also two CH_2Cl_2 molecules in the asymmetric unit; one of them is found to be disordered.

catena-Sb cation-containing salts **9** and **13** crystallize in the monoclinic space groups $P2_1/c$ (**9**; Figure 7) and $P2_1$ (**13**; Figure 8) with four (**9**, **13**) formula units in the unit cell. For **13** an additional CH_2Cl_2 solvent molecule is present in the asymmetric unit. The Sb−Sb bonds found in the antimony backbone of both cations are nearly equidistant with 2.8273(3) in **9** and 2.811(1)/2.830(1) Å in **13** displaying a typical single

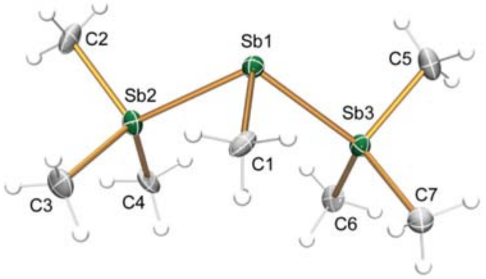


Figure 8. ORTEP drawing[11] of the cation in **13** ($GaCl_4^-$ anion omitted for clarity). Thermal ellipsoids with 30% probability at 173 K. Selected bond distances (Å) and angles (deg) for **13**: Sb1−Sb2 2.811(1); Sb1−Sb3 2.830(1); Sb1−C1 2.20(1); Sb2−C 2.05(1), 2.10(1), 2.10(1); Sb3−C 2.11(1), 2.09(1), 2.11(1); Sb2−Sb1−Sb3 100.83; C−Sb2−C 103.7(2).

bond (cf. Σr_{cov}(Sb−Sb) = 2.80 Å).[24] These Sb−Sb distances are in good agreement with those reported in $[Me_2Sb-SbMe_2-SbMe_2]^+$ (2.8203(4) Å), but are slightly shorter compared to those reported for tetramethyldistibane (Me_4Sb_2, 2.862(2) Å)[31a] and tetraphenyldistibane (Ph_4Sb_2, 2.867(1) Å).[31b] The Sb−C single bonds of the tetracoordinated (stibonium) and the tricoordinated Sb atoms (stibino centers) are observed in the expected range (2.08−2.16 Å, cf. Σr_{cov}(Sb−C) = 2.15 Å).[28] Only weak cation−anion interactions are found for **9**. For instance, four van der Waals interactions are observed for the dicoordinated Sb2 atom (Sb2···Cl distances of 3.3−3.9 Å), and three interactions for the tricoordinated antimony atoms Sb1 (3.4−3.7 Å) are observed leading to a slightly distorted $GaCl_4^-$ anion.

■ CONCLUSION

In summary, we report here on the successful extension of the Lewis acid assisted methyl exchange reactions to silylated aminostibanes. The methyl/chlorine exchange in the reaction of $(Me_3Si)_2N-SbCl_2$ **11** and $GaCl_3$ can be regarded as a valuable application of this concept for the generation of different *catena*-antimony cations, depending on the variation of either temperature or solvent.

Silylated aminostibanes of the type $Ter(Me_3Si)N-SbCl_2$ have been studied in the reaction with AgOTf, AgN_3, KO*t*Bu, $GaCl_3$, and $Me_3SiN_3/GaCl_3$ displaying triflate/methyl, azide/methyl, and chlorine/methyl exchange reactions. The intermediate aminopnictenium cation (**12**) could be isolated at −60 °C when $(Me_3Si)_2N-SbCl_2$ (**11**) was reacted with $GaCl_3$ at low temperatures. The reaction of **11** and $GaCl_3$ at ambient temperatures led to different stibinostibonium cations as tetrachloridogallates in $[(Me_3Sb)SbMe][GaCl_4]$ and $[(Me_3Sb)_2SbMe][GaCl_4]_2$ along with the $GaCl_3$ adduct of $SbMe_3$. The cations in these salts can be regarded as *catena*-antimony cations.

■ EXPERIMENTAL SECTION

General Information. All manipulations were carried out under oxygen- and moisture-free conditions using standard Schlenk and drybox techniques.

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 ppm) or to protic impurities in the deuterated solvent (^1H, $CDHCl_2$, $\delta_{reference}$ = 5.31 ppm; C_6D_6, $\delta_{reference}$ = 7.16 ppm). CD_2Cl_2 was dried over P_4O_{10}; C_6D_6 was dried over Na/benzophenone.

IR. Nicolet 380 FT-IR with a Smart Orbit ATR device was used.

Raman. Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm), was used.

CHN analyses. Analysator Flash EA 1112 from Thermo Quest, or C/H/N/S-Mikronalysator TruSpec-932 from Leco, was used.

Melting points are uncorrected (EZ-Melt, Stanford Research Systems), with heating rate 20 °C/min (clearing points are reported).

MS. Finnigan MAT 95-XP from Thermo Electron was used.

X-ray Structure Determination. X-ray quality crystals of **1**−**14** were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) (Riedel deHaen) at ambient temperatures. All samples were cooled to 173(2) K during measurement. The data were collected on a Bruker-Nonius Apex X8 and Bruker Apex Kappa-II CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73). The structures were solved by direct methods (*SHELXS-97*)[32] and refined by full-matrix least-squares procedures (*SHELXL- 97*).[33] Semi-empirical absorption corrections were applied (SADABS).[34] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the refinement at calculated positions using a riding model.

$Ter(Me_3Si)N-SbCl_2$ (1). To a stirred solution of *N*-(2,6-bis(2,4,6-trimethylphenyl)-phenyl)-*N*-(trimethylsilyl)-amine $TerN(H)SiMe_3$ (2.415 g, 6 mmol) in Et_2O (20 mL) is added 2.5 M *n*-butyl-lithium-solution in *n*-hexane (2.5 mL, 6.25 mmol) over a period of 10 min at ambient temperature. The resulting pale yellow solution is stirred for 1 h and then added dropwise to a solution of $SbCl_3$ (1.37 g, 6 mmol) in Et_2O (10 mL) at −80 °C. The resulting colorless suspension is allowed to warm up to RT over a period of 1 h and stirred for 30 min. The solvent is removed, and the colorless solid is dried for 2 h in vacuum. Then the residue is extracted with 30 mL benzene and filtered. The solvent is removed in vacuum, and the resulting gray solid is sublimed at 160 °C and 1×10^{-3} mbar, yielding 2.44 g (4.1 mmol, 68%) of $TerN(SiMe_3)SbCl_2$ (**1**) as a colorless crystalline solid. Mp = 202 °C (dec). Anal. Calcd % (Found): C 54.66 (54.62); H 5.78 (6.08); N 2.36 (2.33). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): −0.14 (s, 9H, Si(CH_3)$_3$), 2.09 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 2.32 (s, 6H, CH_3), 6.90−7.19 (m, 7H, *CH*). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.475 MHz): 4.78 (s, 3C, Si(CH_3)$_3$), 21.33 (s, 2C, CH_3), 22.25 (s, 2C, CH_3), 22.63 (s, 2C, CH_3), 124.10 (s, 1C, CH), 129.62 (s, 2C, CH), 130.43 (s, 2C, CH), 133.12 (s, 2C, CH), 136.23 (Ar-C), 138.51 (Ar-C), 138.57 (Ar-C), 138.83 (Ar-C), 139.54 (Ar-C), 146.44 (Ar-C). ^{29}Si INEPT NMR (25 °C, CD_2Cl_2, 49.696 MHz): 16.7 (*Si*(CH_3)$_3$).[35]

$Ter[Me_2(OTf)Si]N-SbMe(OTf)$ (2). To a stirred suspension of AgOTf (0.514 g, 2 mmol) in CH_2Cl_2 (10 mL) is added a solution of 1 (0.594 g, 1 mmol) in CH_2Cl_2 (5 mL) quickly at −80 °C. The resulting gray suspension is allowed to warm up to ambient temperature over 30 min and filtered (F4). The solution is concentrated to about 5 mL and stored at −25 °C for several hours which results in deposition of colorless crystals. The supernatant is transferred by syringe, the solvent is removed *in vacuo*, and the colorless residue is recystallized from *n*-hexane. Drying the combined fractions yields 0.710 g (0.86 mmol, 86%) of **2** as a colorless crystalline solid. Mp = 217 °C (dec). Anal. Calcd % (Found): C 42.45 (43.13); H 4.47 (4.76); N 1.71 (1.63). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): −0.35 (s, 3H, Si−CH_3), 0.34 (s, 3H, Si−CH_3), 0.78 (s, 3H, Sb−CH_3), 2.09 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2. 36 (s, 3H, CH_3), 6.95−7.27 (7H, *CH*). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.48 MHz): 2.01 (s, Si-CH_3), 2.36 (s, Si-CH_3), 21.22 (s, CH_3), 21.45 (s, CH_3), 21.68 (s, CH_3), 22.01 (s, CH_3), 22.45 (s, CH_3), 23.02 (s, CH_3), 26.13 (s, Sb-CH_3), 118.85 (q, $^1J(^{13}C^{19}F)$ = 318.0 Hz, CF_3), 118.97 (q, $^1J(^{13}C^{19}F)$ = 317.5 Hz, CF_3), 124.91 (CH), 129.63 (CH), 129.98 (CH), 130.69 (CH), 130.89 (CH), 131.57 (CH), 133.80 (CH), 135.39 (Ar-C), 136.84 (Ar-C), 137.76 (Ar-C), 138.21 (Ar-C), 138.27 (Ar-C), 138.34 (Ar-C), 139.21 (Ar-C), 142.84 (Ar-C), 143.26 (Ar-C), 143.35 (Ar-C), 146.04 (Ar-C). ^{19}F NMR (25 °C, CD_2Cl_2, 282.38 MHz): −76.94 (s, 3F, CF_3), −78.02 (s, 3F, CF_3). ^{29}Si INEPT NMR (25 °C, CD_2Cl_2, 49.70 MHz): 19.90 (*Si*(CH_3)$_2$OTf).[35]

$Ter[Me_2(OTf)Si]N-Sb(Cl)Me$ (3). To a stirred solution of **1** (0.594 g, 1 mmol) in toluene (10 mL), a solution of AgOTf (0.257 g, 1 mmol) in toluene (5 mL) is added dropwise at −75 °C. The resulting gray suspension is allowed to warm up to ambient temperature over 30 min and filtered (F4). The solvent is removed *in vacuo*, and the colorless residue is recystallized from *n*-hexane which yields 0.556 g (0.78 mmol, 78%) of **3** as a colorless crystalline solid. Mp = 134 °C (dec). Anal. Calcd % (Found): C 47.57 (47.95); H 4.85 (4.76); N 1.98 (1.75). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): −0.25 (s, 3H, Si−CH_3), 0.27 (s, 3H, Si−CH_3), 0.72 (s, 3H, Sb−CH_3), 2.08 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 6.92−7.22 (7H, CH). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.48 MHz): 2.83 (s, Si-CH_3), 3.96 (s, Si-CH_3), 21.19 (s, CH_3), 21.34 (s, CH_3), 21.58 (s, CH_3), 22.03 (s, CH_3), 22.27 (s, Sb-CH_3), 22.53 (s, CH_3), 23.10 (s, CH_3), 118.90 (q, $^1J(^{13}C^{19}F)$ = 318 Hz, CF_3), 124.35 (CH), 129.45 (CH), 129.74 (CH), 129.96 (CH), 130.04 (CH), 132.15 (CH), 133.12 (CH), 135.56 (Ar-C), 136.09 (Ar-C), 137.78 (Ar-*C*), 138.47 (Ar-*C*), 138.49 (Ar-*C*), 138.56 (Ar-*C*), 138.70 (Ar-*C*), 140.38 (Ar-*C*), 140.71 (Ar-*C*), 140.80 (Ar-*C*), 146.82 (Ar-*C*). ^{19}F NMR (25 °C, CD_2Cl_2, 282.38 MHz): −76.95 (s, 3F, CF_3). ^{29}Si INEPT NMR (25 °C, CD_2Cl_2, 49.70 MHz): 18.83 (*Si*$(CH_3)_2$OTf).[35]

Ter(Me$_3$Si)N−Sb(O*t*Bu)$_2$ (4). To a stirred solution of TerN(H)-SiMe$_3$ (1.208 g, 3 mmol) in Et_2O (20 mL) is added 2.5 M *n*-butyllithium in *n*-hexane (1.2 mL, 3 mmol) over a period of 10 min at ambient temperatures. The resulting pale yellow solution is stirred for 1 h and then added dropwise to a solution of Sb(O*t*Bu)$_3$ (1.023 g, 3 mmol) in Et_2O (10 mL) at −80 °C. The resulting colorless solution is allowed to warm up to ambient temperatures over a period of 1 h and stirred for 30 min. A solution of Me_3SiCl (0.109 g, 1 mmol) in Et_2O (3 mL) is added dropwise at 0 °C resulting in a colorless suspension which is stirred for 1 h. The solvent is removed, and the colorless solid is dried for 2 h *in vacuo*. The residue is extracted with 30 mL of *n*-hexane and filtered. The solution is concentrated to about 5 mL and stored at −25 °C for several hours which results in deposition of colorless crystals, yielding 1.140 g (1.71 mmol, 57%) of **4** as a colorless crystalline solid. Mp = 165 °C (dec). Anal. Calcd % (Found): C 62.87 (62.45); H 7.84 (8.04); N 2.09 (2.19). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): −0.16 (s, 9H, Si$(CH_3)_3$), 1.16 (s, 18H, OC$(CH_3)_3$), 1.99 (s, 6H, CH_3), 2.24 (s, 6H, CH_3), 2.29 (s, 6H, CH_3), 6.80−7.02 (7H, Ar−CH). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.48 MHz): 5.65 (s, Si$(CH_3)_3$), 21.31 (s, CH_3), 22.07 (s, CH_3), 23.37 (s, CH_3), 33.68 (s, OC$(CH_3)_3$), 73.99 (s, O*C*$(CH_3)_3$), 122.74 (*C*H), 129.11 (*C*H) 129.79 (*C*H), 132.33 (*C*H), 137.25 (Ar-*C*), 138.09 (Ar-*C*), 138.16 (Ar-*C*), 139.08 (Ar-*C*), 140.10 (Ar-*C*), 148.20 (Ar-*C*).[35]

Ter[Me$_2$(N$_3$)Si]N−Sb(Cl)Me (5). To a stirred solution of **1** (0.475 g, 0.8 mmol) in CH_2Cl_2 (8 mL) is added Me_3SiN_3 (0.104 g, 0.9 mmol) in CH_2Cl_2 (3 mL) quickly at −70 °C. Then a solution of $GaCl_3$ (0.159 g, 0.9 mmol) in CH_2Cl_2 (3 mL) is added dropwise over a period of 15 min at this temperature. The resulting greenish solution is allowed to warm up to ambient temperature over 30 min and is stirred for 20 h. Then a solution of 4-*N*-dimethylaminopyridine (0.063 g, 0.51 mmol) is added dropwise at 0 °C resulting in a colorless solution. The solvent is removed *in vacuo*, and the colorless residue is extracted three times with 10 mL of *n*-hexane. Concentration of the colorless filtrate and storage at −25 °C for several hours yields 0.180 g (0.26 mmol, 32%) of **5** as a colorless crystalline solid. Mp = 147 °C. Anal. Calcd % (Found): C 54.06 (53.60); H 5.71 (5.68); N 9.34 (9.48). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): −0.23 (s, 3H, Si−CH_3), −0.16 (s, 3H, Si−CH_3), 0.73 (s, 3H, Sb−CH_3), 2.11 (s, 3H, CH_3), 2.15 (s, 6H, CH_3), 2.29 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 6.89−7.14 (7H, CH). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.48 MHz): 2.19 (s, Si-CH_3), 2.69 (s, Si-CH_3), 21.21 (CH_3), 21.33 (CH_3), 21.66 (CH_3), 21.82 (CH_3), 21.99 (CH_3), 22.30 (CH_3), 23.10 (CH_3), 123.57 (*C*H), 129.18 (*C*H), 129.64 (*C*H), 129.90 (2C, *C*H), 131.74 (*C*H), 133.15 (*C*H), 136.02 (Ar-*C*), 137.09 (Ar-*C*), 137.92 (Ar-*C*), 138.07 (Ar-*C*), 138.14 (Ar-*C*), 138.23 (Ar-*C*), 138.68 (Ar-*C*), 140.29 (Ar-*C*), 140.59 (Ar-*C*), 140.82 (Ar-*C*), 147.84 (Ar-*C*). ^{29}Si INEPT NMR (25 °C, CD_2Cl_2, 49.70 MHz): 3.7 (*Si*$(CH_3)_2N_3$).[35]

Ter(Me$_3$Si)N−Sb(N$_3$)$_2$ (6a). Procedure 1: NaN_3 (0.067 g, 1 mmol) is added to a stirred solution of **1** (0.297 g, 0.5 mmol) in THF at ambient temperatures, and the mixture is stirred for 20 h. Dispersed NaCl is allowed to settle, the solvent is removed *in vacuo*, and the residue is extracted with toluene. Toluene is again removed, and crystallization from *n*-hexane yields 0.165 g (0.27 mmol, 54%) of **6a** as a colorless crystalline solid. Proceedure 2: AgN_3 (0.080 g, 0.53 mmol) is added to a stirred solution of **1** (0.148 g, 0.25 mmol) in THF (5 mL) at ambient temperatures, and the mixture is allowed to stir for 8 h. The solvent is removed *in vacuo* afterward, the residues are extracted with benzene (5 mL), and concentration to 0.3 mL and storage in the freezer (−24 °C) yields 0.090 g (0.15 mmol, 60%) **6a** as colorless crystalline solid.

Mp = 148 °C. Anal. Calcd % (Found): C 53.47 (52.90); H 5.65 (5.66); N 16.17 (15.73). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): −0.24 (s, 9H, Si$(CH_3)_3$), 2.07 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 2.33 (s, 6H, CH_3), 6.92−7.16 (7H, Ar−CH). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.48 MHz): 3.36 (s, Si$(CH_3)_3$), 21.41 (s, 2C, CH_3), 22.26 (s, 2C, CH_3), 22.56 (s, 2C, CH_3), 123.68 (*C*H) 129.56 (*C*H) 130.35 (*C*H), 132.91 (*C*H), 136.03 (Ar-*C*), 138.09 (Ar-*C*), 138.68 (Ar-*C*), 138.94 (Ar-*C*), 139.59 (Ar-C), 146.13 (Ar-*C*). ^{29}Si INEPT NMR (25 °C, CD_2Cl_2, 49.70 MHz): 13.5 (*Si*$(CH_3)_3$).[35]

MeSb(N$_3$)$_2$ (7). NaN_3 (0.033 g, 0.5 mmol) is added to a stirred solution of **5** (0.297 g, 0.5 mmol) in THF at ambient temperatures, and the resulting colorless solution is stirred for 24 h. Afterward the solvent is stripped off, and the residue is redissolved in toluene (0.5 mL). Within three days colorless crystals of **7** have precipitated. Only small amounts could be isolated (*m* < 40 mg). Mp = 120 °C, 138 °C (dec). IR (ATR, 25 °C, 32 scans, cm^{-1}): 2992 (m), 2948 (m), 2067 (s), 1608 (m), 1579 (w), 1574 (w), 1564 (w), 1494 (w), 1483 (w), 1446 (m), 1399 (m), 1396 (m), 1377 (w), 1312 (m), 1250 (m), 1199 (m), 1166 (m), 1097 (m), 1086 (m), 1029 (m), 1016 (m), 1005 (m), 986 (w), 945 (w), 914 (m), 836 (s), 796 (m), 767 (m), 749 (m), 730 (m), 720 (m), 714 (m), 694 (m), 649 (m), 594 (m), 583 (m), 552 (m), 532 (m).

Ter[Me$_2$(Cl)Si]N−Sb(Cl)Me (8). To a stirred solution of **1** (0.297 g, 0.5 mmol) in CH_2Cl_2 (5 mL) is added a solution of $GaCl_3$ (0.089 g, 0.5 mmol) in CH_2Cl_2 dropwise at −75 °C. The resulting orange solution is stirred for an additional 15 min at this temperature and allowed to warm up to 0 °C within 15 min. Then, a solution of 4-*N*-dimethylaminopyridine (0.063 g, 0.51 mmol) is added dropwise, resulting in a colorless solution. The solvent is removed *in vacuo*, and the colorless residue is extracted three times with 10 mL of *n*-hexane. Concentration of the colorless filtrate and storage at −25 °C for several hours yields 0.124 g (0.21 mmol, 42%) of **8** as a colorless crystalline solid. Prolonged drying *in vacuo* leads to complete removal of solvent molecules. Mp = 177 °C (dec). Anal. Calcd % (Found): C 54.66 (54.56); H 5.78 (5.72); N 2.36 (2.47). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): −0.09 (s, 3H, Si−CH_3), 0.04 (s, 3H, Si−CH_3), 0.71 (s, 3H, Sb−CH_3), 2.14 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 6.91−7.16 (7H, CH). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.48 MHz): 7.13 (s, Si-CH_3), 8.49 (s, Si-CH_3), 21.19 (CH_3), 21.32 (CH_3), 22.05 (CH_3), 22.16 (CH_3), 22.67 (CH_3), 23.16 (CH_3), 23.56 (Sb-CH_3), 123.72 (*C*H), 129.06 (*C*H), 129.70 (*C*H), 129.85 (*C*H), 129.98 (*C*H), 131.74 (*C*H), 133.35 (*C*H), 136.18 (Ar-*C*), 137.22 (Ar-*C*), 137.98 (Ar-*C*), 138.08 (Ar-*C*), 138.12 (Ar-*C*), 138.67 (Ar-*C*), 139.04 (Ar-*C*), 140.28 (Ar-*C*), 140.63 (Ar-*C*), 140.86 (Ar-*C*), 148.13 (Ar-*C*). ^{29}Si INEPT NMR (25 °C, CD_2Cl_2, 49.70 MHz): 18.6 (*Si*$(CH_3)_2$Cl).[35]

[Me$_2$SbSbMe$_3$][GaCl$_4$] (9). Procedure 1: To a stirred solution of **1** (0.59 g, 1 mmol) in CH_2Cl_2 (10 mL) is added a solution of $GaCl_3$ (0.180 g, 1 mmol) in CH_2Cl_2 (3 mL) dropwise at 0 °C. The resulting orange solution is stirred for five days at ambient temperatures, the solvent is removed *in vacuo*, and the colorless residue is extracted two times with 10 mL of Et_2O. Concentration of the colorless filtrate and storage at ambient temperatures for several hours yields only a few colorless crystals of **9**. Procedure 2: To a stirred solution of **11** (1 mmol; 354 mg) in CH_2Cl_2 (3 mL) is added a solution of $GaCl_3$ (1 mmol; 177 mg) in CH_2Cl_2 (2 mL) dropwise at −60 °C. The resulting yellow solution is allowed to warm to ambient temperatures, and upon concentration to 1 mL an oily black layer deposits with a clear reddish supernatant on top. The supernatant is removed, and the black oily residue is extracted with Et_2O (5 mL). The Et_2O extract is concentrated to 2 mL and allowed to rest at ambient temperatures for 48 h; during this time span colorless crystalline blocks of **9** have deposited (0.05 g; 5%).

^{1}H NMR (25 °C, CD_2Cl_2, 500.13 MHz): 1.60 (s, $Sb(CH_3)_3$), 1.49 (s, $Sb(CH_3)_2$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 125.76 MHz): −3.3 (s, $Sb(CH_3)_3$).

Mes*[Me$_2$(Cl)Si]N−Sb(Cl)Me (10). To a stirred solution of Mes*(Me_3Si)N−$SbCl_2$ (0.53 g, 1 mmol) in CH_2Cl_2 (10 mL) is added a solution of $GaCl_3$ (0.180 g, 1 mmol) in CH_2Cl_2 (3 mL) dropwise at 0 °C. The resulting orange solution is stirred for 48 h at ambient temperatures, and the solvent is removed *in vacuo*. THF (2 mL) and *n*-hexane (10 mL) are added, and the colorless suspension is filtered. Concentration of the colorless filtrate and storage at +5 °C for several hours yields only a few colorless crystals of **10**.

($Me_3Si)_2N−SbCl_2$ (11). To a stirred solution of $SbCl_3$ (6.844 g, 30 mmol) in toluene (100 mL) is added a solution of $(Me_3Si)_2NLi$ (5.020 g, 30 mmol) in toluene (50 mL) dropwise at −60 °C. The resulting colorless suspension is allowed to warm to ambient temperatures and is stirred for 10 h. The solvent is removed *in vacuo*, and the resulting colorless residue is extracted with *n*-hexane (50 mL) and filtered (F4), resulting in a colorless solution. Removal of solvent *in vacuo* gives a colorless liquid, which is distilled *in vacuo* at 75 °C, yielding **11** (5.506, 52%) as colorless liquid. Storage at −30 °C. Mp = 32 °C. Anal. Calcd % (Found): C 20.41 (19.08); H 5.14 (4.48); N 3.97 (4.08). ^{1}H NMR (25 °C, CD_2Cl_2, 500.13 MHz): 0.35 (s, $^1J(^{13}C^1H)$ = 119 Hz, $^2J(^{29}Si^1H)$ = 6.7 Hz). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 125.76 MHz): 5.3 (s, $^1J(^{29}Si^{13}C)$ = 57 Hz). $^{29}Si\{^1H\}$ NMR (25 °C, CD_2Cl_2, 99.36 MHz): 9.86 (s). $^{14}N\{^1H\}$ NMR (25 °C, CD_2Cl_2, 36.14 MHz): −286 ($\Delta\nu_{1/2}$ = 280 Hz). IR (ATR 25 °C, cm^{-1}): 2954 (m), 2898 (w), 1404 (m), 1251 (s), 1180 (m), 1056 (m), 931 (m), 864 (s) 834 (s), 801 (s), 759 (m), 717 (m), 673 (m), 636 (m), 619 (m). Raman (75 mW, 25 °C, 500 scans, cm^{-1}): 3080 (2), 2962 (8), 2906 (10), 2780 (2), 2713 (2), 1601 (2), 1469 (2), 1446 (2), 1400 (2), 1282 (1), 1234 (1), 1176 (2), 1137 (2), 1101 (1), 1030 (1), 927 (1), 856 (1), 817 (2), 748 (1), 712 (1), 634 (1), 571 (2), 543 (1), 466 (1), 431 (1), 397 (1), 338 (5), 313 (3), 258 (2), 215 (2).

[$(Me_3Si)_2NSbCl$][$(Me_3Si)_2N(GaCl_3)_2$] (12). To a stirred solution of **11** (0.354 g, 1 mmol) in CH_2Cl_2 (3 mL) is added a solution of $GaCl_3$ (0.177 g, 1 mmol) in CH_2Cl_2 (2 mL) dropwise at −60 °C. The resulting yellow solution is allowed to stir for 15 min at this temperature and is concentrated afterward. Storage at −80 °C for one week leads to the deposition of colorless crystals of **12** (yield: 0.240 g; 48%). Anal. Calcd % (Found): C 16.81 (15.95); H 4.03 (3.98); N 2.80 (3.19). IR (ATR 25 °C, cm^{-1}): 2997 (w), 2961 (w), 2901 (w), 1409 (m), 1312 (w), 1278 (m), 1257 (s), 1204 (w), 1160 (w), 1041 (m), 841 (s), 825 (s), 767 (s), 692 (m), 672 (s), 653 (s), 609 (s), 582 (s).

[$MeSb(SbMe_3)_2$][$GaCl_4$]$_2$ (13). Procedure 1: To a stirred solution of **11** (1 mmol; 354 mg) in CH_2Cl_2 (3 mL) is added a solution of $GaCl_3$ (1 mmol, 177 mg) in CH_2Cl_2 (2 mL) dropwise at −60 °C. The resulting yellow solution is allowed to warm to ambient temperatures, and upon concentration to 1 mL an oily black layer deposits with a clear reddish supernatant on top. The supernatant is transferred, and the black oil is washed with hexane and layered with toluene (2 mL) afterward. Within seven days colorless crystalline needles have grown from the black oil, and only a few crystals could be isolated (tetragonal polymorph). The remaining supernatant was concentrated, and colorless crystals of **13** (monoclinic configuration) grew from the solution within 7 days at 5 °C in the fridge. The supernatant was transferred again, and the crystals were washed with CH_2Cl_2 at −30 °C, yielding 100 mg (0.11 mmol; 33%) of **13**. The remaining supernatant was taken to dryness, and crystals of 1,3-bis-(chlorodimethylsilyl)-2,2,4,4-tetramethyl-*cyclo*-disilazane (**15**) were grown from a saturated CH_2Cl_2 solution. Procedure 2: A solution of **12** (0.1 mmol; 100 mg) in CH_2Cl_2 (2 mL) is stirred for 48 h at ambient temperatures, and the solution is concentrated to 1 mL afterward. Colorless crystals of **13** (monoclinic polymorph) grow within 24 h; only a few crystals could be isolated. Mp = 72 °C. Anal. Calcd % (Found): C 9.41 (9.42); H 2.36 (2.37). ^{1}H NMR (25 °C, CD_2Cl_2, 500.13 MHz): 1.58 (s, $Sb(CH_3)_3$)), 2.01 (s, $Sb(CH_3)$)). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 125.76 MHz): −3.5 (s, $Sb(CH_3)_3$). IR (ATR 25 °C, cm^{-1}): 3012 (w), 2959 (w), 2924 (w), 1399 (m), 1257 (m), 1232 (m), 1217 (m), 1203 (m), 844 (s), 787 (m), 739 (m), 707 (m), 552 (m). Raman (75 mW, 25 °C, 500 scans, cm^{-1}): 3012 (1), 2924 (6), 1238 (1), 1219 (1), 708 (1), 553 (5), 527 (8), 503 (2), 346 (4), 166 (10), 118 (4).

$Me_3Sb−GaCl_3$ (14). To a stirred solution of **11** (1 mmol; 354 mg) in CH_2Cl_2 (3 mL) is added a solution of $GaCl_3$ (1 mmol; 177 mg) in CH_2Cl_2 (2 mL) dropwise at −70 °C. The resulting solution is allowed to warm to ambient temperatures and is concentrated to 0.5 mL at 80 °C. The brownish concentrated solution is put to rest at ambient temperatures for 30 days; within this time, minimal amounts of colorless crystals form, which were identified as [$Me_3Sb*GaCl_3$]. Mp = 131 °C (dec). IR (ATR 25 °C, cm^{-1}): 2963 (m), 1407 (m), 1260 (m), 848 (s), 794 (m), 555 (s).

ASSOCIATED CONTENT

Supporting Information

Experimental details, crystallographic information, including CIF, and further experimental data of all considered species. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Balakrishna, M. S.; Eisler, D. J.; Chivers, T. *Chem. Soc. Rev.* **2007**, *36*, 650−664 and references therein. (b) Stahl, L. *Coord. Chem. Rev.* **2000**, *210*, 203−250 and references therein.

(2) Herler, S.; Villinger, A.; Schmedt auf der Günne, J.; Mayer, P.; Schulz, A.; Weigand, J. J. *Angew. Chem.* **2005**, *117*, 7968−7971; *Angew. Chem., Int. Ed.* **2005**, *44*, 7790−7793.

(3) Schulz, A.; Villinger, A. *Angew. Chem.* **2008**, *120*, 614−617; *Angew. Chem., Int. Ed.* **2008**, *47*, 603−606.

(4) Michalik, D.; Schulz, A.; Villinger, A.; Weding, N. *Angew. Chem.* **2008**, *120*, 6565−6568; *Angew. Chem., Int. Ed.* **2008**, *47*, 6465−6468.

(5) Lehmann, M.; Schulz, A.; Villinger, A. *Eur. J. Inorg. Chem.* **2010**, *35*, 5501−5508.

(6) Mayer, P.; Schulz, A.; Villinger, A. *Chem. Commun.* **2006**, 1236−1238.

(7) Lehmann, M.; Schulz, A.; Villinger, A. *Angew. Chem.* **2011**, *123*, 5327−5331; *Angew. Chem., Int. Ed.* **2011**, *50*, 5221−5224.

(8) Schulz, A.; Mayer, P.; Villinger, A. *Inorg. Chem.* **2007**, *46*, 8316−8322.

(9) Michalik, D.; Schulz, A.; Villinger, A. *Inorg. Chem.* **2008**, *47*, 11798−11806.

(10) Althaus, A.; Breunig, H. J.; Lork, E. *Chem. Commun.* **1999**, 1971−1972.

(11) Ortep-3 for Windows: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(12) The methyl positions of the ring-silicon atom are found to be partly occupied by chlorine atoms in the crystal (see Supporting Information). Thus, a formula with three chlorine atoms in the disilazane can be considered, such as $[(Me_2Cl)SiNSi(Me_{1.5}Cl_{0.5})]_2$.

(13) (a) Geymayer, P.; Rochow, E. G. *Angew. Chem.* **1965**, *77*, 618. (b) Breed, L. W.; Elliot, R. L.; Wiley, J. C. *J. Organomet.* **1970**, *24*, 315−325.

(14) Burford, N.; Conrad, E.; McDonald, R.; Ferguson, M. *J. Am. Chem. Soc.* **2009**, *131*, 17000−17008.
(15) (a) Schmidbauer, H.; Findeiss, W. *Angew. Chem.* **1964**, *76*, 752−753. (b) Luo, B.; Young, V. G.; Gladfelter, W. L. *J. Organomet. Chem.* **2002**, 268−275.
(16) Carmalt, C.; Mileham, J. D.; White, A. J. P.; Williams, D. J.; Steed, J. W. *Inorg. Chem.* **2001**, *40*, 6035−6038.
(17) Hubrich, C.; Schulz, A.; Villinger, A. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2362−2366.
(18) (a) Schmidpeter, A.; Lochschmidt, S.; Karaghiosoff, K.; Sheldrick, W. S. *Chem. Commun.* **1985**, 1447−1448. (b) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem., Int. Ed.* **1985**, *24*, 226−227. (c) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. *J. Am. Chem. Soc.* **2003**, *125*, 14404−14410. (d) Dyker, C. A.; Burford, N. *Chem.—Asian J.* **2008**, *3*, 28−36. (e) Weigand, J. J.; Burford, N.; Decken, A. *Eur. J. Inorg. Chem.* **2008**, 4868−4872. (f) Dyker, C. A.; Riegel, S. D.; Burford, N.; Lumsden, M. D.; Decken, A. *J. Am. Chem. Soc.* **2007**, *129*, 7464−7474. (g) Dyker, C. A.; Burford, N.; Menard, G.; Lumsden, M. D.; Decken, A. *Inorg. Chem.* **2007**, *46*, 4277−4285. (h) Carpenter, Y.; Dyker, C. A.; Burford, N.; Lumsden, M. D.; Decken, A. *J. Am. Chem. Soc.* **2008**, *130*, 15732−15741.
(19) Minkwitz, R.; Hirsch, C. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1674−1682.
(20) Breunig, H. J.; Denker, M.; Lork, E. *Angew. Chem.* **1996**, *108*, 1080−1081; *Angew. Chem., Int. Ed.* **1996**, *35*, 1005−1006.
(21) Stevens, J. G.; Trooster, J. M.; Meinema, H. A.; Noltes, J. G. *Inorg. Chem.* **1981**, *20*, 801−803.
(22) Schulz, S.; Lyhs, B.; Jansen, G.; Bläser, D.; Wölper, C. *Chem.−Eur. J.* **2011**, *17*, 4914−4920.
(23) (a) Christe, K. O.; Haiges, R.; Vij, A.; Boatz, J. A.; Schneider, S.; Schroer, T.; Gerken, M. *Chem.—Eur. J.* **2004**, *10*, 508−517. (b) Schulz, B.; Lyhs, S.; Jansen, G.; Bläser, D.; Wölper, C. *Chem. Commun.* **2011**, *47*, 3401−3403.
(24) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 12770−12779.
(25) Tornieporth-Oetting, I. C.; Klapötke, T. M. *Angew. Chem.* **1995**, *107*, 559−568; *Angew. Chem., Int. Ed.* **1995**, *34*, 511−520.
(26) Klapötke, T. M.; Nöth, H.; Schütt, T.; Warchold, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 81−84.
(27) (a) Haiges, R.; Vij, A.; Boatz, J. A.; Schneider, S.; Schroer, T.; Gerken, M.; Christe, K. O. *Chem.—Eur. J.* **2004**, *10*, 508−517. (b) Klapötke, T. M.; Schulz, A.; McNamara, J. *J. Chem. Soc., Dalton Trans.* **1996**, 2985−2987.
(28) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 12770−12779.
(29) Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M.; Westmoreland, D. L. *J. Organomet. Chem.* **1988**, *341*, C1−C5.
(30) Matano, Y.; Nomura, H.; Suzuki, H. *Inorg. Chem.* **2000**, *39*, 1340−1341.
(31) (a) Ashe, A. J.; Ludwig, E. G., Jr.; Oleksyszyn, J.; Huffman, J. C. *Organometallics* **1984**, *3*, 337−338. (b) Becker, G.; Freudenblum, H.; Witthauer, C. *Z. Anorg. Allg. Chem.* **1982**, *492*, 37.
(32) Sheldrick, G. M. *SHELXS-97: Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
(33) Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
(34) Sheldrick, G. M. *SADABS. Version 2*; University of Göttingen: Göttingen, Germany, 2004.
(35) Raman and IR data can be found in the Supporting Information.