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Lewis-Acid-Assisted Methyl Exchange Reactions In Silylated Aminodichloroarsanes

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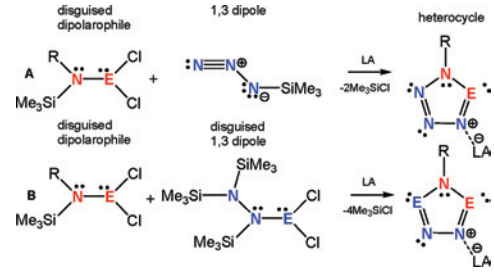
Lewis-acid-assisted methyl/chlorine, methyl/azide, and methyl/triflate exchange reactions between silicon and arsenic centers have been studied and applied to different silylated aminoarsane species leading to a number of new methylarsane compounds: bis(trimethylsilyl)amino(dichloro)arsane (**3**) was reacted with $GaCl_3$ yielding a bis(chlorodimethylsilyl)-tetramethyl-*cyclo*-disilazane (**4**) accompanied by the release of Me_2AsCl, while trimethylsilyl(*m*-terphenyl)amino(dichloro)arsane (**5**) (*m*-terphenyl = 2,6-Mes_2-C_6H_3, Mes = 2,4,6-$Me_3C_6H_2$) reacted with $GaCl_3$ to give dichloromethylsilyl(*m*-terphenyl)aminodimethylarsane (**6**). In the presence of trimethylsilylazide, trimethylsilyl(*m*-terphenyl)amino(dichloro)arsane displays a methyl/azide exchange triggered by the action of $GaCl_3$ yielding azidodimethylsilyl(*m*-terphenyl)amino(chloro)methylarsane (**7**). Moreover, methyl/triflate exchange reactions have been observed in the reaction of trimethylsilyl(*m*-terphenyl)amino(dichloro)arsane (i) with 1 equiv of AgOTf (OTf = triflate) yielding *N*-(trifluoromethylsulfonatodimethylsilyl)-*N*-(*m*-terphenyl)amino(methyl)chloroarsane (**8**) and (ii) with 2 equiv of AgOTf yielding *N*-(trifluoromethylsulfonatodimethylsilyl)-*N*-(*m*-terphenyl)trifluoromethylsulfonatomethylarsane (**9**). All new compounds (**3**−**9**) have been fully characterized by means of vibrational spectroscopy, X-ray, CHN analysis, MS, and NMR studies. A possible reaction mechanism is discussed starting from an initial chloride abstraction and the intermediate formation of a cationic iminoarsane species. In a second step, a methyl shift from the silicon to the arsenic center occurs.

Introduction

In a series of papers, Lewis-acid-assisted Me_3Si-Cl elimination reactions followed by [3 + 2] cycloadditions[1] have been established in phosphorous/nitrogen chemistry only recently.[2] This reaction type was also successfully applied in arsenic/nitrogen chemistry to the reaction of silylated supermesityl(dichloro)arsane, Mes*-N(Me_3Si)$AsCl_2$, (Mes* = 2,4,6-$tBu_3C_6H_2$) and Me_3Si-N_3 in the presence of $GaCl_3$ resulting in the formation of neutral tetrazarsole, Mes*-N_4As, stabilized as a $GaCl_3$ adduct (Scheme 1).[3] Lewis acids such as $AlCl_3$, $GaCl_3$, or $B(C_6F_5)_3$[4] are needed to release the "disguised" dipolarophile and 1,3-dipole by catalyzing the Me_3Si-Cl elimination.

Scheme 1. Lewis-Acid-Assisted [3 + 2] Cycloaddition Utilizing Disguised Dipolarophiles and 1,3 Dipoles[a]



[a] LA = Lewis acid = $AlCl_3$, $GaCl_3$, or $B(C_6F_5)_3$; E = P, As; R = $N(SiMe_3)_2$, *m*-terphenyl[5] = Ar[#] = 2,6-Mes_2-C_6H_3, supermesityl[6]).

Astonishingly, in contrast to the analogous phosphorus species, *N*,*N*′,*N*′-[tris(trimethylsilyl)]hydrazino(dichloro)arsane, $(Me_3Si)_2N-N(SiMe_3)-AsCl_2$ (**1**), did not react to the

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(1) (a) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; pp 1−176. (b) Padwa, A. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon, Oxford, 1991; Vol. 4, pp 1069−1109. (c) For a review of asymmetric 1,3-dipolar cycloaddition reactions, see: Gothelf, K. V.; Jorgensen, K. A. *Chem. Rev* **1998**, *98*, 863–909. (d) For a review of synthetic applications, see: Mulzer, J. *Org. Synth. Highlights* **1991**, 77–95.

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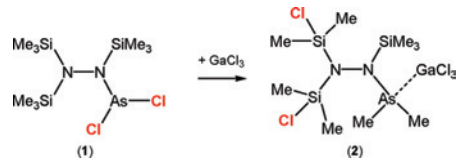
Scheme 2. $GaCl_3$-Assisted Methyl/Chlorine Exchange in Hydrazino(dichloro)arsane, $(Me_3Si)_2N-N(SiMe_3)-AsCl_2$.



triazadiarsole according to Scheme 1 (reaction B), but instead **1** was transformed into the corresponding *N*-trimethylsilyl-*N*′,*N*′-bis-(dimethylchlorosilyl)hydrazinodimethylarsane (**2**) (Scheme 2).[7] Obviously, in case of the arsenic compound (**1**), there is a second reaction channel that is faster and results in a methyl/chlorine exchange at the silicon and the arsenic centers induced by the action of the Lewis acid. The thermodynamic stabilization of this chlorinated system in **2** appears in the important antiperiplanar interactions between nitrogen/chlorine lone pairs and adjacent σ^* acceptor orbitals.

In this study, we report that this methyl/chlorine exchange reaction triggered by the action of $GaCl_3$ can be generalized and applied to different silylated amino(dichloro)arsane species.

Results and Discussion

Reactions with Si−C bond cleavage catalyzed by the action of $GaCl_3$ are known.[8] For instance, a methyl migration from silicon to gallium was found in the reaction of $GaCl_3$ and $SiMe_4$ for which an intermediate with bridging Cl and Me between Si and Ga was suggested, finally resulting in the formation of Me_3SiCl and $(MeGaCl_2)_2$. In the intramolecular Me/Cl exchange reaction of **1** (Scheme 2), $GaCl_3$ mediates the substitution and forms an adduct (**2**) at the end of the exchange reaction. Reaction of **2** with a Lewis base, for example, 4-(dimethylamino)pyridine (DMAP), yields the adduct-free hydrazinodimethylarsane,[7] so $GaCl_3$ can be considered a catalyst in contrast to the Si−C bond cleavage reaction described above where methylgalliumchlorides are formed. Carmalt et al. have observed a similar Si−C bond cleavage in the reaction of $GaCl_3$ with $(Me_3Si)_3N$ yielding among other things dimeric $(MeGaCl_2)_2$.[9]

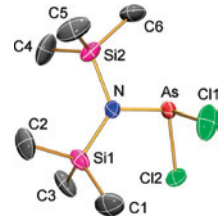
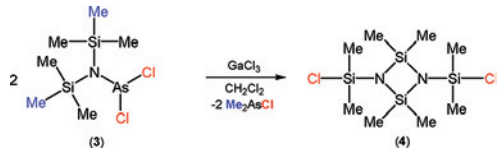


Figure 1. ORTEP drawing of the molecular structure of **3** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity).

Scheme 3. $GaCl_3$-Assisted Methyl/Chlorine Exchange in Bis(trimethylsilyl)amino(dichloro)arsane (**3**), Yielding *cyclo*-Disilazane (**4**) via Release of Me_2AsCl



Methyl-Exchange Reactions in Bis(trimethylsilyl)amino(dichloro)arsane (3). To gain further insight into $GaCl_3$-assisted methyl/chlorine exchange reactions, we applied this reaction type to **3** and other arsenic species. In a modified synthetic procedure,[10] bis(trimethylsilyl)amino(dichloro)arsane (Figure 1) is easily prepared from *N*-lithio-*N*,*N*-bis-(trimethylsilyl)amide and $AsCl_3$ in *n*-hexane at −40 °C. Filtration and removal of the solvent and the excess of $AsCl_3$ gave a viscous liquid of **3** (yield = 70%, mp = −11 °C, bp = 53 °C (10^{-3} mbar)).

According to Scheme 3, amino(dichloro)arsane **3** dissolved in CH_2Cl_2 was added dropwise to a solution of $GaCl_3$ in CH_2Cl_2 at −20 °C resulting in a yellowish solution. Removal of CH_2Cl_2 yielded a residue, which was extracted with *n*-hexane. Subsequent sublimation gave the unexpected 1,3-bis(chlorodimethylsilyl)-2,2,4,4-tetramethyl-*cyclo*-disilazane (**4**) (Scheme 3) in good yields (75 %). The formation of **4** was unequivocally proven by NMR and X-ray studies, and it was fully characterized. Furthermore, the methyl/chlorine exchange was confirmed by the identification of Me_2AsCl (^1H NMR). *cyclo*-Disilazane **4** has been reported before and was prepared, for example, in the condensation reaction of dichlorodimethylsilane, 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, $[Me_2SiNH]_4$.[11]

Presumably, the unexpected formation of **4** in the reaction of **3** with $GaCl_3$ is triggered by a chloride abstraction (formation of $GaCl_4^-$) in the first reaction step as illustrated

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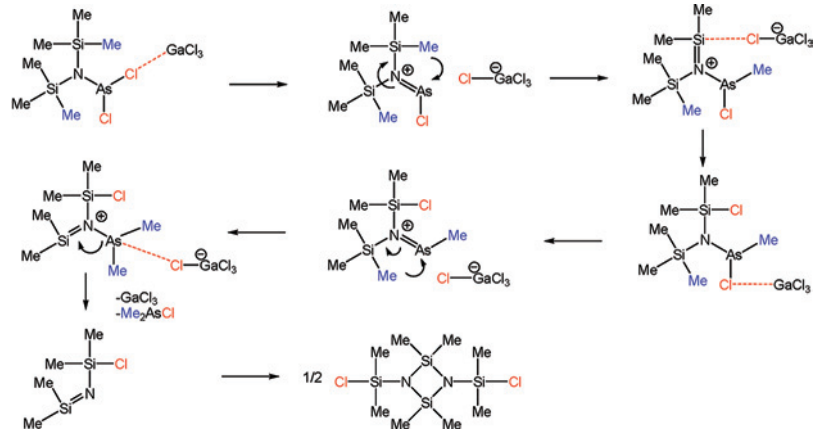
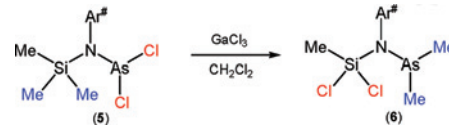
Scheme 4. Suggested Reaction Mechanism of the $GaCl_3$-Assisted Methyl/Chlorine Exchange in Bis(trimethylsilyl)amino(dichloro)arsane (**3**), Yielding *cyclo*-Disilazane (**4**) via Release of Me_2AsCl



in Scheme 4. The formed cationic As−N species undergoes a shift of one methyl group from the Me_3Si unit to the cationic arsenic center. Now $GaCl_4^-$ transfers the chloride to the Me_2Si═N moiety. The same process can be discussed for the second methyl/chlorine exchange, which is followed by a release of Me_2AsCl and the dimerization of the *in situ* generated Me_2Si═N−$SiMe_2Cl$.

Methyl/Chlorine Exchange Reactions in Trimethylsilyl(*m*-terphenyl)aminodichloroarsane (5). Compound **5** (Figure 2) may be regarded a "disguised" dipolarophile, since an intrinsic elimination of Me_3Si−Cl should give an imino(chloro)arsane, $Ar^{\#}$−N═As−Cl, which can react with a 1,3 dipole molecule such as Me_3Si−N_3 to give a tetrazarsole (*m*-terphenyl[5d] = $Ar^{\#}$ = 2,6-Mes_2-C_6H_3, Mes = 2,4,6-$Me_3C_6H_2$).[3] This at least was the idea, which worked well for the analogue phosphorus compound but not for **5**.[2f] Upon adding a solution of $GaCl_3$ in CH_2Cl_2 to a solution of **5** in CH_2Cl_2, the formation of an iminoarsane was not observed but again a chlorine/methyl exchange reaction occurred as displayed by ^{29}Si, ^1H, and ^{13}C NMR studies. Recrystallization from toluene gave crystals suitable for an X-ray structure determination, revealing again a methyl/chlorine exchange product, now with two chlorine atoms attached to the silicon and a dimethylarsane unit according to Scheme 5 (Figure 3). Obviously, when only one Me_3Si unit is present in the molecule, a double methyl/chlorine exchange at this Si center (Scheme 5) occurs, while a single methyl/chlorine exchange at two different Si centers is observed when two Me_3Si groups are present (Schemes 2 and 3). The novel dichloromethylsilyl(*m*-terphenyl)aminodimethylarsane (**6**) is soluble

Scheme 5. $GaCl_3$-Assisted Methyl/Chlorine Exchange in Trimethylsilyl(*m*-terphenyl)amino(dichloro)arsane (**5**), Yielding Dichloromethylsilyl(*m*-terphenyl)aminodimethylarsane (**6**)



in toluene, CH_2Cl_2, and ether and is thermally stable up to 156 °C. Aminodimethylarsane **6** is air- and moisture-sensitive, but under argon, it is stable over a long period in both solid and common organic solvents. Interestingly, in contrast to **1**, which forms a $GaCl_3$ adduct **2**, compound **6** does not form an adduct presumably due to steric reasons.

Methyl/Azide Exchange Reactions in Trimethylsilyl(*m*-terphenyl)aminodichloroarsane. Although we noticed that $GaCl_3$ already reacts with **5** in a methyl/chlorine exchange reaction, we changed the synthetic approach with respect to the order of adding the Lewis acid to determine whether a formal [3 + 2] cyclization[2,3] is faster than the methyl/chlorine or methyl/azide exchange reaction. Hence, in a further experiment, a solution of $GaCl_3$ in CH_2Cl_2 was added to a solution of **5** and Me_3Si−N_3 in CH_2Cl_2 at −70 °C, resulting in an orange solution (Scheme 6). After being stirred at −30 °C for 30 min, the solution was concentrated and recrystallized at −80 °C yielding a colorless, crystalline solid (yield = 95%). A Raman experiment immediately revealed the existence of a covalently bound azide (ν_{as} = 2141 cm^{-1}), and by means of X-ray structure determination, the formation of azidodimethylsilyl(*m*-terphenyl)amino(chloro)methylar-

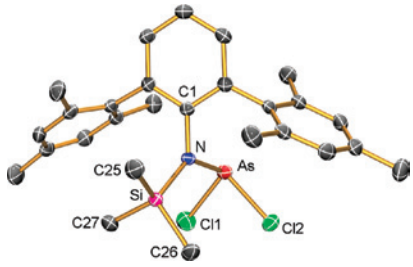


Figure 2. ORTEP drawing of the molecular structure of **5** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity).

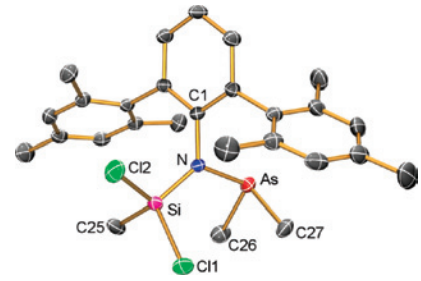


Figure 3. ORTEP drawing of the molecular structure of **6** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity).

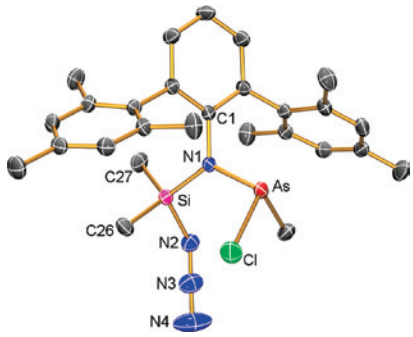
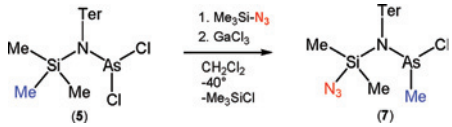


Figure 4. ORTEP drawing of the molecular structure of **7** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity).

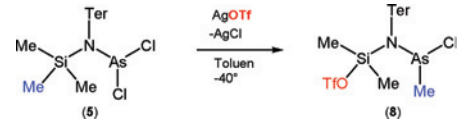
Scheme 6. $GaCl_3$-Assisted Methyl/Azide Exchange in Trimethylsilyl(*m*-terphenyl)amino(dichloro)arsane (**5**), Yielding Azidomethylsilyl(*m*-terphenyl)amino(chloro)methylarsane (**7**)



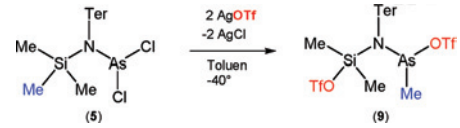
sane (**7**) was unequivocally proven (Figure 4).[12] It is interesting to note that in the presence of Me_3Si-N_3 the Lewis acid $GaCl_3$ facilitates a methyl/azide exchange even at low temperatures (T always below −30 °C). Without $GaCl_3$ no reaction was observed between **5** and Me_3Si-N_3. Interestingly, the novel azidodimethylsilyl(*m*-terphenyl)amino(chloro)methylarsane (**7**) represents one of the rare examples of structurally characterized neutral azidosilanes.[13] Compound **7** is thermally stable to over 149 °C and is neither heat- nor shock-sensitive. Moreover, **7** is extremely air- and moisture-sensitive, but under argon, it is stable over a long period in solid at ambient temperatures and in common organic solvents (e.g., toluene, CH_2Cl_2, ether) at low temperatures ($T < -40$ °C). It is interesting to mention that when an excess of Me_3Si-N_3 was used, a $Me_3Si-N_3 \cdot GaCl_3$ adduct crystallizes together with **7**. This adduct was first described by Kouvetakis et al.[14]

Azidosilanes are frequently used for the introduction of azide groups, for the generation of silylenes and the synthesis of silyl-iminophosphoranes via Staudinger reaction.[12b,15−20]

Scheme 7. Methyl/Triflate Exchange in Trimethylsilyl(*m*-terphenyl)amino(dichloro)arsane (**5**), Yielding *N*-(Trifluoromethylsulfonatodimethylsilyl)-*N*-(*m*-terphenyl)amino-(methyl)chloroarsane (**8**) (Utilization of 1 equiv of AgOTf)



Scheme 8. Methyl/Triflate Exchange in Trimethylsilyl(*m*-terphenyl)amino(dichloro)arsane (**5**), Yielding *N*-(Trifluoromethylsulfonatodimethylsilyl)-*N*-(*m*-terphenyl)amino-trifluoromethylsulfonatomethylarsane (**9**) (Utilization of 2 equiv of AgOTf)



Methyl/Triflate Exchange Reactions in Trimethylsilyl(*m*-terphenyl)aminodichloroarsane. In a second series of experiments we studied the reaction of silver triflate, AgOTf (OTf = SO_3CF_3 = trifluoromethylsulfonate = triflate), with **5**, again observing interesting methyl exchange reactions, this time triggered by the action of the Lewis acid Ag^+ (Scheme 7 and 8). First, 1 equiv of AgOTf was added to a solution of **5** in CH_2Cl_2 at −30 °C under exclusion of light, resulting in the formation of *N*-(trifluoromethylsulfonatodimethylsilyl)-*N*-(*m*-terphenyl)amino(methyl)chloroarsane (**8**) (mp = 163 °C) in high yields (98 %) (Scheme 7, Figure 5). Usage of 2 equiv of AgOTf led to the formation of *N*-(trifluoromethylsulfonatodimethylsilyl)-*N*-(*m*-terphenyl)-amino-trifluoromethylsulfonatomethylarsane (**9**) (yield = 96%, mp = 186 °C). Both compounds (**8** and **9**) have been fully characterized. As expected, when 1 equiv AgOTf was added a methyl/triflate exchange occurs at the silicon center (Scheme 7). However, when 2 equiv of AgOTf are used, again only one methyl/triflate exchange was observed. The second equivalent of AgOTf attacks the arsenic center finally forming an As−OTf bond (Scheme 8).

Both novel amino(methyl)chloroarsanes (**8** and **9**) are thermally stable to over 160 °C. Both crude products (of **8** and **9**) are easily purified by recrystallization and are extremely air- and moisture-sensitive, but under argon they are stable over a long period.

Generalized Reaction Mechanism of Methyl Exchange Reactions in Amino Substituted Dichloroarsanes. Independent of the Lewis acid, the first reaction step is characterized by a chloride abstraction and the intermediate formation of a cationic species with the formal positive charge localized at the nitrogen atom as displayed in Scheme 9. According to NBO analysis for the cationic model compound $Me_3Si-N(R)-AsCl^+$ (R = H), the As−N bonds and the Si−N bonds are highly polarized, and the calculated partial

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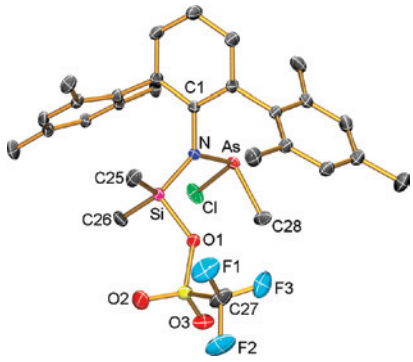
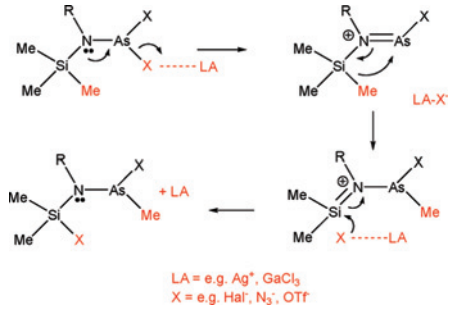


Figure 5. ORTEP drawing of the molecular structure of **8** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity).

Scheme 9. Generalized Reaction Mechanism of Methyl Exchange Reactions in Amino-Substituted Dichloroarsanes



charges are +1.93 for Si, +1.30 for As, and −1.28 *e* for N.[21] As further indicated by NBO analysis,[22] there are significant interactions of the π(N═As) bond with two unoccupied, antibonding σ^* orbitals of the Si−C bond system.[7] This intramolecular donor−acceptor interaction (hyperconjugation)[23] accounts for the rather long Si−C bond and describes the delocalization of the π(N═As). This rather long Si−C bond presumably facilitates the methyl group shift from the Si to the As center, while the basic anion X^- (X = Cl, N_3, OTf) attacks the positively charged Si atom, finally forming an As−C and a Si−X bond.

X-ray Structure Determination. The solid-state structures of the aminoarsane derivatives **3** and **5**−**9** are shown in Figures 1−6. Selected bond lengths and angles are listed in Table 1; crystallographic details are given in Tables 2 and 3.[24] X-ray quality crystals of **4**−**9** were selected in Kel-F-oil (Riedel deHaen) at ambient temperatures, while an X-ray quality crystal of **3** had to be selected in Galden-HT230 oil

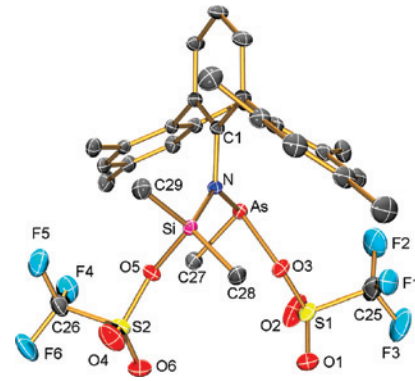


Figure 6. ORTEP drawing of the molecular structure of **9** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity).

(Solvay Solexis) at 173 K due to the low melting point of **3** (mp = −11 °C). All samples were cooled to 173(2) K during the measurement. To the best of our knowledge, only a few silyltriflates[25] and dichloromethylsilanes have been structurally characterized.[26]

In all aminoarsane derivatives, as expected, the central nitrogen atom is almost trigonal planar, the arsenic atom is trigonal pyramidal, and the silicon atom is tetrahedrally coordinated. The sum of the bond angles at the amino nitrogen atom N is always very close to 360° indicating a planar environment and hence a formal sp^2-hybridization (Table 1). The sum of the bond angles at the arsenic atom ranges between 300−302° for compounds **3**−**8**, while in the triflate-subtituted aminoarsane **9** a sum of 292° is found. The R^1−As−N and R^2−As−N angles are all between 91° and 108° with the smallest angle (∠O−As−N = 91.42(6)°) and the largest (∠C−As−N = 107.96(8)°) in case of triflate substitution in compound **9**. Obviously, a more electronegative substituent allows a smaller bond angle.[27]

As depicted in Figures 2−6, in all *m*-terphenyl-substituted aminoarsanes, the N−AsR_2−Si moiety sits almost central inside the pocket formed by the m-terphenyl group but always twisted (the torsion angle between the N−Si−As plane and the central phenyl ring of the *m*-terphenyl group is always between 45° and 65°).

It should be mentioned that the $AsCl_2$ unit in **3** is twisted towards Si1 (∠Si1−N−As−Cl2 = 23.03(8)°) resulting in a C_1 symmetric molecule (Figure 1). Hence the Si1−N−As angle is considerably larger (creates more space for the $AsCl_2$ moiety) then the Si2−N−As angle (125.37(7)° vs 112.03(6)°). Both Me_3Si groups adopt a staggered conformation.

The As−N distances are all between 1.802(1) (compound **3**) and 1.920(1) Å (compound **6**), with smaller As−N distances always found for the more electronegative R^1 and

(21) Computational details and a summary of the NBO output are given in the Supporting Information. As model compound, $Me_3SiN(H)-AsCl^+$ has been used.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) in $(Me_3Si)_2N-AsCl_2$ (**3**) and *m*-Terphenylaminoarsanes of the Type Ter−N(silyl)−As(R^1)R^2 (**5**−**9**)

	3, $R^1 = R^2 = Cl$	**5**, $R^1 = R^2 = Cl$	**6**, $R^1 = R^2 = CH_3$	**7**, $R^1 = Cl$, $R^2 = CH_3$	**8**, $R^1 = Cl$, $R^2 = CH_3$	**9**, $R^1 = CH_3$, $R^2 = OTf$
As−N	1.802(1)	1.828(2)	1.920(1)	1.878(1)	1.877(1)	1.849(2)
As−R^1	2.2265(8)	2.2116(7)	1.959(2)	2.2340(7)	2.2221(6)	1.946(2)
As−R^2	2.211(1)	2.2260(7)	1.965(2)	1.961(2)	1.950(2)	1.987(2)
N−Si	1.778(1)[a]	1.796(2)	1.703(1)	1.745(1)[b]	1.732(2)	1.747(2)
	1.781(1)			1.780(1)		
R^1−As−N	103.27(4)	106.66(6)	105.96(7)	100.47(3)	101.83(5)	107.96(8)
R^2−As−N	102.15(4)	99.53(6)	100.73(7)	105.86(6)	104.47(7)	91.42(6)
R^1−As−R^2	96.38(4)	94.27(3)	95.53(8)	93.67(5)	94.46(8)	93.11(8)
As−N−Si	125.37(7)[a]	126.6(1)	123.82(7)	125.99(6)	127.48(8)	128.10(8)
	112.03(6)					
∑∠N	360.0	360.0	359.5	360.0	359.9	360.0
∑∠As	301.8	300.5	302.2	300.0	300.8	292.5

[a] First value corresponds to Si1, second to Si2. [b] First distance Si−N_{amino}, second Si−N_3 bond.

Table 2. Crystallographic Details of Compounds **3**−**5**

	3	**4**	**5**
empirical formula	$C_6H_{18}AsCl_2NSi_2$	$C_8H_{24}Cl_2N_2Si_4$	$C_{27}H_{34}AsCl_2NSi$
M_r	306.21	331.55	546.46
cryst syst	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	*Pbca*
a (Å)	8.0250(16)	16.096(3)	16.150(3)
b (Å)	8.7700(18)	15.286(3)	17.950(4)
c (Å)	11.352(2)	22.432(5)	18.470(4)
α (deg)	90.53(3)	90.00	90.00
β (deg)	93.99(3)	112.20(2)	90.00
γ (deg)	117.10(3)	90.00	90.00
V (Å^3)	708.7(2)	907.5(4)	5354.3(2)
Z	2	2	8
D_{calcd} (g cm^{-3})	1.435	1.213	1.356
μ (mm^{-1})	2.905	0.604	1.530
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073
T (K)	173 (2)	173 (2)	173 (2)
reflns collected	20165	23812	97966
independent reflns	5038	2062	6244
reflns with $I > 2\sigma(I)$	4454	1652	4578
R_{int}	0.0194	0.0510	0.0735
F(000)	312	352	2272
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0242	0.0389	0.0312
wR_2 (F^2)	0.0637	0.1141	0.0767
GOF	1.046	1.035	1.048
params	115	77	298
CCDC no.	693309	693310	693311

R^2 (Table 1). For comparison, partial double bond character was discussed in tetrazaarsols[3] with As−N distance between 1.784(2) and 1.805(2) Å or between 1.82 and 1.84 Å in cations of 1,3,2-diazaarsolenes[28] (cf. sum of the covalent radii d_{cov}(N−As) = 1.91 and d_{cov}(N=As) = 1.71 Å).[29] Hence, it can be assumed that in the case of compounds **3** and **5** ($R^{1,2}$ = Cl) also partial double bond character can be discussed, which is introduced by hyperconjugation.[2b] Since the nitrogen atom sits in a planar environment, the lone pair is localized in a pure p-type atomic orbital. As a consequence, this p-type lone pair at the N_{amino} atom (notation p-LP) is slightly further delocalized resulting in intramolecular interactions (noncovalent effects). As indicated by an investigation of the noncovalent effects,[22] there are two significant interactions of the nitrogen lone pair (p-LP) with the two unoccupied localized antibonding *σ**(As−Cl) orbitals. These intramolecular LP(N) → *σ**(As−Cl) donor−acceptor interactions (hyperconjugation, 15.2 and 2.5 kcal/mol in case of species **3**) account for the rather short As−N distance by introducing a small amount of *π* interaction (Figure S1, Supporting Information).[21] Similar structural features with short As−N distances have already been observed in a series of aminoarsanes ($R_2N-AsR^1R^2$; with R^1,R^2 = Cl or Me).[6,7,30]

Aminoarsane **7** can also be regared as an azidosilane of which only a few have been structurally characterized. Azidotriphenylsilane is the first structurally characterized azidosilane, which was published in 1973.[31] Furthermore, the structures of trimesitylazidosilane, 1,1-dimesityl-2,2-diphenyl-2-*tert*-butylazidodisilane,[32] a 2,4-diazido-*cyclo*-disiladiazane,[33] and $Me_3SiN_3 \cdot GaCl_3$[14] have been reported. As shown on numerous occasions,[34] covalently bound azide groups such as Si−NNN display a *trans*-bent configuration (regarding the Si atom) with a N−N−N bond angle of 175.4(2)° and a Si−N distance of 1.780(1) Å (cf. 175.3(2)° and 1.866−1.881 Å in $Si(N_3)_6^-$).[35] The N−N distances *d*(N3−N4) = 1.130(2) and *d*(N2−N3) = 1.215(2) Å are substantially shorter than the sum of the covalent radii (d_{cov}(N−N) = 1.48 and d_{cov}(N=N) = 1.20),[8] which indicates partial triple and double bond character for both N−N bonds.

Conclusion

Lewis-acid-assisted methyl exchange reactions have been established as an interesting new route to substituted silylamino(methyl)arsane compounds bearing either one or two electronegative groups R (R = Cl, N_3, and OTf) at the silicon atom. These novel exchange reactions were unambiguously proven by IR, Raman, NMR, and X-ray studies. A general-

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Table 3. Crystallographic Details of Compounds **6**−**9**

	6·(toluene)	**7**	**8**	**9**·(toluene)
empirical formula	$C_{34}H_{42}AsCl_2NSi$	$C_{27}H_{34}AsClN_4Si$	$C_{28}H_{34}AsClF_3NO_3SSi$	$C_{36}H_{42}AsF_6NO_6S_2Si$
M_r	638.60	553.04	660.08	865.84
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	12.813(3)	10.681(2)	8.5100(17)	12.241(2)
b (Å)	12.597(3)	15.587(3)	12.946(3)	20.940(4)
c (Å)	20.432(4)	16.446(3)	28.447(6)	15.639(3)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	98.80(3)	94.55(3)	95.70(3)	99.51(3)
γ (deg)	90.00	90.00	90.00	90.00
V (Å^3)	3259.0(11)	2729.4(9)	3118.5(11)	3953.6(14)
Z	4	4	4	4
D_{calcd} (g cm^{-3})	1.302	1.346	1.406	1.455
μ (mm^{-1})	1.267	1.410	1.328	1.068
λ(Mo Kα) [Å]	0.71073	0.71073	0.71073	0.71073
T (K)	173 (2)	173 (2)	173 (2)	173 (2)
reflns collected	46291	50108	41346	54566
independent reflns	9460	12009	9052	11496
reflns with $I > 2\sigma(I)$	7386	8870	7156	9046
R_{int}	0.0362	0.0226	0.0282	0.0251
F(000)	1336	1152	1360	1784
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0330	0.0355	0.0363	0.0405
wR_2 (F^2)	0.0841	0.1026	0.0919	0.1189
GOF	1.032	1.069	1.031	1.065
params	420	316	361	523
CCDC no.	693312	693313	693314	693315

ized reaction mechanism is proposed with an initial formation of an iminochloroarsenium cation followed by a shift of one methyl group from the silicon to the arsenic. In case of bis(trimethylsilyl)amino(dichloro)arsane (**3**), Me_2AsCl was eliminated finally yielding a cyclic silazane (**4**) after dimerization of the intermediate silazene $Me_2Si{=}N-SiMe_2Cl$.

As expected for silylated aminoarsanes, all considered species revealed similar structural features with respect to the $N-AsR_2$ moiety: The geometries at nitrogen and arsenic are distinguished by the sums of the three angles at each site, defining an almost planar geometry at each nitrogen center (almost 360°; Table 1) and a distinctly pyramidal geometry at each arsenic center (substantially less than 360°). Hence, as displayed by NBO analysis, the one lone pair at the amino nitrogen atom is localized in a pure p-type atomic orbital. Investigation of intramolecular donor−acceptor interaction displayed significant interactions of this lone pair into $\sigma^*(As-R_1)$ orbitals and into $\sigma^*(Si-C)$ orbitals.

Moreover, only a few neutral azidosilanes and aminoarsanes are known, which have been structurally characterized. Hence, the X-ray data of compounds **3** and **5**−**9**, respectively, may fill this gap.

Experimental Procedures

Caution! *Due the high toxicity of organoarsenic compounds proper safety precautions are necessary. It should be noted that only the dimethylarsane compound (***6***) is a very malodorous substance.*

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques. Dichloromethane was purified according to a literature procedure,[36] dried over P_4O_{10}, and freshly distilled prior to use. Diethylether and toluene were dried over Na/benzophenone and freshly distilled prior to use. *n*-Hexane was dried over Na/benzophenone/tetraglyme and freshly distilled prior to use.

N,*N*-Bis(trimethylsilyl)amino-dichloroarsane (**3**) and *N*-trimethylsilyl-2,6-bis-(2,4,6-trimethylphenyl)aniline (**10**) were previously reported and were prepared according to modified literature procedures.[37,38] 2,6-Bis-(2,4,6-trimethylphenyl)aniline was prepared according to a literature procedure.[38] Chlorotrimethylsilane (99%, Merck), trimethylsilylazide (99%, Fluka), and $AsCl_3$ (99.99%, Merck) were freshly distilled prior to use. $GaCl_3$ (99.999%, Sigma-Aldrich), $AgSO_3CF_3$ (99%, Fluka), *N*-lithio-*N*,*N*-bis-trimethylsilylamide (98%, Fluka) and *n*-BuLi (2.5 M, Acros) were used as recieved.

NMR. $^{14}N\{^1H\}$, $^{19}F\{^1H\}$, ^{29}Si INEPT, ^1H, and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker spectrometers AVANCE 250, 300, or 500. The ^1H and ^{13}C NMR chemical shifts were referenced to the solvent signals (^{13}C, $\delta_{CD_2Cl_2} = 54.0$; ^1H, $\delta_{CDHCl_2} = 5.31$). The ^{14}N, ^{19}F, and ^{29}Si chemical shifts are referred ($\delta = 0$) to $MeNO_2$, $CFCl_3$, and Me_4Si, respectively.

IR. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR device or Nicolet 380 FT-IR with Smart Orbit ATR module.

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Raman. Raman spectra were recorded on a Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm).

MS. Mass spectrometry was performed with a Finnigan MAT 95-XP from Thermo Electron.

CHN Analyses. CHN analysis was carried out using Analysator Flash EA 1112 from Thermo Quest.

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

DSC. Differential scanning calorimetry was performed with a DSC 823e from Mettler-Toledo at a heating rate of 5 °C/min.

Synthesis of 3. *N*-Lithio-*N*,*N*-bis-(trimethylsilyl)amide (6.693 g, 40.0 mmol) was dissolved in *n*-hexane (60 mL) and filtered (F4). The colorless solution was then added dropwise to a solution of $AsCl_3$ (14.50 g, 80.0 mmol) in *n*-hexane (30 mL) at −40 °C over a period of 30 min. The resulting colorless suspension was stirred for 1 h at ambient temperature and was then filtered (F4), resulting in a colorless solution. Removal of solvent and excess $AsCl_3$ *in vacuo* results in a colorless, viscous liquid. Fractionated distillation *in vacuo* yields 8.590 g (28.1 mmol, 70%) of pure **3**. Mp −11 °C; bp 53 °C (10^{-3} mbar). Anal. calcd % (found): C, 23.53 (23.53); H, 5.92 (6.02); N, 4.57 (4.74). ^{14}N NMR (36.1 MHz, CD_2Cl_2, 25 °C): $\delta = 278.4$ ($\nu_{1/2} \approx 280$ Hz). ^{29}Si NMR (99.4 MHz, CD_2Cl_2, 25 °C): $\delta = 11.4$. ^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): $\delta = 0.40$. ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 °C): $\delta = 4.8$. MS (CI, positive, 70 eV (isobutane), *m*/*z*, >10 %): 71, 91 $[NAsH_3]^+$. Crystals suitable for X-ray crystallographic analysis were obtained by cooling a neat sample of **3** slowly to −25°C.

Synthesis of 4. To a stirred solution of *N*,*N*-bis-(trimethylsilyl)-amino-dichloroarsane (**3**) (0.612 g, 2.0 mmol) in CH_2Cl_2 (10 mL), $GaCl_3$ (0.387 g, 2.2mmol) in CH_2Cl_2 (10 mL) was added dropwise at −20 °C over a period of 15 min. The resulting yellowish solution was stirred for 1 h at ambient temperature resulting in a colorless solution. The solvent was removed *in vacuo*, resulting in a colorless crystalline solid. *n*-Hexane (10 mL) was added, which gave a brownish oil (which is discarded) and a colorless supernatant, which is separated. The solvent is removed *in vacuo* resulting in a colorless crystalline solid. Sublimation at 40 °C (10^{-3} mbar) for 1 h yields 0.631 g (1.904 mmol, 75%) of **4** as colorless crystals. Mp 67 °C. Anal. calcd % (found): C, 28.98 (29.35); H, 7.30 (7.26); N, 8.45 (8.35). ^{29}Si NMR (59.6 MHz, CD_2Cl_2, 25 °C): $\delta = 6.4, 7.2$. ^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): $\delta = 0.37$ (s, 12H), 0.40 (s, 12H). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 °C): $\delta = 5.0, 5.1$. Crystals suitable for X-ray crystallographic analysis were obtained by sublimation of **4** at 40 °C (10^{-3} mbar).

Synthesis of 5. To a stirred solution of *N*-trimethylsilyl-2,6-bis-(2,4,6-trimethylphenyl)aniline (**10**) (2.008 g, 5.0 mmol) in Et_2O (50 mL), *n*-BuLi (2.5 M, 5.05 mmol) was added dropwise at −10 °C. The resulting golden solution was stirred for 1 h and was then added dropwise to a stirred solution of $AsCl_3$ (0.733 g, 6.5 mmol) in Et_2O (10 mL) at −50 °C over a period of 30 min, resulting in a pale yellowish suspension, which is stirred for 2 h at ambient temperature. The solvent is removed *in vacuo*, and the orange residue is extracted with benzene (15 mL) and filtered (F4). Slow removal of solvent over a period of 1 h gives a yellowish crystalline solid, which is surrounded by an orange viscous oil. Ice-cold diethyl ether (10 mL) is then added, and the resulting suspension is filtered (F4) rapidly. The pale yellowish residue is then washed by repeated back distillations of solvent. Drying *in vacuo* yields 1.211 g (2.21 mmol, 44%) of **5** as a colorless, crystalline solid. Mp 216 °C. Anal. calcd % (found): C, 59.34 (59.49); H, 6.27 (6.46); N, 2.56 (2.35). ^{29}Si NMR (59.6 MHz, CD_2Cl_2, 25 °C): $\delta = 18.4$. ^{1}H NMR (250.13 MHz, CD_2Cl_2, 25 °C): $\delta = -0.09$ (s, 9H, $Si(CH_3)_3$), 2.02 (s, 6H, CH_3), 2.22 (s, 6H, CH_3), 2.31 (s, 6H, CH_3), 6.93 (m, broad, 2H, CH-Mes), 6.98 (m, broad, 2H, CH-Mes), 7.07 (d, 1H, $^3J(^1H-^1H) = 8.0$ Hz, *m*-Ph), 7.07 (d, 1H, $^3J(^1H-^1H) = 7.0$ Hz, *m*-Ph), 7.26 (dd, 1H, $^3J(^1H-^1H) = 8.0$ Hz, $^3J(^1H-^1H) = 7.0$ Hz, *p*-Ph). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25 °C): $\delta = 4.7$ ($Si(CH_3)_3$), 21.3 (CH_3), 22.1 (CH_3), 22.2 (CH_3), 126.0 (CH), 129.5 (CH), 129.8 (CH), 132.9 (CH), 136.7, 137.6, 138.3, 138.9, 140.4, 144.5. MS (CI, positive, 70 eV (isobutane), *m*/*z*, >10%): 330 $[TerNH_3]^+$, 402 $[M - SiMe_3Cl - Cl]^+$, 476 $[M - 2Cl]^+$, 510 $[M - Cl]^+$, 545 $[M]^+$. Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated dichloromethane solution of **5** to −25 °C.

Synthesis of 6. To a stirred solution of *N*-trimethylsilyl-*N*-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-dichloroarsane (**5**) (0.546 g, 1.0 mmol) in CH_2Cl_2 (20 mL), $GaCl_3$ (0.194 g, 1.1 mmol) in CH_2Cl_2 (10 mL) was added dropwise at −40 °C. The resulting clear red solution was stirred at ambient temperatures for 1 h. The solvent is removed *in vacuo*, resulting in a red crystalline residue, which is dissolved in toluene (2 mL). Crystallization at −80 °C over a period of 1 week gives a colorless crystalline solid. Removal of supernatant by syringe and drying *in vacuo* yields 0.351 g (0.64 mmol, 64%) of **4** as a colorless, crystalline solid. Mp 156 °C (dec.). Anal. calcd % (found): C, 59.34 (59.14); H, 6.27 (6.26); N, 2.56 (2.22). ^{29}Si NMR (59.6 MHz, CD_2Cl_2, 25 °C): $\delta = -4.9$. ^{1}H NMR (300.13 MHz, CD_2Cl_2, 25 °C): $\delta = 0.06$ (s, 3H, $SiCH_3$), 0.83 (s, 6H, $As(CH_3)_2$), 2.08 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 2.29 (s, 6H, CH_3), 6.91 (m, broad, 2H, CH-Mes), 6.94 (m, broad, 2H, CH-Mes), 6.99 (d, 1H, $^3J(^1H-^1H) = 8.0$ Hz, *m*-Ph), 6.99 (d, 1H, $^3J(^1H-^1H) = 7.0$ Hz, *m*-Ph), 7.18 (dd, 1H, $^3J(^1H-^1H) = 8.0$ Hz, $^3J(^1H-^1H) = 7.0$ Hz, *p*-Ph). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25 °C): $\delta = 11.0$ ($SiCH_3$), 17.2 ($As(CH_3)_2$), 21.2 (CH_3), 22.3 (CH_3), 22.7 (CH_3), 125.0 (CH), 129.0 (CH), 129.2 (CH), 132.1 (CH), 137.0, 137.8, 138.1, 138.2, 140.7, 147.2. MS (CI, positive, 70 eV (isobutane), *m*/*z*, >10 %): 330 $[TerNH_3]^+$, 406, 448, 510 $[M - Cl]^+$, 530 $[M - CH_3]^+$, 545 $[M + H]^+$. Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated toluene solution of **6** to −80 °C.

Synthesis of 7. To a stirred solution of *N*-trimethylsilyl-*N*-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-dichloroarsane (**5**) (0.546 g, 1.0 mmol) in CH_2Cl_2 (30 mL), Me_3SiN_3 (0.461 g, 4.0 mmol) in CH_2Cl_2 (10 mL) was added dropwise at −75 °C resulting in a colorless solution. $GaCl_3$ (0.194 g, 1.1 mmol) in CH_2Cl_2 (10 mL) was added dropwise at −70 °C over a period of 10 min. The resulting orange suspension was stirred at −70 °C for 10 min and was then warmed to −50 °C. The solvent is removed *in vacuo* at this temperature, resulting in an orange crystalline residue, which is redissolved in CH_2Cl_2 (10 mL) at −30 °C, resulting in an orange solution. After being stirred at −30 °C for 30 min, the solution is concentrated *in vacuo* to a volume of 3 mL. Crystallization at −80 °C over a period of 10 h gives an orange, crystalline solid. Removal of supernatant by syringe and drying *in vacuo* yields 0.526 g (0.95 mmol, 95%) of **7** as a colorless, crystalline solid. Mp 149 °C (dec.). Anal. calcd % (found): C, 58.64 (58.44); H, 6.20 (6.07); N, 10.13 (10.00). ^{1}H NMR (500.13 MHz, CD_2Cl_2, −40 °C): $\delta = -0.29$ (s, broad, 3H, $SiCH_3$), −0.18 (s, broad, 3H, $SiCH_3$), 0.85 (s, 3H, $AsCH_3$), 2.02 (s, 6H, CH_3), 2.04 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 6.88 (s, broad, 1H, CH-Mes), 6.90 (s, broad, 1H, CH-Mes), 6.95 (s, broad, 1H, CH-Mes), 6.96 (s, broad, 1H, CH-Mes), 6.96 (dd, 1H, $^3J(^1H-^1H) = 7.6$ Hz, $^4J(^1H-^1H) = 1.9$ Hz, *m*-Ph), 7.03 (dd, 1H, $^3J(^1H-^1H) = 7.6$ Hz, $^4J(^1H-^1H) = 1.9$ Hz, *m*-Ph), 7.19 ('t', 1H, $^3J(^1H-^1H) = 7.6$ Hz, *p*-Ph). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, −40 °C): $\delta = 1.6$ ($SiCH_3$), 2.9 (broad, $SiCH_3$), 20.9 (CH_3), 21.0 (CH_3), 21.1 (CH_3),

21.1 (CH_3), 21.5 (CH_3), 22.3 (CH_3), 24.9 ($AsCH_3$), 124.8 (*p*-Ph), 128.3 (CH-Mes), 128.5 (CH-Mes), 128.7 (CH-Mes), 129.0 (CH-Mes), 130.8 (*m*-Ph), 131.9 (*m*-Ph), 136.2, 136.2, 137.1, 137.4, 137.6, 138.1 (*o*-Ph), 138.8, 138.8, 139.5, 139.5 (*o*-Ph), 145.3 (*i*-Ph). MS (EI, *m*/*z*, >10 %): 43 (35) $[HN_3]^+$, 299 (16) $[Ter - CH_3]^+$, 314 (45) $[Ter - H]^+$, 329 (100) $[TerNH_3]^+$, 370 (48) $[M - N_3 - AsClCH_3 - CH_3]^+$, 385 (92), $[M - N_3 - AsClMe]^+$, 552 (2) $[M]^+$. Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated CH_2Cl_2 solution of **7** to −80 °C.

Synthesis of 8. To a stirred solution of *N*-trimethylsilyl-*N*-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-dichloroarsane (**5**) (0.546 g, 1.0 mmol) in toluene (10 mL), $AgSO_3CF_3$ (0.283 g, 1.1 mmol) in toluene (10 mL) was added dropwise at −30 °C under exclusion of light. The resulting colorless suspension was stirred at ambient temperatures for 3 h and was then filtered (F4), resulting in a colorless solution. The solvent was concentrated to a volume of 1 mL resulting in a pale brownish solution, which was stored at −25 °C, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying *in vacuo* yielded 0.648 g (0.98 mmol, 98%) of **8** as colorless, crystalline solid. Mp 163 °C. Anal. calcd % (found): C, 50.95 (50.63); H, 5.19 (5.37); N, 2.12 (2.03). ^{29}Si NMR (59.6 MHz, CD_2Cl_2, 25 °C): $\delta = 18.3$. ^{19}F{^{1}H} NMR (282.4 MHz, CD_2Cl_2, 25 °C): $\delta = -77.3$. ^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): $\delta = -0.15$ (s, 3H, $SiCH_3$), 0.33 (s, 3H, $SiCH_3$), 0.98 (s, 3H, $AsCH_3$), 2.03 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 6.94 (s, broad, 1H, CH-Mes), 6.96 (s, broad, 1H, CH-Mes), 6.97 (s, broad, 1H, CH-Mes), 6.98 (s, broad, 1H, CH-Mes), 7.06 (dd, 1H, $^3J(^1H-^1H) = 7.6$ Hz, $^4J(^1H-^1H) = 1.9$ Hz, *m*-Ph), 7.14 (dd, 1H, $^3J(^1H-^1H) = 7.6$ Hz, $^4J(^1H-^1H) = 1.9$ Hz, *m*-Ph), 7.28 ('t', 1H, $^3J(^1H-^1H) = 7.6$ Hz, *p*-Ph). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 °C): $\delta = 3.0$ ($SiCH_3$), 3.6 ($SiCH_3$), 21.2 (CH_3), 21.3 (CH_3), 21.5 (CH_3), 22.4 (CH_3), 22.5 (CH_3), 22.7 (CH_3), 25.8 ($AsCH_3$), 118.8 (q, $^1J(^{13}C-^{19}F) = 318$ Hz, CF_3), 126.0 (*p*-Ph), 129.1 (CH-Mes), 129.3 (CH-Mes), 129.5 (CH-Mes), 129.6 (CH-Mes), 131.9 (*m*-Ph), 132.5 (*m*-Ph), 136.0, 136.5, 137.1, 138.4, 138.6, 138.8, 139.6, 139.6, 140.0, 140.8, 145.2. MS (CI, positive, 70 eV (isobutane), *m*/*z*, >10 %): 329 $[TerNH_3]^+$, 370 $[M - OTf - AsClCH_3 - CH_3]^+$, 385, $[M - OTf - AsClCH_3]^+$, 402, 415, 458, 520 $[M - AsClCH_3 + H]^+$, 540, 624 $[M - Cl]^+$, 654 $[M - Cl + 2CH_3]^+$, 669 $[M - Cl + 3CH_3]^+$. Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated toluene solution of **8** to −25 °C.

Synthesis of 9. To a stirred solution of $AgSO_3CF_3$ (0.565 g, 2.2 mmol) in toluene (20 mL), *N*-trimethylsilyl-*N*-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-dichloroarsane (**5**) (0.546 g, 1.0 mmol) in toluene (20 mL) was added dropwise at ambient temperatures under exclusion of light. The resulting pale brownish suspension was stirred at ambient temperatures for 2 h and was then filtered (F4), resulting in a colorless solution. The solvent was concentrated to a volume of 1 mL resulting in a pale brownish solution, which was stored at −25 °C, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying *in vacuo* yielded 0.745 g (0.96 mmol, 96%) of **9** as colorless, crystalline solid. Mp 186 °C (dec.). Anal. calcd % (found): C, 45.02 (44.94); H, 4.43 (4.64); N, 1.81 (1.73). ^{29}Si NMR (59.6 MHz, CD_2Cl_2, 25 °C): $\delta = 19.4$. ^{19}F{^{1}H} NMR (235.4 MHz, CD_2Cl_2, 25 °C): $\delta = -77.8, -77.3$. ^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): $\delta = -0.26$ (s, 3H, $SiCH_3$), 0.40 (s, 3H, $SiCH_3$), 1.05 (s, 3H, $AsCH_3$), 2.02 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 6.97 (s, broad, 1H, CH-Mes), 6.98 (s, broad, 1H, CH-Mes), 7.00 (s, broad, 1H, CH-Mes), 7.06 (s, broad, 1H, CH-Mes), 7.13 (dd, 1H, $^3J(^1H-^1H) = 7.6$ Hz, $^4J(^1H-^1H) = 1.9$ Hz, *m*-Ph), 7.22 (dd, 1H, $^3J(^1H-^1H) = 7.6$ Hz, $^4J(^1H-^1H) = 1.9$ Hz, *m*-Ph), 7.36 ('t', 1H, $^3J(^1H-^1H) = 7.6$ Hz, *p*-Ph). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 °C): $\delta = 2.1$ ($SiCH_3$), 2.2 ($SiCH_3$), 21.2 (CH_3), 21.3 (CH_3), 21.6 (CH_3), 22.3 (CH_3), 22.4 (CH_3), 22.5 (CH_3), 25.8 ($AsCH_3$), 118.8 (q, $^1J(^{13}C-^{19}F) = 318$ Hz, CF_3), 118.8 (q, $^1J(^{13}C-^{19}F) = 318$ Hz, CF_3), 126.9 (*p*-Ph), 129.6 (CH-Mes), 129.7 (CH-Mes), 129.8 (CH-Mes), 130.1 (CH-Mes), 131.5 (*m*-Ph), 133.1 (*m*-Ph), 134.9, 135.0, 137.1, 138.6, 139.0, 139.2, 139.8, 139.8, 141.4, 141.8, 143.9 (*i*-Ph). MS (CI, positive, 70 eV (isobutane), *m*/*z*, >10 %): 314, 329 $[TerNH_3]^+$, 372 $[M - OTf - AsClCH_3 - CH_3]^+$, 385 (92), $[M - OTf - AsClMe]^+$, 402, 520 $[M - AsClCH_3 + H]^+$, 550 $[M - AsOTf]^+$, 624 $[M - Cl]^+$, 654 $[M - OTf + 2CH_3]^+$, 669 $[M - OTf + 3CH_3]^+$, 728 $[M - CH_3 - F]^+$. Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated toluene solution of **9** to −25 °C.

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Supporting Information Available: CIF files for all crystal structures, relative and absolute energies, NBO data, and theoretically optimized structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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