Synthesis and Characterization of A Stable Non-cyclic Bis(amino)arsenium Cation

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Dedicated to Prof. Dr. Neil Burford

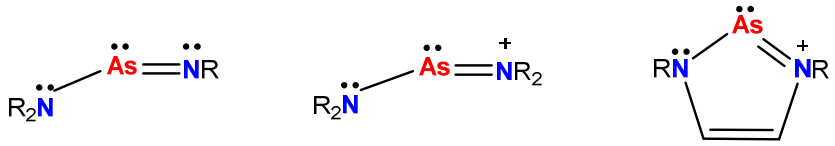
Abstract:

The reaction of Li[Mes*NH] (**1**, Mes * = 2,4,6-tri-*tert*-butylphenyl) with aminoarsane Mes*N(H)$AsCl_2$ (**2**, Mes* = 2,4,6-*t*-$Bu_3C_6H_2$) at –80 °C resulted in the formation of bisamino(chloro)arsane $(Mes*NH)_2AsCl$ (**3**Cl) by elimination of LiCl. **3**Cl reacted with the Lewis acids such as $AlCl_3$, $GaCl_3$ and Ag[X] (X = AsF_6^-, OTf^-, BF_4^-; OTf = trifluoromethanesulfonate = $OSO_2CF_3^-$) upon chloride ion abstraction to give salts bearing the cation $[(Mes*NH)_2As]^+$ (**3**[X]; X = AsF_6^-, OTf^-, BF_4^-, ECl_4; E = Al, Ga). $\mathbf{3}^+$ represents the first NH-functionalized acyclic bis(amino)arsenium cation. The formation of the salts bearing $\mathbf{3}^+$ could also be observed in the reaction of *cyclo*-1,3-diarsa-2,4-diazane $[ClAs(\mu\text{-}NMes*)]_2$ (**4**) with Lewis acids ($AlCl_3$, $GaCl_3$) in the presence of proton sources in solution. All presented salts **3**[X] were stable at room temperature and fully characterized.

Keywords: arsenic, cation, bis(amino)arsenium cation, crystal structure

Introduction

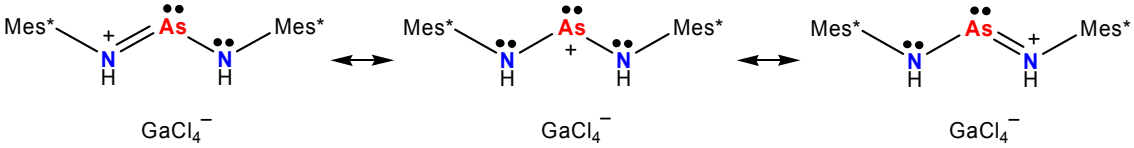
In the last decades the possibility to generate dicoordinate nitrogen bound arsenic compounds was shown not only for a series of amino(imino)arsanes (**I**, Scheme 1) but also for non-cyclic and cyclic bis(amino)arsenium ions (**II**, **III**).[1–7] Furthermore, base stabilized mono[8] and di cations of arsenic have been reported.[9]



I **II** **III**

Scheme 1. **I**: aminoiminoarsane, **II**: bis(amino)arsenium cation, **III**: (6π)-diazarsolium cation.

As depicted in Scheme 2, for acyclic bis(amino)arsenium cations, at least three Lewis representations need to be considered. The second resonance structure in Scheme 2 displays a divalent As atom with an unsaturated cationic (six valence) electron-deficit center and an empty p_z-orbital. That is why in contrast to species **I**, compounds such as **II** and **III** can be regarded as carbene analogues with respect to the isoelectronic situation in the valence shell.



Scheme 2. Resonance structures of acyclic bis(amino)arsenium cations.

While numerous acyclic diaminophosphenium ions are known,[10] up to now only two structures of salts with an acyclic diaminoarsenium cation $[(R_2N)_2As]^+$ (R = $SiMe_3$) were published in 2013.[5] Contrarily, cationic four-, five- and six-membered cyclic bis(amino)arsenium salts have been known for years.[6,7,11–13]

The phosphenium ion $[(Mes^*NH)_2P]^+$ was synthesized by Burford *et al*. in the reaction of $[Mes^*NP]^+$ with Mes^*NH_2 (supermesityl = Mes* = 2,4,6-*t*-$Bu_3C_6H_2$).[14] This reaction was described as a nucleophilic addition of a N–H bond to the phosphadiazonium cation displaying a formal insertion of a NP unit into a N–

H bond. Recently, we could isolate and characterize an arsadiazonium cation $[Mes*NAs]^+$ allowing further systematic investigations for the syntheses of dicoordinated arsenium ions $[R_2As]^+$.[15]

We describe here the generation of the cation $[(Mes*NH)_2As]^+$ (**3**$^+$) as $[GaCl_4]^-$-salt in the reaction of $[Mes*NAs]^+[GaCl_4^-]$ (**5**$[GaCl_4]$) with $Mes*NH_2$. For the direct syntheses of other salts bearing **3**$^+$, we present a convenient synthetic protocol starting from $(Mes*NH)_2AsCl$ (**3**Cl), which can be considered as an ideal precursor for salts of **3**$^+$, when treated with chloride ion abstracting Lewis acids. Furthermore, we report on reactions of $Mes*NAs^+$-salts with Lewis bases such as $PnPh_3$ (Pn = P, As, Sb).

Experimental

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

Preparation of starting materials. All solvents were freshly distilled prior to use. Methylene dichloride was purified according to a literature procedure,[16] dried over P_4O_{10}, and distilled from CaH_2. Diethylether and toluene were dried over Na/benzophenone, *n*-hexane was dried over Na/benzophenone/tetraglyme. *N*-butyllithium (2.5M solution in hexanes, Acros Organics) was used as received. $GaCl_3$ (Sigma-Aldrich) was freshly sublimed prior to use. 1,3-Dichloro-2,4-bis-(2,4,6-tri-*tert*-butylphenyl)*cyclo*-1,3-diarsa-2,4-diazane $[Mes*NAsCl]_2$ (**4**) was prepared according to a literature procedure.[12,15] This procedure includes the synthesis of **1**. 4-Dimethylaminopyridine (DMAP) was used as received. PPh_3, $AsPh_3$ and $SbPh_3$ were freshly sublimed prior to use.

X-ray: BRUKER Apex Kappa-II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073).

NMR: BRUKER Avance 250, 300 and 500 NMR spectrometers. Spectra were referenced internally to corresponding deuterated solvents (^1H: δ_{ref} ($CDHCl_2$) = 5.31 ppm, within CD_2Cl_2, ^{13}C: δ_{ref} (CD_2Cl_2) = 54 ppm).

IR: NICOLET 380 FT-IR spectrometer (Smart Orbit ATR module).

RAMAN: BRUKER Vertex70 FT-IR with RAM II FT-RAMAN module, Nd:YAG laser (1064 nm) *or* HORIBA Scientific LabRAM HR800 system, diode laser (785 nm, 100 mW), He-Ne laser (633 nm, 17 mW), frequency doubling Nd:YAG laser (532 nm, 50 mW).

MS: THERMO ELECTRON Finnigan MAT 95-XP spectrometer.

CHN-Analysis: THERMO QUEST Flash EA 1112 analysator.

Melting points: STANFORD RESEARCH SYSTEMS EZ-Melt, automated analysator, data uncorrected. Heating rate 20 °C/min (clearing-points are reported).

DSC: METTLER-TOLEDO DSC 823e (Heating rate 5 °C/min)

Synthesis of 3Cl

To a solution of 2,4,6-tri-*tert*-butylaniline (Mes*NH_2, 261 mg, 1.0 mmol) in Et_2O (10 ml) *n*-Butyllithium (1.0 mmol) is added at room temperature and stirred for 1.5 hours. The reaction solution is added to a stirred solution of $AsCl_3$ (181 mg, 1.0 mmol) in Et_2O (3 ml) at room temperature. The resulting rose suspension of generated Mes*N(H)$AsCl_2$ and LiCl is stirred for 30 minutes. The precipitated LiCl is separated by filtration. Li[Mes*NH], obtained from reaction of Mes*NH_2, (261 mg, 1.0 mmol) and *n*-Butyllithium (1.0 mmol) in Et_2O (3 ml), is added to the filtrate at –80 °C over a period of 10 minutes. The solvent is removed *in vacuo* at room temperature and the product extracted with 5 ml *n*-hexane. **3**Cl is purified by re-crystallization from Et_2O solution. Decomp. 115 °C. Anal. calc. % (found) for $C_{36}H_{60}AsClN_2$ (631.25): C, 68.50 (66.28); H, 9.58 (9.17); N, 4.44 (4.41). ^{1}H NMR (25°C, CD_2Cl_2, 300.13 MHz): δ = 1.29 (s, 18 H, *p*-C(CH_3)$_3$), 1.53 (s, 36 H, *o*-C(CH_3)$_3$), 5.57 (s, 2 H, N*H*), 7.33 (s, 4 H, C*H*). ^{13}C{^{1}H} NMR (25°C, CD_2Cl_2, 75.48 MHz): δ = 31.76 (s, *p*-C(CH_3)$_3$), 33.89 (s, *o*-C(CH_3)$_3$), 35.04 (s, *p*-*C*(CH_3)$_3$), 36.74 (s, *o*-*C*(CH_3)$_3$), 124.04 (s, *C*H, Ar), 137.88 (s, *p*-Ar), 144.59 (s, *o*-Ar), 145.32 (s, *ipso*-Ar). IR (ATR, 64 scans, cm^{-1}): 3352 (m), 2959 (s), 2951 (s), 2903 (m), 2868 (m), 1597 (m), 1477 (m), 1463 (m), 1422 (s), 1392 (m), 1361 (s), 1304 (w), 1288 (m), 1241 (m), 1214 (s), 1200 (m), 1111 (s), 1022 (w), 933 (w), 922 (w), 912 (w), 878 (m), 828 (s), 816 (m), 780 (m), 750 (m), 732 (w), 667 (w), 649 (w), 629 (m), 594 (m), 568 (w), 546 (w). Raman (460 mW, 25 °C, 150 scans, cm^{-1}): 3088 (1), 2965 (10), 2909 (9), 2784 (1), 2712 (2), 1601 (5), 1461 (3), 1449 (4), 1430 (3), 1366 (1), 1345 (1), 1293 (3), 1256 (2), 1245 (2), 1225 (3), 1202 (4), 1183 (3), 1146 (3), 1119 (1), 1029 (1), 934 (3), 926 (3), 826 (4), 803 (1), 755 (2), 635 (2), 573 (3), 477 (1), 373 (2), 323 (1), 263

(4), 149 (5), 113 (2), 87 (2). MS (CI pos. Isobutane): 262 $[Mes*NH_3]^+$, 334 $[Mes*NAs]^+$, 595 $[(Mes*NH)_2As]^+$.

Synthesis of 3[AlCl$_4$]

A) To a stirred colorless solution of **3**Cl (0.124 mmol, 78 mg) in toluene (5 ml) powdered $AlCl_3$ (0.124 mmol, 17 mg) is added at –80 °C. The color of the resulting solution alters to yellow within a few minutes. The solution is warmed up to ambient temperatures and stirred for two hours resulting in a yellow precipitate and a clear colorless supernatant which is removed by a syringe. The precipitate is washed with toluene and dried *in vacuo*. **3**[$AlCl_4$] is obtained as a yellow powder (90 mg, 0.118 mmol, 95 %).

B) To a stirred solution of **4**, (0.118 mmol, 87 mg) in toluene (1 ml) a solution of $AlCl_3$ (0.235 mmol, 31 mg) in toluene (8 ml) is added dropwise at –80 °C to give a clear orange solution. Crystals of **3**[$AlCl_4$] are obtained by subsequent removal of solvent at –70 °C. The supernatant is removed by decantation. **3**[$AlCl_4$] is isolated as a yellow crystalline solid. Decomp. 156 °C. Anal. calc. % (found) for $C_{36}H_{60}AlAsCl_4N_2$ (764.59): C, 56.55 (56.27); H, 7.91 (7.89); N, 3.66 (3.69). ^{1}H NMR (25°C, CD_2Cl_2, 250.13 MHz): δ = 1.32 (s, 18 H, *p*-C(C*H*$_3$)$_3$), 1.57 (s, 36 H, *o*-C(C*H*$_3$)$_3$), 7.53 (s, 4 H, C*H*), 10.44 (s, 2 H, N*H*). ^{13}C{^{1}H} NMR (25°C, CD_2Cl_2, 62.90 MHz): δ = 31.5 (s, *p*-C(*C*H$_3$)$_3$), 34.6 (s, *o*-C(*C*H$_3$)$_3$), 35.6 (s, *p*-*C*(CH$_3$)$_3$), 37.5 (s, *o*-*C*(CH$_3$)$_3$), 124.8 (s, *C*H, Ar), 131.4 (s, *p*-Ar), 148.5 (s, *o*-Ar), 152.5 (s, *ipso*-Ar). IR (ATR, 64 scans, cm^{-1}): 3236 (m), 3009 (w), 2956 (s), 2872 (m), 1600 (m), 1476 (m), 1463 (m), 1419 (m), 1395 (m), 1362 (m), 1294 (w), 1269 (m), 1243 (m), 1214 (s), 1181 (m), 1106 (s), 1025 (w), 938 (w), 926 (w), 912 (w), 881 (m), 852 (s), 820 (w), 798 (w), 779 (w), 762 (w), 666 (w), 648 (w), 634 (w), 627 (w), 582 (s). Raman (784 nm, lat10X, 25 °C, 4 sc/60 sec, cm^{-1}): 2962 (2), 2929 (2), 2904 (2), 2870 (1), 2780 (1), 2708 (1), 1600 (3), 1468 (2), 1454 (2), 1422 (2), 1396 (1), 1363 (1), 1347 (2), 1289 (2), 1254 (1), 1243 (1), 1218 (4), 1186 (5), 1146 (4), 1117 (2), 1024 (1), 927 (2), 861 (10), 821 (6), 798 (5), 762 (3), 698 (4), 648 (2), 569 (3), 465 (2), 418 (1), 349 (3), 263 (2), 183 (2), 134 (6), 119 (6), 107 (7), 70 (10). MS (CI pos. Isobutane): 206 $[Mes*NH_3 - {}^tBu]^+$, 262 $[Mes*NH_3]^+$. Crystals of **3**[$AlCl_4$] suitable for X-ray crystallographic analysis are obtained by re-crystallization from CH_2Cl_2.

Synthesis of 3[GaCl$_4$]

A) To a stirred solution of **3**Cl (0.182 mmol, 115 mg) in toluene (3 ml) a solution of $GaCl_3$ (0.182 mmol, 32 mg) in toluene (2 ml) is added dropwise at room temperature and stirred for one hour resulting in a yellow precipitate and a clear colorless supernatant which is removed by a syringe. The precipitate is washed with toluene and dried *in vacuo*. **3**[$GaCl_4$] is obtained as a yellow powder (138 mg, 0.171 mmol, 94 %).

B) To a stirred solution of **4** (0.087 mmol, 64 mg) in toluene (2 ml) a solution of $GaCl_3$ (0.173 mmol, 31 mg) in toluene (1 ml) is added dropwise at –80 °C, followed by dropwise addition of 2,4,6-tri-*tert*-butylaniline (Mes*NH_2, 44 mg, 0.170 mmol) in toluene (2 ml). The reaction mixture is warmed to room temperature and stirred for two hours. Removal of solvent, washing with toluene and drying *in vacuo* yields **3**[$GaCl_4$] as a yellow powder (65 mg, 0.081 mmol, 92 %). Decomp. 135 °C. Anal. calc. % (found) for $C_{36}H_{60}AsCl_4GaN_2$ (807.33): C, 53.56 (52.69); H, 7.49 (7.02); N, 3.47 (3.42). ^{1}H NMR (25°C, CD_2Cl_2, 300.13 MHz): δ = 1.32 (s, 18 H, *p*-C(C*H*$_3$)$_3$), 1.57 (s, 36 H, *o*-C(C*H*$_3$)$_3$), 7.53 (s, 4 H, C*H*), 10.50 (s, 2 H, N*H*). ^{13}C{^{1}H} NMR (25°C, CD_2Cl_2, 75.48 MHz): δ = 31.51 (s, *p*-C(*C*H$_3$)$_3$), 34.62 (s, *o*-C(*C*H$_3$)$_3$), 35.63 (s, *p*-*C*(CH$_3$)$_3$), 37.50 (s, *o*-*C*(CH$_3$)$_3$), 124.80 (s, *C*H, Ar), 131.42 (s, *p*-Ar), 148.43 (s, *o*-Ar), 152.48 (s, *ipso*-Ar). IR (ATR, 64 scans, cm^{-1}): 3231 (m), 3009 (m), 2956 (s), 2872 (m), 1600 (m), 1475 (m), 1471 (m), 1463 (m), 1418 (m), 1395 (m), 1362 (m), 1294 (w), 1269 (w), 1243 (m), 1213 (s), 1180 (m), 1105 (s), 1025 (w), 938 (w), 926 (w), 912 (w), 881 (m), 851 (s), 820 (w), 798 (w), 779 (w), 762 (w), 666 (w), 647 (w), 634 (w), 627 (w), 581 (m), 543 (w). Raman (460 mW, 25 °C, 150 scans, cm^{-1}): 3237 (1), 3129 (1), 3109 (1), 2971 (10), 2911 (9), 2785 (2), 2712 (2), 1603 (7), 1470 (4), 1457 (3), 1451 (3), 1426 (3), 1399 (2), 1366 (2), 1351 (3), 1293 (3), 1256 (2), 1246 (2), 1221 (5), 1189 (8), 1148 (6), 1119 (3), 1030 (1), 930 (3), 865 (9), 824 (7), 801 (5), 782 (1), 764 (3), 701 (4), 651 (2), 573 (4), 469 (1), 421 (1), 350 (6), 265 (2), 155 (2), 132 (5), 114 (4), 111 (4). MS (CI pos. Isobutane): 262 [Mes*NH_3]$^+$, 334 [Mes*NAs]$^+$, 595 [(Mes*NH)$_2$As]$^+$. Crystals of **3**[$GaCl_4$] suitable for X-ray crystallographic analysis are obtained by re-crystallization from a CH_2Cl_2 solution of **3**[$GaCl_4$].

Synthesis of 3[OTf] • toluene

A) To a stirred colorless solution of **3**Cl (78 mg, 0.124 mmol) in CH_2Cl_2 (5 ml) powdered Ag[OTf] (0.124 mmol, 32 mg) is added at −80 °C. The color of the resulting solution alters to yellow within a few

minutes. The solution is warmed up to room temperature under stirring within one hour. Afterwards, the solution is stirred for another hour resulting in a colorless precipitate and a clear orange supernatant. After filtration (F4) and removal of the solvent *in vacuo* **3**[OTf] is obtained as a yellow powder (87 mg, 0.117 mmol, 94 %).

B) To a stirred solution of **4** (0.134 mmol, 99 mg) in toluene (6 ml) powdered Ag[OTf] (0.284 mmol, 73 mg) is added at –80 °C. The resulting orange suspension is warmed to room temperature over a period of one hour and is then filtered (F4), resulting in a yellow solution. Subsequent, the solution is cooled to –80 °C again and a solution of PPh_3 (0.402 mmol, 105 mg) in toluene (3 ml) is added under stirring. The reaction solution is warmed to room temperature and stirred for two hours resulting in a colorless solid and a clear orange supernatant. The solid is separated from the liquid by filtration. The filtrate is concentrated and cooled to 5 °C. Crystals of **3**[OTf] · toluene are obtained by storage of the solution at 5 °C for some hours. Crystals of $[Ag(PPh_3)_3][OTf] \cdot 2\ CH_2Cl_2$ (**9**) suitable for X-ray crystallographic analysis are obtained by re-crystallization of the colorless solid from a CH_2Cl_2 solution. Decomp. 165 °C. Anal. calc. % (found) for $C_{37}H_{60}AsF_3N_2O_3S$ (744.87): C, 59.66 (56.97); H, 8.12 (7.74); N, 3.76 (3.67). ^{1}H NMR (25°C, CD_2Cl_2, 250.13 MHz): δ = 1.32 (s, 18 H, *p*-C(C*H*$_3$)$_3$), 1.56 (s, 36 H, *o*-C(C*H*$_3$)$_3$), 7.52 (s, 4 H, C*H*), 11.93 (s, 2 H, N*H*). ^{13}C{^{1}H} NMR (25°C, CD_2Cl_2, 62.90 MHz): δ = 31.6 (s, *p*-C(*C*H$_3$)$_3$), 34.3 (s, *o*-C(*C*H$_3$)$_3$), 35.6 (s, *p*-*C*(CH$_3$)$_3$), 37.4 (s, *o*-*C*(CH$_3$)$_3$), 124.4 (s, *C*H, Ar), 132.4 (s, *p*-Ar), 148.5 (s, *o*-Ar), 151.7 (s, *ipso*-Ar). IR (ATR, 32 scans, cm^{-1}): 2958 (s), 2872 (m), 1599 (m), 1478 (w), 1464 (m), 1456 (w), 1435 (w), 1423 (w), 1397 (m), 1362 (m), 1292 (m), 1269 (m), 1242 (m), 1219 (m), 1209 (s), 1162 (m), 1155 (m), 1108 (m), 1022 (s), 930 (w), 914 (w), 880 (m), 855 (m), 806 (m) 757 (w), 707 (w), 633 (s), 574 (m). Raman (784 nm, lat10X, 25 °C, 5 sc/40 sec, cm^{-1}): 3024 (1), 2970 (2), 2911 (2), 2875 (1), 1600 (3), 1473 (1), 1455 (1), 1442 (2), 1425 (3), 1397 (1), 1365 (1), 1345 (1), 1292 (2), 1244 (1), 1221 (4), 1191 (4), 1148 (4), 1120 (2), 1022 (3), 930 (2), 917 (2), 867 (10), 824 (7), 804 (5), 785 (1), 763 (3), 756 (3), 705 (4), 648 (2), 573 (3), 471 (1), 436 (1), 423 (1), 386 (1), 347 (1), 313 (1), 268 (1), 134 (6), 110 (9), 71 (9). MS (CI pos. Isobutane): 206 [Mes*NH$_3$ - ^{t}Bu]$^+$, 244 [Mes* - 2H]$^+$, 246 [Mes*]$^+$, 262 [Mes*NH$_3$]$^+$. Crystals of **3**[OTf] · toluene suitable for X-ray crystallographic analysis are obtained by re-crystallization from toluene.

Synthesis of 3[BF$_4$] • toluene

A) To a stirred colorless solution of **3**Cl (78 mg, 0.124 mmol) in CH_2Cl_2 (5 ml) powdered Ag[BF_4] (0.124 mmol, 24 mg) is added at −80 °C. The color of the resulting solution alters to yellow within a few minutes. The solution is warmed up to room temperature and stirred for two hours resulting in a colorless precipitate and a clear orange supernatant. After filtration (F4) and removing of solvent *in vacuo* **3**[BF_4] is obtained as an orange liquid. The product can be obtained as a yellow powder from a *n*-hexane solution (77 mg, 0.113 mmol, 91 %).

B) To a stirred solution of **4** (0.108 mmol, 80 mg) in CH_2Cl_2 (5 ml) powdered Ag[BF_4] (0.216 mmol, 42 mg) was added at –80 °C resulting in a deep red solution that was stirred for 30 minutes. Afterwards the reaction solution was warmed to room temperature at which the color of the solution changed to yellow. The colorless precipitate is separated from the liquid by filtration (F4). Subsequently, the solvent was removed under reduced pressure and the product extracted with *n*-hexane. Mp. 144 °C. Anal. calc. % (found) for $C_{36}H_{60}AsBF_4N_2$ (682.6): C, 63.34 (62.34); H, 8.86 (8.81); N, 4.10 (4.42). ^{1}H NMR (25°C, CD_2Cl_2, 250.13 MHz): δ = 1.32 (s, 18 H, *p*-C(C*H*$_3$)$_3$), 1.55 (s, 36 H, *o*-C(C*H*$_3$)$_3$), 7.52 (s, 4 H, C*H*), 11.21 (s, 2 H, N*H*). ^{11}B{^{1}H} NMR (25°C, CD_2Cl_2, 80.25 MHz): δ = −0.81. ^{13}C{^{1}H} NMR (25°C, CD_2Cl_2, 62.90 MHz): δ = 31.5 (s, *p*-C(*C*H$_3$)$_3$), 34.3 (s, *o*-C(*C*H$_3$)$_3$), 35.6 (s, *p*-*C*(CH$_3$)$_3$), 37.4 (s, *o*-*C*(CH$_3$)$_3$), 124.5 (s, *C*H, Ar), 132.1 (s, *p*-Ar), 148.5 (s, *o*-Ar), 151.9 (s, *ipso*-Ar). IR (ATR, 32 scans, cm^{-1}): 3232 (m), 3162 (m), 3007 (m), 2960 (s), 2910 (m), 2872 (m), 1596 (m), 1477 (m), 1471 (m), 1464 (m), 1456 (w), 1435 (w), 1421 (m), 1397 (m), 1363 (m), 1288 (w), 1269 (w), 1241 (m), 1211 (m), 1180 (m), 1134 (s), 1104 (s), 1070 (s), 1028 (w), 941 (s), 913 (m), 883 (m), 850 (s), 819 (w), 784 (w), 759 (m), 673 (m), 667 (m), 648 (m), 617 (w), 602 (w), 569 (w). Raman (784 nm, lat10X, 25 °C, 6 sc/30 sec, cm^{-1}): 2974 (1), 2907 (1), 1598 (2), 1468 (1), 1445 (1), 1423 (2), 1398 (1), 1367 (1), 1289 (2), 1243 (1), 1216 (2), 1188 (3), 1144 (3), 1117 (2), 1023 (1), 926 (1), 915 (2), 859 (10), 823 (5), 806 (4), 786 (1), 762 (3), 709 (2), 649 (1), 572 (2), 470 (1), 436 (1), 422 (1), 368 (1), 354 (1), 260 (1), 135 (4), 108 (5), 71 (7). MS (CI pos. Isobutane): 206 [Mes*NH$_3$ - ^{t}Bu]$^+$, 262 [Mes*NH$_3$]$^+$. Crystals of **3**[BF_4] · toluene suitable for X-ray crystallographic analysis are obtained by re-crystallization from a toluene solution of **3**[BF_4].

Synthesis of 3[AsF$_6$] • 2 CH$_2$Cl$_2$

To a stirred solution of Ag[AsF$_6$] (0.55 mmol, 0.163 g) in CH_2Cl_2 (5 ml), a yellow solution of **4** (0.5 mmol, 0.370 g) in CH_2Cl_2 (3 ml), is added dropwise at –90 °C over a period of five minutes. The resulting red suspension is warmed to –50 °C over a period of one hour and filtered (F4). The solution is slowly cooled to –80 °C, resulting in the deposition of orange crystals. The supernatant was removed by decantation and the residue was dried *in vacuo* which yields **3**[AsF$_6$] · 2 CH_2Cl_2 as an orange crystalline solid. Decomp. 127 °C. Anal. calc. % (found) for **3**[AsF$_6$] · CH_2Cl_2 ($C_{37}H_{62}As_2Cl_2F_6N_2$ (869.64): C, 51.10 (51.81); H, 7.19 (7.36); N, 3.22 (3.73). ^{1}H NMR (25°C, CD_2Cl_2, 300.13MHz): δ = 1.33 (s, 18 H, *p*-C(C*H*$_3$)$_3$), 1.56 (s, 36 H, *o*-C(C*H*$_3$)$_3$), 7.53 (s, 4 H, *m*-C*H*), 10.49 (s, 2 H, N*H*). ^{13}C{^{1}H} NMR (25°C, CD_2Cl_2, 75.5MHz): δ = 31.5 (s, *p*-C(*C*H$_3$)$_3$), 34.3 (s, *o*-C(*C*H$_3$)$_3$), 35.6 (s, *p*-*C*(CH$_3$)$_3$), 37.5 (s, *o*-*C*(CH$_3$)$_3$), 124.7 (s, *C*H, Ar), 131.7 (s, *p*-Ar), 148.6 (s, *o*-Ar), 152.3 (s, *ipso*-Ar). ^{19}F{^{1}H} NMR (25°C, CD_2Cl_2, 282.4MHz): δ = 61 (s, *broad*). IR (ATR, 32 scans, cm^{-1}): 3272 (w), 2959 (m), 2873 (w), 1597 (w), 1470 (w), 1455 (w), 1434 (w), 1417 (w), 1396 (w), 1362 (m), 1297 (w), 1269 (w), 1242 (w), 1211 (m), 1178 (w), 1144 (w), 1104 (m), 1025 (w), 927 (w), 913 (w), 881 (m), 854 (m), 847 (m), 820 (w), 802 (m), 787 (w), 762 (w), 693 (s), 670 (s), 650 (m), 608 (m), 595 (m). Raman (50 mW, 25 °C, 402 scans, cm^{-1}): 2968 (10), 2913 (10), 2789 (2), 2760 (12), 2714 (2), 1601 (7), 1469 (3), 1448 (4), 1416 (3), 1399 (3), 1367 (2), 1292 (3), 1248 (3), 1224 (7), 1193 (6), 1149 (5), 1121 (2), 1030 (1), 930 (2), 870 (4), 826 (5), 802 (2), 766 (1), 754 (1), 698 (2), 679 (2), 648 (1), 632 (1), 573 (3), 476 (1), 430 (1), 415 (1), 392 (1), 369 (2), 324 (3), 284 (2), 261 (2), 149 (5). MS (FAB+, Cs, 20keV, *p*-NBA matrix): 262 [Mes*-NH$_3$]$^+$, 334 [Mes*-NAs]$^+$. Crystals of **3**[AsF$_6$] · 2 CH_2Cl_2 suitable for X-ray crystallographic analysis are obtained directly from the reaction solution of **3**[AsF$_6$].

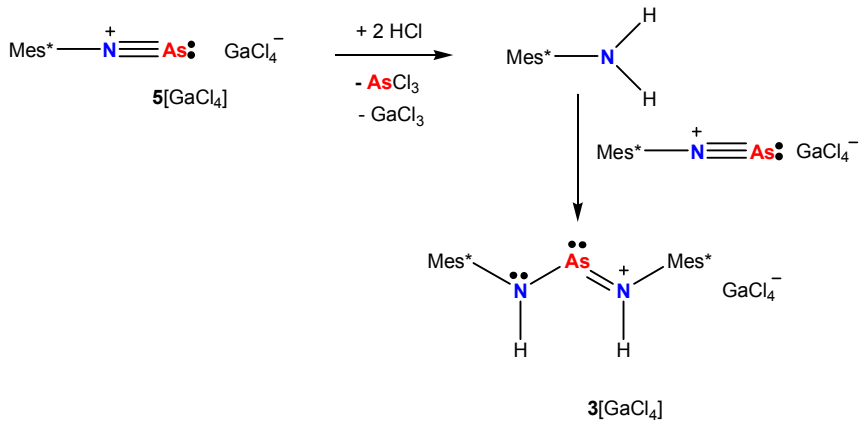
Synthesis of 7

To a stirred solution of **5** (0.216 mmol, 138 mg) in toluene (5 ml) a solution of $SbPh_3$ (0.216 mmol, 76 mg) in toluene (3 ml) was added dropwise at –60 °C. The obtained deep red solution was warmed to room temperature. The reaction solution was concentrated under reduced pressure and stored for some hours resulting in the deposition of crystals of **7** (110 mg, 0.188 mmol, 87 %). Mp. 164 °C. Anal. calc. % (found) for $C_{24}H_{34}AsCl_3GaN$ (587.54): C, 49.06 (51.06); H, 5.83 (5.42); N, 2.38 (1.98). ^{1}H NMR (25°C, CD_2Cl_2,

300.13 MHz): δ = 1.33 (s, 9 H, C6(CH_3)$_3$), 1.60 (s, 9 H, C4(CH_3)$_3$), 1.66 (s, 9 H, C2(CH_3)$_3$), 7.39-7.47 (m, 5 H, Ar), 7.54 (s, 2 H, C*H*). ^{13}C{^{1}H} NMR (25°C, CD_2Cl_2, 75.48 MHz): δ = 31.58 (C15(*C*H$_3$)$_3$), 33.42 (C4(*C*H$_3$)$_3$), 35.27 (C15), 36.33 (C7(*C*H$_3$)$_3$), 37.07 (C11), 37.98 (C7), 50.38 (C6), 125.27 (C3, C5), 130.05 (*p*-Ph), 130.99 (*m*-Ph), 133.54 (C4), 133.81 (*o*-Ph), 138.87 (C19), 146.77 (C2), 149.77 (C1). Due to the high sensitivity of **7** against air and moisture no effective purification for further analytics of **7** is possible. Crystals of **7** suitable for X-ray crystallographic analysis can only be obtained directly from the reaction solution of **7**.

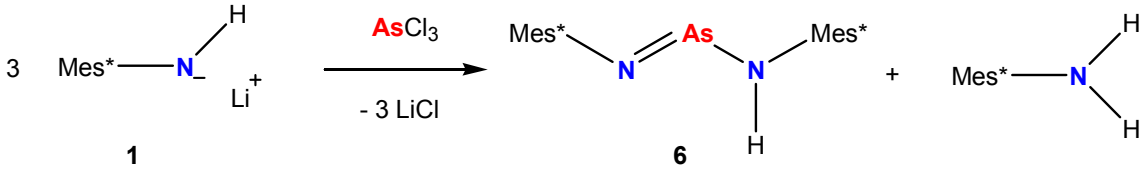
Results and Discussion:

In solution, dimeric [ClAs(μ-NMes*)]$_2$ (**4**) readily monomerized to give Mes*NAsCl. The reaction with $GaCl_3$ resulted in the formation of the arsadiazonium salt [Mes*N≡As][$GaCl_4$] (**5**[$GaCl_4$]).[15] However, in cases of long time storage of **5**[$GaCl_4$] in solutions of toluene or CH_2Cl_2 the slow formation of [(Mes*NH)$_2$As][$GaCl_4$] (**3**[$GaCl_4$]) could be observed. A similar reaction sequence was observed when **4** was treated with $AlCl_3$ yielding salt **3**[$AlCl_4$]. These results indicated the presence of proton sources e.g. HCl in solution or the slow generation of protons in these reactions (Scheme 3). Already Burford *et al*. described the formation of [(Mes*NH)$_2$P][$GaCl_4$] in the reaction of [Mes*N≡P][$GaCl_4$] with Mes*NH_2.[14] Analogously, we treated **5**[$GaCl_4$] with Mes*NH_2 affording quantitatively **3**[$GaCl_4$] (Scheme 3). To explain the formation of salts bearing the **3**$^+$ ion starting from **4** or **5**$^+$ in the presence of Lewis acids we studied possible proton sources along the synthesis of the starting materials. The generation of starting material **4** was achieved by elimination of NEt_3·HCl from Mes*N(H)$AsCl_2$ (**2**) upon addition of NEt_3. Despite several purification steps for **4** most likely small amounts of HCl still remain e.g. as NEt_3·HCl salt. It is also known that CH_2Cl_2 slowly decomposes in the presence of Lewis acids or light generating HCl. Therefore, we believe that storage of dissolved **5**[$GaCl_4$] for longer periods led to the reaction of **5**$^+$ with two equivalents of HCl yielding $GaCl_3$, $AsCl_3$ and Mes*NH_2 which reacted in a subsequent reaction with a further equivalent of **5**$^+$ to give **3**[$GaCl_4$] (Scheme 3). A similar slow decomposition of **4** can be assumed generating free Mes*NH_2.



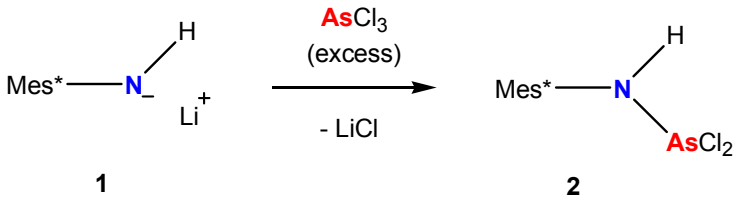
Scheme 3. Proposed reaction pathway of the formation of **3**[$GaCl_4$] in the reaction of $\mathbf{5}^+$ with HCl.

We have already demonstrated that the chloride abstraction in $(TerNH)_2PCl$ by Lewis acids such as $GaCl_3$ or several silver salts led to the formation of salts containing the cation $[(TerNH)_2P]^+$.[17] Analogously, it was shown by Gudat and co-workers that the reaction of 2-chloro-1,3,2-diazarsolene with $GaCl_3$ gave species III as $[GaCl_4]^-$ salt (Scheme 1, R = Mes).[7] During the course of our work we tried to receive salts containing $\mathbf{3}^+$ by treatment of $(Mes*NH)_2AsCl$ (**3**Cl) with different Lewis acids. Since **3**Cl has not been described in literature yet, it was necessary to find first synthetic access to this molecule, which proved to be rather difficult. For this reason, we studied the reaction of LiN(H)Mes* with $AsCl_3$ (Scheme 4). On the basis of ^1H NMR spectroscopic data we found that **1** reacted with $AsCl_3$ in a molar ratio of 3:1 at ambient temperature affording deeply red colored crystals of amino(imino)arsane Mes*N(H)AsNMes* (**6**) and $Mes*NH_2$ in accord with observations by Lappert *et al.* in 1986.[1]



Scheme 4. Reaction of **1** with $AsCl_3$ in a molar ratio of 3:1.

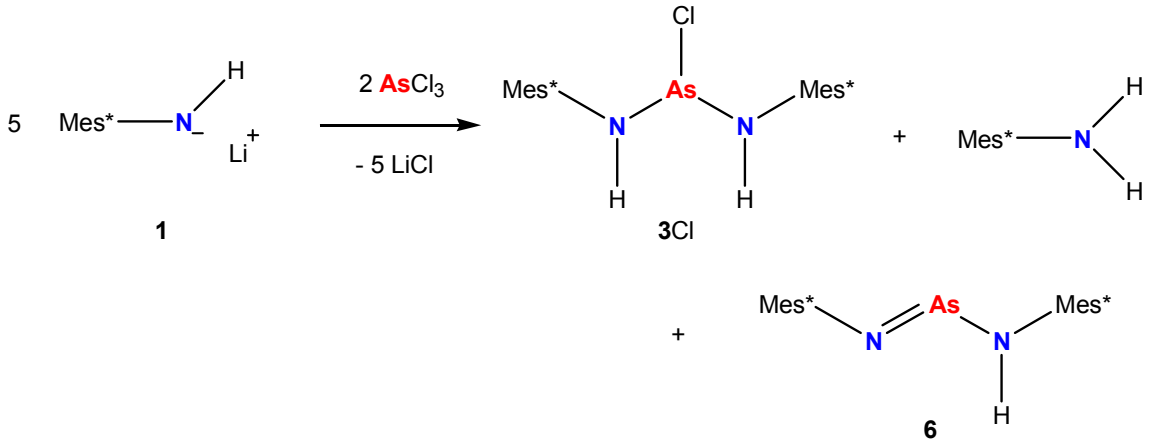
It is noteworthy that Burford *et al.* obtained the aminoarsane **2** in 19 % yield in the reaction of **1** with an excess of $AsCl_3$ in Et_2O at room temperature (Scheme 5).[18] Interestingly, the reactions of three equivalents of **1** with the heavy Pn(III)-halides resulted in a quantitative amination finally yielding $Pn[N(H)Mes*]_3$ (Pn = Sb, Bi).[19]



1 **2**

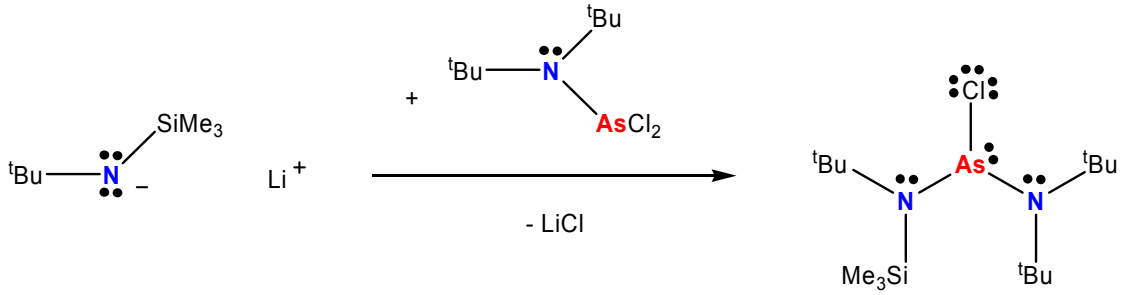
Scheme 5. Reaction of **1** with an excess of $AsCl_3$ according to Burford *et al.* [18]

The dropwise addition of a solution of $AsCl_3$ to a solution of Li[Mes*NH] (**1**) in Et_2O at –80 °C did not only yield **6** and $Mes*NH_2$ but additionally **3**Cl by elimination of LiCl (Scheme 6).



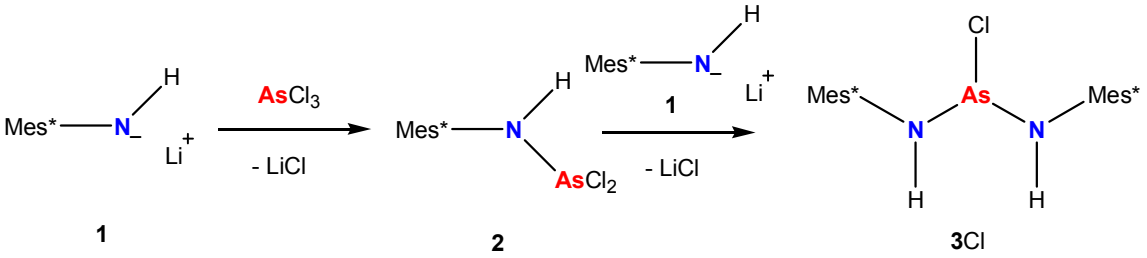
1 **3**Cl **6**

Scheme 6. Observed products for the dropwise addition of $AsCl_3$ to **1**.

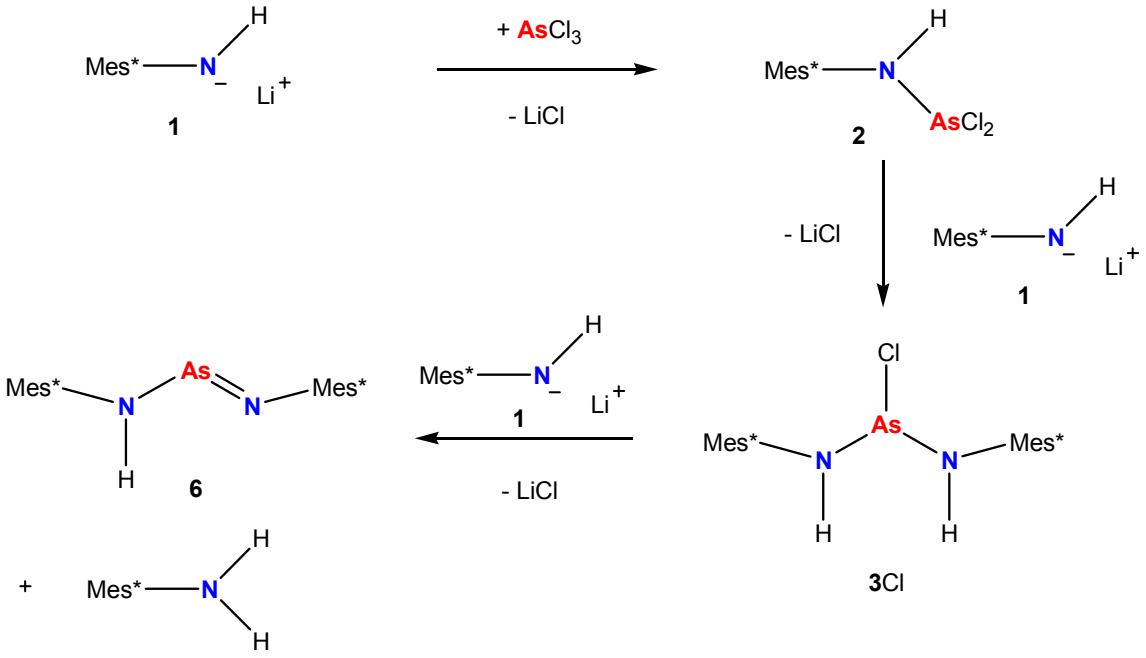


Scheme 7. Synthesis of bisamino(chloro)arsane $(^tBu)_2NAs(Cl)N(^tBu)SiMe_3$ according to Scherer *et al.*[20]

On the basis of NMR spectroscopic investigations Scherer *et al.* reported on the stoichiometric reaction of amino(dichloro)arsane R_2NAsCl_2 with $Li[N(R)SiMe_3]$ which resulted in the formation of the bisamino(chloro)arsane $R_2NAs(Cl)N(R)SiMe_3$ (R = ^{t}Bu) (Scheme 7).[20] Accordingly, in the analogous reaction a solution of **2** was added in stoichiometric amounts to a solution of **1** in Et_2O at –80 °C (Scheme 8) and pure **3**Cl could be obtained after re-crystallization in rather good yields (ca. 80 %).



Scheme 8. Synthesis of **3**Cl in a two-step synthesis.

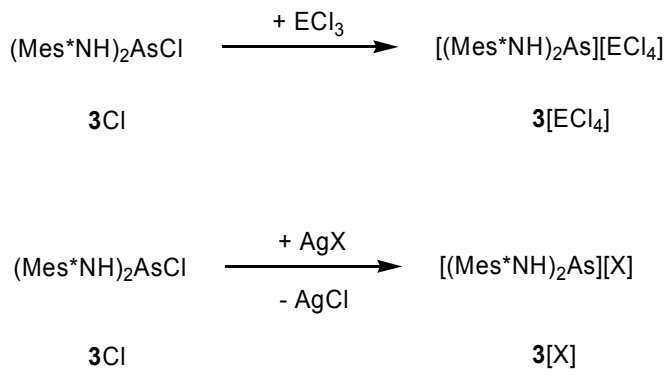


Scheme 9. Reaction pathway for the formation of **6** resulting from the addition of **1** and $AsCl_3$ in a molar ratio of 3:1.

To summarize these results, an excess of $AsCl_3$ resulted in the formation of **2**, while an excess of **1** led to formation of **6** and Mes*NH_2 (as shown in Scheme 9). Obviously in the latter case, **1** induced upon contact with **3**Cl an indirect "HCl-elimination" in the final step by formation of LiCl and Mes*NH_2. As a consequence, for a successful generation of **3**Cl there had to be neither an excess of $AsCl_3$ nor an excess of **1** during the course of reaction. A two-step synthesis as shown in Scheme 8 was found to give the best results.

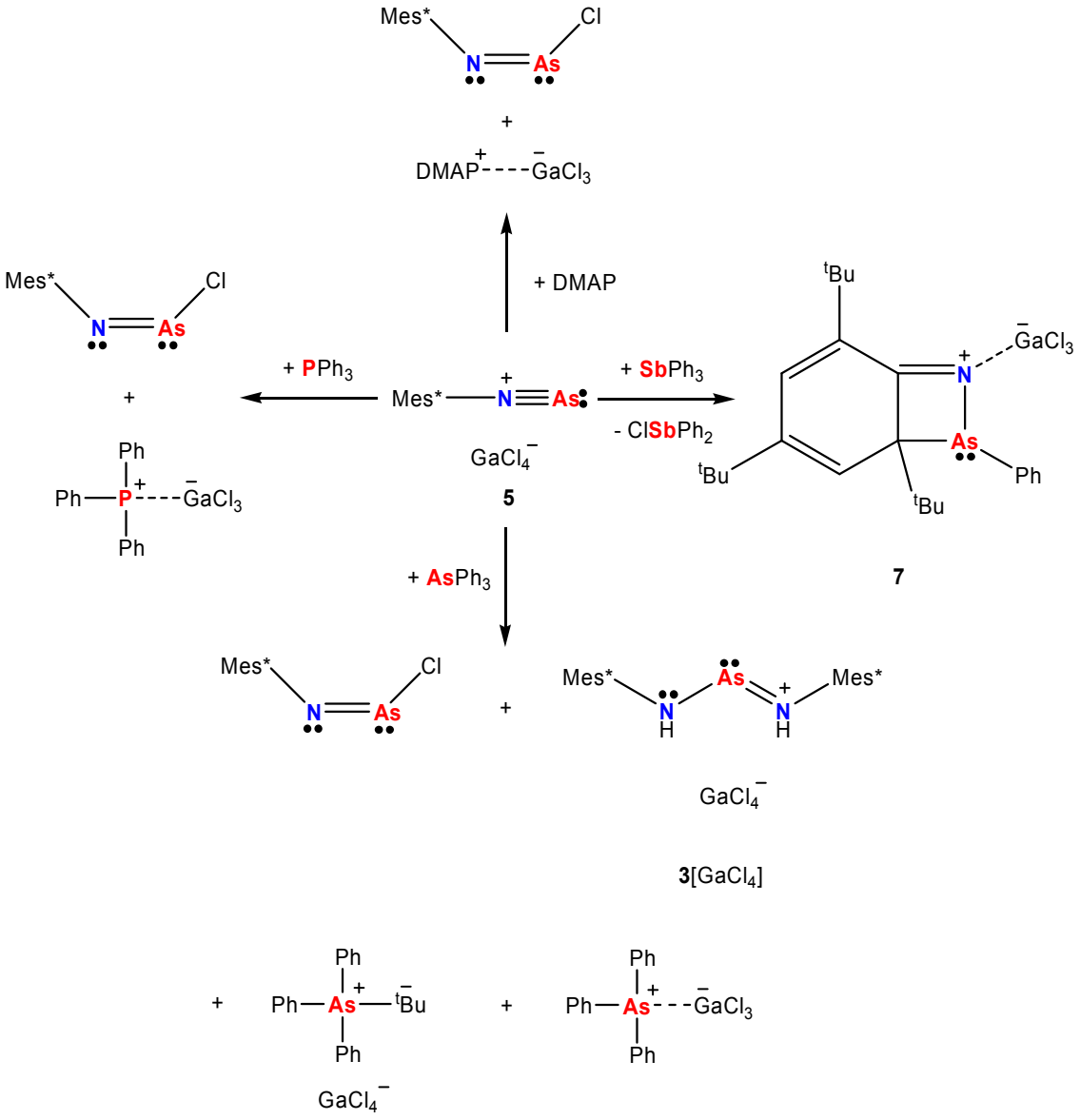
Subsequently, **3**Cl was treated with the Lewis acids $AlCl_3$ and $GaCl_3$, affording the salts **3**[$AlCl_4$] and **3**[$GaCl_4$] with yields over 90%. Furthermore, **3**Cl was treated with the silver salts Ag[OTf] and Ag[BF_4] (Scheme 10). After extraction from precipitated silver chloride the solvates **3**[OTf] · toluene and

3[BF_4] · toluene could be obtained from toluene solution also with yields over 90 %. In contrast, the silylaminoarsane [$(Me_3Si)_2N]_2AsCl$ reacted with Ag[OTf] to give the *cyclo*-1,3-diarsa-2,4-diazane [$(Me_3Si)_2NAs$-μ-$NSiMe_3]_2$ by elimination of Me_3SiOTf.[5] In the reaction of **3**Cl with Ag[AsF_6], surprisingly a quantitative conversion of **3**Cl to Mes*NH_2 was detected by ^{1}H NMR spectroscopy, presumably due to the presence of HF in solution.



Scheme 10. Top: Reaction of **3**Cl with ECl_3 (E = Al, Ga). Bottom: Reaction of **3**Cl with AgX (X = OTf^-, BF_4^-).

In a next series of experiments we were interested in the reactivity of [Mes*N≡As][$GaCl_4$] (**5**[$GaCl_4$]) towards classical Lewis bases such as pyridine or triphenylpnictanes of the type $PnPh_3$ (Pn = P, As, Sb) and to compare these results with those of the lighter phosphorus congener reported by Burford *et al.*[21–24] The reaction of **5**[$GaCl_4$] with DMAP (4-dimethylaminopyridine) at –80 °C yielded monomeric Mes*NAsCl and DMAP·$GaCl_3$ adduct. A similar reaction was found when **5**[$GaCl_4$] was treated with PPh_3 at –80 °C affording also the chloroiminoarsane along with the Ph_3P·$GaCl_3$ adduct (Scheme 7). Contrarily, treatment of **5**[$GaCl_4$] with $AsPh_3$ at –80 °C resulted in a product mixture containing also Mes*NAsCl and Ph_3As·$GaCl_3$ besides arsonium salt [^{t}BuAsPh_3][$GaCl_4$] · toluene (**8**) and **3**[$GaCl_4$] which could be co-crystallized both as main products in moderate yields (~40 %). The formation of an iminodiarsenium salt [Mes*NAsAsPh_3][$GaCl_4$] could not be observed. A further unexpected molecule could be isolated from the reaction of **5**[$GaCl_4$] with $SbPh_3$ which yielded after formal elimination of $ClSbPh_2$ a four-membered ring with an inner-cyclic As-N-bond, stabilized as $GaCl_3$ adduct (**7**, Scheme 11).

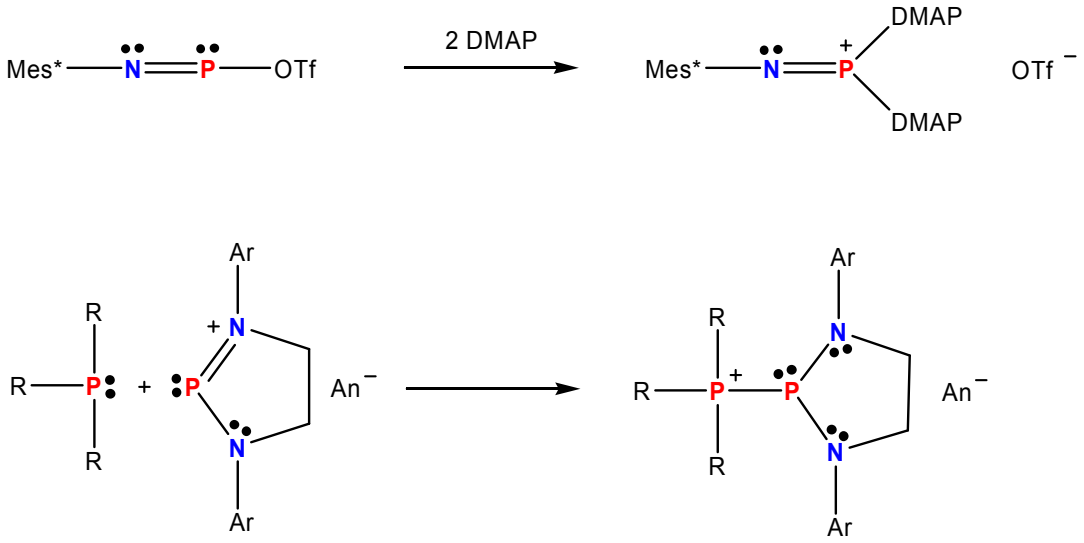


Scheme 11. Summary of the obtained product mixtures in the reactions of **5**[$GaCl_4$] with DMAP and $PnPh_3$ (Pn = P, As, Sb).

To summarize these findings, on the one hand the stability of the formed adducts by release of one chloride ion from the gallate anion involving the formation of a covalent As–Cl bond in Mes*NAsCl seemed to be the driving force of the reactions in case of DMAP and PPh_3. As already mentioned above, utilization of **5**[$GaCl_4$] also led to the introduction of amounts of HCl into the reaction systems, which we unfortunately could not avoid. While Mes*NAsCl seemed to be stable in the presence of traces of HCl, **5**[$GaCl_4$]

immediately showed decomposition. DMAP·$GaCl_3$ and Ph_3P·$GaCl_3$ can be regarded as chemically and thermodynamically robust species. In contrast to the latter, adduct formation of Ph_3As·$GaCl_3$ seemed not to be favored since the formation of several other products were observed at the same time (Scheme 7). In case of $SbPh_3$ formation of Ph_3Sb·$GaCl_3$ was not observed indicating a smaller Lewis basic character leading to a different reaction channel (Ph transfer to arsenic) with the formation of Ph_2SbCl and **7**. On the other hand, it was shown for the chosen reaction systems, that no formation of DMAP adducts of the arsadiazonium ion occurred as well as no formation of phosphinoarsenium or arsinoarsenium ions as observed for the lighter phosphorus congener (Scheme 12).[14,24,25]

We also tried to react in situ generated Mes*NAsCl with $Ag[B(C_6F_5)_4]$, however, only a complex product mixture was obtained. Thus, we carried out the same reaction in the presence of $SbPh_3$ in the hope to quench $[Mes^*NAs\text{-}SbPh_3]^+$, which did not work. Again a complex mixture was obtained, from which we were able to crystallize $[Ag(SbPh_3)_4][B(C_6F_5)_4]$ (**9**).



Scheme 12. Top: Reaction of Mes*NPOTf with DMAP reported by Burford *et al.*[24] Bottom: Synthesis of a bis(arylamino)phosphinophosphenium salt with R = Me, Ar = 2,6-$(CHMe_2)_2C_6H_3$; An = OTf.[25]

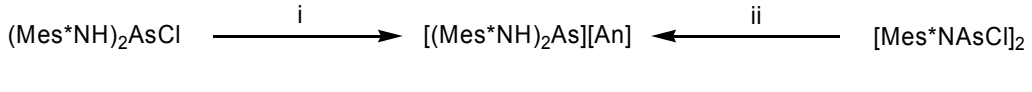
Interestingly, when **5**$[GaCl_4]$ was treated with $AsPh_3$ at –80 °C the beginning formation of the product mixture obviously served as a proton providing medium because of the detected fast formation of **3**$[GaCl_4]$ after warming up the reaction solution. For this reaction, a similar reaction sequence as depicted in Scheme

3 can be assumed. Thus, two general reaction channels for the formation of **3**[$GaCl_4$] are possible with either **3**Cl or **4** as starting materials.

In comparison to the synthesis of **3**[$GaCl_4$] starting from **4**, the reaction of **4** with Ag[AsF_6] yielded **3**[AsF_6]. Again small amounts of HF or HCl within the reaction system are inevitable. It is known that the reaction of **4** with Ag[OTf] resulted in the formation of cyclic [Mes*N-μ-AsOTf]$_2$ by elimination of silver halide.[26]

Burford *et al*. explored the electrophilic character of the phosphadiazonium ion [Mes*N≡P]$^+$, e.g. they were able to isolate and fully characterize the iminophosphinphosphonium salt [Mes*NPPPh_3][OTf] obtained when Mes*NPOTf was treated with PPh_3.[14] To compare the reactivity of **5**$^+$ towards PPh_3 with the results of the Burford group, additionally, the reaction of [Mes*N-μ-AsOTf]$_2$ with PPh_3 was explored. The main product of this reaction was the formation of **3**[OTf] indicating ring-opening upon attack of the base PPh_3. As side product, solvated [Ag(PPh_3)$_3$][OTf] (**10**) was isolated in low quantities and fully characterized. Keeping in mind that [Mes*N-μ-AsOTf]$_2$ was prepared by silver halide elimination it was not surprising that dissolved Ag^+ salts can easily form solvated [Ag(PPh_3)$_3$][OTf], which was first described in 2000 by Laguna.[27]

The reaction of **4** with Ag[BF_4] proved that among other products the formation of **3**[BF_4] also occurred. Scheme 13 summarizes the two general synthetic methods to obtain salts of **3**, either starting from **3**Cl by chloride elimination with Lewis acids (i) or starting from **4** in the reaction with Lewis acids in the presence of proton sources (ii).



Scheme 13. Synthetic methods to obtain salts of **3**. Reaction with halides of group 13: (i) ECl_3, An = ECl_4, E = Al, Ga; (ii) ECl_3/ 2 HCl, An = ECl_4, E = Al, Ga. Reaction with silver salts: (i) Ag[OTf], An = OTf, Ag[BF_4], An = BF_4; (ii) 2 Ag[OTf]/ PPh_3/ 2 HCl, An = OTf; 2 Ag[BF_4]/ 2 HX, X = F or Cl, An = BF_4; 2 Ag[AsF_6]/ 2 HX, X = F or Cl, An = AsF_6.

376 Since in case of route (ii) always the formation of product mixtures was found, reaction channel (i) is to be
377 preferred when preparing **3**Cl. All presented salts of **3** were thermally stable and could be stored unlimited at
378 room temperature under inert conditions. They decomposed at temperatures between 127 °C
379 (**3**[AsF_6] · 2 CH_2Cl_2) and 165 °C (**3**[OTf] · toluene). The As–Cl stretching mode for **3**Cl could be detected in
380 the Raman spectrum at 323 cm^{-1} (cf. 326 cm^{-1} for $[(Me_3Si)_2N]_2AsCl$). A significant feature of all described
381 salts of **3** is their pronounced low-field shift of the N*H*-resonance in the ^1H NMR spectra depending of the
382 cationic character. While in **3**Cl a polarized As–Cl bond was found (N–H: $\delta[^1H]$ = 5.57), all **3**[X] (X =
383 $AlCl_4$, $GaCl_4$, BF_4, OTf, AsF_6) salts form ion pairs and hence their N–*H* resonance was detected in the low-
384 field range between 10.44 for **3**[$AlCl_4$] and 11.93 ppm for **3**[OTf] (see Table 1).

385

Table 1: ^{1}H NMR shifts [ppm] in CD_2Cl_2 for **3**[X] (X = $AlCl_4$, $GaCl_4$, BF_4, OTf, AsF_6) and for comparison Mes^*NH_2 and **2**.

	3Cl	**3**[$AlCl_4$]	**3**[$GaCl_4$]	**3**[BF_4]	**3**[OTf]	**3**[AsF_6]	Mes^*NH_2	**2**
p-C(CH_3)$_3$	1.29	1.32	1.32	1.32	1.32	1.33	1.27	1.28
o-C(CH_3)$_3$	1.53	1.57	1.57	1.55	1.56	1.56	1.45	1.49
C*H*,Ar	7.33	7.53	7.53	7.52	7.52	7.53	7.19	7.36
N*H*	5.57	10.44	10.50	11.21	11.93	10.49	4.01	5.83

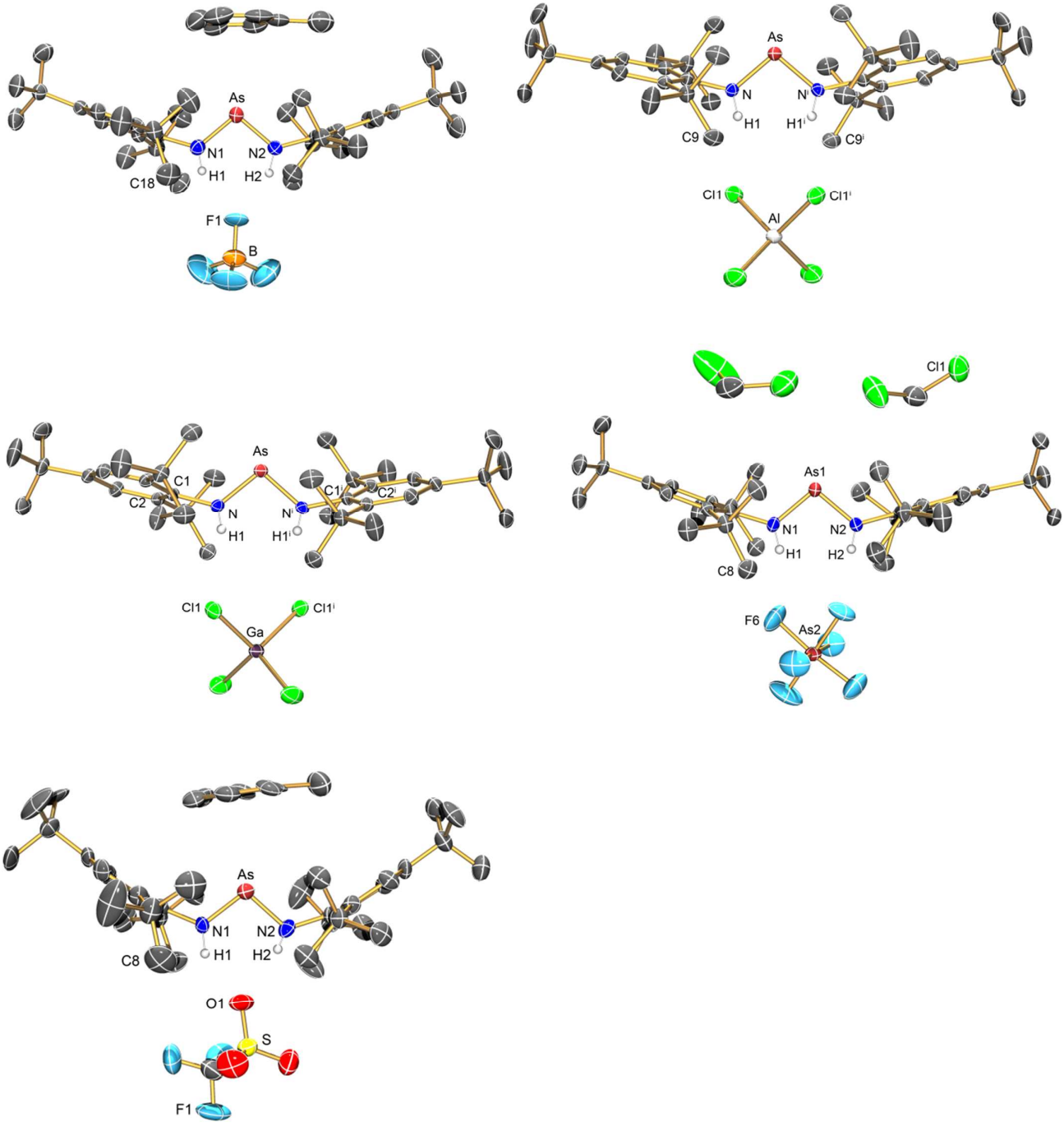


Figure 1. ORTEP drawing of the molecular structures of **3**[X] (X = BF_4, $AlCl_4$, $GaCl_4$, AsF_6, OTf) in the crystal. Thermal ellipsoids drawn with 50% probability at 173 K. Only *N*-bonded hydrogen atoms are depicted for clarity. Selected bond length and angles are listed in Table 2.

All characterized $\mathbf{3}^+$ cations (Figure 1) exhibit similar metrical parameters which are summarized in Table 2. The shortest distances between the arsenic centers and the anions are around 3.6 Å in all structures, indicating rather weak cation···anion interactions and similar coordination behavior of all used anions. One of the electronegative atoms of the anion is positioned in such a way that it fits into the pocket formed by the two Mes* substituents directing towards the opened N–As–N unit. Therefore, N–H···X interactions can be assumed. This arrangement and the N–H···X interactions are comparable with those found for the analogous $[(TerNH)_2P]^+$ salts.[17]

3[$AlCl_4$] and **3**[$GaCl_4$] crystallized solvent free, whereas compounds **3**[OTf], **3**[BF_4] and **3**[AsF_6] crystallized as the mono-solvates **3**[OTf] · toluene, **3**[BF_4] · toluene and the di-solvate **3**[AsF_6] · 2 CH_2Cl_2. The toluene molecules in **3**[OTf] · toluene and **3**[BF_4] · toluene adopt comparable positions above the angulated N–As–N unit. It is important to note that in both structures the As centers and the centroids (Ct) of the toluene rings are not arranged on a crystallographic slide axis in the crystal. The shortest distances As···Ct are 3.161 Å in **3**[OTf] · toluene and 3.302 Å in **3**[BF_4] · toluene stabilizing these salts by weak interactions (Σr_{vdW}(As···C) = 3.55 Å).[28] Moreover, these η^6-interactions confirm the electrophilic character of the As center and pack its coordination sphere so that it is effectively protected against nucleophilic attack what is quite favorable for long-time storage. Such Mentschutkin-type complexes of arsenic halides are already known in the literature.[29,30]

The most prominent structural feature is the bent N–As–N unit (99-100°) with rather short As–N bond lengths between 1.748 and 1.757Å clearly indicating double bond character (Σr_{cov}(As–N) = 1.92 Å, Σr_{cov}(As=N) = 1.74 Å).[31] The first compound bearing an As=N double bond (1.714(7) and 1.745(7) Å) was *N,N'*-bis(2,4,6-tri-tert-butylphenyl)amino-iminoarsane, reported by Lappert *et al.* in 1986.[1] Moreover cationic diazarsenium (1.763-1.814 Å)[5] and neutral tetrazaarsole (1.784 - 1.805 Å)[32] heterocycles containing partial As-N double bonds are known. Recently, neutral triazarsoles heterocycles were synthesized either by insertion of isonitriles into arsatriazanediyls [As(μ-NTer)$_2$N] (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl,

419 1.875 Å)[33] and by making use of a [3+2] cycloaddition reaction between an organic azide and an arsaalkyne

420 (1.839 Å).[34]

421 ***Table 2:*** Selected parameters (distances [Å], angles [°]) for derivatives of **3**[X] (X = BF_4, $AlCl_4$, $GaCl_4$, AsF_6, OTf).

	3[$AlCl_4$]	**3**[$GaCl_4$]	**3**[OTf]	**3**[BF_4]	**3**[AsF_6]
N–As(*)	1.757(3)	1.750(2)	1.760(5)	1.750(3)	1.748(2)
C–N(*)	1.453(4)	1.461(3)	1.444(7)	1.453(4)	1.456(3)
N–As–N`	99.5(2)	99.6(1)	100.6(2)	99.1(1)	100.0(1)
As–N–C(*)	125.1(2)	125.7(2)	119.6(4)	123.9(2)	123.9(2)
Σ(∡N1)	359.1	359.5	359.1	359.7	359.6
Σ(∡N2)	359.1	359.5	360.0	360.1	360.2
$As^+\cdots X^-$	3.633	3.624	3.539	3.637	3.659

422 (*) average values

423 ***Table 3:*** Crystallographic details of the structures of **3**[X] (X = BF_4, $AlCl_4$, $GaCl_4$, AsF_6, OTf) and **7**.

	3[$AlCl_4$]	**3**[$GaCl_4$]	**3**[OTf] · toluene	**3**[BF_4] · toluene	**3**[AsF_6] · 2 CH_2Cl_2	**7**
Chem. Formula	$C_{36}H_{60}AlAsCl_4N_2$	$C_{36}H_{60}AsCl_4GaN_2$	$C_{44}H_{68}AsF_3N_2O_3S$	$C_{43}H_{68}AsBF_4N_2$	$C_{38}H_{64}As_2Cl_4F_6N_2$	$C_{24}H_{34}AsCl_3GaN$
Form. Wght. [g mol^{-1}]	764.56	807.30	836.98	774.72	954.55	587.51
Colour	yellow	yellow	yellow	yellow	orange	yellow
Cryst. system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [Å]	24.945(1)	24.9686(7)	10.6600(5)	10.0267(3)	10.3463(2)	9.7496(3)
b [Å]	10.0767(5)	10.0804(3)	11.4046(5)	24.5792(8)	24.6479(5)	18.9671(5)
c [Å]	16.3057(9)	16.3100(4)	37.459(2)	17.6919(5)	18.1301(4)	14.7660(4)
α [°]	90.00	90.00	90.00	90.00	90.00	90.00
β [°]	93.000(4)	92.793(2)	90.00	92.337(2)	92.460(1)	95.991(1)
γ [°]	90.00	90.00	90.00	90.00	90.00	90.00
V [$Å^3$]	4093.0(4)	4100.2(2)	4554.0(4)	4356.5(2)	4619.2(2)	2715.6(1)
Z	4	4	4	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.241	1.308	1.221	1.181	1.373	1.437
μ [mm^{-1}]	1.139	1.758	0.842	0.827	1.730	2.529
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)	203(2)	173(2)	173(2)
Measured reflections	20489	30858	35975	94859	60716	68291
Independent reflections	4698	6248	7919	10952	10606	7216

Reflections with $I > 2\sigma(I)$	2814	3942	4341	6255	7346	5078
$R_{int.}$	0.1087	0.0802	0.1255	0.0841	0.0364	0.0627
$F(000)$	1616	1688	1784	1656	1976	1200
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0532	0.0442	0.0598	0.0603	0.0417	0.0386
wR_2 (F^2)	0.1162	0.0930	0.1103	0.1278	0.1063	0.0898
GooF	1.008	0.998	1.002	1.094	1.016	1.072
Parameters	212	213	510	573	527	280
CCDC #	1572163	1572160	1572161	1572162	1572159	1572157

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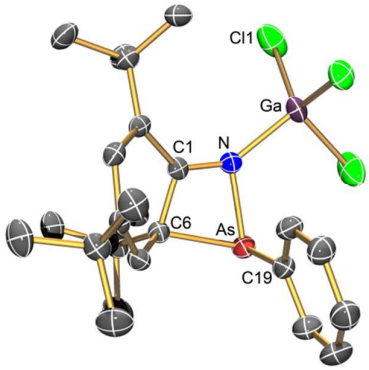


Figure 2. ORTEP drawing of the molecular structure of **7** in the crystal. Thermal ellipsoids drawn with 50% probability at 173 K. Hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [°]: As–N 1.958(2), N–C1 1.309(3), C1–C6 1.500(3), As–C6 2.038(2), As–C19 1.937(3), N–Ga 1.951(2); N–As–C19 98.5(1), C1–N–Ga 145.5(2), C6–As–N–C1 6.8(1).

7 represents a rare example of a four-membered heterocycle consisting of As, N and two C-atoms (Figure 2).[35,36] Yellow needles of **7** crystallized in the monoclinic space group $P2_1/n$ with four molecules per unit cell. As depicted in Figure 2, the four-membered ring is almost planar with a maximum deviation from planarity of 6.8° (∡(C6–As–N–C1)), while the six-membered condensed ring is stronger distorted from planarity (21.2°). Both rings are arranged almost orthogonally to each other (∡(N–As–C6–C5) = 117.6°). The C1–N bond with 1.309(3) Å displays some double bond character (*cf.* Σr_{cov}(N–C) = 1.46 Å, Σr_{cov}(N=C) = 1.27 Å),[31] whereas the As–N (1.958(2) Å), As–C6 (2.038(2) Å) and C6–C1 (1.500(3) Å) distances can be regarded as classical single bonds. The Ga–N donor-acceptor bond with 1.951(2) Å lies in the expected range (Σr_{cov}(N–Ga) = 1.95 Å).[31]

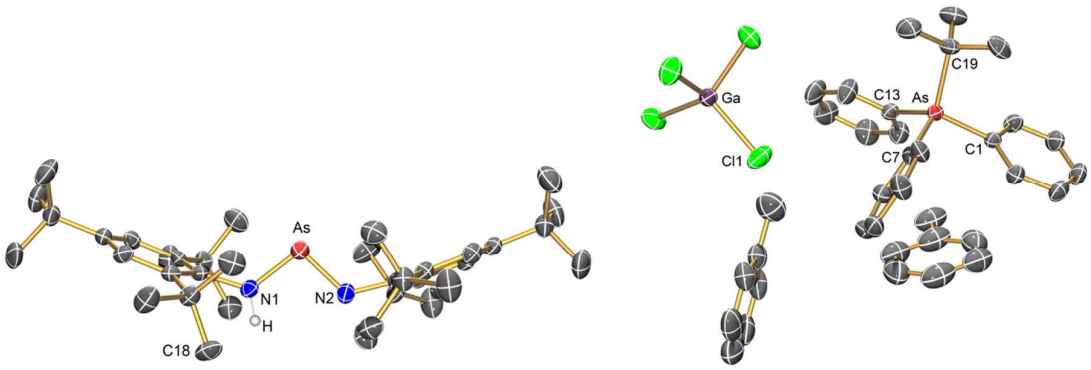


Figure 3. ORTEP drawing of the molecular structure of **6** and **8** in the crystal. Thermal ellipsoids drawn with 50% probability at 173 K. Hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [°] are listed in Tables S8 and Table S10.

Compound **6** crystallized in the orthorhombic space group $P2_12_12_1$ with for units per cell (Figure 3). The bent N-As-N (99.0(1)°) moiety displayed rather short N-As bonds (1.733(2), 1.752(2) Å) in accord with the situation found for species **3**[X] (vide infra, Table 2). Compound **8** crystallized in the triclinic space group $P\bar{1}$ with two formula units per cell (Figure 3). The molecular structure of the cation featured a distorted tetrahedral environment around the central arsenic atom with two distinctly different As–C bonds (As–C_{Ph} 1.911(3)-1.920(3) Å vs. As–C_{tBu} 1.985(3) Å). There are no significant cation···anion interactions.

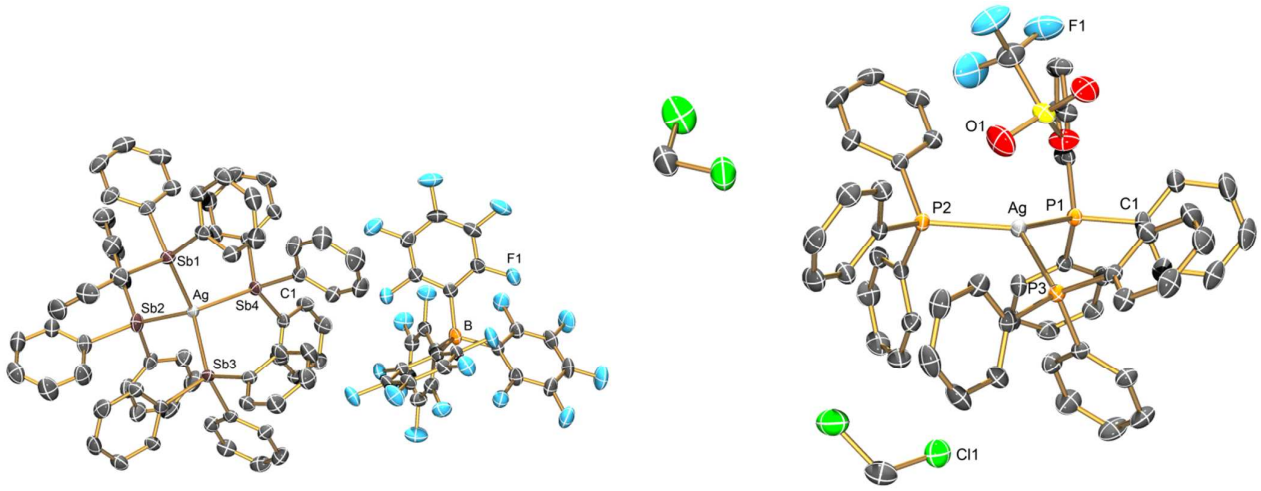


Figure 4. ORTEP drawing of the molecular structure of **9** and **10** in the crystal. Thermal ellipsoids drawn with 50% probability at 173 K. Hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [°] are listed in Tables S11 and Table S12.

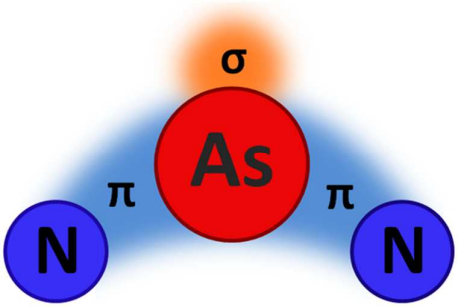
Both silver salts **9** and **10** crystallized in the triclinic space group $P\bar{1}$ with two formula units per cell (Figure 4). While **9** displayed a Ag^+ ion surrounded by four $SbPh_3$ ligands (Ag–Sb: between 2.692 – 2.700 Å, *cf.* Σr_{cov}(Ag–Sb) = 2.68 Å),[31] thus exhibiting a slightly distorted tetrahedral coordination environment, silver salt **10** is only surrounded by three neutral PPh_3 ligands (Ag–P: between 2.482 – 2.512 Å, *cf.* Σr_{cov}(Ag–P) =

2.39 Å)[31] but one oxygen atom of the CF_3-SO_3^- anion is also rather close with 2.657(2) Å, *cf.* Σr_{cov}(Ag–O) = 1.91 Å[31] vs. Σr_{vdW}(Ag···O) = 3.24 Å,[28] hence the coordination is best described by a [3+1] mode.

Conclusion:

In conclusion, the library of salts with dicoordinated arsenium cations $[R_2As]^+$ has been expanded by a series of acyclic bis(amino)arsenium salts. Additionally, the reactivity of the arsadiazonium ion $[Mes^*N{\equiv}As]^+$ towards protons has been explored as well as its Lewis acidic character towards classical Lewis bases such as $PnPh_3$ (Pn = P, As, Sb). A high-yielding synthetic protocols to obtain room temperature stable salts of acyclic NH-functionalized bis(amino)arsenium cation $[(Mes^*NH)_2As]^+$ is reported. These new salts represent an interesting building block for the synthesis of low coordinated electrophilic arsenic centers.

TOC Graphic



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