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

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Dedicated to Prof. Dr. Neil Burford

11

12 **Abstract:**

13 The reaction of Li[Mes*NH] (**1**, Mes * = 2,4,6-tri-*tert*-butylphenyl) with aminoarsane Mes*N(H)AsCl₂ (**2**,
14 Mes* = 2,4,6-*t*-Bu₃C₆H₂) at -80 °C resulted in the formation of bisamino(chloro)arsane (Mes*NH)₂AsCl
15 (**3**Cl) by elimination of LiCl. **3**Cl reacted with the Lewis acids such as AlCl₃, GaCl₃ and Ag[X] (X = AsF₆⁻,
16 OTf⁻, BF₄⁻; OTf = trifluoromethanesulfonate = OSO₂CF₃⁻) upon chloride ion abstraction to give salts
17 bearing the cation [(Mes*NH)₂As]⁺ (**3**[X]; X = AsF₆⁻, OTf⁻, BF₄⁻, ECl₄; E = Al, Ga). **3**⁺ represents the first
18 NH-functionalized acyclic bis(amino)arsenium cation. The formation of the salts bearing **3**⁺ could also be
19 observed in the reaction of *cyclo*-1,3-diarsa-2,4-diazane [ClAs(μ-NMes*)]₂ (**4**) with Lewis acids (AlCl₃,
20 GaCl₃) in the presence of proton sources in solution. All presented salts **3**[X] were stable at room
21 temperature and fully characterized.

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

23 **Introduction**

24 In the last decades the possibility to generate dicoordinate nitrogen bound arsenic compounds was shown
 25 not only for a series of amino(imino)arsanes (**I**, Scheme 1) but also for non-cyclic and cyclic
 26 bis(amino)arsenium ions (**II**, **III**).¹⁻⁷ Furthermore, base stabilized mono⁸ and di cations of arsenic have been
 27 reported.⁹

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

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

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

38 While numerous acyclic diaminophosphenium ions are known,¹⁰ up to now only two structures of salts
 39 with an acyclic diaminoarsenium cation $[(R_2N)_2As]^+$ ($R = SiMe_3$) were published in 2013.⁵ Contrarily,
 40 cationic four-, five- and six-membered cyclic bis(amino)arsenium salts have been known for years.^{6,7,11-13}

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

44 H bond. Recently, we could isolate and characterize an arsadiazonium cation $[\text{Mes}^*\text{NAs}]^+$ allowing further
45 systematic investigations for the syntheses of dicoordinated arsenium ions $[\text{R}_2\text{As}]^+$.¹⁵

46 We describe here the generation of the cation $[(\text{Mes}^*\text{NH})_2\text{As}]^+ (\mathbf{3}^+)$ as $[\text{GaCl}_4]^-$ -salt in the reaction of
47 $[\text{Mes}^*\text{NAs}]^+[\text{GaCl}_4]^- (\mathbf{5}[\text{GaCl}_4])$ with Mes^*NH_2 . For the direct syntheses of other salts bearing $\mathbf{3}^+$, we
48 present a convenient synthetic protocol starting from $(\text{Mes}^*\text{NH})_2\text{AsCl} (\mathbf{3Cl})$, which can be considered as an
49 ideal precursor for salts of $\mathbf{3}^+$, when treated with chloride ion abstracting Lewis acids. Furthermore, we
50 report on reactions of Mes^*NAs^+ -salts with Lewis bases such as PnPh_3 ($\text{Pn} = \text{P}, \text{As}, \text{Sb}$).

51

52 Experimental

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

55 **Preparation of starting materials.** All solvents were freshly distilled prior to use. Methylene dichloride
56 was purified according to a literature procedure,¹⁶ dried over P_4O_{10} , and distilled from CaH_2 . Diethylether
57 and toluene were dried over Na/benzophenone, *n*-hexane was dried over Na/benzophenone/tetraglyme. *N*-
58 butyllithium (2.5M solution in hexanes, Acros Organics) was used as received. GaCl_3 (Sigma-Aldrich) was
59 freshly sublimed prior to use. 1,3-Dichloro-2,4-bis-(2,4,6-tri-*tert*-butylphenyl)*cyclo*-1,3-diarsa-2,4-diazane
60 $[\text{Mes}^*\text{NAsCl}]_2 (\mathbf{4})$ was prepared according to a literature procedure.^{12,15} This procedure includes the
61 synthesis of **1**. 4-Dimethylaminopyridine (DMAP) was used as received. PPh_3 , AsPh_3 and SbPh_3 were
62 freshly sublimed prior to use.

63 **X-ray:** BRUKER Apex Kappa-II CCD diffractometer using graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda =$
64 0.71073).

65 **NMR:** BRUKER Avance 250, 300 and 500 NMR spectrometers. Spectra were referenced internally to
66 corresponding deuterated solvents (^1H : $\delta_{\text{ref}}(\text{CDHCl}_2) = 5.31$ ppm, within CD_2Cl_2 , ^{13}C : $\delta_{\text{ref}}(\text{CD}_2\text{Cl}_2) =$
67 54 ppm).

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

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

72 **MS:** THERMO ELECTRON Finnigan MAT 95-XP spectrometer.

73 **CHN-Analysis:** THERMO QUEST Flash EA 1112 analyser.

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

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

77 *Synthesis of 3Cl*

78 To a solution of 2,4,6-tri-*tert*-butylaniline (Mes*NH₂, 261 mg, 1.0 mmol) in Et₂O (10 ml) *n*-Butyllithium
79 (1.0 mmol) is added at room temperature and stirred for 1.5 hours. The reaction solution is added to a stirred
80 solution of AsCl₃ (181 mg, 1.0 mmol) in Et₂O (3 ml) at room temperature. The resulting rose suspension of
81 generated Mes*N(H)AsCl₂ and LiCl is stirred for 30 minutes. The precipitated LiCl is separated by
82 filtration. Li[Mes*NH], obtained from reaction of Mes*NH₂, (261 mg, 1.0 mmol) and *n*-Butyllithium
83 (1.0 mmol) in Et₂O (3 ml), is added to the filtrate at -80 °C over a period of 10 minutes. The solvent is
84 removed *in vacuo* at room temperature and the product extracted with 5 ml *n*-hexane. **3Cl** is purified by re-
85 crystallization from Et₂O solution. Decomp. 115 °C. Anal. calc. % (found) for C₃₆H₆₀AsClN₂ (631.25): C,
86 68.50 (66.28); H, 9.58 (9.17); N, 4.44 (4.41). ¹H NMR (25°C, CD₂Cl₂, 300.13 MHz): δ = 1.29 (s, 18 H, *p*-
87 C(CH₃)₃), 1.53 (s, 36 H, *o*-C(CH₃)₃), 5.57 (s, 2 H, NH), 7.33 (s, 4 H, CH). ¹³C{¹H} NMR (25°C, CD₂Cl₂,
88 75.48 MHz): δ = 31.76 (s, *p*-C(CH₃)₃), 33.89 (s, *o*-C(CH₃)₃), 35.04 (s, *p*-C(CH₃)₃), 36.74 (s, *o*-C(CH₃)₃),
89 124.04 (s, CH, Ar), 137.88 (s, *p*-Ar), 144.59 (s, *o*-Ar), 145.32 (s, *ipso*-Ar). IR (ATR, 64 scans, cm⁻¹): 3352
90 (m), 2959 (s), 2951 (s), 2903 (m), 2868 (m), 1597 (m), 1477 (m), 1463 (m), 1422 (s), 1392 (m), 1361 (s),
91 1304 (w), 1288 (m), 1241 (m), 1214 (s), 1200 (m), 1111 (s), 1022 (w), 933 (w), 922 (w), 912 (w), 878 (m),
92 828 (s), 816 (m), 780 (m), 750 (m), 732 (w), 667 (w), 649 (w), 629 (m), 594 (m), 568 (w), 546 (w). Raman
93 (460 mW, 25 °C, 150 scans, cm⁻¹): 3088 (1), 2965 (10), 2909 (9), 2784 (1), 2712 (2), 1601 (5), 1461 (3),
94 1449 (4), 1430 (3), 1366 (1), 1345 (1), 1293 (3), 1256 (2), 1245 (2), 1225 (3), 1202 (4), 1183 (3), 1146 (3),
95 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

96 (4), 149 (5), 113 (2), 87 (2). MS (CI pos. Isobutane): 262 [Mes*NH₃]⁺, 334 [Mes*NA_s]⁺, 595
 97 [(Mes*NH)₂As]⁺.

98 *Synthesis of 3[AlCl₄]*

99 **A)** To a stirred colorless solution of **3**Cl (0.124 mmol, 78 mg) in toluene (5 ml) powdered AlCl₃
 100 (0.124 mmol, 17 mg) is added at –80 °C. The color of the resulting solution alters to yellow within a few
 101 minutes. The solution is warmed up to ambient temperatures and stirred for two hours resulting in a yellow
 102 precipitate and a clear colorless supernatant which is removed by a syringe. The precipitate is washed with
 103 toluene and dried *in vacuo*. **3**[AlCl₄] is obtained as a yellow powder (90 mg, 0.118 mmol, 95 %).

104 **B)** To a stirred solution of **4**, (0.118 mmol, 87 mg) in toluene (1 ml) a solution of AlCl₃ (0.235 mmol,
 105 31 mg) in toluene (8 ml) is added dropwise at –80 °C to give a clear orange solution. Crystals of **3**[AlCl₄]
 106 are obtained by subsequent removal of solvent at –70 °C. The supernatant is removed by decantation.
 107 **3**[AlCl₄] is isolated as a yellow crystalline solid. Decomp. 156 °C. Anal. calc. % (found) for
 108 C₃₆H₆₀AlAsCl₄N₂ (764.59): C, 56.55 (56.27); H, 7.91 (7.89); N, 3.66 (3.69). ¹H NMR (25°C, CD₂Cl₂,
 109 250.13 MHz): δ = 1.32 (s, 18 H, *p*-C(CH₃)₃), 1.57 (s, 36 H, *o*-C(CH₃)₃), 7.53 (s, 4 H, CH), 10.44 (s, 2 H,
 110 NH). ¹³C{¹H} NMR (25°C, CD₂Cl₂, 62.90 MHz): δ = 31.5 (s, *p*-C(CH₃)₃), 34.6 (s, *o*-C(CH₃)₃), 35.6 (s, *p*-
 111 C(CH₃)₃), 37.5 (s, *o*-C(CH₃)₃), 124.8 (s, CH, Ar), 131.4 (s, *p*-Ar), 148.5 (s, *o*-Ar), 152.5 (s, *ipso*-Ar). IR
 112 (ATR, 64 scans, cm^{–1}): 3236 (m), 3009 (w), 2956 (s), 2872 (m), 1600 (m), 1476 (m), 1463 (m), 1419 (m),
 113 1395 (m), 1362 (m), 1294 (w), 1269 (m), 1243 (m), 1214 (s), 1181 (m), 1106 (s), 1025 (w), 938 (w), 926
 114 (w), 912 (w), 881 (m), 852 (s), 820 (w), 798 (w), 779 (w), 762 (w), 666 (w), 648 (w), 634 (w), 627 (w), 582
 115 (s). Raman (784 nm, lat10X, 25 °C, 4 sc/60 sec, cm^{–1}): 2962 (2), 2929 (2), 2904 (2), 2870 (1), 2780 (1),
 116 2708 (1), 1600 (3), 1468 (2), 1454 (2), 1422 (2), 1396 (1), 1363 (1), 1347 (2), 1289 (2), 1254 (1), 1243 (1),
 117 1218 (4), 1186 (5), 1146 (4), 1117 (2), 1024 (1), 927 (2), 861 (10), 821 (6), 798 (5), 762 (3), 698 (4), 648
 118 (2), 569 (3), 465 (2), 418 (1), 349 (3), 263 (2), 183 (2), 134 (6), 119 (6), 107 (7), 70 (10). MS (CI pos.
 119 Isobutane): 206 [Mes*NH₃ - ^tBu]⁺, 262 [Mes*NH₃]⁺. Crystals of **3**[AlCl₄] suitable for X-ray
 120 crystallographic analysis are obtained by re-crystallization from CH₂Cl₂.

121 *Synthesis of 3[GaCl₄]*

122 **A)** To a stirred solution of **3**Cl (0.182 mmol, 115 mg) in toluene (3 ml) a solution of GaCl₃ (0.182 mmol,
123 32 mg) in toluene (2 ml) is added dropwise at room temperature and stirred for one hour resulting in a
124 yellow precipitate and a clear colorless supernatant which is removed by a syringe. The precipitate is
125 washed with toluene and dried *in vacuo*. **3**[GaCl₄] is obtained as a yellow powder (138 mg, 0.171 mmol,
126 94 %).

127 **B)** To a stirred solution of **4** (0.087 mmol, 64 mg) in toluene (2 ml) a solution of GaCl₃ (0.173 mmol,
128 31 mg) in toluene (1 ml) is added dropwise at –80 °C, followed by dropwise addition of 2,4,6-tri-*tert*-
129 butylaniline (Mes*NH₂, 44 mg, 0.170 mmol) in toluene (2 ml). The reaction mixture is warmed to room
130 temperature and stirred for two hours. Removal of solvent, washing with toluene and drying *in vacuo* yields
131 **3**[GaCl₄] as a yellow powder (65 mg, 0.081 mmol, 92 %). Decomp. 135 °C. Anal. calc. % (found) for
132 C₃₆H₆₀AsCl₄GaN₂ (807.33): C, 53.56 (52.69); H, 7.49 (7.02); N, 3.47 (3.42). ¹H NMR (25°C, CD₂Cl₂,
133 300.13 MHz): δ = 1.32 (s, 18 H, *p*-C(CH₃)₃), 1.57 (s, 36 H, *o*-C(CH₃)₃), 7.53 (s, 4 H, CH), 10.50 (s, 2 H,
134 NH). ¹³C {¹H} NMR (25°C, CD₂Cl₂, 75.48 MHz): δ = 31.51 (s, *p*-C(CH₃)₃), 34.62 (s, *o*-C(CH₃)₃), 35.63 (s,
135 *p*-C(CH₃)₃), 37.50 (s, *o*-C(CH₃)₃), 124.80 (s, CH, Ar), 131.42 (s, *p*-Ar), 148.43 (s, *o*-Ar), 152.48 (s, *ipso*-Ar).
136 IR (ATR, 64 scans, cm⁻¹): 3231 (m), 3009 (m), 2956 (s), 2872 (m), 1600 (m), 1475 (m), 1471 (m), 1463
137 (m), 1418 (m), 1395 (m), 1362 (m), 1294 (w), 1269 (w), 1243 (m), 1213 (s), 1180 (m), 1105 (s), 1025 (w),
138 938 (w), 926 (w), 912 (w), 881 (m), 851 (s), 820 (w), 798 (w), 779 (w), 762 (w), 666 (w), 647 (w), 634 (w),
139 627 (w), 581 (m), 543 (w). Raman (460 mW, 25 °C, 150 scans, cm⁻¹): 3237 (1), 3129 (1), 3109 (1), 2971
140 (10), 2911 (9), 2785 (2), 2712 (2), 1603 (7), 1470 (4), 1457 (3), 1451 (3), 1426 (3), 1399 (2), 1366 (2), 1351
141 (3), 1293 (3), 1256 (2), 1246 (2), 1221 (5), 1189 (8), 1148 (6), 1119 (3), 1030 (1), 930 (3), 865 (9), 824 (7),
142 801 (5), 782 (1), 764 (3), 701 (4), 651 (2), 573 (4), 469 (1), 421 (1), 350 (6), 265 (2), 155 (2), 132 (5), 114
143 (4), 111 (4). MS (CI pos. Isobutane): 262 [Mes*NH₃]⁺, 334 [Mes*NAs]⁺, 595 [(Mes*NH)₂As]⁺. Crystals of
144 **3**[GaCl₄] suitable for X-ray crystallographic analysis are obtained by re-crystallization from a CH₂Cl₂
145 solution of **3**[GaCl₄].

146 *Synthesis of 3[OTf] • toluene*

147 **A)** To a stirred colorless solution of **3**Cl (78 mg, 0.124 mmol) in CH₂Cl₂ (5 ml) powdered Ag[OTf]
148 (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 $-80\text{ }^{\circ}\text{C}$. 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 $-80\text{ }^{\circ}\text{C}$ 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 $5\text{ }^{\circ}\text{C}$. Crystals of **3**[OTf] · toluene are obtained by storage of the solution at $5\text{ }^{\circ}\text{C}$ for some hours. Crystals of $[\text{Ag}(\text{PPh}_3)_3][\text{OTf}] \cdot 2\text{ CH}_2\text{Cl}_2$ (**9**) suitable for X-ray crystallographic analysis are obtained by re-crystallization of the colorless solid from a CH_2Cl_2 solution. Decomp. $165\text{ }^{\circ}\text{C}$. Anal. calc. % (found) for $\text{C}_{37}\text{H}_{60}\text{AsF}_3\text{N}_2\text{O}_3\text{S}$ (744.87): C, 59.66 (56.97); H, 8.12 (7.74); N, 3.76 (3.67). ^1H NMR (25°C , CD_2Cl_2 , 250.13 MHz): $\delta = 1.32$ (s, 18 H, *p*- $\text{C}(\text{CH}_3)_3$), 1.56 (s, 36 H, *o*- $\text{C}(\text{CH}_3)_3$), 7.52 (s, 4 H, CH), 11.93 (s, 2 H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (25°C , CD_2Cl_2 , 62.90 MHz): $\delta = 31.6$ (s, *p*- $\text{C}(\text{CH}_3)_3$), 34.3 (s, *o*- $\text{C}(\text{CH}_3)_3$), 35.6 (s, *p*- $\text{C}(\text{CH}_3)_3$), 37.4 (s, *o*- $\text{C}(\text{CH}_3)_3$), 124.4 (s, CH, 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, $25\text{ }^{\circ}\text{C}$, 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 $[\text{Mes}^*\text{NH}_3 - \text{tBu}]^+$, 244 $[\text{Mes}^* - 2\text{H}]^+$, 246 $[\text{Mes}^*]^+$, 262 $[\text{Mes}^*\text{NH}_3]^+$. Crystals of **3**[OTf] · toluene suitable for X-ray crystallographic analysis are obtained by re-crystallization from toluene.

176 *Synthesis of 3[BF₄] • toluene*

177 A) To a stirred colorless solution of **3**Cl (78 mg, 0.124 mmol) in CH₂Cl₂ (5 ml) powdered Ag[BF₄]
178 (0.124 mmol, 24 mg) is added at –80 °C. The color of the resulting solution alters to yellow within a few
179 minutes. The solution is warmed up to room temperature and stirred for two hours resulting in a colorless
180 precipitate and a clear orange supernatant. After filtration (F4) and removing of solvent *in vacuo* **3**[BF₄] is
181 obtained as an orange liquid. The product can be obtained as a yellow powder from a *n*-hexane solution
182 (77 mg, 0.113 mmol, 91 %).

183 B) To a stirred solution of **4** (0.108 mmol, 80 mg) in CH₂Cl₂ (5 ml) powdered Ag[BF₄] (0.216 mmol,
184 42 mg) was added at –80 °C resulting in a deep red solution that was stirred for 30 minutes. Afterwards the
185 reaction solution was warmed to room temperature at which the color of the solution changed to yellow. The
186 colorless precipitate is separated from the liquid by filtration (F4). Subsequently, the solvent was removed
187 under reduced pressure and the product extracted with *n*-hexane. Mp. 144 °C. Anal. calc. % (found) for
188 C₃₆H₆₀AsBF₄N₂ (682.6): C, 63.34 (62.34); H, 8.86 (8.81); N, 4.10 (4.42). ¹H NMR (25°C, CD₂Cl₂, 250.13
189 MHz): δ = 1.32 (s, 18 H, *p*-C(CH₃)₃), 1.55 (s, 36 H, *o*-C(CH₃)₃), 7.52 (s, 4 H, CH), 11.21 (s, 2 H, NH).
190 ¹¹B{¹H} NMR (25°C, CD₂Cl₂, 80.25 MHz): δ = –0.81. ¹³C{¹H} NMR (25°C, CD₂Cl₂, 62.90 MHz): δ = 31.5
191 (s, *p*-C(CH₃)₃), 34.3 (s, *o*-C(CH₃)₃), 35.6 (s, *p*-C(CH₃)₃), 37.4 (s, *o*-C(CH₃)₃), 124.5 (s, CH, Ar), 132.1 (s, *p*-
192 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),
193 2910 (m), 2872 (m), 1596 (m), 1477 (m), 1471 (m), 1464 (m), 1456 (w), 1435 (w), 1421 (m), 1397 (m),
194 1363 (m), 1288 (w), 1269 (w), 1241 (m), 1211 (m), 1180 (m), 1134 (s), 1104 (s), 1070 (s), 1028 (w), 941
195 (s), 913 (m), 883 (m), 850 (s), 819 (w), 784 (w), 759 (m), 673 (m), 667 (m), 648 (m), 617 (w), 602 (w), 569
196 (w). Raman (784 nm, lat10X, 25 °C, 6 sc/30 sec, cm^{–1}): 2974 (1), 2907 (1), 1598 (2), 1468 (1), 1445 (1),
197 1423 (2), 1398 (1), 1367 (1), 1289 (2), 1243 (1), 1216 (2), 1188 (3), 1144 (3), 1117 (2), 1023 (1), 926 (1),
198 915 (2), 859 (10), 823 (5), 806 (4), 786 (1), 762 (3), 709 (2), 649 (1), 572 (2), 470 (1), 436 (1), 422 (1), 368
199 (1), 354 (1), 260 (1), 135 (4), 108 (5), 71 (7). MS (CI pos. Isobutane): 206 [Mes*NH₃ - ^tBu]⁺, 262
200 [Mes*NH₃]⁺. Crystals of **3**[BF₄] • toluene suitable for X-ray crystallographic analysis are obtained by re-
201 crystallization from a toluene solution of **3**[BF₄].

202

203 **Synthesis of $3[\text{AsF}_6] \cdot 2 \text{CH}_2\text{Cl}_2$**

204 To a stirred solution of $\text{Ag}[\text{AsF}_6]$ (0.55 mmol, 0.163 g) in CH_2Cl_2 (5 ml), a yellow solution of **4**
 205 (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
 206 resulting red suspension is warmed to -50°C over a period of one hour and filtered (F4). The solution is
 207 slowly cooled to -80°C , resulting in the deposition of orange crystals. The supernatant was removed by
 208 decantation and the residue was dried *in vacuo* which yields $3[\text{AsF}_6] \cdot 2 \text{CH}_2\text{Cl}_2$ as an orange crystalline
 209 solid. Decomp. 127°C . Anal. calc. % (found) for $3[\text{AsF}_6] \cdot \text{CH}_2\text{Cl}_2$ ($\text{C}_{37}\text{H}_{62}\text{As}_2\text{Cl}_2\text{F}_6\text{N}_2$ (869.64): C, 51.10
 210 (51.81); H, 7.19 (7.36); N, 3.22 (3.73). ^1H NMR (25°C , CD_2Cl_2 , 300.13MHz): δ = 1.33 (s, 18 H, *p*-
 211 $\text{C}(\text{CH}_3)_3$), 1.56 (s, 36 H, *o*- $\text{C}(\text{CH}_3)_3$), 7.53 (s, 4 H, *m*-CH), 10.49 (s, 2 H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (25°C ,
 212 CD_2Cl_2 , 75.5MHz): δ = 31.5 (s, *p*- $\text{C}(\text{CH}_3)_3$), 34.3 (s, *o*- $\text{C}(\text{CH}_3)_3$), 35.6 (s, *p*- $\text{C}(\text{CH}_3)_3$), 37.5 (s, *o*- $\text{C}(\text{CH}_3)_3$),
 213 124.7 (s, CH, Ar), 131.7 (s, *p*-Ar), 148.6 (s, *o*-Ar), 152.3 (s, *ipso*-Ar). $^{19}\text{F}\{^1\text{H}\}$ NMR (25°C , CD_2Cl_2 ,
 214 282.4MHz): δ = 61 (s, broad). IR (ATR, 32 scans, cm^{-1}): 3272 (w), 2959 (m), 2873 (w), 1597 (w), 1470
 215 (w), 1455 (w), 1434 (w), 1417 (w), 1396 (w), 1362 (m), 1297 (w), 1269 (w), 1242 (w), 1211 (m), 1178 (w),
 216 1144 (w), 1104 (m), 1025 (w), 927 (w), 913 (w), 881 (m), 854 (m), 847 (m), 820 (w), 802 (m), 787 (w), 762
 217 (w), 693 (s), 670 (s), 650 (m), 608 (m), 595 (m). Raman (50 mW, 25°C , 402 scans, cm^{-1}): 2968 (10), 2913
 218 (10), 2789 (2), 2760 (12), 2714 (2), 1601 (7), 1469 (3), 1448 (4), 1416 (3), 1399 (3), 1367 (2), 1292 (3),
 219 1248 (3), 1224 (7), 1193 (6), 1149 (5), 1121 (2), 1030 (1), 930 (2), 870 (4), 826 (5), 802 (2), 766 (1), 754
 220 (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),
 221 261 (2), 149 (5). MS (FAB+, Cs, 20keV, *p*-NBA matrix): 262 $[\text{Mes}^*-\text{NH}_3]^+$, 334 $[\text{Mes}^*-\text{NAs}]^+$. Crystals of
 222 $3[\text{AsF}_6] \cdot 2 \text{CH}_2\text{Cl}_2$ suitable for X-ray crystallographic analysis are obtained directly from the reaction
 223 solution of $3[\text{AsF}_6]$.

224 **Synthesis of **7****

225 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)
 226 in toluene (3 ml) was added dropwise at -60°C . The obtained deep red solution was warmed to room
 227 temperature. The reaction solution was concentrated under reduced pressure and stored for some hours
 228 resulting in the deposition of crystals of **7** (110 mg, 0.188 mmol, 87 %). Mp. 164°C . Anal. calc. % (found)
 229 for $\text{C}_{24}\text{H}_{34}\text{AsCl}_3\text{GaN}$ (587.54): C, 49.06 (51.06); H, 5.83 (5.42); N, 2.38 (1.98). ^1H NMR (25°C , CD_2Cl_2 ,

300.13 MHz): δ = 1.33 (s, 9 H, C6(CH₃)₃), 1.60 (s, 9 H, C4(CH₃)₃), 1.66 (s, 9 H, C2(CH₃)₃), 7.39-7.47 (m, 5 H, Ar), 7.54 (s, 2 H, CH). ¹³C{¹H} NMR (25°C, CD₂Cl₂, 75.48 MHz): δ = 31.58 (C15(CH₃)₃), 33.42 (C4(CH₃)₃), 35.27 (C15), 36.33 (C7(CH₃)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 GaCl₃ resulted in the formation of the arsadiazonium salt [Mes*N $\equiv$ As][GaCl₄] (**5**[GaCl₄]).¹⁵ However, in cases of long time storage of **5**[GaCl₄] in solutions of toluene or CH₂Cl₂ the slow formation of [(Mes*NH)₂As][GaCl₄] (**3**[GaCl₄]) could be observed. A similar reaction sequence was observed when **4** was treated with AlCl₃ yielding salt **3**[AlCl₄]. 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)₂P][GaCl₄] in the reaction of [Mes*N $\equiv$ P][GaCl₄] with Mes*NH₂.¹⁴ Analogously, we treated **5**[GaCl₄] with Mes*NH₂ affording quantitatively **3**[GaCl₄] (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 NEt₃·HCl from Mes*N(H)AsCl₂ (**2**) upon addition of NEt₃. Despite several purification steps for **4** most likely small amounts of HCl still remain e.g. as NEt₃·HCl salt. It is also known that CH₂Cl₂ slowly decomposes in the presence of Lewis acids or light generating HCl. Therefore, we believe that storage of dissolved **5**[GaCl₄] for longer periods led to the reaction of **5**⁺ with two equivalents of HCl yielding GaCl₃, AsCl₃ and Mes*NH₂ which reacted in a subsequent reaction with a further equivalent of **5**⁺ to give **3**[GaCl₄] (Scheme 3). A similar slow decomposition of **4** can be assumed generating free Mes*NH₂.

Scheme 3. Proposed reaction pathway of the formation of $3[\text{GaCl}_4]$ in the reaction of 5^+ with HCl.

We have already demonstrated that the chloride abstraction in $(\text{TerNH})_2\text{PCl}$ by Lewis acids such as GaCl_3 or several silver salts led to the formation of salts containing the cation $[(\text{TerNH})_2\text{P}]^+$.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 $[\text{GaCl}_4]^-$ salt (Scheme 1, $\text{R} = \text{Mes}$).⁷ During the course of our work we tried to receive salts containing 3^+ by treatment of $(\text{Mes}^*\text{NH})_2\text{AsCl}$ (3Cl) with different Lewis acids. Since 3Cl 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 $\text{LiN}(\text{H})\text{Mes}^*$ 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 $\text{Mes}^*\text{N}(\text{H})\text{AsN}(\text{H})\text{Mes}^*$ (**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 $\text{Pn}(\text{III})$ -halides resulted in a quantitative amination finally yielding $\text{Pn}[\text{N}(\text{H})\text{Mes}^*]_3$ ($\text{Pn} = \text{Sb}, \text{Bi}$).¹⁹

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 $\text{Li}[\text{Mes}^*\text{NH}]$ (**1**) in Et_2O at -80°C did not only yield **6** and Mes^*NH_2 but additionally **3Cl** by elimination of LiCl (Scheme 6).

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

Scheme 7. Synthesis of bisamino(chloro)arsane $(\text{tBu})_2\text{NAs}(\text{Cl})\text{N}(\text{tBu})\text{SiMe}_3$ 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 $\text{Li}[\text{N}(\text{R})\text{SiMe}_3]$ which resulted in the formation of the bisamino(chloro)arsane $\text{R}_2\text{NAs}(\text{Cl})\text{N}(\text{R})\text{SiMe}_3$ ($\text{R} = \text{tBu}$) (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 **3Cl** could be obtained after re-crystallization in rather good yields (ca. 80 %).

Scheme 8. Synthesis of **3Cl** 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 **3Cl** an indirect “HCl-elimination” in the final step by formation of LiCl and Mes^*NH_2 . As a consequence, for a successful generation of **3Cl** 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, **3Cl** was treated with the Lewis acids AlCl_3 and GaCl_3 , affording the salts **3** $[\text{AlCl}_4]$ and **3** $[\text{GaCl}_4]$ with yields over 90%. Furthermore, **3Cl** was treated with the silver salts $\text{Ag}[\text{OTf}]$ and $\text{Ag}[\text{BF}_4]$ (Scheme 10). After extraction from precipitated silver chloride the solvates **3** $[\text{OTf}] \cdot \text{toluene}$ and

303 $3[\text{BF}_4] \cdot \text{toluene}$ could be obtained from toluene solution also with yields over 90 %. In contrast, the
 304 silylaminoarsane $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AsCl}$ reacted with $\text{Ag}[\text{OTf}]$ to give the *cyclo*-1,3-diarsa-2,4-diazane
 305 $[(\text{Me}_3\text{Si})_2\text{NAs}-\mu\text{-NSiMe}_3]_2$ by elimination of Me_3SiOTf .⁵ In the reaction of 3Cl with $\text{Ag}[\text{AsF}_6]$, surprisingly
 306 a quantitative conversion of 3Cl to Mes^*NH_2 was detected by ^1H NMR spectroscopy, presumably due to the
 307 presence of HF in solution.

308

309

310 **Scheme 10.** Top: Reaction of 3Cl with ECl_3 ($\text{E} = \text{Al}, \text{Ga}$). Bottom: Reaction of 3Cl with AgX ($\text{X} = \text{OTf}^-, \text{BF}_4^-$).

311

312 In a next series of experiments we were interested in the reactivity of $[\text{Mes}^*\text{N}\equiv\text{As}][\text{GaCl}_4]$ ($5[\text{GaCl}_4]$)
 313 towards classical Lewis bases such as pyridine or triphenylpnictanes of the type PnPh_3 ($\text{Pn} = \text{P}, \text{As}, \text{Sb}$) and
 314 to compare these results with those of the lighter phosphorus congener reported by Burford *et al.*^{21–24} The
 315 reaction of $5[\text{GaCl}_4]$ with DMAP (4-dimethylaminopyridine) at -80°C yielded monomeric Mes^*NAsCl and
 316 $\text{DMAP}\cdot\text{GaCl}_3$ adduct. A similar reaction was found when $5[\text{GaCl}_4]$ was treated with PPh_3 at -80°C
 317 affording also the chloroiminoarsane along with the $\text{Ph}_3\text{P}\cdot\text{GaCl}_3$ adduct (Scheme 7). Contrarily, treatment of
 318 $5[\text{GaCl}_4]$ with AsPh_3 at -80°C resulted in a product mixture containing also Mes^*NAsCl and $\text{Ph}_3\text{As}\cdot\text{GaCl}_3$
 319 besides arsonium salt $[\text{tBuAsPh}_3][\text{GaCl}_4] \cdot \text{toluene}$ (**8**) and $3[\text{GaCl}_4]$ which could be co-crystallized both as
 320 main products in moderate yields ($\sim 40\%$). The formation of an iminodiarsenium salt
 321 $[\text{Mes}^*\text{NAsAsPh}_3][\text{GaCl}_4]$ could not be observed. A further unexpected molecule could be isolated from the
 322 reaction of $5[\text{GaCl}_4]$ with SbPh_3 which yielded after formal elimination of ClSbPh_2 a four-membered ring
 323 with an inner-cyclic As-N-bond, stabilized as GaCl_3 adduct (**7**, Scheme 11).

8

Scheme 11. Summary of the obtained product mixtures in the reactions of $5[\text{GaCl}_4]$ with DMAP and PnPh_3 ($\text{Pn} = \text{P}, \text{As}, \text{Sb}$).

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 $\text{As}-\text{Cl}$ 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 $5[\text{GaCl}_4]$ 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 , $5[\text{GaCl}_4]$

immediately showed decomposition. DMAP·GaCl₃ and Ph₃P·GaCl₃ can be regarded as chemically and thermodynamically robust species. In contrast to the latter, adduct formation of Ph₃As·GaCl₃ seemed not to be favored since the formation of several other products were observed at the same time (Scheme 7). In case of SbPh₃ formation of Ph₃Sb·GaCl₃ was not observed indicating a smaller Lewis basic character leading to a different reaction channel (Ph transfer to arsenic) with the formation of Ph₂SbCl 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**N*AsCl with Ag[B(C₆F₅)₄], however, only a complex product mixture was obtained. Thus, we carried out the same reaction in the presence of SbPh₃ in the hope to quench [Mes**N*As-SbPh₃]⁺, which did not work. Again a complex mixture was obtained, from which we were able to crystallize [Ag(SbPh₃)₄][B(C₆F₅)₄] (**9**).

Scheme 12. Top: Reaction of Mes**N*POTf with DMAP reported by Burford *et al.*²⁴ Bottom: Synthesis of a bis(arylamino)phosphinophosphenium salt with R = Me, Ar = 2,6-(CHMe₂)₂C₆H₃; An = OTf.²⁵

Interestingly, when **5**[GaCl₄] was treated with AsPh₃ 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**[GaCl₄] after warming up the reaction solution. For this reaction, a similar reaction sequence as depicted in Scheme

352 3 can be assumed. Thus, two general reaction channels for the formation of **3**[GaCl₄] are possible with either
 353 **3**Cl or **4** as starting materials.

354 In comparison to the synthesis of **3**[GaCl₄] starting from **4**, the reaction of **4** with Ag[AsF₆] yielded
 355 **3**[AsF₆]. Again small amounts of HF or HCl within the reaction system are inevitable. It is known that the
 356 reaction of **4** with Ag[OTf] resulted in the formation of cyclic [Mes*N-μ-AsOTf]₂ by elimination of silver
 357 halide.²⁶

358 Burford *et al.* explored the electrophilic character of the phosphadiazonium ion [Mes*N≡P]⁺, e.g. they
 359 were able to isolate and fully characterize the iminophosphinphosphonium salt [Mes*NPPPh₃][OTf]
 360 obtained when Mes*NPOTf was treated with PPh₃.¹⁴ To compare the reactivity of **5**⁺ towards PPh₃ with the
 361 results of the Burford group, additionally, the reaction of [Mes*N-μ-AsOTf]₂ with PPh₃ was explored. The
 362 main product of this reaction was the formation of **3**[OTf] indicating ring-opening upon attack of the base
 363 PPh₃. As side product, solvated [Ag(PPh₃)₃][OTf] (**10**) was isolated in low quantities and fully
 364 characterized. Keeping in mind that [Mes*N-μ-AsOTf]₂ was prepared by silver halide elimination it was not
 365 surprising that dissolved Ag⁺ salts can easily form solvated [Ag(PPh₃)₃][OTf], which was first described in
 366 2000 by Laguna.²⁷

367 The reaction of **4** with Ag[BF₄] proved that among other products the formation of **3**[BF₄] also occurred.
 368 Scheme 13 summarizes the two general synthetic methods to obtain salts of **3**, either starting from **3**Cl by
 369 chloride elimination with Lewis acids (i) or starting from **4** in the reaction with Lewis acids in the presence
 370 of proton sources (ii).

372 **Scheme 13.** Synthetic methods to obtain salts of **3**. Reaction with halides of group 13: (i) ECl₃, An = ECl₄, E = Al, Ga;
 373 (ii) ECl₃/ 2 HCl, An = ECl₄, E = Al, Ga. Reaction with silver salts: (i) Ag[OTf], An = OTf, Ag[BF₄], An = BF₄; (ii) 2
 374 Ag[OTf]/ PPh₃/ 2 HCl, An = OTf; 2 Ag[BF₄]/ 2 HX, X = F or Cl, An = BF₄; 2 Ag[AsF₆]/ 2 HX, X = F or Cl, An = AsF₆.

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**[AsF₆] · 2 CH₂Cl₂) 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 [(Me₃Si)₂N]₂AsCl). A significant feature of all described
381 salts of **3** is their pronounced low-field shift of the *NH*-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: δ[¹H] = 5.57), all **3**[X] (X =
383 AlCl₄, GaCl₄, BF₄, OTf, AsF₆) salts form ion pairs and hence their N–*H* resonance was detected in the low-
384 field range between 10.44 for **3**[AlCl₄] and 11.93 ppm for **3**[OTf] (see Table 1).

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Table 1: ^1H 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**.

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

392 **Figure 1.** ORTEP drawing of the molecular structures of **3**[X] (X = BF₄, AlCl₄, GaCl₄, AsF₆, OTf) in the crystal. Thermal
 393 ellipsoids drawn with 50% probability at 173 K. Only N-bonded hydrogen atoms are depicted for clarity. Selected bond
 394 length and angles are listed in Table 2.

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

402 **3**[AlCl₄] and **3**[GaCl₄] crystallized solvent free, whereas compounds **3**[OTf], **3**[BF₄] and **3**[AsF₆]
 403 crystallized as the mono-solvates **3**[OTf] · toluene, **3**[BF₄] · toluene and the di-solvate **3**[AsF₆] · 2 CH₂Cl₂.
 404 The toluene molecules in **3**[OTf] · toluene and **3**[BF₄] · toluene adopt comparable positions above the
 405 angulated N–As–N unit. It is important to note that in both structures the As centers and the centroids (Ct) of
 406 the toluene rings are not arranged on a crystallographic slide axis in the crystal. The shortest distances
 407 As···Ct are 3.161 Å in **3**[OTf] · toluene and 3.302 Å in **3**[BF₄] · toluene stabilizing these salts by weak
 408 interactions ($\Sigma r_{\text{vdW}}(\text{As} \cdots \text{C}) = 3.55 \text{ Å}$).²⁸ Moreover, these η⁶-interactions confirm the electrophilic character
 409 of the As center and pack its coordination sphere so that it is effectively protected against nucleophilic attack
 410 what is quite favorable for long-time storage. Such Mentschutkin-type complexes of arsenic halides are
 411 already known in the literature.^{29,30}

412 The most prominent structural feature is the bent N–As–N unit (99-100°) with rather short As–N bond
 413 lengths between 1.748 and 1.757 Å clearly indicating double bond character ($\Sigma r_{\text{cov}}(\text{As}=\text{N}) = 1.92 \text{ Å}$,
 414 $\Sigma r_{\text{cov}}(\text{As}=\text{N}) = 1.74 \text{ Å}$).³¹ The first compound bearing an As=N double bond (1.714(7) and 1.745(7) Å) was
 415 N,N'-bis(2,4,6-tri-tert-butylphenyl)amino-iminoarsane, reported by Lappert *et al.* in 1986.¹ Moreover
 416 cationic diazarsenium (1.763-1.814 Å)⁵ and neutral tetrazaarsole (1.784 - 1.805 Å)³² heterocycles containing
 417 partial As–N double bonds are known. Recently, neutral triazarsoles heterocycles were synthesized either by
 418 insertion of isonitriles into arsatriazanediyals [As(μ-NTer)₂N] (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 = BF₄, AlCl₄, GaCl₄, AsF₆, 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 ⁺ ...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 = BF₄, AlCl₄, GaCl₄, AsF₆, OTf) and **7**.

	3 [AlCl ₄]	3 [GaCl ₄]	3 [OTf] · toluene	3 [BF ₄] · toluene	3 [AsF ₆] · 2 CH ₂ Cl ₂	7
Chem. Formula	C ₃₆ H ₆₀ AlAsCl ₄ N ₂	C ₃₆ H ₆₀ AsCl ₄ GaN ₂	C ₄₄ H ₆₈ AsF ₃ N ₂ O ₃ S	C ₄₃ H ₆₈ AsBF ₄ N ₂	C ₃₈ H ₆₄ As ₂ Cl ₄ F ₆ N ₂	C ₂₄ H ₃₄ AsCl ₃ GaN
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	C2/c	C2/c	P2 ₁ 2 ₁ 2 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
ρ _{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
λ _{MoKα} [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° ($\angle(\text{C6–As–N–C1})$), while the six-membered condensed ring is stronger distorted from planarity (21.2°). Both rings are arranged almost orthogonally to each other ($\angle(\text{N–As–C6–C5}) = 117.6^\circ$). The C1–N bond with 1.309(3) Å displays some double bond character (*cf.* $\Sigma r_{\text{cov}}(\text{N–C}) = 1.46$ Å, $\Sigma r_{\text{cov}}(\text{N=C}) = 1.27$ 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 ($\Sigma r_{\text{cov}}(\text{N–Ga}) = 1.95$ Å).³¹

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

445

446 Compound **6** crystallized in the orthorhombic space group $P2_12_12_1$ with four units per cell (Figure 3). The
 447 bent N-As-N ($99.0(1)^\circ$) moiety displayed rather short N-As bonds (1.733(2), 1.752(2) Å) in accord with the
 448 situation found for species **3**[X] (vide infra, Table 2). Compound **8** crystallized in the triclinic space group
 449 $P\bar{1}$ with two formula units per cell (Figure 3). The molecular structure of the cation featured a distorted
 450 tetrahedral environment around the central arsenic atom with two distinctly different As-C bonds (As-C_{Ph}
 451 1.911(3)-1.920(3) Å vs. As-C_{tBu} 1.985(3) Å). There are no significant cation $\cdots$ anion interactions.

452

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

456

457 Both silver salts **9** and **10** crystallized in the triclinic space group $P\bar{1}$ with two formula units per cell (Figure
 458 4). While **9** displayed a Ag^+ ion surrounded by four SbPh_3 ligands (Ag-Sb: between 2.692 – 2.700 Å, cf.
 459 $\Sigma r_{\text{cov}}(\text{Ag-Sb}) = 2.68 \text{ Å}$),³¹ thus exhibiting a slightly distorted tetrahedral coordination environment, silver
 460 salt **10** is only surrounded by three neutral PPh_3 ligands (Ag-P: between 2.482 – 2.512 Å, cf. $\Sigma r_{\text{cov}}(\text{Ag-P}) =$

461 2.39 Å)³¹ but one oxygen atom of the CF₃-SO₃⁻ anion is also rather close with 2.657(2) Å, *cf.* $\Sigma r_{\text{cov}}(\text{Ag}-\text{O}) =$
462 1.91 Å³¹ vs. $\Sigma r_{\text{vdW}}(\text{Ag}\cdots\text{O}) = 3.24 \text{ Å}$,²⁸ hence the coordination is best described by a [3+1] mode.

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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 arsediazonium 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.

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