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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

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Abstract:

The reaction of Li[Mes*NH] (1, Mes * = 2,4,6-tri-tert-butylphenyl) with aminoarsane Mes*N(H)AsCl₂ (2, Mes* = 2,4,6-t-Bu₃C₆H₂) at –80 °C resulted in the formation of bisamino(chloro)arsane (Mes*NH₂AsCl) (3Cl) by elimination of LiCl. 3Cl reacted with the Lewis acids such as AlCl₃, GaCl₃ and Ag[X] (X = AsF₆⁻, OTf⁻, BF₄⁻; OTf = trifluoromethanesulfonate = OSO₂CF₃⁻) upon chloride ion abstraction to give salts bearing the cation [(Mes*NH₂As)]⁺ (3[X]; X = AsF₆⁻, OTf⁻, BF₄⁻, ECl₄; E = Al, Ga). 3⁺ represents the first NH-functionalized acyclic bis(amino)arsenium cation. The formation of the salts bearing 3⁺ could also be observed in the reaction of cyclo-1,3-diarsa-2,4-diazane [ClAs(µ-NMes*)]₂ (4) with Lewis acids (AlCl₃, GaCl₃) 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.\(^9\)

**Scheme 1.** I: aminoiminoarsane, II: bis(amino)arsenium cation, III: (6\(\pi\))-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 \textit{et al.} in the reaction of [Mes*NP]\(^+\) with Mes*NH\(_2\) (supermesityl = Mes* = 2,4,6-\(\text{t}-\text{Bu}_3C_6H_2\)).\(^14\) 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$_2$As]$^+$.\textsuperscript{15}

We describe here the generation of the cation [(Mes*NH)$_2$As]$^+$ (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)$_2$AsCl (3Cl), 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,\textsuperscript{16} dried over P$_4$O$_{10}$, 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.\textsuperscript{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 ($\lambda = 0.71073$).

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

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

Synthesis of 3Cl

To a solution of 2,4,6-tri-tert-butylaniline (Mes*NH₂, 261 mg, 1.0 mmol) in Et₂O (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 AsCl₃ (181 mg, 1.0 mmol) in Et₂O (3 ml) at room temperature. The resulting rose suspension of generated Mes*N(H)AsCl₂ and LiCl is stirred for 30 minutes. The precipitated LiCl is separated by filtration. Li[Mes*NH], obtained from reaction of Mes*NH₂, (261 mg, 1.0 mmol) and n-Butyllithium (1.0 mmol) in Et₂O (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. 3Cl is purified by re-crystallization from Et₂O solution. Decomp. 115 °C. Anal. calc. % (found) for C₃₆H₆₀AsCl₂N₂ (631.25): C, 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- 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, 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), 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 (m), 2959 (s), 2903 (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
[(Mes*NH)$_2$As]$^+$.

**Synthesis of 3[AlCl$_4$]**

A) To a stirred colorless solution of 3Cl (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$_4$N$_2$ (764.59): C, 56.55 (56.27); H, 7.91 (7.89); N, 3.66 (3.69). $^1$H NMR (25°C, CD$_2$Cl$_2$,
250.13 MHz): δ = 1.32 (s, 18 H, p-C(CH$_3$)$_3$), 1.57 (s, 36 H, o-C(CH$_3$)$_3$), 7.53 (s, 4 H, CH), 10.44 (s, 2 H,
NH). $^{13}$C{$^1$H} NMR (25°C, CD$_2$Cl$_2$, 62.90 MHz): δ = 31.5 (s, p-C(CH$_3$)$_3$), 34.6 (s, o-C(CH$_3$)$_3$), 35.6 (s, p-
C(CH$_3$)$_3$), 37.5 (s, o-C(CH$_3$)$_3$), 124.8 (s, CH, 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.
crystallographic analysis are obtained by re-crystallization from CH$_2$Cl$_2$.

**Synthesis of 3[GaCl$_4$]**
A) To a stirred solution of 3Cl (0.182 mmol, 115 mg) in toluene (3 ml) a solution of GaCl₃ (0.182 mmol, 122 mg) 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[GaCl₄] 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 GaCl₃ (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*NH₂, 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[GaCl₄] as a yellow powder (65 mg, 0.081 mmol, 92%). Decomp. 135 °C. Anal. calc. % (found) for C₃₆H₆₀AsCl₄GaN₂ (807.33): C, 53.56 (52.69); H, 7.49 (7.02); N, 3.47 (3.42). ¹H NMR (25°C, CD₂Cl₂, 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, C₆H), 10.50 (s, 2 H, 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, o-C(CH₃)₃), 124.80 (s, CH, 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), 1474 (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*NH₃]⁺, 334 [Mes*NAS]⁺, 595 [(Mes*NH₂)₂As]⁺. Crystals of 3[GaCl₄] suitable for X-ray crystallographic analysis are obtained by re-crystallization from a CH₂Cl₂ solution of 3[GaCl₄].

**Synthesis of 3[OTf] • toluene**

A) To a stirred colorless solution of 3Cl (78 mg, 0.124 mmol) in CH₂Cl₂ (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 PPh₃ (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(PPh₃)₃][OTf] · 2 CH₂Cl₂ (9) suitable for X-ray crystallographic analysis are obtained by re-crystallization of the colorless solid from a CH₂Cl₂ solution. Decomp. 165 °C. Anal. calc. % (found) for C₃₇H₆₀AsF₃N₂O₃S (744.87): C, 59.66 (56.97); H, 8.12 (7.74); N, 3.76 (3.67). ¹H NMR (25°C, CD₂Cl₂, 250.13 MHz): δ = 1.32 (s, 18 H, p-C(CH₃)₃), 1.56 (s, 36 H, o-C(CH₃)₃), 7.52 (s, 4 H, CH), 11.93 (s, 2 H, NH). ¹³C{¹H} NMR (25°C, CD₂Cl₂, 62.90 MHz): δ = 31.6 (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), 124.4 (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 °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*NH₃ - tBu⁺], 244 [Mes* - 2H⁺], 246 [Mes*⁺], 262 [Mes*NH₃⁺]. Crystals of 3[OTf] · toluene suitable for X-ray crystallographic analysis are obtained by re-crystallization from toluene.
**Synthesis of 3[BF₄] • toluene**

**A** To a stirred colorless solution of 3Cl (78 mg, 0.124 mmol) in CH₂Cl₂ (5 ml) powdered Ag[BF₄] (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[BF₄] 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 CH₂Cl₂ (5 ml) powdered Ag[BF₄] (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 C₃₆H₆₀AsBF₄N₂: C, 63.34 (62.34); H, 8.86 (8.81); N, 4.10 (4.42). ¹H NMR (25°C, CD₂Cl₂, 250.13 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). ¹¹B{¹H} NMR (25°C, CD₂Cl₂, 80.25 MHz): δ = −0.81. ¹³C{¹H} NMR (25°C, CD₂Cl₂, 62.90 MHz): δ = 31.5 (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-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*NH₃⁺ - tBu]⁺, 262 [Mes*NH₃]⁺. Crystals of 3[BF₄] · toluene suitable for X-ray crystallographic analysis are obtained by recrystallization from a toluene solution of 3[BF₄].

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

To a stirred solution of Ag[$\text{AsF}_6$] (0.55 mmol, 0.163 g) in CH$_2$Cl$_2$ (5 ml), a yellow solution of 4 (0.5 mmol, 0.370 g) in CH$_2$Cl$_2$ (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 $3\text{[AsF}_6\text{]} \cdot 2\text{CH}_2\text{Cl}_2$ as an orange crystalline solid. Decomp. 127 °C. Anal. calc. % (found) for $3\text{[AsF}_6\text{]} \cdot \text{CH}_2\text{Cl}_2$ (C$_{37}$H$_{62}$As$_2$Cl$_2$F$_6$N$_2$ (869.64): C, 51.10 (51.81); H, 7.19 (7.36); N, 3.22 (3.73). $^1$H NMR (25°C, CD$_2$Cl$_2$, 300.13MHz): δ = 1.33 (s, 18 H, $p$. C(C$_3$H$_3$)$_3$), 1.56 (s, 36 H, $o$. C(C$_3$H$_3$)$_3$), 7.53 (s, 4 H, $m$. CH), 10.49 (s, 2 H, NH). $^{13}$C{$^1$H} NMR (25°C, CD$_2$Cl$_2$, 75.5MHz): δ = 31.5 (s, $p$. C(CH$_3$)$_3$), 34.3 (s, $o$. C(CH$_3$)$_3$), 35.6 (s, $p$. C(CH$_3$)$_3$), 37.5 (s, $o$. C(CH$_3$)$_3$), 124.7 (s, CH, Ar), 131.7 (s, $p$. Ar), 148.6 (s, $o$. Ar), 152.3 (s, ipso-Ar). $^{19}$F{$^1$H} NMR (25°C, CD$_2$Cl$_2$, 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), 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 $3\text{[AsF}_6\text{]} \cdot 2\text{CH}_2\text{Cl}_2$ suitable for X-ray crystallographic analysis are obtained directly from the reaction solution of $3\text{[AsF}_6\text{]}$.

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$_3$GaN (587.54): C, 49.06 (51.06); H, 5.83 (5.42); N, 2.38 (1.98). $^1$H NMR (25°C, CD$_2$Cl$_2$, 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$_2$Cl$_2$ suitable for X-ray crystallographic analysis are obtained directly from the reaction solution of 3[AsF$_6$].
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(C6(CH3)3)), 33.42 (C4(C6(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*NAcCl. The reaction with GaCl3 resulted in the formation of the arsonazidonium salt [Mes*N≡As][GaCl4] (5[GaCl4]). 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≡P][GaCl4] with Mes*NH2. 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[GaCl₄] in the reaction of 5⁺ with HCl.

We have already demonstrated that the chloride abstraction in (TerNH)₂PCl by Lewis acids such as GaCl₃ 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 GaCl₃ gave species III as [GaCl₄]⁻ salt (Scheme 1, R = Mes).⁷ During the course of our work we tried to receive salts containing 3⁺ by treatment of (Mes*NH)₂AsCl (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 LiN(H)Mes* with AsCl₃ (Scheme 4). On the basis of ¹H NMR spectroscopic data we found that 1 reacted with AsCl₃ 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*NH₂ in accord with observations by Lappert et al. in 1986.¹

Scheme 4. Reaction of 1 with AsCl₃ 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 AsCl₃ in Et₂O 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
Scheme 5. Reaction of 1 with an excess of AsCl₃ according to Burford et al.¹⁸

The dropwise addition of a solution of AsCl₃ to a solution of Li[Mes*NH] (1) in Et₂O at –80 °C did not only yield 6 and Mes*NH₂ but additionally 3Cl by elimination of LiCl (Scheme 6).

Scheme 6. Observed products for the dropwise addition of AsCl₃ to 1.

Scheme 7. Synthesis of bisamino(chloro)arsane (¹Bu₂)₂NAs(Cl)N(¹Bu)SiMe₃ 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 R₂NAsCl₂ with Li[N(R)SiMe₃] which resulted in the formation of the bisamino(chloro)arsane R₂NAs(Cl)N(R)SiMe₃ (R = ¹Bu) (Scheme 7).²⁰ Accordingly, in the analogous reaction a solution of 2 was added in stoichiometric amounts to a solution of 1 in Et₂O 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 AsCl₃ in a molar ratio of 3:1.

To summarize these results, an excess of AsCl₃ resulted in the formation of 2, while an excess of 1 led to formation of 6 and Mes*NH₂ (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*NH₂. As a consequence, for a successful generation of 3Cl there had to be neither an excess of AsCl₃ 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 AlCl₃ and GaCl₃, affording the salts 3[AlCl₄] and 3[GaCl₄] with yields over 90%. Furthermore, 3Cl was treated with the silver salts Ag[OTf] and Ag[BF₄] (Scheme 10). After extraction from precipitated silver chloride the solvates 3[OTf]·toluene and
3[BF₄] · toluene could be obtained from toluene solution also with yields over 90%. In contrast, the silylaminoarsane [(Me₃Si)₂N]₂AsCl reacted with Ag[OTf] to give the cyclo-1,3-diarsa-2,4-diazane [(Me₃Si)₂As-µ-NSiMe₃]₂ by elimination of Me₃SiOTf. In the reaction of 3Cl with Ag[AsF₆], surprisingly a quantitative conversion of 3Cl to Mes*NH₂ was detected by ¹H NMR spectroscopy, presumably due to the presence of HF in solution.

\[
\begin{align*}
&\text{(Mes*NH)₂AsCl} + \text{ECl₃} \rightarrow [(\text{Mes*NH})₂\text{As}[\text{ECl₄}]] \\
&\text{3Cl} \quad \text{3[ECI₄]} \\
&\text{(Mes*NH)₂AsCl} + \text{AgX} \rightarrow [(\text{Mes*NH})₂\text{As}[\text{X}]] \\
&\text{3Cl} \quad \text{3[X]}
\end{align*}
\]

**Scheme 10.** Top: Reaction of 3Cl with ECl₃ (E = Al, Ga). Bottom: Reaction of 3Cl with AgX (X = OTf⁻, BF₄⁻).

In a next series of experiments we were interested in the reactivity of [Mes*N≡As][GaCl₄] (5[GaCl₄]) towards classical Lewis bases such as pyridine or triphenylpnictanes of the type PnPh₃ (Pn = P, As, Sb) and to compare these results with those of the lighter phosphorus congener reported by Burford *et al.* 

The reaction of 5[GaCl₄] with DMAP (4-dimethylaminopyridine) at −80 °C yielded monomeric Mes*NAsCl and DMAP-GaCl₃ adduct. A similar reaction was found when 5[GaCl₄] was treated with PPh₃ at −80 °C affording also the chloroiminoarsane along with the Ph₃P-GaCl₃ adduct (Scheme 7). Contrarily, treatment of 5[GaCl₄] with AsPh₃ at −80 °C resulted in a product mixture containing also Mes*NAsCl and Ph₃As-GaCl₃ besides arsonium salt [³BuAsPh₃][GaCl₄] · toluene (8) and 3[GaCl₄] which could be co-crystallized both as main products in moderate yields (~40 %). The formation of an iminodiarsenium salt [Mes*NAsAsPh₃][GaCl₄] could not be observed. A further unexpected molecule could be isolated from the reaction of 5[GaCl₄] with SbPh₃ which yielded after formal elimination of ClSbPh₂ a four-membered ring with an inner-cyclic As-N-bond, stabilized as GaCl₃ adduct (7, Scheme 11).
**Scheme 11.** Summary of the obtained product mixtures in the reactions of $\text{GaCl}_4^{-}$ 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 $\text{GaCl}_4^{-}$ 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, $\text{GaCl}_4^{-}$...
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 Ph₂Sb-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*NAsCl 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*NAs-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*NPOCl with DMAP reported by Burford et al.²⁴ Bottom: Synthesis of a bis(arylamo)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
3 can be assumed. Thus, two general reaction channels for the formation of $[\text{GaCl}_4]$ are possible with either $\text{3Cl}$ or $\text{4}$ as starting materials.

In comparison to the synthesis of $[\text{GaCl}_4]$ starting from $\text{4}$, the reaction of $\text{4}$ with $\text{Ag}[\text{AsF}_6]$ yielded $[\text{AsF}_6]$. Again small amounts of HF or HCl within the reaction system are inevitable. It is known that the reaction of $\text{4}$ with $\text{Ag}[\text{OTf}]$ resulted in the formation of cyclic $[\text{Mes}^*\text{N}_{-}\mu-\text{AsOTf}]_2$ by elimination of silver halide.$^{26}$

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

The reaction of $\text{4}$ with $\text{Ag}[\text{BF}_4]$ proved that among other products the formation of $[\text{3}[\text{BF}_4]$ also occurred.

Scheme 13 summarizes the two general synthetic methods to obtain salts of $\text{3}$, either starting from $\text{3Cl}$ by chloride elimination with Lewis acids (i) or starting from $\text{4}$ in the reaction with Lewis acids in the presence of proton sources (ii).

\begin{align*}
\text{(MesNH)$_2$AsCl} & \xrightarrow{\text{i}} [(\text{MesNH)$_2$As][\text{An}] \xrightarrow{\text{ii}} [\text{MesNAsCl}]_2}
\end{align*}

\begin{align*}
\text{3Cl} & \quad \text{3[An]} & \quad \text{4}
\end{align*}

**Scheme 13.** Synthetic methods to obtain salts of $\text{3}$. Reaction with halides of group 13: (i) $\text{ECl}_3$, An = $\text{ECl}_4$, E = Al, Ga; (ii) $\text{ECl}_3$/ 2 HCl, An = $\text{ECl}_4$, E = Al, Ga. Reaction with silver salts: (i) $\text{Ag[OTf]}$, An = $\text{OTf}$, $\text{Ag[BF}_4]$, An = $\text{BF}_4$; (ii) 2 $\text{Ag[OTf]}$/ $\text{PPh}_3$/ 2 HCl, An = $\text{OTf}$; 2 $\text{Ag[BF}_4]$/ 2 HX, X = F or Cl, An = $\text{BF}_4$; 2 $\text{Ag[AsF}_6]$/ 2 HX, X = F or Cl, An = $\text{AsF}_6$. 

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Since in case of route (ii) always the formation of product mixtures was found, reaction channel (i) is to be preferred when preparing 3Cl. All presented salts of 3 were thermally stable and could be stored unlimited at room temperature under inert conditions. They decomposed at temperatures between 127 °C (3[AsF₆] · 2 CH₂Cl₂) and 165 °C (3[OTf] · toluene). The As–Cl stretching mode for 3Cl could be detected in the Raman spectrum at 323 cm⁻¹ (cf. 326 cm⁻¹ for [(Me₃Si)₂N]₂AsCl). A significant feature of all described salts of 3 is their pronounced low-field shift of the NH-resonance in the ¹H NMR spectra depending of the cationic character. While in 3Cl a polarized As–Cl bond was found (N–H: δ[¹H] = 5.57), all 3[X] (X = AlCl₄, GaCl₄, BF₄, OTf, AsF₆) salts form ion pairs and hence their N–H resonance was detected in the low-field range between 10.44 for 3[AlCl₄] and 11.93 ppm for 3[OTf] (see Table 1).
Table 1: $^1$H NMR shifts [ppm] in CD$_2$Cl$_2$ for 3[X] (X = AlCl$_4$, GaCl$_4$, BF$_4$, OTf, AsF$_6$) and for comparison Mes*NH$_2$ and 2.

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**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 $3^+$ 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.$^{17}$


The toluene molecules in $3[OTf] \cdot$ toluene and $3[BF_4] \cdot$ 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 $3[OTf] \cdot$ toluene and 3.302 Å in $3[BF_4] \cdot$ toluene stabilizing these salts by weak interactions ($\Sigma r_{vdW}(As \cdot\cdot\cdot C) = 3.55$ Å).$^{28}$ Moreover, these $\eta^6$-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 1.757 Å clearly indicating double bond character ($\Sigma r_{cov}(As\cdot\cdot\cdot N) = 1.92$ Å, $\Sigma r_{cov}(As=N) = 1.74$ 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($\mu$-NTer)$_2$N] (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl, $\mu$-NTer) and $N$-alkylamino-$N$'-arylaminoarsane ($N$-alkylamino-$N'$-arylaminoarsane, reported by Lappert et al. in 1986.$^1$
1.875 Å) and by making use of a [3+2] cycloaddition reaction between an organic azide and an arsaalkyne (1.839 Å).

Table 2: Selected parameters (distances [Å], angles [°]) for derivatives of 3[X] (X = BF₄, AlCl₄, GaCl₄, AsF₆, OTf).

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<th>3[OTf]</th>
<th>3[BF₄] · toluene</th>
<th>3[AsF₆] · 2 CH₂Cl₂</th>
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(*) average values

Table 3: Crystallographic details of the structures of 3[X] (X = BF₄, AlCl₄, GaCl₄, AsF₆, OTf) and 7.

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<th>Chem. Formula</th>
<th>3[AlCl₄]</th>
<th>3[GaCl₄]</th>
<th>3[OTf] · toluene</th>
<th>3[BF₄] · toluene</th>
<th>3[AsF₆] · 2 CH₂Cl₂</th>
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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). 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° ($\angle$(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 ($\angle$(N–As–C6–C5) = 117.6°). The C1–N bond with 1.309(3) Å displays some double bond character (cf. $\Sigma r_{cov}(N–C) = 1.46$ Å, $\Sigma r_{cov}(N=C) = 1.27$ Å), 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 ($\Sigma r_{cov}(N–Ga) = 1.95$ Å).
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 two 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 $P\overline{1}$ 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 $P\overline{1}$ 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. $\Sigma_{r_{cov}(Ag–Sb)} = 2.68$ 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. $\Sigma_{r_{cov}(Ag–P)} =$
2.39 Å)\textsuperscript{31} but one oxygen atom of the CF\textsubscript{3}-SO\textsubscript{3}– anion is also rather close with 2.657(2) Å, \textit{cf}. \( \Sigma r_{\text{cov}}(\text{Ag–O}) = \)

1.91 Å\textsuperscript{31} vs. \( \Sigma r_{\text{vdW}}(\text{Ag···O}) = 3.24 \) Å,\textsuperscript{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(amo)no)arsenium salts. Additionally, the reactivity of the arsadiazonium ion \([\text{Mes}*\text{N}=\text{As}]^+\) towards protons has been explored as well as its Lewis acidic character towards classical Lewis bases such as \(\text{PnPh}_3\) (\(\text{Pn} = \text{P}, \text{As}, \text{Sb}\)). A high-yielding synthetic protocols to obtain room temperature stable salts of acyclic \(\text{NH}\)-functionalized bis(amo)no)arsenium cation \([\text{(Mes}^*\text{NH})_2\text{As}]^+\) is reported. These new salts represent an interesting building block for the synthesis of low coordinated electrophilic arsenic centers.

References


2000, 2087.


