

Supporting information for:

## A base-stabilized arsenic(III) dication

*Allison L. Brazeau, Anton S. Nikouline and Paul J. Ragogna\**

Department of Chemistry, *The University of Western Ontario*, 1151 Richmond St.,  
London, Ontario, N6A 5B7, Canada

### Experimental Details...S1

**Figure S-1:** Solid-state structure of **1**...S5

### Experimental Details

**General Procedures.** All manipulations were performed in an inert atmosphere in a nitrogen filled MBraun Labmaster dp glovebox or using standard Schlenk techniques unless stated otherwise. Reagents were obtained from commercial sources. Triethylamine was distilled from CaH<sub>2</sub>, arsenic(III) chloride was distilled prior to use, while all other reagents were used without further purification. All solvents were dried using an MBraun controlled atmospheres solvent purification system and stored in Strauss flasks under an N<sub>2</sub> atmosphere or over 4 Å molecular sieves in the glovebox. Chloroform-d was dried over calcium hydride, distilled prior to use, and stored in the glovebox over 4 Å molecular sieves. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>19</sup>F{<sup>1</sup>H} data were collected on a 400 MHz Varian Inova spectrometer (399.762 MHz for <sup>1</sup>H, 100.52 MHz for <sup>13</sup>C and 376.15 MHz for <sup>19</sup>F) Spectra were recorded at room temperature, unless otherwise indicated, in CDCl<sub>3</sub> or CD<sub>3</sub>CN using the residual protons of the deuterated solvent for reference and are listed in ppm. Fluorine NMR spectra were recorded unlocked relative to an external standard

(CF<sub>3</sub>C<sub>6</sub>H<sub>5</sub>,  $\delta$  -63.9). Single crystal X-ray diffraction data were collected on a Nonius Kappa-CCD area detector or a Bruker Apex II-CCD detector using Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Crystals were selected under N-paratone oil, mounted on nylon loops then immediately placed in a cold stream of N<sub>2</sub>. Structures were solved and refined using SHELXTL. FT-IR spectra were collected on samples as KBr pellets using a Bruker Tensor 27 spectrometer, with a resolution of 4 cm<sup>-1</sup>. Samples for FT-Raman spectroscopy were packed in capillary tubes and flame-sealed. Data was collected using a Bruker RFS 100/S spectrometer, with a resolution of 4 cm<sup>-1</sup>. Melting and decomposition points were recorded in flame sealed capillary tubes using a Gallenkamp Variable Heater. High (HRMS) resolution mass spectrometry was collected using a Finnigan MAT 8200 instrument. Elemental analyses (C, H, N) were performed by Guelph Chemical Laboratories, Guelph, ON, Canada.

**Synthesis of 1.** A THF (6 mL) solution of 2,4,6-trimethylaniline (0.68 mL, 4.8 mmol) at 0°C was treated with *n*-BuLi (1.6 M in hexanes, 3.6 mL, 5.76 mmol) *via* cannula and the cooled yellow solution stirred for an additional 20 min. The solution was warmed to room temperature and a solution of *N,N'*-bis(2,4,6-trimethylphenyl)carbodiimide (1.35 g, 4.8 mmol) in THF (6 mL) was added dropwise *via* cannula. The dark orange mixture was refluxed for two hours and after cooling to room temperature, deionized H<sub>2</sub>O (1.5 mL) was added and the mixture was dried over anhydrous MgSO<sub>4</sub>. Concentrating the orange filtrate on the rotary evaporator yielded an orange solid, which washed with CH<sub>3</sub>CN (2 x 3 mL). The white product (1.46 g, 3.5 mmol) was dried *in vacuo*. Yield 73%; d.p.: 245-248 °C. X-ray quality colourless crystals were obtained from a CH<sub>2</sub>Cl<sub>2</sub>

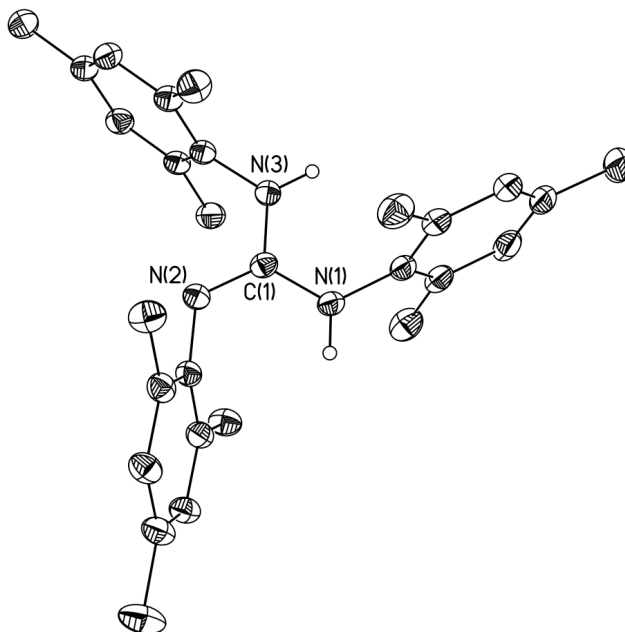
solution layered with hexanes after three weeks at  $-20^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.92 (s, 2H, *m-CH*), 6.83 (s, 2H, *m-CH*), 6.86 (s, 2H, *m-CH*), 4.97 (s, 1H, *NH*), 4.72 (s, 1H, *NH*), 2.37 (s, 6H, *o-CH}\_3*), 2.34 (s, 6H, *o-CH}\_3*), 2.26 (s, 9H, *p-CH}\_3*), 2.22 (s, 6H, *o-CH}\_3*).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  146.2, 144.3, 137.7, 136.5, 136.4, 133.3, 132.3, 130.9, 130.9, 129.6, 129.2, 128.9, 21.1, 20.9, 18.9, 18.8. FT-IR ( $\text{cm}^{-1}$  (ranked intensity))  $\nu$  = 544(9), 693(11), 778(13), 849(2), 947(15), 1032(8), 1152(10), 1224(5), 1291(7), 1311(12), 1474(6), 1646(1), 2917(3), 3360(4), 3392(14); FT-Raman ( $\text{cm}^{-1}$  (ranked intensity))  $\nu$  = 235(8), 278(14), 424(6), 504(12), 582(2), 1162(13), 1246(11), 1308(5), 1379(4), 1480(10), 1609(3), 1647(9), 2859(15), 2918(1), 3005(7). HRMS:  $\text{C}_{28}\text{H}_{35}\text{N}_3$  calcd (found) 413.2831 (413.2848). Anal. Calc. for  $\text{C}_{28}\text{H}_{35}\text{N}_3$ : C 81.31; H 8.53; N 10.16. Found: C 80.44; H 8.25; N 10.00.

**Data for  $2\text{Cl}_2$ :**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $-30^{\circ}\text{C}$ ):  $\delta$  7.05 (s, 2H, *m-CH*), 6.50 (s, 4H, *m-CH*), 5.65 (s, 1H, *NH*), 2.53 (s, 6H, *p-CH}\_3*), 2.33 (s, 3H, *p-CH}\_3*), 2.19 (s, 6H, *o-CH}\_3*), 2.09 (s, 12H, *o-CH}\_3*).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $-30^{\circ}\text{C}$ ):  $\delta$  153.0, 138.6, 138.5, 137.5, 136.4, 135.6, 134.1, 133.5, 131.5, 129.9, 128.8, 129.4, 128.5, 128.4, 128.0, 127.9, 21.3(br), 20.9(br), 19.6(br), 19.1. FT-IR ( $\text{cm}^{-1}$  (ranked intensity))  $\nu$  = 584(14), 740(9), 857(3), 915(11), 1033(7), 1141(15), 1200(12), 1276(5), 1303(13), 1334(8), 1375(10), 1500(1), 1556(6), 2919(2), 3321(4); FT-Raman ( $\text{cm}^{-1}$  (ranked intensity)) 97(10), 179(8), 273(5), 349(4), 370(15), 438(14), 579(3), 1278(13), 1308(12), 1333(6), 1383(7), 1482(11), 1610(1), 2921(2), 3014(9). Anal. Calc. for  $\text{C}_{28}\text{H}_{34}\text{N}_3\text{Cl}_2\text{As}$ : C 60.22; H 6.14; N 7.52. Found: C 59.92; H 5.85; N 7.55.

**Data for 2Cl[OTf]:**  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ,  $-40^\circ\text{C}$ ):  $\delta$  8.15 (s, 1H, NH), 7.11 (s, 2H, *aryl*), 6.72 (s, 2H, *aryl*), 6.47 (s, 1H, *aryl*), 6.42 (s, 1H, *aryl*), 2.56 (s, 3H,  $\text{CH}_3$ ), 2.52 (s, 3H,  $\text{CH}_3$ ), 2.44 (br s, 3H,  $\text{CH}_3$ ), 2.31 (s, 3H,  $\text{CH}_3$ ), 2.27 (s, 3H,  $\text{CH}_3$ ), 2.10 (br s, 3H,  $\text{CH}_3$ ), 2.07 (s, 3H,  $\text{CH}_3$ ), 2.05 (s, 3H,  $\text{CH}_3$ ), 1.91 (br s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ,  $-40^\circ\text{C}$ ):  $\delta$  161.8, 140.6, 140.2, 139.3, 138.4, 138.0, 136.2, 132.7, 130.6, 130.3, 129.2, 129.1, 128.1, 127.8, 20.8, 20.5, 19.6, 18.4.  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  - 78.8. FT-IR ( $\text{cm}^{-1}$  (ranked intensity))  $\nu$  = 516(10), 574(12), 637(3), 843(11), 923(9), 963(13), 1016(4), 1178(14), 1203(1), 1227(15), 1289(6), 1360(8), 1483(7), 1584(2), 2923(5). FT-Raman ( $\text{cm}^{-1}$  (ranked intensity))  $\nu$  = 174(9), 235(15), 324(11), 348(7), 483(6), 576(2), 763(12), 1014(5), 1323(4), 1360(8), 1484(10), 1610(3), 2061(13), 2923(1), 3024(14). Anal. Calc. for  $\text{C}_{29}\text{H}_{34}\text{O}_3\text{N}_3\text{F}_3\text{SAsCl}$ : C 51.83; H 5.10; N 6.25. Found: C 51.99; H 5.25; N 6.36.

**Data for 2[OTf] $_2$ :**  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  8.81 (d, 1H, *aryl*,  $^3J_{\text{HH}} = 5.6$ ), 8.74 (d, 1H, *aryl*,  $^3J_{\text{HH}} = 8.0$ ), 8.67 (m, 2H, *aryl*), 8.52 (t, 1H, *aryl*,  $^3J_{\text{HH}} = 8.0$ ), 8.47 (d, 1H, *aryl*,  $^3J_{\text{HH}} = 5.6$ ), 8.03 (t, 1H, *aryl*,  $^3J_{\text{HH}} = 6.0$ ), 7.78 (t, 1H, *aryl*,  $^3J_{\text{HH}} = 6.0$ ), 7.61 (s, 1H, NH), 7.17 (s, 1H, *m-CH*), 6.83 (s, 1H, *m-CH*), 6.78 (s, 1H, *m-CH*), 6.64 (s, 1H, *m-CH*), 6.49 (s, 1H, *m-CH*), 6.46 (s, 1H, *m-CH*), 2.78 (s, 3H,  $\text{CH}_3$ ), 2.60 (s, 3H,  $\text{CH}_3$ ), 2.28 (s, 3H,  $\text{CH}_3$ ), 2.13 (s, 3H,  $\text{CH}_3$ ), 2.10 (s, 3H,  $\text{CH}_3$ ), 1.98 (s, 3H,  $\text{CH}_3$ ), 1.91 (s, 3H,  $\text{CH}_3$ ), 1.77 (s, 3H,  $\text{CH}_3$ ), 1.76 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  158.03, 148.39, 147.06, 146.58, 146.47, 145.94, 140.41, 139.11, 138.46, 137.84, 137.73, 136.85, 136.24, 135.71, 135.68, 134.01, 130.87, 130.51, 129.93, 129.89, 129.55, 129.49, 129.1, 128.95, 128.71, 125.39, 125.03, 122.95, 119.77, 21.08, 20.74, 20.50, 20.45, 19.93, 19.21, 18.76, 18.60, 17.94.  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  -78.9. FT-IR ( $\text{cm}^{-1}$  (ranked intensity))  $\nu$  = 518(9), 573(11), 636(3),

723(7), 780(6), 1029(2), 1158(4), 1256(1), 1287(15), 1352(12), 1449(14), 1476(13),  
1501(8), 1590(5), 2928(10); FT-Raman ( $\text{cm}^{-1}$  (ranked intensity))  $\nu = 185(9), 233(15),$   
316(8), 570(7), 769(12), 1031(2), 1286(14), 1329(3), 1351(13), 1381(11), 1501(5),  
1570(6), 1601(1), 2928(4), 3093(10). Anal. Calc. for  $\text{C}_{40}\text{H}_{42}\text{O}_6\text{N}_5\text{F}_6\text{S}_2\text{As}$ : C 51.01; H  
4.49; N 7.44. Found: C 50.14; H 4.53; N 7.24.



**Figure S1:** Solid-state structure of **1**. Ellipsoids are drawn to 30% probability. Non-essential hydrogen atoms are removed for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): C(1)–N(1) 1.363(3), C(1)–N(2) 1.318(3), C(1)–N(3) 1.353(3), N(1)–C(1)–N(2) 122.8(2), N(1)–C(1)–N(3) 117.1(2), N(2)–C(1)–N(3) 120.1(2).