Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Diamidonaphthalene-Supported Pnictogenium Cations: Synthesis of an N-Heterocyclic Stibenium Cation by a Novel Protonation Route

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Experimental

General Methods: All reactions were performed under nitrogen using standard Schlenk techniques or in a dry box with a nitrogen atmosphere. Triethylamine was dried by fractional distillation from KOH and then CaH_2. Dichloromethane was distilled over CaH_2 prior to use. All other solvents were sparged with nitrogen and then dried by passage through a column of activated alumina using an apparatus purchased from Anhydrous Engineering. Deuterated benzene and dichloromethane were dried by addition of molecular sieves. Tris(dimethylamino)antimony was purchased from Strem Chemicals and used as received. All other chemicals were purchased from Aldrich and used without further purification. 1,8-Di(isopropylamino)naphthalene was prepared according to a previously reported procedure (Bazinet, P., Yap, G. P. A., DiLabio, G. A., and Richeson, D. S. *Inorg. Chem.* **2005**, *44*, 4616). NMR spectra were run on Bruker Avance 300 MHz and 500 MHz spectrometers with deuterated benzene or dichloromethane as a solvent and internal standard. Infrared spectra were collected on samples prepared as Nujol mulls on NaCl plates using a ABB Bomem MB Series FT-IR spectrometer, and are reported in wavenumbers (cm^{-1}) followed by ranked intensities in parentheses, where a value of one corresponds to the most intense peak in the spectrum. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, ON, Canada.

Preparation of $ClAs(^iPrN)_2C_{10}H_6$ (7As): To a solution of 1,8-$(^iPrNH)_2C_{10}H_6$ (1.0 g, 4.1 mmol) in 30 mL of toluene was added sequentially $AsCl_3$ (0.45 mL, 5.4 mmol) followed by NEt_3 (1.5 mL, 10.7 mmol). The reaction mixture was stirred for four days, during which time a copious amount of white precipitate formed and the solution turned yellow. All volatiles were removed under vacuum, toluene was added to the solid reaction mixture, and the solution was filtered through a glass frit packed with celite. The filtrate was concentrated, an equal volume of hexane was added to the flask, and the toluene/hexane mixture was placed in the freezer at -20 °C overnight to yield yellow crystals of **7As** (0.80 g, 55 %). ^1H NMR (C_6D_6): 1.1 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.3 (d, $^3J_{HH}$ = 6 Hz, 6H, CH_3), 3.9 (septet, $^3J_{HH}$ = 7 Hz, 2H, $CHMe_2$), 6.6 (d, $^3J_{HH}$ = 8 Hz, 2H, *H*Ar), 7.2 (t, $^3J_{HH}$ = 8 Hz, 2H, *H*Ar), 7.3 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 0.9 Hz, 2H, *H*Ar). $^{13}C\{^1H\}$ NMR (C_6D_6): 22 (s, CH_3), 25 (s, CH_3), 50 (s, $CHMe_2$), 108 (s, *C*HAr), 120.7 (s, *C*Ar), 121.4 (s, *C*HAr), 127 (s, *C*HAr), 138 (s, *C*Ar), 142 (s, *C*Ar). IR : 1923(13), 1821(18), 1740(15), 1727(14), 1640(18), 1606(9), 1569(8), 1519(14), 1297(12), 1249(16), 1331(12), 1129(8), 1165(10), 1104(10), 1081(10), 1048(7), 955(4), 878(6), 812(3), 870(4), 784(5), 762(1), 668(17), 632(2), 565(11), 520(8). Anal. Calcd for $C_{16}H_{20}N_2AsCl$: C 54.79, H 5.75, N 7.99; Found: C 55.15, H 6.15, N 8.02.

Preparation of ClSb(^{i}PrN)$_2$C$_{10}$H$_6$ (7Sb): To a solution of 1,8-(^{i}PrNH)$_2$C$_{10}$H$_6$ (1.0 g, 4.1 mmol) in 15 mL of toluene was added sequentially $SbCl_3$ (0.94 g, 4.1 mmol) followed by NEt_3 (1.5 mL, 10.7 mmol). The reaction mixture was stirred for four days, during which time a copious amount of white precipitate formed and the solution turned orange. All volatiles were removed under vacuum, toluene was added to the solid reaction mixture, and the solution was filtered through a glass frit packed with celite. The filtrate was concentrated, an equal volume of hexane was added to the flask, and the toluene/hexane mixture was placed in the freezer at -20 °C overnight to yield orange crystals of **7Sb** (0.63 g, 38 %). ^{1}H NMR (C_6D_6): 1.1 (d, $^3J_{HH}$ = 6 Hz, 6H, C*H*$_3$), 1.2 (d, $^3J_{HH}$ = 6 Hz, 6H, C*H*$_3$), 4.1 (septet, $^3J_{HH}$ = 6 Hz, 2H, C*H*Me$_2$), 6.7 (d, $^3J_{HH}$ = 8 Hz, 2H, *H*Ar), 7.3 (t, $^3J_{HH}$ = 8 Hz, 2H, *H*Ar), 7.4 (d, $^3J_{HH}$ = 7 Hz, 2H, *H*Ar). ^{13}C{^{1}H} NMR (C_6D_6): 25 (s, *C*H$_3$), 26 (s, *C*H$_3$), 50 (s, *C*HMe$_2$), 109 (s, *C*HAr), 121 (s, *C*HAr), 122 (s, *C*Ar), 127 (s, *C*HAr), 138 (s, *C*Ar), 145 (s, *C*Ar). IR : 2725(16), 1708(16), 1586(14), 1558(3), 1316(3), 1292(1), 1242(11), 1162(6), 1134(4), 1106(8), 1072(5), 1045(9), 958(10), 944(8), 930(10), 873(13), 854(13), 808(3), 780(12), 762(7), 753(2), 740(7), 630(15). Anal. Calcd for $C_{16}H_{20}N_2SbCl$: C 48.34, H 5.07, N 7.05; Found: C 47.77, H 5.47, N 6.68.

Preparation of [As(^{i}PrN)$_2$C$_{10}$H$_6$][GaCl$_4$] (8As): To a solution of ClAs(^{i}PrN)$_2$C$_{10}$H$_6$ **7As** (0.30 g, 0.86 mmol) in 5 mL of toluene was added a solution of $GaCl_3$ (0.15 g, 0.86 mmol) in 3 mL of toluene, causing immediate precipitation of a dark blue powder. The solvent was removed by filtration, the solid washed with 2 × 5 mL portions of hexane, and then dried under vacuum. As much of the solid as possible was dissolved in 15 mL of CH_2Cl_2, and the solution was filtered and placed in the freezer at -20 ºC to yield dark blue crystals of **8As** after one week (0.17 g, 37 %). X-ray quality crystals were obtained by dissolving a very small amount of **8As** in toluene and placing the solution in the freezer (-20 ºC) for two weeks. ^{1}H NMR (CD_2Cl_2): 1.7 (d, $^3J_{HH}$ = 4 Hz, 12H, C*H*$_3$) 4.5 (broad, 2H, C*H*Me$_2$), 6.7 (broad, 2H, *H*Ar), 7.3 (broad, 4H, *H*Ar). ^{13}C{^{1}H} NMR: The low solubility of this compound prevented collection of a ^{13}C NMR with a good enough signal to noise ratio to report a listing of peaks. IR: 2725(13), 2670(14), 1618(18), 1569(12), 1311(5), 1284(3), 1215(15), 1169(11), 1138(6), 1111(8), 1067(9), 1049(17), 961(10), 937(7), 811(4), 786(13), 777(16), 754(2), 734(1), 697(18), 613(14). Anal. Calcd for $C_{16}H_{20}N_2AsCl_4Ga$: C 36.48, H 3.83, N 5.32; Found: C 36.37, H 4.13, N 5.28.

Preparation of $(NMe_2)Sb(^iPrN)_2C_{10}H_6$ (9): A Schlenk flask containing a solution of tris(dimethylamino)antimony (2.10 g, 8.3 mmol) in 30 mL of toluene was cooled in a dry ice/acetone bath to -78 ºC. A solution of 1,8-$(^iPrNH)_2C_{10}H_6$ (2.00 g, 8.3 mmol) in 10 mL of toluene was transferred into the flask *via* cannula, producing a purple solution. The reaction mixture was stirred at low temperature for an additional 30 minutes and then slowly allowed to warm to room temperature, during which time the colour of the reaction mixture turned from purple to orange and $NH(CH_3)_2$ gas evolved. After stirring for an additional 2 hours, all volatiles were removed to give an orange oil. The oil was dissolved in a 50/50 toluene/hexane mixture and placed in the freezer at -20 °C overnight to yield yellow crystals of **9** (1.82 g, 54 %). ^1H NMR (C_6D_6): 1.2 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.3 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 2.4 (s, 6H, NCH_3), 4.1 (septet, $^3J_{HH}$ = 6 Hz, 2H, $CHMe_2$), 6.7 (t, $^3J_{HH}$ = 5 Hz, 2H, *H*Ar), 7.3 (d, $^3J_{HH}$ = 5 Hz, 4H, *H*Ar). $^{13}C\{^1H\}$ NMR (C_6D_6): 25 (s, CH_3), 26 (s, CH_3), 42 (s, NCH_3), 50 (s, $CHMe_2$), 107 (s, *C*HAr), 119 (s, *C*HAr), 122 (s, *C*Ar), 127 (s, *C*HAr), 138 (s, *C*Ar), 148 (s, *C*Ar). IR : 2373(16), 1893(17), 1692(18), 1563(1), 1387(2), 1321(3), 1296(4), 1171(5), 1138(5), 1108(9), 1073(6), 1047(10), 930(8), 868(12), 807(9), 781(11), 762(9), 748(7), 641(15), 631(14), 554(13). Anal. Calcd for $C_{18}H_{26}N_3Sb$: C 53.23, H 6.45, N 10.35; Found: C 52.44, H 6.33 N 10.03

Preparation of $[Sb(^iPrN)_2C_{10}H_6{\cdot}NHMe_2][OSO_2CF_3]$ (10): A Schlenk flask containing a solution of $(NMe_2)Sb(^iPrN)_2C_{10}H_6$ **9** (0.50 g, 1.2 mmol) in 20 mL of toluene was cooled in a dry ice/acetone bath to -78 ºC. A solution of triflic acid (0.11 mL, 1.2 mmol) in 5 mL of toluene was transferred into the flask *via* cannula, causing an immediate colour change from light to dark orange. The reaction mixture was stirred at low temperature for an additional 20 minutes, during which time a yellow solid precipitated. As the reaction warmed to room temperature, the solid dissolved, returning the reaction mixture to its dark orange colour. All volatiles were removed, resulting in an orange oil. The oil was dissolved in a 50/50 toluene/hexane mixture and placed in the freezer at -20 °C overnight to yield yellow crystals of **10** (0.47 g, 68 %). ^1H NMR (C_6D_6): 1.4 (broad, 12H, CH_3), 1.9 (s, 6H, NCH_3), 4.0 (septet, $^3J_{HH}$ = 6 Hz, 2H, $CHMe_2$), 6.3 (broad, 1H, N*H*), 6.5 (d, $^3J_{HH}$ = 8 Hz, 2H, *H*Ar), 7.1 (t, $^3J_{HH}$ = 8 Hz, 2H, *H*Ar), 7.2 (d, $^3J_{HH}$ = 8 Hz, 2H, *H*Ar). $^{13}C\{^1H\}$ NMR (C_6D_6): 25 (s, *C*H$_3$), 38 (s, N*C*H$_3$), 53 (s, *C*HMe$_2$), 110 (s, *C*HAr), 121.2 (s, *C*HAr), 121.5 (s, *C*Ar), 122 (q, $^1J_{FC}$ = 320 Hz, *C*F$_3$), 127 (s, *C*HAr), 138 (s, *C*Ar), 145 (s, *C*Ar). IR : 3167(19), 1912(14), 1832(17), 1807(16), 1723(15), 1603(11), 1559(1), 1510(12), 1405(18), 1329(9), 1317(8), 1291(7), 1218(6), 1113(6), 1158(6), 1062(5), 1021(4), 961(5), 943(6), 930(7), 876(4), 812(3), 780(10), 757(2), 636(8), 574(13). Anal. Calcd for $C_{19}H_{27}N_3O_3F_3SSb$: C 41.02, H 4.89, N 7.55; Found: C 40.45, H 4.54, N 7.27.

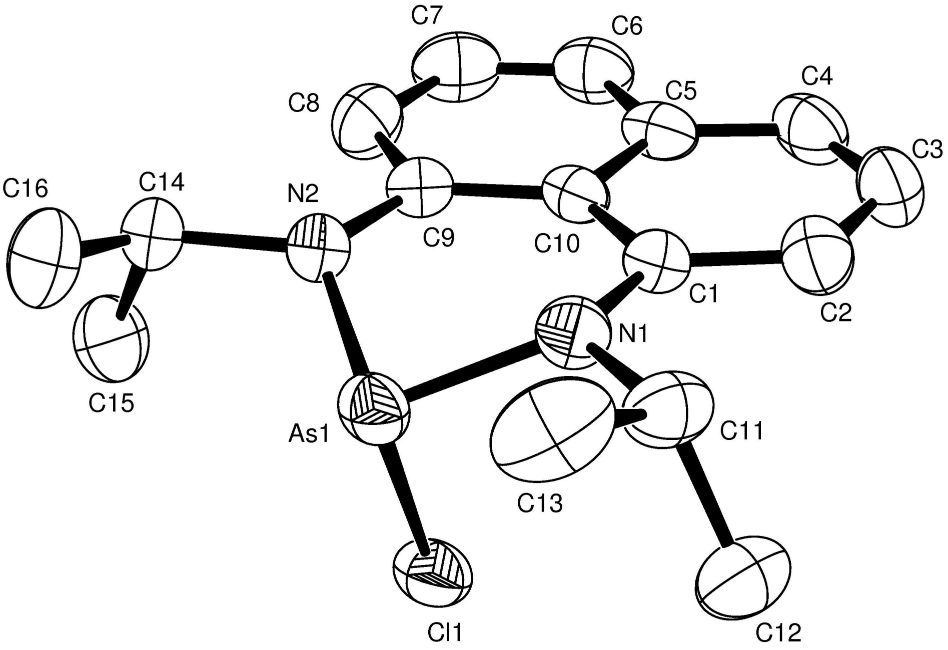

Figure S1. Thermal ellipsoid plot showing the molecular structure and atom numbering scheme for compound **7As**. Hydrogen atoms have been omitted for clarity.

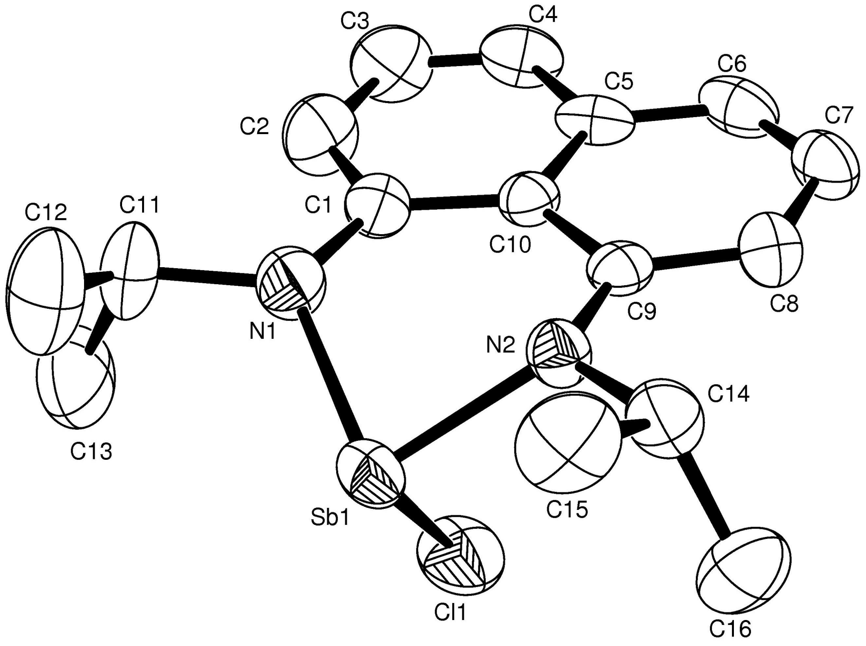

Figure S2. Thermal ellipsoid plot showing the molecular structure and atom numbering scheme for compound **7Sb**. Hydrogen atoms and a toluene solvate molecule have been omitted for clarity.