Bridged Heterocyclium Di-Cationic *closo*-Icosahedral Perfluoroborane, Borane, and Carborane Salts via Aqueous, Open-Air Benchtop Synthesis

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SUPPLEMENTAL INFORMATION

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References/Notes.

References (1) – (20) appear in the main paper.

(21) See under **X-ray Analyses** section below on this page.

(22) *Handbook of Chemistry and Physics*, 49th ed.; Weast, R. C., Ed.; CRC: Cleveland, OH, 1968. See under Ion Chromatography Results section below (page 23).

General Experimental Comments.

Caution! *While no special protective equipment or handling were used with salts **6-18**, be aware that these are high energy materials and can be initiated to rapid energy releasing phenomena.* Thermal initiation can occur on a hot plate surface *(c.a.* >200 °C) to rapid combustion with salt **6** while salt **8** only undergoes a slow thermochemical decomposition.[2] Recent standard impact, friction, and electrostatic discharge (ESD) hazards testing were conducted on salts **6-8**, **10**, **12**, and **18**. All five salts displayed spark sensitivity at 0.09 Joules (ESD test). Impact test results were determined at the 100% non-initiation level, and salt **12** proved most sensitive to impact at 54 Kg-cm while salt **18** was the least sensitive at 147 Kg-cm. These two 100% "No-Go" values compare with known explosives for which the following more sensitive 50% initiation Kg-cm values are available: CL-20 at 33; PETN at 67; HMX at 115; and, RDX at 117. Salt **12** was the most sensitive to friction at 16.0 Kg-cm, while salts **7**, **10**, and **18** gave no initiation at the maximum 21.6 Kg-cm machine friction threshold.

All neutral heterocycles used to synthesize the bridged heterocyclium salts **1-18** were purchased commercially with one exception. The 1-amino-1,2,3-triazole compound was

synthesized according to the procedure cited.[18] De-ionized (DI) water was obtained from an in-house Millipore MILL-Q Reagent Grade Water System at an 18 megaohm cm purity level. All organic solvents were commercially purchased as either Reagent Grade or HPLC purity, and were used as received.

NMR Analyses. A Bruker Avance 400 Digital NMR instrument was used to obtain both proton (^{1}H) and ^{13}C spectra.

FTIR Analyses. Fourier transform infrared spectra (FTIR) were taken as powder samples using a Nicolet 6700 Spectrometer in air using with an HATR optical system. Reported are the significant peaks observed. An FTIR spectrum of the $K_2[B_{12}F_{12}]$ reactant salt reveals only two very strong peaks at 1221 cm^{-1} and 719 cm^{-1}. Therefore, the presence of the $[B_{12}F_{12}]^{2-}$ di-anion is revealed in three product salts **16-18** by two very strong peaks in the 1220 cm^{-1} and 720 cm^{-1} regions. The $[B_{12}F_{12}]^{2-}$ di-anion symbol was also placed behind the appropriate FTIR peaks (cm^{-1}) to identify these two characteristic peaks for each product salt **16** (pages 10 and 11), **17** (page 14), and **18** (pages 10 and 16).

High Resolution Mass Spectometry Analyses. High resolution mass specta (HRMS) analyses were conducted at UCR Mass Spectrometry Facility, Department of Chemistry, University of California, 501 Big Springs Road (CS1), Riverside, CA 92521, Dr. Richard W. Kondrat, Academic Coordinator, and Mr. Ronald B. New, Staff Research Associate. Analyses were conducted in either the +ev or –ev mode. In all five borane product salts (**2**, **4**, **6**, **8**) and two perfluoroborane salts (**17**, **18**), the Na atom appeared in the resolved salt specta. According to UCR Mass Spectrometry Facility personnel, Na is endemic to the environment, is easily ionized; and therefore, often appears in HRMS results, and the Na seen in several salt products could have come from solvents stored in glass. All seven salts were verified by these HRMS analyses.

Single Crystal X-ray Analyses. The single-crystal X-ray diffraction data were collected on a Bruker 3-circle-platform diffractometer equipped with a SMART APEX 2 detector with the χ-axis fixed at 54.74° and using MoK_α or CuK_α radiation from a fine-focus tube. The goniometer head, equipped with a nylon Cryoloop and magnetic base, was used to mount the crystals using perfluoropolyether oil. The data collection as well as structure solution and refinement were carried out using standard procedures with the APEX2 V.2.1-4, SMART V.5.622, SAINT 7.24A, SADABS, and SHELXTL software packages and programs.[21] Crystal data and refinement details of crystals of **16-18** are given in Table 1-3. Crystallographic data are also available in CIF-format.

(21) APEX2 V.2.1-4, SMART V.5.622, SAINT 7.24A, SADABS, SHELXTL ed.; Bruker-AXS, INC.: Madison, WI USA, 2007.

Melting Point Determination. Visually-determined melting point values come from a Stanford Research Systems OptiMelt MPA100-Automated Melting Point Apparatus equipped with digital image video playback software. Observed melting point behavior tends to differ somewhat from what is seen with neutral covalent organic compounds; so, more detail is provided in **Table 4** at the end of this section.

Ion Chromatography Cl^- or Br^- Analysis Results. Ionic Cl^- or Br^- concentrations were determined for product salts (**6-18**), obtained from intermediate di-bromide and di-chloride salts (**1-5**), by Ion Chromatography using a Waters HPLC equipped with a Waters 432 conductivity detector and a Phenomenex STAR-ION A300 100 x 4.6 mm ID (PEEK) analytical column. A Borate/Gluconate eluent was used and system conditions were set according to Waters method #980895.

General Conventional Alkylation Procedure for the Intermediate Bridged Heterocyclium Di-Cation Di-Halide Salt Reactants (1-5).

Either the 1,4-di-halo-2-butene or 1,4-di-halo-2-butyne reagent and the selected neutral triazole or 1-methylimiazole heterocycle were dissolved in Reagent Grade CH_3CN solvent and stirred under reflux using a Teflon®-coated magnetic stirring bar until the precipitated salt product was obtained. Cooling the reaction suspension, vacuum filtration, rinsing the resultant filter cake with several mL of CH_3CN or Et_2O, and drying gave one of the selected bridged heterocyclium di-cation di-halide salts **1-4**. Slight exceptions to the above procedure are noted in the individual salt product descriptions below. In these alkylations, the millimoles recorded reflect the stated purity of the specific reagent used. The heterocyclium di-cation di-bromide salt **5** was synthesized using a microwave-assisted synthesis procedure.

[1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butyne][Br]$_2$ (1): A 100 mL 24/40 jointed single-necked recovery flask was charged with 2.013 g (9.027 mmol) of 95% pure 1,4-dibromo-2-butyne, 10 mL CH_3CN, 1.502 g (17.685 mmol) of 99% 4-amino-1,2,4-triazole, and 30 mL additional CH_3CN. Refluxing 22 h, cooling for 95 min in the refrigerator, filtration, rinsing with 5 mL pre-chilled (+3.0 °C) in several portions, and drying under high vacuum for 22 h at rt afforded 3.261 g of light tan salt **1** (97% yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.33 (s, 2H), 9.29 (s, 2H), (7.08 (brs, 4H), 5.53 (s, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.63, 142.94, 78.88, 41.89; FTIR (HATR) cm^{-1}, 3255, 3116, 3086, 2986, 2948, 2903, 1618, 1562, 1516, 1417, 1359, 1204, 1155, 1070, 995, 884, 771, 645, 609; HRMS calcd for $[Cation^{2+} + Br^-]^+$ 299.0363, found 299.0367.

[*trans*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][Br]$_2$ (2): A 100 mL 24/40 jointed single-necked recovery flask was charged with 1.506 g (6.831 mmol) of 97% pure trans-1,4-dibromo-2-butene, 1.160 g (13.658 mmol) of 99% 4-amino-1,2,4-triazole, and 40 mL CH_3CN. Refluxing 6.5 h, cooling to rt overnight, filtration, rinsing with 3 x 5 mL CH_3CN, and drying under high vacuum (40 – 50 mTorr) at 60 °C for 50 h, 20 min afforded 2.560 g of white salt **2** (98% yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ10.25 (s, 2H), 9.24 (s, 2H), 7.05 (brs, 4H), 6.08-6.06 (m, 2H), 5.10-5.08 (m, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.38, 142.82, 128.29, 52.44; FTIR (HATR) cm^{-1}, 3254, 3142, 3096, 3041, 2997, 1614, 1583, 1558, 1514, 1439, 1406, 1352, 1326, 1269, 1226, 1207, 1174, 1150, 1071, 1023, 994, 940, 909, 858, 769, 732, 682, 647, 617; HRMS calcd for $[Cation^{2+} + Br^-]^+$ 301.0519, found 301.0521.

[*trans*-1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butene][Br]$_2$ (3): Six Biotage (*nee* Personal Microwave) Initiator Emrys™ 10-20 mL process vials containing a coated magnetic stir bar are each are charged with an average of 0.600 g (2.721 mmol) 97% *trans*-1,4-di-(1-amino-1,2,3,-triazolium)-2-butene di-bromide, an average of 0.472 g (5.614 mmol) 1-amino-1,2,3-triazole (1AT),[18] with 20 mL CH_3CN solvent in each reaction vessel. Each reaction vessel was capped/sealed and automatically microwaved at 100 °C for 45 min successively using the reaction vessel transfer feature that is part of the software set-up. The white solid suspension is cooled to rt and is then placed into a freezer (–13.5 °C). The suspension of each vial is combined and vacuum filtered; then, each reaction vessel is successively rinsed with 2 mL pre-chilled (–13.5 °C) CH_3CN which is filtered through the combined solid cake. The solid cake is then rinsed with 4 mL additional pre-chilled CH_3CN in to portions. Finally, the white cake is rinsed with 5 mL Et_2O and is then dried at 50 °C for 3 d on the house vacuum to yield 1.398 g (22%) of slightly off-white solid salt **3** containing less than 1% unreacted (1AT): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 8.87 (d, 2H), 8.69 (d, 2H), 8.43 (brs, 4H), 6.18-6.16 (m, 2H), 5.31-5.30 (m, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 130.91, 128.56, 126.76, 53.35; FTIR (HATR) cm^{-1}, 3171, 3131, 3112, 3083, 3041, 2972, 2961, 2842, 2800, 1622, 1534, 1476, 1426, 1364, 1330, 1234, 1187, 1160, 1079, 1055, 1025, 975, 962, 905, 810, 751, 697, 654, 628; HRMS calcd for [Cation^{2+} + Br$^-$]$^+$ 301.0519, found 301.0524.

[*cis*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][Cl]$_2$ (4): A 50 mL 24/40 jointed single-necked recovery flask was charged with 0.590 g (4.480 mmol) of 95% pure cis-1,4-dichloro-2-butene, 15 mL CH_3CN, 0.746 g (8.778 mmol) of 99% 4-amino-1,2,4-triazol (4AT), and another 5 mL CH_3CN. Refluxing 95 h, cooling to rt, and decanting left the dark brown solid stuck to the insides of the reaction flask. Next, 6 mL fresh CH_3CN were added to the reaction flask. Refluxing 6 min, cooling to rt, and decanting the CH_3CN ensued. This CH_3CN reflux trituration was repeated with a 5 min reflux and decanting the solvent to leach out all but 5.6% of unreacted 4AT. Drying 6 days and 17 h, or161 h, at rt under a high vacuum afforded 1.267 g of clear, hard dark brown salt **4** (98% yield incl. 5.6 % 4AT): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ10.46 (s, 2H), 9.26 (s, 2H), 8.86 (s, unreacted 4AT), 7.20 (brs, 4H), 6.05-6.03 (m, 2H), 5.33-5.32 (m, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.24, 143.95 (unreacted 4AT), 142.64, 127.54, 48.42; FTIR (HATR) cm^{-1}, 3179 (sh), 3089, 3015, 1630, 1560, 1409, 1324, 1156, 1070, 1001, 964, 809, 612; HRMS calcd for [Cation^{2+} + Cl$^-$]$^+$ 257.1024, found 257.1029.
Note: Regarding assignment of the ^{13}C NMR peak at δ 143.95 as being unreacted 4AT, a smaller reaction scale gave a ^{13}C NMR with three peaks clustered at 145.24 (large), 143.95 (small), 142.64 (large). The 143.95 peak also was suspected to come from 18% unreacted 4AT seen in the proton NMR spectra. Trituration in hot CH_3CN removed most of the unreacted 4AT so that the triturated sample gave ^{13}C NMR peaks only at 145.25 and 142.66 further confirming that the smaller middle peak is unreacted 4AT.

[*trans*-1,4-di-(1-methylimidazoium-3N)-2-butene][Br]$_2$ (5): A 100 mL 24/40 jointed single-necked recovery flask was charged with 1.500 g (6.803 mmol) of 97% pure trans-1,4-dibromo-2-butene, 1.117 g (13.604 mmol) of 99$^+$% 1-methylimidazole, and 15 mL additional CH_3CN. Refluxing 6 h, cooling in the freezer (–13.5 °C) over the weekend, filtration, rinsing with 4 x 10 mL Et_2O, and drying 24 h at 60 °C on the house vacuum

afforded 2.442 g of white salt **5** (95% yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 9.24 (s, 2H), 7.76 (d, 4H), 6.01-5.99 (m, 2H), 4.91-4,90 (m, 4H), 3.88 (s, 6H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 136.66, 129.02, 123.78, 1.22.34; 49.40, 35.87; FTIR (HATR) cm^{-1}, 3136, 3074, 3043, 2938, 1777, 1675, 1563, 1475, 1409, 1387, 1371, 1335, 1296, 1256, 1159, 1137, 1093, 1074, 984, 956, 890, 846, 792, 754, 652, 616; HRMS calcd for $[Cation^{2+} + Br^{-}]^{+}$ 297.0709, found 297.0715.

Larger-Scale General Metathesis Reaction Procedure for Bridged Heterocyclium Di-Cation *closo*-Perfluoroborane, *closo*-Borane, and *closo*-Carborane Salt Products (6-15 and 18).

In order to minimize the presence of residual potassium halide by-product salt, the following general procedure was used for the large scale synthesis runs. An initial aqueous precipitation of the desired product occurred at 78-80 °C, followed by slow cooling to rt, placement in a refrigerator overnight, and isolation of the salt product by filtration. A subsequent aqueous digestion of the isolated precipitated solid product salt was conducted at 78-80 °C, followed by slow cooling, and placement in a refrigerator overnight. Filtration, and final drying in an Electrothermal Chem-Dry® vacuum drying apparatus afforded solid salt products **6-15** and **18**.

A 100 mL beaker, containing with a one-half inch Teflon-Coated magnetic stirring bar, was charged with the selected bridged heterocyclium di-cation di-halide salt (**1-5**) which was dissolved at rt in de-ionized (DI) water. A second 100 mL beaker was charged with a nearly stoichiometric amount of potassium *closo*-perfluoroborane, *closo*-borane, or *closo*-carborane which was then dissolved at rt in DI water. Both beakers were then placed for 15 min on a hot plate/stirrer that was calibrated to hold 25 mL DI water at 78 to 80 °C after a 15 min warming time. The beaker with the di-halide reactant salt was stirred while the beaker with the potassium *closo*-borane-based salt was occasionally swirled. Constant volume in both beakers was maintained by use of glass covers and/or by adding DI water as needed. The aqueous potassium borane-based solution was then added dropwise to the stirred aq di-halide reactant salt solution over several minutes duration using a disposable capillary pipette. Immediately or nearly so, precipitation was noted. The spent potassium *closo*-borane-based beaker was rinsed with 2 x 1mL DI water, and each rinse was added to the stirred aqueous suspension in the beaker containing the reaction suspension (Total addition time was from 5 to 17 min, including addition of the DI water rinses, is noted for each product salt). The beaker containing the suspension was covered and allowed to cool to rt before being covered with Parafilm™ and placed in the refrigerator (+3.0 °C) at least overnight. The cold suspension was suction filtered to give a solid cake of the desired product salt, the beaker was rinsed with 2 x 1 mL pre-chilled (+3.0 °C) DI water and each rinse was passed through the solid cake which was air dried of excess water under suction. The semi-dried solid cake was placed back into the same 50 mL beaker with the same stirring bar, and a defined amount of fresh DI water was added to affect a suspension. The stirred suspension was digested on the same hot plate/stirrer in the glass covered 50 mL beaker for 30 min at 78-80 °C to remove any residual potassium halide. The beaker and its contents were cooled to rt; the beaker was covered with Parafilm™, and then, was placed into the refrigerator (3.0 °C) at least overnight. Cold vacuum filtration, rinsing the beaker with 2 x 1 mL pre-chilled DI water, and air drying a defined time gave a semi-dry solid

which was transferred to a tarred 4 dram bottle that was subjected to high vacuum drying at 65 °C (50 °C for product salt **9** to give the final bridged heterocyclium di-cation *closo*-perfluoroborane, borane, or carborane salt product.

[1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne][*closo*-$B_{12}H_{12}$] (6): Reacting 1.550 g (4.078 mmol) of 1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne di-bromide **(1)** in 8 mL DI water with 0.879 g (3.996 mmol) of $K_2[B_{12}H_{12}]$ in 12 mL DI water, added over 8 min, gave a solid product salt. Digestion of the solid product salt with 7 mL fresh DI water, when dried under high vacuum at 65 °C for 71 h, gave 1.347 g of a slightly off-white solid product salt **6** (93.1 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.23 (s, 2H), 9.27 (s, 2H), (7.00 (brs, 4H), 5.50 (s, 4H), 1.30-0.38 (very brm, 12H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.69, 143.01, 78.88, 41.92; FTIR (HATR) cm^{-1}, 3336, 3269, 3118, 3054, 2969, 2936, 2524 (B-H), 2449 (B-H), 1602, 1556, 1523, 1414, 1350, 1272, 1198, 1160, 1061, 1014, 944, 895, 772, 706, 635, 607; HRMS calcd for $[Cation^{2+} + 2Anion^{2-} + Na^+]^-$ 527.5345, found 527.5351.

[1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne][*closo*-$CB_{11}H_{12}$] (7): Reacting 1.450 g (3.815 mmol) of 1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne di-bromide **(1)** in 7 mL DI water with 1.362 g (7.477 mmol) of $K[CB_{11}H_{12}]$ in 7 mL DI water, added over 6 min, gave a solid product salt. [Note: Care must be taken to ensure thorough mixing is acheived with this reaction.] Digestion of the solid product salt with 7 mL fresh DI water, when dried under high vacuum at 65 °C for 71 h, gave 1.736 g of a light brown solid product salt **7** (91.7 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.24 (s, 2H), 9.27 (s, 2H), (7.01 (brs, 4H), 5.49 (s, 4H), 2.38 (brs, 2H), 2.11-0.90 (very brm, 22H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.68, 143.02, 78.87, 50.71, 41.90; FTIR (HATR) cm^{-1}, 3352, 3278, 3239, 3135, 3093, 2980, 2946, 2559 (B-H), 2520 (B-H), 1626, 1426, 1414, 1354, 1171, 1141, 1090, 1023, 999, 931, 894, 860, 840, 758, 717, 687, 638, 609; HRMS calcd for $[Cation^{2+} + Anion^-]^+$ 363.3215, found 363.3214.

[*trans*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][*closo*-$B_{12}H_{12}$] (8): Reacting 1.438 g (3.763 mmol) of *trans*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene di-bromide **(2)** in 9 mL DI water with 0.827 g (3.759 mmol) of $K_2[B_{12}H_{12}]$ in 12 mL DI water, added over 10 min, gave a solid product salt. Digestion of the solid product salt with 10 mL fresh DI water, when dried under high vacuum at 50 °C for 90 h, gave 1.272 g of a white solid product salt **8** (92.9 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.13 (s, 2H), 9.22 (s, 2H), (6.96 (brs, 4H), 6.06-6.05 (m, 2H), 5.07-5.06 (m, 4H), 1.32-0.38 (very brm, 12H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.45, 142.88, 128.28, 52.52; FTIR (HATR) cm^{-1}, 3332, 3266, 3120, 3051, 2967, 2517 (B-H), 2464 (B-H), 2444 (B-H), 1604, 1556, 1521, 1422, 1360, 1187, 1157, 1060, 1017, 982, 957, 894, 770, 707, 612; HRMS calcd for $[Cation^{2+} + 2Anion^{2-} + Na^+]^-$ 529.5501, found 529.5484.

[*trans*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][*closo*-$CB_{11}H_{12}$] (9): Reacting 1.031 g (2.698 mmol) of *trans*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene di-bromide **(2)** in 7 mL DI water with 0.982 g (5.391 mmol) of $K[CB_{11}H_{12}]$ in 6 mL DI water, added over 7 min, gave a solid product salt. Digestion of the solid product salt with 7 mL fresh DI water, when dried under high vacuum for 75 h at 50 °C, gave 1.262 g of a white solid product salt **9** (92.1 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.14 (s,

2H), 9.22 (s, 2H), (6.98 (brs, 4H), 6.06-6.05 (m, 2H), 5.06-5.05 (m, 4H), 2.38 (brs, 2H), 2.11-0.90 (very brm, 22H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.41, 142.84, 128.31, 52.50, 50.76; FTIR (HATR) cm^{-1}, 3346, 3282, 3240, 3131, 3089, 2547(B-H), 2510 (B-H), 1707, 1625, 1558, 1434, 1361, 1312, 1150, 1149, 1088, 1066, 1022, 979, 922, 864, 765, 714, 608; HRMS calcd for [Cation^{2+} + Anion^{-}]$^{+}$ 365.3371, found 365.3382.

[*trans*-1,4-di-(1-amino-1,2,3,-triazolium-3N)-2-butene][*closo*-$B_{12}H_{12}$] (10): Reacting 1.329 g (3.478 mmol) of *trans*-1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butene di-bromide **(3)** in 7 mL DI water with 0.765 g (3.478 mmol) of $K_2[B_{12}H_{12}]$ in 8 mL DI water, added over 9 min, gave a solid product salt. Digestion of the solid product salt with 6 mL fresh DI water, when dried for 96 h at 65 °C under high vacuum to give 1.192 g of a white solid product salt **10** (94.1 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 8.80-8.79 (d, 2H), 8.66 (d, 2H), 8.37 (brs, 4H), 6.17-6.16 (m, 2H), 5.29-5.28 (m, 4H), 1.30-0.38 (very brm, 12H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 130.93, 128.57, 126.83, 53.42; FTIR (HATR) cm^{-1}, 3324, 3255, 3174, 3128, 3041, 2980, 2942, 2475 (B-H), 2455 (B-H), 2438 (B-H), 1599, 1523, 1473, 1411, 1341, 1248, 1210, 1187, 1088, 1060, 971, 926, 791, 753, 708, 652, 620; HRMS calcd for [Cation^{2+} + 2Anion^{2-} + Na^{+}]$^{-}$ 528.5538 found 528.5549.

[*trans*-1,4-di-(1-amino-1,2,3,-triazolium-3N)-2-butene][*closo*-$CB_{11}H_{12}$] (11): Reacting 1.356 g (3.549 mmol) of *trans*-1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butene di-bromide **(3)** in 7 mL DI water with 1.293 g (7.100 mmol) of $K[CB_{11}H_{12}]$ in 7 mL DI water, added over 8 min, gave a solid product salt. Digestion of the solid product salt with 7 mL fresh DI water, when dried for 96 h at 65 °C under high vacuum to give 1.760 g of a cream-colored solid product salt **11** (97.5 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 8.80 (d, 2H), 8.66-8.65 (d, 2H), 8.38 (brs, 4H), 6.16-6.15 (m, 2H), 5.28-5.27 (m, 4H), 2.39 (brs, 2H), 2.11-0.90 (very brm, 22H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 130.94, 128.57, 126.79, 53.41, 50.71; FTIR (HATR) cm^{-1}, 3338, 3266, 3146, 3132, 3090, 2998, 2529 (B-H), 1523, 1196, 1167, 1087, 1022, 968, 901, 786, 759, 717, 651; HRMS calcd for [Cation^{2+} + Anion^{-}]$^{+}$ 365.3371, found 365.3374.

[*cis*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][*closo*-$B_{12}H_{12}$] (12): Reacting 1.256 g (4.286 mmol) of *cis*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene di-chloride **(4)** in 3 mL DI water with 0.848 g (3.856 mmol) of $K_2[B_{12}H_{12}]$ in 14 mL DI water, added over 17 min, gave a solid product salt. Digestion of the solid product salt with 5 mL fresh DI water, when dried under high vacuum at 65 °C for 96 h, gave 1.299 g of a light brown solid product salt **12** (92.5 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.15 (s, 2H), 9.22 (s, 2H), (6.97 (brs, 4H), 6.04-6.02 (m, 2H), 5.24-5.23 (m, 4H), 1.30-0.38 (very brm, 12H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.36, 142.80, 127.38, 48.62; FTIR (HATR) cm^{-1}, 3337, 3316, 3306, 3213, 3123, 3070, 3003, 2467 (B-H), 2442 (B-H), 1613, 1564, 1532, 1436, 1406, 1323, 1164, 1057, 1006, 960, 950, 867, 806, 711, 651, 637, 605; HRMS calcd for [Cation^{2+} + 2Anion^{2-} + Na^{+}]$^{-}$ 529.5501, found 529.5493.

[*cis*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][*closo*-$CB_{11}H_{12}$] (13): Reacting 0.849 g (2.896 mmol) of *cis*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene di-chloride **(4)** in 4 mL DI water with 0.949 g (5.211 mmol) of $K[CB_{11}H_{12}]$ in 6 mL DI water, added over 5

min, gave a solid product salt. [Note: Initially, oil droplets formed, but as more potassium carborane solution was added, the brown oil solidified to a precipitate.] Digestion of the solid product salt with 7 mL fresh DI water, when dried under high vacuum at 65 °C for 96 h, gave 1.233 g of a light brown solid product salt **13** (93.1 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.16 (s, 2H), 9.23 (s, 2H), (6.99 (brs, 4H), 6.04-6.02 (m, 2H), 5.23-5.22 (m, 4H), 2.38 (brs, 2H), 2.11-0.90 (very brm, 22H); ^{13}C NMR (1 00 MHz, std. DMSO-d_6 (δ 39.51); δ 145.33, 142.79, 127.41, 50.71, 48.56; FTIR (HATR) cm^{-1}, 3355, 3288, 3248, 3135, 3099, 2537 (B-H), 1637, 1466, 1443, 1403, 1325, 1149, 1088, 1021, 891, 836, 713, 649; 610 HRMS calcd for [Cation^{2+} + Anion^{-}]$^{+}$ 365.3371, found 365.3382.

[*trans*-1,4-di-(1-methylimidazolium-3N)-2-butene][*closo*-$B_{12}H_{12}$] (14): Reacting 1.437 g (3.802 mmol) of *trans*-1,4-di-(1-methylimidazolium-3N)-2-butene di-bromide **(5)** in 5 mL DI water with 0.823 g (3.762 mmol) of $K_2[B_{12}H_{12}]$ in 10 mL DI water, added over 9 min gave a solid product salt. Digestion of the solid product salt with 10 mL fresh DI water, when dried for 69.5 h at 65 °C under high vacuum (45-50 mTorr) to gave 1.307 g of a white solid product salt **14** (96.4 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 9.07 (s, 2H), 7.74-7.73 (m, 2H), 7.70-7.69 (m, 2H), 5.98-5.97 (m, 2H), 4.88-4.87 (m, 4H), 3.86 (s, 6H), 1.31-0.38 (very brm, 12H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 136.61, 129.00, 123.84, 122.32, 49.44, 35.89; FTIR (HATR) cm^{-1}, 3146, 3108, 3030, 2943, 2828, 2475 (B-H), 2452 (B-H), 2435 (B-H), 1723, 1678, 1618, 1574, 1557, 1452, 1368, 1333, 1295, 1266, 1190 1155, 1066, 974, 838, 752, 720, 656, 620; HRMS calcd for [Cation^{2+} + 2Anion^{2-} + Na^{+}]$^{-}$ 525.5691 found 525.5708.

[*trans*-1,4-di-(1-methylimidazolium-3N)-2-butene][*closo*-$CB_{11}H_{12}$] (15): Reacting 1.029 g (2.720 mmol) of *trans*-1,4-di-(1-methylimidazolium-3N)-2-butene di-bromide **(5)** in 4 mL DI water with 0.990 g (5.438 mmol) of $K[CB_{11}H_{12}]$ in 6 mL DI water, added over 10 min gave a solid product salt. Digestion of the solid product salt with 7 mL fresh DI water, when dried for 69.5 h at 65 °C under high vacuum (45-50 mTorr) to gave 1.332 g of a white solid product salt **15** (97.1 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 9.08 (s, 2H), 7.74-7.73 (m, 2H), 7.70-7.69 (m, 4H), 5.97-5.96 (m, 2H), 4.87-4.86 (m, 4H), 3.86 (s, 6H), 2.39 (brs, 2H), 2.08-0.90 (very brm, 22H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 136.63, 129.01, 123.85, 122.31, 49.43, 35.86; FTIR (HATR) cm^{-1}, 3281, 3235, 3162, 3147, 3102, 2537 (B-H), 1595, 1565, 1444, 1384, 1358, 1334, 1295, 1159, 1087, 1021, 980, 890, 827, 739, 716, 617; HRMS calcd for [Cation^{2+} + Anion^{-}]$^{+}$ 361.3561, found 361.3577.

[*trans*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene][*closo*-$B_{12}F_{12}$] (16): Reacting 0.773 g (2.024 mmol) of *trans*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene di-bromide **(2)** in 4 mL DI water with 0.865 g (1.984 mmol) of $K_2[B_{12}F_{12}]$ in 6 mL DI water, added over 9 min, gave a solid product salt. Digestion of the solid product salt with 6 mL fresh DI water, when dried for 72 h at rt under a high vacuum line to 18 mTorr, gave 1.058 g of a white solid product salt **16** (92.0 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.14 (s, 2H), 9.22 (s, 2H), (6.97 (brs, 4H), 6.06-6.05 (m, 2H), 5.06-5.05 (m, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.40, 142.83, 128.30, 52.94; FTIR (HATR) cm^{-1}, 3393, 3321, 3150, 3107, 3009, 2975, 1620, 1560, 1440, 1371, 1221 $[B_{12}F_{12}]^{2-}$, 1149, 1072, 1003, 971, 935, 875, 723 $[B_{12}F_{12}]^{2-}$, 640, 612; HRMS (from smaller scale sample shown

below) calcd for [Cation^{2+} - H^{+}]$^{+}$ 221.1263, found 221.1258 in positive mode, and HRMS calcd for [Cation^{2+} + Anion^{2-} - H^{+}]$^{-}$ 579.2266, found 579.2284 in the negative mode.

[1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne][*closo*-$B_{12}F_{12}$] (18): Reacting 0.821 g (2.159 mmol) of 1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne di-bromide **(1)** in 4 mL DI water with 0.922 g (2.115 mmol) of $K_2[B_{12}F_{12}]$ in 11 mL DI water, added over 9 min, gave a solid product salt. Digestion of the solid product salt with 5 mL fresh DI water, when dried for 38 h at rt on a high vacuum to 12 mTorr, gave 1.084 g of a cream-colored solid product salt **18** (88.7 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.24 (s, 2H), 9.26 (s, 2H), (7.01 (brs, 4H), 5.49 (s, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.65, 142.99, 78.84, 41.88; FTIR (HATR) cm^{-1}, 3372, 3309, 3149, 3107, 3013, 2985, 2966, 1630, 1568, 1429, 1361, 1219 $[B_{12}F_{12}]^{2-}$, 1074, 1002, 957, 886, 724 $[B_{12}F_{12}]^{2-}$, 650, 612; HRMS calcd for [Cation^{2+} + Anion^{2-} – H^{+}]$^{-}$ 577.2110, found 577.2093.

Smaller-Scale General Metathesis Reaction Procedure and X-ray Data for Bridged Heterocyclium Di-Cation *closo*-Perfluoroborane Salt Products (16-18). Because of the limited supply of $K_2[B_{12}F_{12}]$ and $Cs_2[B_{12}F_{12}]$ reactant salts, the [Heterocyclium di-cation][$B_{12}F_{12}$] salts initially were synthesized on a smaller reaction scale at rt with no digestion of the initial product salt. These three perfluoroborane salts are very soluble in CH_3CN at rt; so, this solvent was used to obtain crystals suitable for single-crystal X-ray analyses shown below.

A 10 mL 14/20 jointed single-neck recovery flask was charged with the selected bridged heterocyclium di-cation di-halide salt (**2**, **3**, or **5**) which was dissolved at rt in de-ionized (DI) water. A 50 mL beaker was charged with a nearly stoichiometric amount of potassium *closo*-perfluoroborane or cesium *closo*-perfluoroborane which was then dissolved at rt in DI water. The aqueous potassium or cesium perfluoroborane solution was added dropwise, using a disposable capillary pipette, to the aqueous solution in the 10 mL single-necked recovery flask, and a precipitate immediately began to form. During addition, the flask occasionally was swirled. After complete addition, the beaker was rinsed with 0.4 to 1 mL DI water in two portions which was added to the 10 ml recovery flask. The capped 10 mL recovery flask and its contents were placed overnight in a refrigerator (+3.0 °C). Vacuum filtration, rinsing the 10 mL recovery flask with 1 (salt **16**), 2 (salt **17**), or 3 (salt **18**) mL of DI water, in two, two, and three portions, respectively, passing the rinses through the solid cake in the filtration funnel, and drying the resultant solid cake for at least 18 h at 75 °C in a vacuum oven gave the desired product salt.

[*trans*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene][*closo*-$B_{12}F_{12}$] (16): Reacting 0.0443 g (0.1159 mmol) of 1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene di-bromide **(2)** in 0.6 mL DI water with 0.0500 g (0.1147mmol) of $K_2[B_{12}F_{12}]$ in 0.6 mL DI water, added over less than one min, to give 0.0649 g (97.6%) of solid product salt **16**: ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.14 (s, 2H), 9.22 (s, 2H), (6.98 (s, 4H), 6.06-6.05 (m, 2H), 5.06-5.05, (m, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.39, 142.82, 128.29, 52.48; FTIR (HATR) cm^{-1}, 3391, 3322, 3150, 3097, 3003, 1622, 1556, 1438, 1372, 1221 $[B_{12}F_{12}]^{2-}$, 1148, 1017, 1005, 972, 935, 874, 723 $[B_{12}F_{12}]^{2-}$, 641, 612; HRMS calcd for [Cation^{2+} - H^{+}]$^{+}$ 221.1263, found 221.1258 in positive mode, and HRMS calcd for [Cation^{2+} + Anion^{2-} - H^{+}]$^{-}$ 579.2266, found 579.2284 in the negative mode.

Recystallization from CH_3CN to a very concentrated sample permitted single-crystal X-ray analysis. Recrystallization from DI water also gave acceptable X-ray crystals: 23.3 mg of salt **16** was dissolved in 20 mL boiling DI water. Filtration, cooling to rt, very slow air evaporation and concentration of the solution to 5 mL, removal of excess water solvent with a disposable capillary pipette, and slow air drying of the resultant crystals gave 20.4 mg of salt **16** for use in single-crystal X-ray analysis.

Table 1. Crystal and structure refinement data for **16.**

	(16) $(4AT)_2C_4H_6\ B_{12}F_{12}$
Formula	C8 H14 N8, B12 F12
Space group	$P2_1/c$ monoclinic
a (Å)	8.220(1)
b (Å)	12.027(1)
c (Å)	11.690(1)
β (°)	105.839(1)
V/Å^3	1111.87(16)
$\rho_{calc.}$/g cm^{-3}	1.73
Z	2
Formula weight	579.99
μ/mm^{-1}	0.172
Temperature (K)	296(2)
λ(MoKα)	0.71073
Crystal size	0.1x0.2x0.2
Theta range θ/°	2.48 to 28.64
Index range	-10≤h≤10, -15≤k≤15, -15≤l≤15
Reflection collected	13074
Independent [R(int)]/	2700 [0.0286]
Obs. refl. ([I > 2.0 σ(I)])	1823
F(000)	572
GooF	1.069
R_1, wR [I > 2σ(I)]	0.0483, 0.1388
R_1, wR_2 (all data)	0.0726, 0.1559
L.diff. peak/hole eÅ^3	0.28 and -0.21
Absorption correct.	multiscan SADABS
T_{min}, T_{max}	0.662, 0.746
Data/restraints/param.	2700/0/193
Refinement method	Full-matrix least squares on F^2

$R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2]\}^{½}$

CCDC-776032 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif.

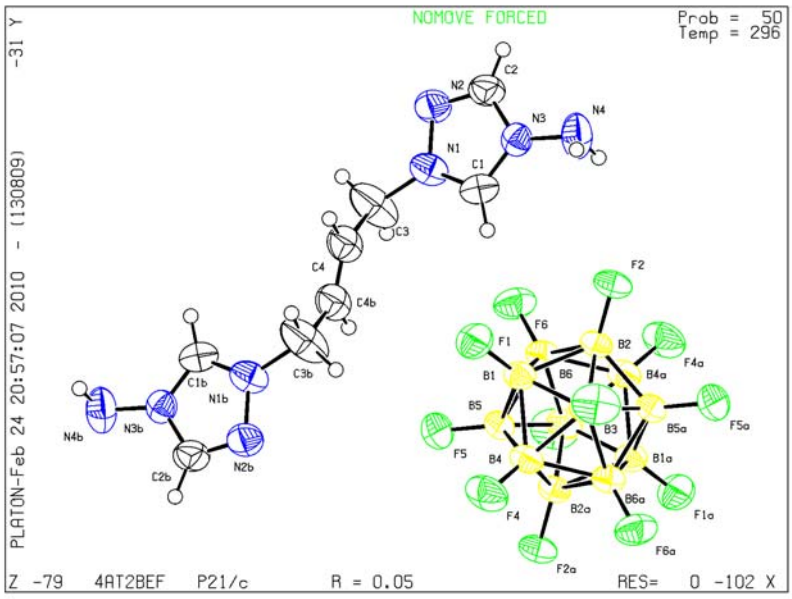


Figure 1. Molecular drawing of **16**. Thermal ellipsoids are shown at 50% probability level.

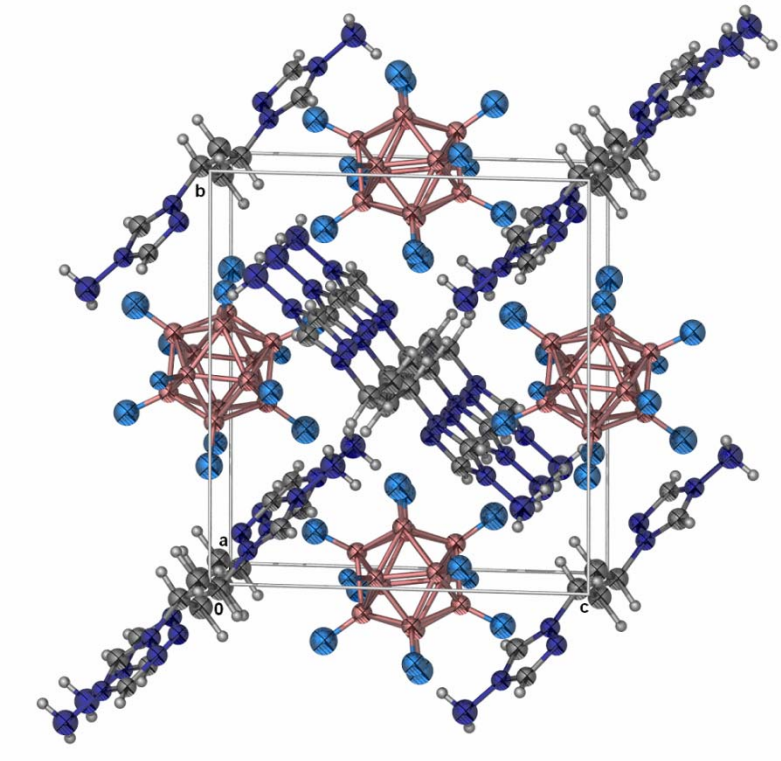


Figure 2. Crystal packing of **16** viewed along the *a*-axis (tiltel forward)

[*trans*-1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butene][*closo*-$B_{12}F_{12}$] (17): Reacting 0.0490 g (0.1282 mmol) of 1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butene di-bromide **(3)** in 0.6 mL DI water with 0.0539 g (0.1236mmol) of $K_2[B_{12}F_{12}]$ in 0.6 mL DI water, added over less than one min, to give 0.0679 g (94.7%) of solid product salt **17**: ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 8.79 (d, 2H), 8.65 (d, 2H), (8.38 (brs, 4H), 6.16-6.14 (m, 2H), 5.28-5.26, (m, 4H);^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 130.91, 128.56, 126.79, 53.40; FTIR (HATR) cm^{-1}, 3386, 3311, 3189, 3174, 1623, 1530, 1476, 1414, 1357, 1330, 1222 $[B_{12}F_{12}]^{2-}$, 1087, 980, 904, 790, 726 $[B_{12}F_{12}]^{2-}$, 659, 628; HRMS calcd for [$Cation^{2+}$ + $Anion^{2-}$ - H^+]$^-$ 579.2266, found 579.2246.

Dissolving crude salt product **17** in CH_3CN and evaporating to dryness gives crystals suitable for single-crystal X-ray analysis.

Table 2. Crystal and structure refinement data for **17.**

	(17) $(1AT)_2C_4H_4$ $B_{12}F_{12}$
Formula	B12 F12, C8 H14 N8
Space group	$P2_1/n$ monoclinic
a (Å)	8.318(1)
b (Å)	13.311(1)
c (Å)	10.994(1)
β (°)	110.847(1)
V/Å^3	1137.55(5)
$\rho_{calc.}$/g cm^{-3}	1.69
Z	2
Formula weight	579.99
μ/mm^{-1}	0.168
Temperature (K)	296(2)
λ(MoKα)	0.71073
Crystal size	0.1x0.1x0.2
Theta range θ/°	2.50 to 25.46
Index range	-10≤h≤10, -16≤k≤16, -13≤l≤13
Reflection collected	21415
Independent [R(int)]/	2099 [0.0359]
Obs. refl. ([I > 2.0 σ(I)])	1600
F(000)	572
GooF	1.041
R_1, wR [I > 2σ(I)]	0.0385, 0.1023
R_1, wR_2 (all data)	0.0539, 0.1129
L.diff. peak/hole eÅ^3	0.27 and -0.19
Absorption correct.	multiscan SADABS
T_{min}, T_{max}	0.702, 0.745
Data/restraints/param.	2099/398/289
Refinement method	Full-matrix least squares on F^2

$R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2]\}^{½}$

CCDC-776033 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif.

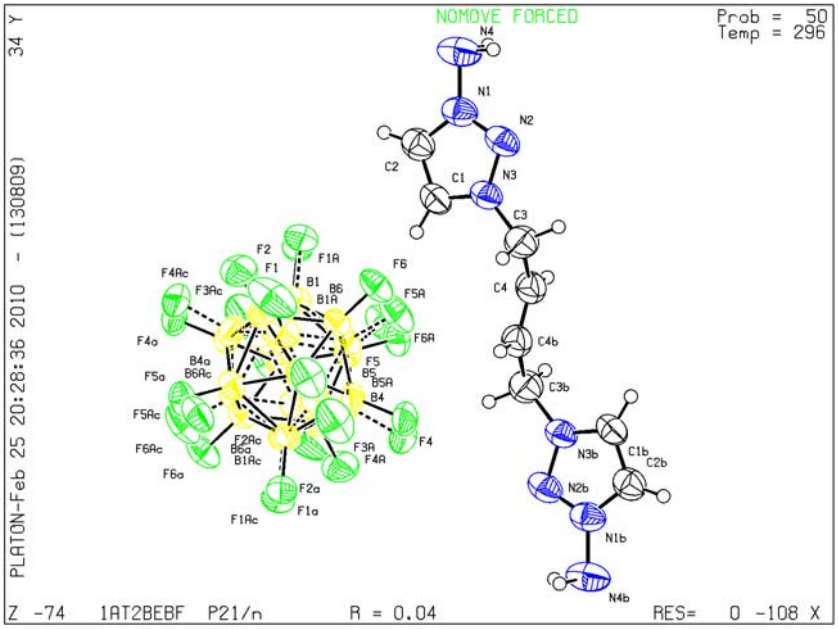


Figure 3. Molecular drawing of **17**. Thermal ellipsoids are shown at 50% probability level ($B_{12}F_{12}^{2-}$ anion is disordered).

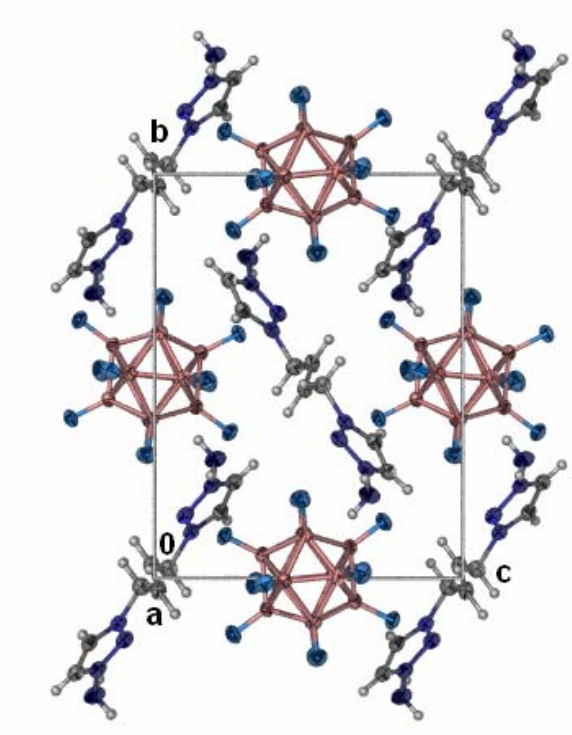


Figure 4. Crystal packing of **17** viewed along the *a*-axis (disorder removed for clarity).

[1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne][*closo*-$B_{12}F_{12}$] (18): Reacting 0.1084 g (0.2852 mmol) of 1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne di-bromide **(1)** in 0.4 mL DI water with 0.1774 g (0.2845 mmol) of $Cs_2[B_{12}F_{12}]$ in 5 mL (minimum amount needed) DI water, added over a couple of minutes, to give 0.1524 g (92.7%) of cream-colored solid product salt **18**: ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.24 (s, 2H), 9.27 (s, 2H), (7.01 (s, 4H), 5.49, (s, 4H);^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.66, 142.99, 78.85, 41.88; FTIR (HATR) cm^{-1}, 3375, 3308, 3151, 3107, 2985, 2966, 1631, 1570, 1430, 1363, 1218 $[B_{12}F_{12}]^{2-}$, 959, 887, 725 $[B_{12}F_{12}]^{2-}$, 716, 652, 613; HRMS calcd for $[Cation^{2+} + Anion^{2-} - H^+]^-$ 577.2110, found 577.2093.

Dissolving crude salt product **18** in CH_3CN and evaporating to dryness gives crystals suitable for single-crystal X-ray analysis.

Table 3. Crystal and structure refinement data for **18**

	(18) $(1AT)_2C_4H_6$ $B_{12}F_{12}$
Formula	C8 H12 N8, B12 F12
Space group	*P*bca orthorhombic
a (Å)	17.066(1)
b (Å)	14.648(1)
c (Å)	17.812(1)
σ,β,γ (°)	90
V/Å^3	4452.7(6)
$\rho_{calc.}$/g cm^{-3}	1.72
Z	8
Formula weight	577.98
μ/mm^{-1}	1.542
Temperature (K)	296(2)
λ(CuKα)	1.54178
Crystal size	0.1x0.1x0.2
Theta range θ/°	4.69 to 65.21
Index range	-20≤h≤16, -16≤k≤14, -13≤l≤20
Reflection collected	15709
Independent [R(int)]/	3670 [0.0241]
Obs. refl. ([I > 2.0 σ(I)])	2768
F(000)	2272
GooF	1.048
R_1, w*R* [I > 2σ(I)]	0.0468, 0.1313
R_1, wR_2 (all data)	0.0630, 0.1444
L.diff. peak/hole eÅ^3	0.36 and -0.37
Absorption correct.	multiscan SADABS
T_{min}, T_{max}	0.643, 0.753
Data/restraints/param.	3670/0/377
Refinement method	Full-matrix least squares on F^2

$R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2]\}^{½}$

CCDC-776034 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif.

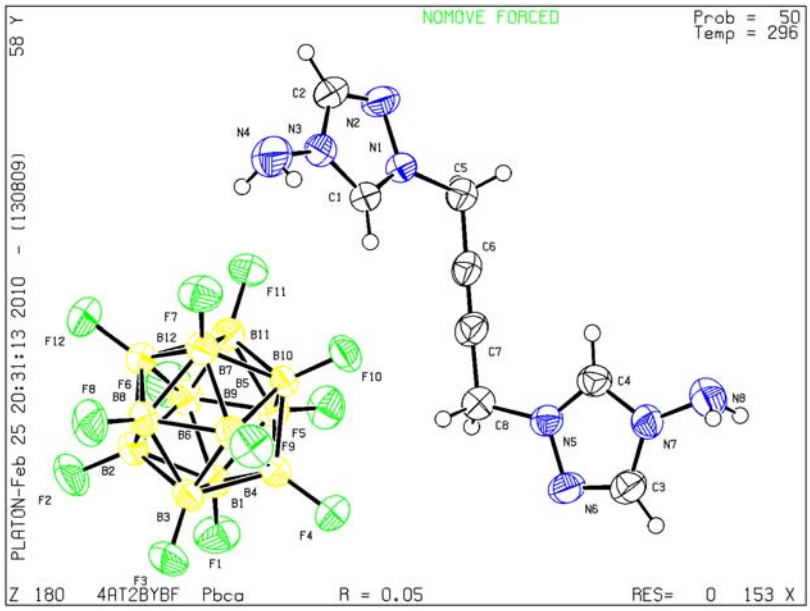


Figure 5. Molecular drawing of **18**. Thermal ellipsoids are shown at 50% probability level.

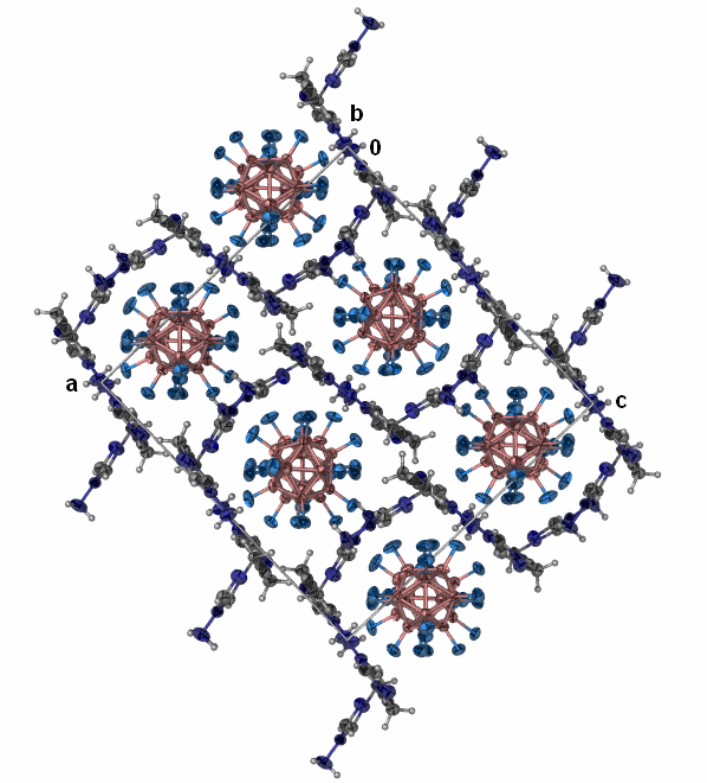


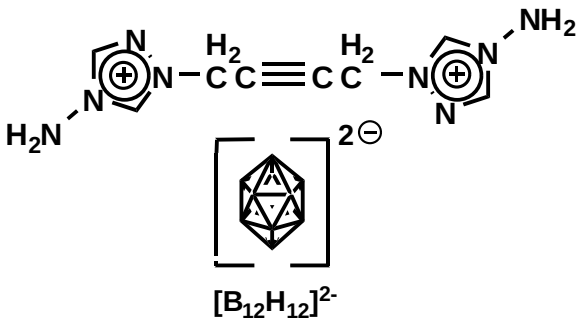
Figure 6. Crystal packing of **18** viewed along the *b*-axis.

Melting Point Data.

Detailed visual melting point behavior for all product salts (**6–18**) is presented in Supplemental **Table 4**. These values were determined as follows. First, a run was made at a 10 °C/minute temperature rise to obtain an approximate melting point value for each salt sample; then, a second run was made with each salt sample using a 1 °C/minute temperature rise beginning about 10 °C below the initial melt response.

This second run data was used to establish the published melting point or decomposition temperature values (**Table 4**) from iteratively comparing visual observations of each sample directly in the apparatus melting point compartment and the resultant video replay of that same sample. Softening means that the crystalline salt appeared to lose its sharp crystalline character to a more velvet-like solid that was devoid of sharp corners on the solid particles.

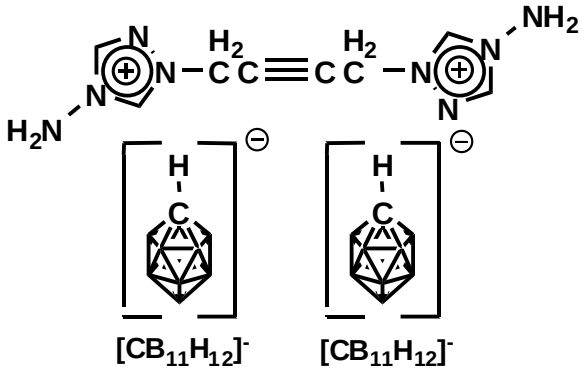
Table 4. Melting Point Data Determined with the SRS MPA100 Apparatus.



$[B_{12}H_{12}]^{2-}$

6

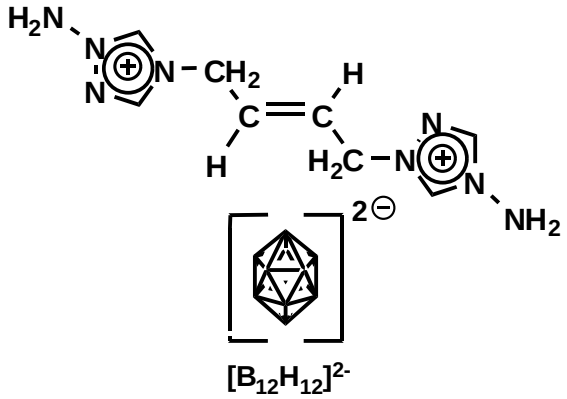
DECOMPOSES with solid state gas evolution to a dark residue: 217.4 - 219.6 °C



$[CB_{11}H_{12}]^{-}$ $[CB_{11}H_{12}]^{-}$

7

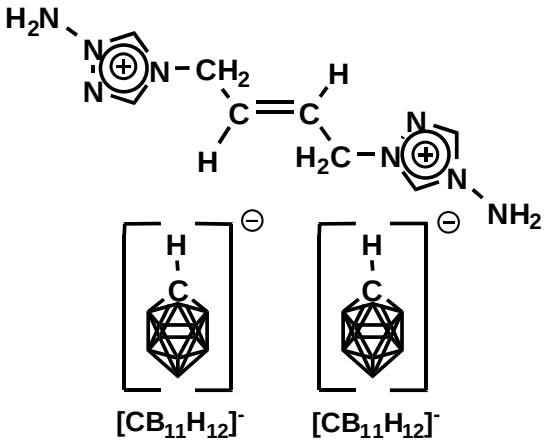
LIQUIFIES to a brown oil with decomposition: 175.5 - 178.5 °C



$[B_{12}H_{12}]^{2-}$

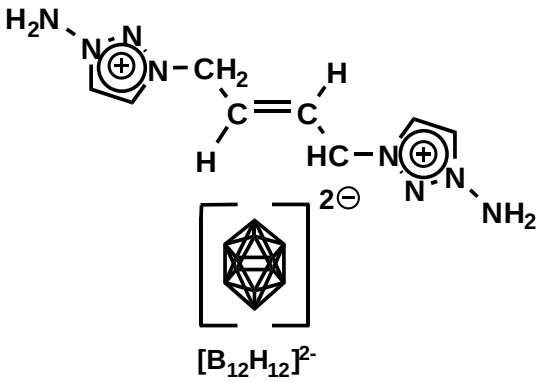
8

LIQUIFIES with rapid gas evolution: 238.7 - 239.6 °C



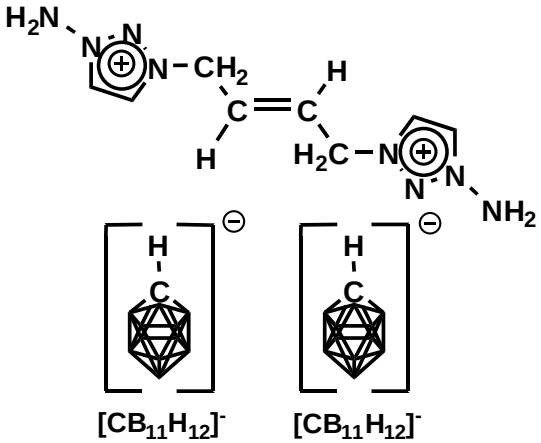
9

LIQUIFIES with gas evolution:
216.9 - 221.2 °C



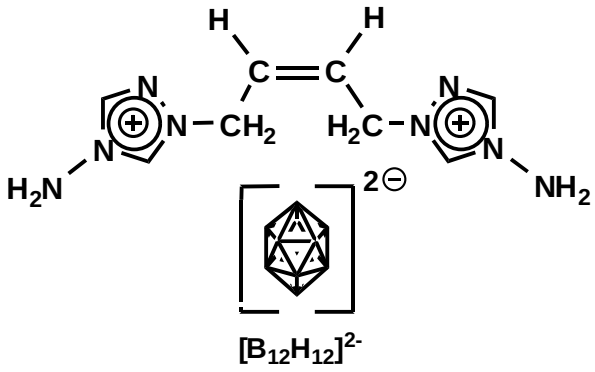
10

LIQUIFIES with rapid gas evolution:
229.7 - 230.6 °C



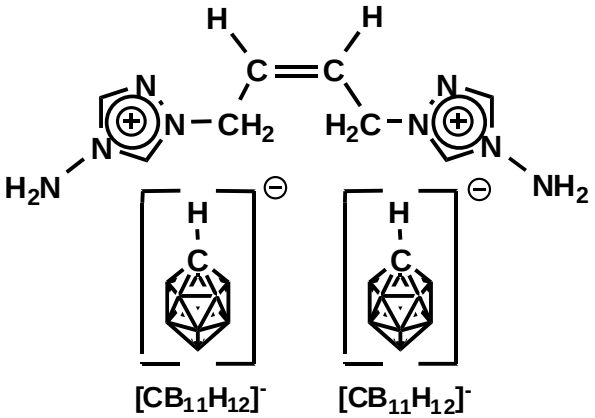
11

LIQUIFIES with rapid gas evolution:
206.2 - 208.6 °C



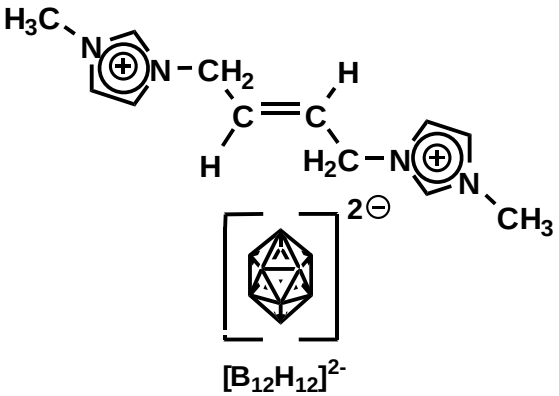
12

LIQUIFIES with gas evolution:
238.9 - 240.0 °C



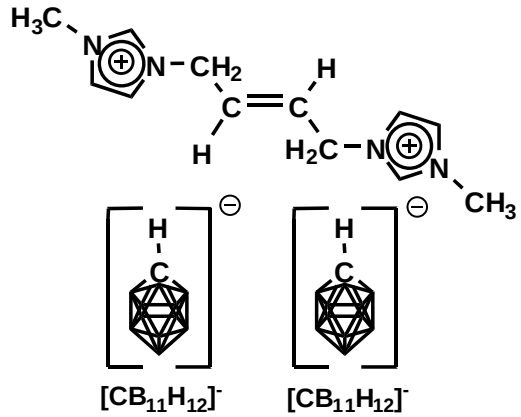
13

LIQUIFIES slowly to a brown oil:
170.0 - 174.0 °C



14

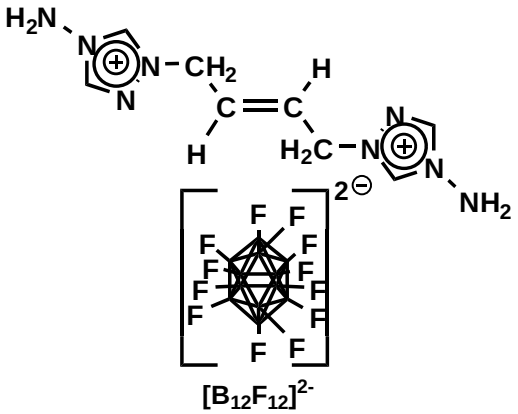
DECOMPOSITION in the solid state
with very slow gas evolution
to a brown residue:
305.1 - 398.0 °C



15

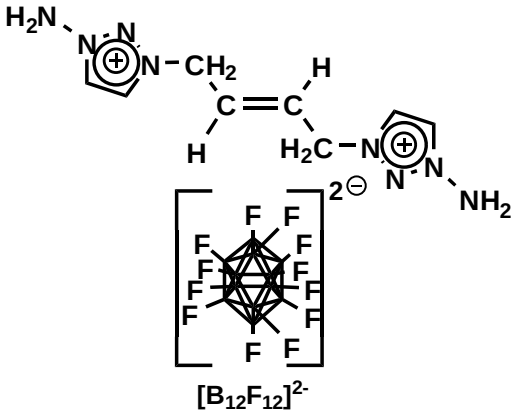
SOFTENS with possible morphology change:
210.1 - 231.4 °C

LIQUIFIES with slight oil discoloration:
251.9 - 255.2 °C



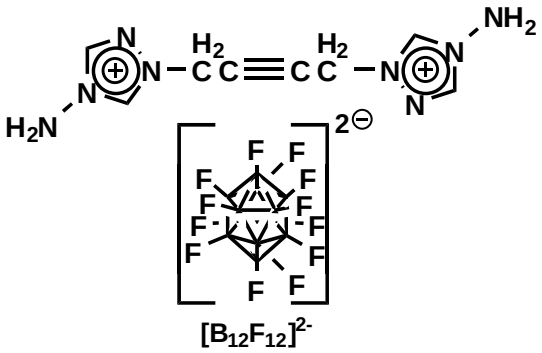
16 (Large Scale Digested Sample)

LIQUIFIES and darkens
302.8 - 303.4 °C with
slow gas evolution noted
at 303.6 °C



17 (Small Scale Sample)

LIQUIFIES and darkens
with slow gas evolution:
237.6 - 239.6 °C



LIQUIFIES and darkens to a dark brown oil with very slow gas evolution: 236.5 - 238.5 °C

18 (Large Scale Digested Sample)

Ion Chromatography Cl^- or Br^- Analysis Results.

Ionic concentration was determined by Ion Chromatography using a Waters 1525 HPLC Binary Pump equipped with a Waters 432 conductivity detector and a Phenomenex™ STAR-ION™ A300 100 x 4.6 mm ID (PEEK™) column. Each salt sample was weighed between 0.01 mg to 0 0.08 mg, and in one case 0.03 mg, into a plastic class B centrifuge tube and diluted to 25 mL using Type 1 ultra pure water. Samples that did not readily dissolve were heated to 80 °C with a plastic reflux cap. Each sample was passed through an IC Millex LG 0.2 µm syringe filter prior to injection. A three point calibration curve was generated using blank reagent water, 1 and 10 ppm NIST traceable Chloride and Bromide standards. Concentrations were determined by comparing peak area response of the samples to the standard calibration curve. Run detection limits displayed for each salt vary depending upon the sample mass used in each analysis. As can be seen from **Table 5** (page 24), the chloride ion content, from the residual KCl by-product, ranged from 0.3 to 0.5 weight percent, while the bromide content, from the residual KBr by-product (CsBr in the case of salt **18**), ranged from less than 0.04 weight percent to 0.83 weight percent.

Table 5. Ion Chromatography Residual Cl^- or Br^- Content in the Unsaturated Bridged Heterocyclium Di-Cation *closo*-Perfluoroborane, *closo*-Borane, and *closo*-Carborane Salts.

Bridged Salt Product[a]	**Run Detection Limit (wt. %)**	**Cl^- (wt. %)**	**Br^- (wt. %)**
6	0.08	---	< 0.08
7	0.08	---	0.10
8	0.08	---	0.28
9	0.08	---	< 0.08
10	0.03	0.03	---
11	0.03	0.05	---
12	0.08	---	< 0.08
13	0.07	---	< 0.07
14	0.08	---	0.33
15	0.08	---	0.83
16	0.04	---	< 0.04
17 (small scale)	0.12	---	< 0.12
18	0.08	---	< 0.08
16 (small scale)	0.10	---	0.50
18 (small scale)	0.08	---	< 0.08

[a]All bridged heterocyclium dication product salts were synthesized using either the potassium borane, carborane, or perfluoroborane reactant salt except for the small scale salt **18** sample where a cesium perfluoroborane reactant was used. Water solubility of the CsBr by-product salt is more than two times greater than that of the KBr by-product salt.[22]