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

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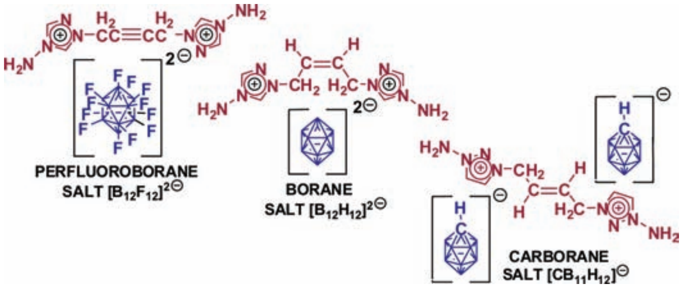
ABSTRACT



Thirteen bridged triazolium and imidazolium dicationic salts, which uniquely pair *closo*-icosahedral perfluoroborane $[B_{12}F_{12}]^{2-}$, borane $[B_{12}H_{12}]^{2-}$, or carborane $[CB_{11}H_{12}]^{-}$ anionic species with unsaturated bridged heterocyclium dications, were synthesized using an aqueous benchtop method. This considerably extends the scope of a reported aqueous synthesis of binary [heterocyclium]$_2$[$B_{12}H_{12}$] and [heterocyclium][$CB_{11}H_{12}$] salts. Also, the one-step preparation of five new precursor bridged heterocyclium dicationic dihalide salts using conventional procedures and in one case a microwave-assisted method is described.

Compared to neutral organic compounds, heterocyclic salts enhance the flexibility to attain rational structural design and resultant predicted ingredient properties, which can permit a tailorable behavioral response.[1,2] Tailoring thermal initiation of heterocyclium borane and dinitrate salts to an air-sustained combustion is one example,[2] as explained by a current initiation sensitivity concept.[3]

We report the first synthesis of heterocyclium perfluoroborane $[B_{12}F_{12}]^{2-}$ salts and the first pairing of $[B_{12}F_{12}]^{2-}$, $[B_{12}H_{12}]^{2-}$, and $[CB_{11}H_{12}]^{-}$ anionic species with unsaturated bridged [heterocyclium dications]$^{2+}$ in 89−98% yields. The functional unsaturated site centered in the alkyl-based bridge structure, which in turn possesses a heterocylium cation

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(1) Shackelford, S. A.; Belletire, J. L.; Boatz, J. A.; Schneider, S.; Wheaton, A. K.; Wight, B. A.; Hudgens, L. M.; Ammon, H. L.; Strauss, S. H. *Org. Lett.* **2009**, *11*, 2623.

(2) (a) Shackelford, S. A.; Belletire, J. L. *Centr. Europ. J. Energ. Mater.* **2009**, *6*, 219. (b) Shackelford, S. A.; Belletire, J. L. 12th New Trends in Research of Energetic Materials (NTREM) International Seminar, Pardubice, Czech Republic, April 1−3 2009.

(3) Shackelford, S. A. *Centr. Europ. J. Energ. Mater.* **2008**, *5*, 75.

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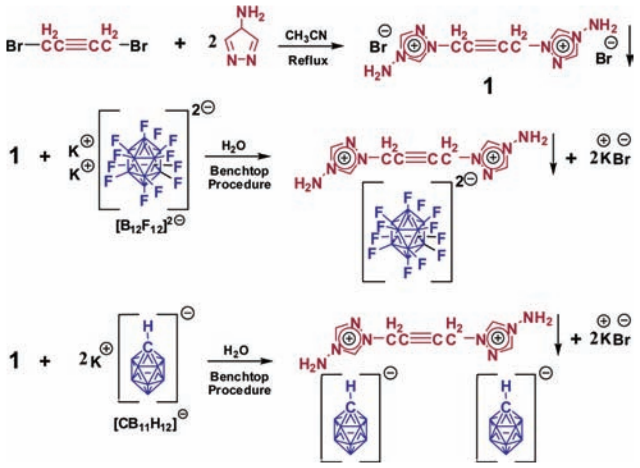
tethered at each terminal end, is a unique dication feature (Scheme 1).

The aqueous, open-air benchtop synthesis of 13 unique high-energy bridged heterocyclium dication salts of $[B_{12}F_{12}]^{2-}$, $[B_{12}H_{12}]^{2-}$, and $[CB_{11}H_{12}]^{-}$ by a rapid, one-step, high-yield metathesis reaction significantly extends the scope of the recently reported preparation of high-energy binary triazolium and imidazolium *closo*-icosahedral borane $[B_{12}H_{12}]^{2-}$ and carborane $[CB_{11}H_{12}]^{-}$ salts in water solvent.[1] An open-air metathesis method for similar binary triazolium and tetrazolium borane based salts of high water solubility and for mixed borane salts that pair two different heterocyclium cations in a 1:1 ratio also is possible.[4] All five precursor bridged heterocyclium dication dihalide salts **1**−**5** (Figure 1) used in the aqueous metathesis reaction were obtained by a one-step alkylation in CH_3CN solvent. Salts **1**−**4** have no literature precedent.

Two bridged 2-butenyl heterocyclium dicationic dihalide salts, such as salt **5**, have been reported,[5,6] and both contain an *N*-methylimidazolium cation at the terminal ends of the alkenyl bridge structure. No bridged heterocyclium dicationic salts based on the 2-butynyl bridge structure or terminal triazolium cations, seen in salts **1**−**4**, have been described.

Scheme 1. Two-Step Synthesis of Bridged Heterocyclium Dicationic Salts of $[B_{12}F_{12}]^{2-}$, $[B_{12}H_{12}]^{2-}$, and $[CB_{11}H_{12}]^{-}$



Analogous to the *closo*-icosahedral $[B_{12}H_{12}]^{2-}$ and $[CB_{11}H_{12}]^{-}$ anionic species previously reported[7−11] and seen in the bridged heterocyclic salts **6**−**15** (Table 1), the $[B_{12}F_{12}]^{2-}$ dianion first was synthesized in 1992 as the cesium salt in 38% yield.[12] Recently, the $K_2[B_{12}F_{12}]$ salt was synthesized by $K_2[B_{12}H_{12}]$ perfluorination in 74% yield and 99.5%$^+$ purity by continuously bubbling 20/80 F_2/N_2 in CH_3CN solvent using ordinary glassware.[13] Two bridged [heterocyclium]$[B_{12}F_{12}]$ salts **16** and **17** were synthesized using the $K_2[B_{12}F_{12}]$ reactant salt, and a third **18** was synthesized twice, once with the $Cs_2[B_{12}F_{12}]$ salt (Table 2). The bridged $[B_{12}H_{12}]$, and $[CB_{11}H_{12}]$ salts were synthesized using the $K_2[B_{12}H_{12}]$ and $K[CB_{11}H_{12}]$ reactant salts, respectively, in the correct stoichiometry.[14]

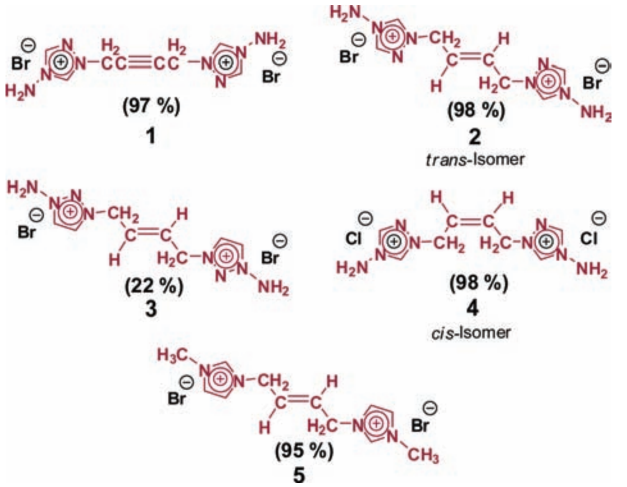


Figure 1. Five bridged heterocyclium dicationic dihalide reactant salts prepared with yields obtained.

These 13 2-alkenyl- and 2-alkynyl-based bridged heterocyclium dicationic salts of $[B_{12}F_{12}]^{2-}$, $[B_{12}H_{12}]^{2-}$, and $[CB_{11}H_{12}]^{-}$ were synthesized in a two-step sequence (Scheme 1). First, five new intermediate bridged heterocyclium dicationic dihalogen salts **1**−**5**, needed to prepare the final bridged heterocyclium dicationic salts **6**−**18**, precipitated from refluxing CH_3CN solution during a high-yield, one-step alkylation of 1,4-dihalo-2-butene or 1,4-dibromo-2-butyne with the selected neutral triazole or imidazole compound (Figure 1). Intermediate salts **1**−**5**, once filtered and dried, were pure enough for direct use in the second metathesis step (e.g., salt **1**). One intermediate, bridged salt **4** (Figure 1), contained 6−7% of unreacted 4-amino-1,2,4-triazole (4AT), but water solvent removed the 4AT impurity during the subsequent metathesis reaction. Reaction times needed to synthesize intermediate bridged dihalide salts **1**−**5** varied. A typical procedure for salts **1**−**4** is given by *trans*-

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(4) Belletire, J. L.; Shackelford, S. A.; Schneider, S.; Wight, B. A.; Strauss, S. H. *Synth. Commun.* Submitted for publication.

(5) Zhang, Y.; Ngeow, K. C.; Ying, J. Y. *Org. Lett.* **2007**, *9*, 3495.

(6) Jokanovic, M.; Maksimovic, M.; Killbarda, V.; Jovanovic, D.; Savic, D. *Toxicol. Lett.* **1996**, *85*, 35.

(7) Pitochelli, A. R.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 3228.

(8) Kaszynski, P. *Collect. Czech. Chem. Commun.* **1999**, *64*, 895, and references therein.

(9) Muetterties, E. L.; Knoth, W. H. *Polyhedral Boranes*; Marcel Dekker: New York, 1969.

(10) Grimes, R. N. *Angew. Chem. Int. Ed.* **2003**, *42*, 1198, and references therein.

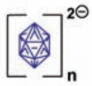
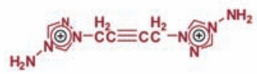
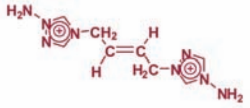
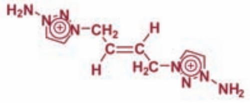
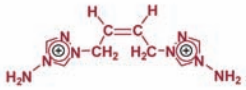
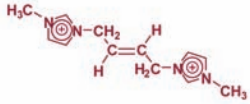
(11) Knoth, W. H. *J. Am. Chem. Soc.* **1967**, *89*, 1274.

(12) Solntsev, K. A; Mebel, A. M.; Votinova, N. A.; Kuznetsov, N. T.; Charkin, O. P. *Koord. Khim.* **1992**, *18*, 340.

(13) Peryshkov, D. V.; Popov, A. A.; Strauss, S. H *J. Am. Chem. Soc.* **2009**, *131*, 18393.

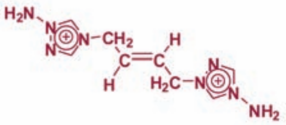
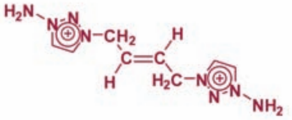
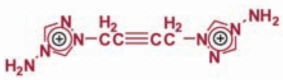
(14) The $K_2[B_{12}H_{12}]$ and $K[CB_{11}H_{12}]$ reactant salts were purchased from Katchem Ltd., E. Krasnohorske 6, 110 00 Prague 1, Czech Republic and were used as received.

Table 1. Properties Data for Bridged Heterocyclium Dicationic Salts **6**−**15** of $[B_{12}H_{12}]^{2-}$ and $[CB_{11}H_{12}]^{-}$

[HETEROCYCLIUM DICATION]$^{2\oplus}$ CHEMICAL STRUCTURE	BORANE  n = 1 $[B_{12}H_{12}]^{2\ominus}$	CARBORANE  n = 2 $[CB_{11}H_{12}]^{\ominus}$
	isolated yield density (g/cc) pycnometry (predicted) melting/dec. point (°C)	isolated yield density (g/cc) pycnometry (predicted) melting/dec. point (°C)
	**6** 93% 1.23 (1.23) dec. 217-220[a]	**7** 92% 1.16 (1.14) dec. 176-178[a]
	**8** 93% 1.21 (1.22) melt. 239-240[a]	**9** 92% 1.16 (1.14) melt. 217-221[a]
	**10** 94% 1.21 (1.25) melt. 230-231[a]	**11** 98% 1.12 (1.16) melt. 206-209[a]
	**12** 92% 1.24 (1.22) melt. 239-240[a]	**13** 93% 1.12 (1.14) melt.. 170-174
	**14** 96% 1.12 (1.25) dec. 305-398[a]	**15** 97% 1.09 (1.16) melt. 252-255

[a] Proceeds with gas evolution

Table 2. Properties Data for Bridged Heterocyclium Dicationic Salts **16**−**18** of $[B_{12}F_{12}]^{2-}$

[HETEROCYCLIUM DICATION]$^{2\oplus}$ CHEMICAL STRUCTURE	 n = 1 $[B_{12}F_{12}]^{2\ominus}$
	isolated yield density (g/cc at 23 °C) single crystal x-ray melting/dec. point (°C)
	**16** 98% (small scale) 92% (large scale) 1.73 liquifies 303-304[a]
	**17** 95% (small scale) 1.69 liquifies 238-240[a]
	**18** 93% (small scale) 89% (large scale) 1.72 liquifies 237-238[a]

[a] Proceeds with gas evolution

1,4-di(4-amino-1,2,4,-triazolium-1*N*)-2-butene dibromide **2**.[15] Synthesis details for salts **1**−**5** are in Supporting Information.

Synthesis of the intermediate bridged heterocyclium dichloride salt analogue of dibromide salt **1** was possible using 1,4-dichloro-2-butyne, but a noticeable amount of the 4-amino-1,2,4-triazole (4AT) reactant (11−16%) remained in the isolated dichloride salt. Two tedious reprecipitations in a MeOH/CH_3CN mixed solvent, with large losses, removed the 4AT. The availability of 1,4-dibromo-2-butyne, however, provided 4AT-free bridged dibromide salt **1** in high yield and purity.[16]

Microwave-assisted synthesis reduced alkylation reaction time and gave a comparable yield and purity. Bridged intermediate dibromide salt **2** was synthesized in 6.5 h conventionally in refluxing CH_3CN (98% yield) but in 50 min at 100 °C under microwave conditions (96% yield). Bridged intermediate salt **5** required 6 h conventionally but only 45 min at 100 °C in the microwave. A key advantage existed in the synthesis of intermediate bridged salt **3**. Whereas a conventional one-step alkylation yielded acceptably pure bridged salts **1**, **2**, **4**, and **5**, intermediate salt **3** was obtained in a 90% crude yield and contained 11% of unreacted 1-amino-1,2,3-triazole (1AT) and other trace impurities. The neutral 1AT heterocycle was removed by reprecipitation from a methanol/ethanol mixed solvent with an 82% recovery, but the other trace impurities remained. Microwave-assisted synthesis precipitated 1AT-free salt **3** as a pure white solid.[17,18]

While microwaving the reaction solution in a defined concentration at 100 °C for 45 min afforded the best reaction conditions, a 22% yield of precipitated intermediate salt **3** must be an acceptable option.[17] A parametric study that increased concentration, increased or decreased reaction time, and increased or decreased temperature gave either a lower purified yield or a less pure tan-colored, gummy solid salt **3** that was similar to the conventional alkylation reaction results.

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(15) [*trans*-1,4-Di(4-amino-1,2,4,-triazolium-1*N*)-2-butene]$[Br]_2$ (**2**). A 100 mL single-necked recovery flask with Teflon-coated stir bar was charged with 1.506 g (6.831 mmol) of 97% *trans*-1,4-dibromo-2-butene, 1.160 g (13.658 mmol) of 99% 4-amino-1,2,4-triazole, and 40 mL of CH_3CN and was refluxed for 6.5 h. The resultant suspension was cooled to rt, vacuum filtered, and vacuum dried to yield 2.560 g (98%) of white solid salt **2**.

(16) The 1,4-dibromo-2-butyne was purchased from BromOrganics Corporation, P.O. Box 722, Elk Grove, IL 60009.

(17) [*trans*-1,4-Di(1-amino-1,2,3-triazolium-3N)-2-butene]$[Br]_2$ (**3**). Six Biotage (nee Personal Chemistry) Initiator Emrys 10−20 mL vials with Teflon-coated magnetic stir bars were each charged with 0.600 g (2.72 mmol) of 97% *trans*-1,4-di(1-amino-1,2,3,-triazolium-3*N*)-2-butene dibromide, 0.472 g (0.561mmol) of 1-amino-1,2,3-triazole,[18] and 20 mL of CH_3CN. Each capped vial was microwaved at 100 °C for 45 min and then was cooled in a freezer (−13.5 °C). The suspensions of each vial were combined and vacuum filtered. Vacuum drying at 50 °C for 3 d yielded 1.398 g (22%) of white solid salt **3**.

(18) Kaplan, G.; Drake, G.; Tollison, K.; Hall, L.; Hawkins, T. *J. Heterocyclic Chem.* **2005**, *42*, 19.

The chemical structure of bridged salts **1**−**5** demonstrate the flexibilty that these salts provide for systematic structure design to achieve properties modifications that are needed for tailoring chemical performance behavior.[1,2] The unsaturated bond at the bridge center can be varied, the chemical stucture of the tethered heterocyclium cation can be altered, the terminal heterocyclium cations can be changed for another type, and/or the paired anionic species can be exchanged from dihalides to a perfluoroborane, borane, carborane, or a dinitrate.[2]

A second aqueous, open-air, one-step metathesis reacted intermediate salts **1**−**5** with either $K_2[B_{12}F_{12}]$, $K_2[B_{12}H_{12}]$, or $K[CB_{11}H_{12}]$ to produce the 13 new bridged heterocyclium dication *closo*-icosahedral salts of $[B_{12}H_{12}]^{2-}$, $[CB_{11}H_{12}]^{-}$ **6**−**15** (Table 1), and of $[B_{12}F_{12}]^{2-}$ **16**−**18** (Table 2) as solid precipitates. A typical synthesis procedure is given for the [1,4-di(4-amino-1,2,4-triazolium-1*N*)-2-butyne]$[B_{12}F_{12}]$ salt **16**.[19] Detailed data for salts **6**−**18** are found in Supporting Information.

Initially, smaller scale metatheses (47−320 mg of intermediate bridged salts **1**−**5**) were conducted at rt by immediately mixing the two aqueous reactants. To minimize the presence of possible KBr or KCl byproduct residue, subsequent larger scale aqueous metatheses (849−1550 mg) were run at 78−80 °C by a dropwise addition of aqueous $K_2[B_{12}F_{12}]$, $K_2[B_{12}H_{12}]$, or $K[CB_{11}H_{12}]$ solutions to a solution of salts **1**−**5**. After precipitation and filtration, the product salt suspension was digested 30 min at 78−80 °C in fresh deionized water before final isolation.

Because intermediate bridged heterocyclium dichloride salt **4** is a clear dark brown glass-like solid with a hard rock candy texture, weighing the exact mass needed for subsequent aqueous metathesis reactions is difficult. Therefore, the amount of salt **4** needed to synthesize bridged heterocyclium dication salts of $[B_{12}H_{12}]^{2-}$ **12** and $[CB_{11}H_{12}]^{-}$ **13** was prepared individually in two portions.

Isolated yield, density, and melting/decomposition point data for each bridged heterocyclium dication borane, carborane, and perfluoroborane salt are listed in Tables 1 and 2. Pycnometry-determined densities at rt, and predicted values are compared for salts **6**−**15** using a newly developed predictive density additivity code (Table 1).[20] This additivity code predicts an average 3.3% variance from the 10 pycnometry density values despite two unusually large variances with salts **14** and **15**.

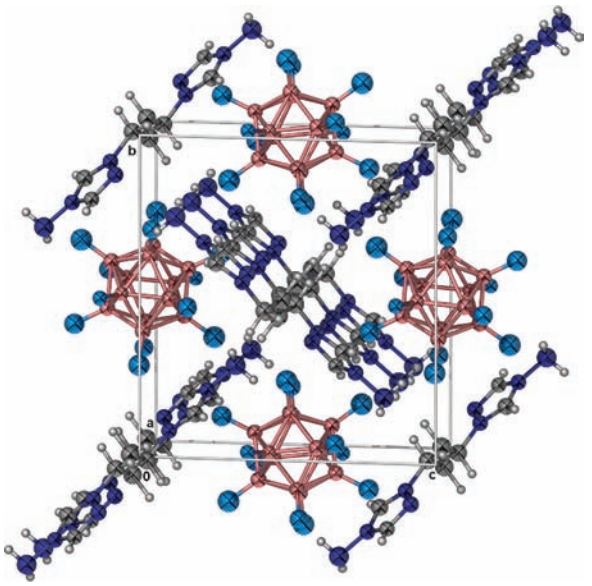

Figure 2. Crystal packing of bridged $[B_{12}F_{12}]$ salt **16** viewed along a slightly tilted crystallographic α-axis.

As expected, bridged [heterocyclium dication]$[B_{12}F_{12}]$ salts **16**−**18** (Table 2) displayed a single crystal X-ray density at rt that is significantly higher than the analogous bridged [heterocyclium dication]$[B_{12}H_{12}]$ and [heterocyclium dication]$[CB_{11}H_{12}]_2$ salts **6**−**15** (Table 1). Limited $K_2[B_{12}F_{12}]$ reactant initially dictated that bridged [heterocyclium dication]$[B_{12}F_{12}]$ salts **16**−**18** be synthesized at rt on a 44−49 mg scale based on reactant salts **1**−**3**. Bridged salts **16** and **18** later were scaled to 773 and 821 mg, respectively, using the 78−80 °C digestion procedure.[19]

The similar densities for the bridged salts **16**−**18** (Table 2) result from the formation of planar perpendicular intersecting bridged [heterocyclium dication]$^{2+}$ layers that alternate with icosahedral $[B_{12}F_{12}]^{2-}$ dianion layers (Figure 2). Therefore, the structure of the unsaturated bridged heterocyclium dication exerts little effect in altering crystal packing and resultant density values.

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Supporting Information Available: Experimental procedures, spectroscopy data, HRMS (all salts), ion chromatography Cl^-/Br^- analyses, melting/decomposition points, single crystal X-ray (salts **16**−**18**). This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] [1,4-Di(4-amino-1,2,4-triazolium)-*trans*-2-butene-1*N*]$B_{12}F_{12}$] **16**. A 50 mL beaker was charged with a Teflon-coated magnetic stir bar and 0.773 g (2.02 mmol) of salt **2** that was dissolved in 4 mL of DI water. Another 50 mL beaker was charged with 0.865 g (1.98 mmol) of $K_2[B_{12}F_{12}]$ that was dissolved in 6 mL of DI water. Both beakers were placed on a hot plate that maintained water at 78−80 °C. The water volume was maintained for 15 min by adding DI water as needed. The aq salt **2** solution was stirred vigorously, and the aq $K_2[B_{12}F_{12}]$ occasionally was swirled. The aq $K_2[B_{12}F_{12}]$ solution was added dropwise to the stirred aq solution of salt **2** with a disposable capillary pipette plus 2 × 1 mL rinses of the aq $K_2[B_{12}F_{12}]$, beaker (9 min total add time). The aq suspension was cooled to rt and placed into a refrigerator (3.0 °C). Vacuum filtration and rinsing of the solid cake with 2 × 1 mL of pre-chilled (3.0 °C) DI water followed. The semi-dried cake was placed in the same 50 mL beaker with the same stir bar, and 6 mL of fresh DI water were added. The stirred suspension was digested at 78−80 °C for 30 min, cooled to rt, and placed into the refrigerator 16 h. Vacuum filtration, rinsing of the solid cake with 2 × 1 mL of pre-chilled DI water, and high vacuum drying to 18 mTorr at rt yielded 1.060 g (92%) of white salt **16**.

[20] Ammon, H. L. *Propellants, Explos., Pyrotech.* **2008**, *33*, 92.