Reactions of N-heterocyclic carbene boranes with 5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione: Synthesis of mono- and bis-hydrazonyl NHC-boranes

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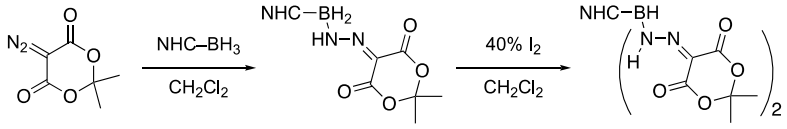


Abstract: N-Heterocyclic carbene boranes (NHC-boranes) react with 5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione at 40 ˚ C in dichloromethane to provide NHC-boryl hydrazone derivatives of 2,2-dimethyl-1,3-dioxane-4,6-dione. These hydrazones disproportionate to bis-hydrazones on treatment with diiodine in dichloromethane at room temperature. The mono- and bis-hydrazones are yellow solids that are stable to chromatography and storage.

Boron-hydrogen bond insertion reactions of ligated-boranes and diazoesters can be catalyzed by both transition metals and borenium ion equivalents. For example, the reaction between 1,3-dimethylimidazol-2-ylidene borane **1** and ethyl 2-phenyldiazoacetate **2** is catalyzed either by addition of rhodium salts (or other transition metal catalysts)[1] or by addition of diiodine (I_2) to form a boryl iodide catalyst (Figure 1a).[2] The product is a stable α-boryl ester **3** that results from B–H insertion with concomitant loss of dinitrogen.

This type of reaction is rather general,[1,2] and succeeds because most ligated-boranes and diazoesters do not spontaneously react with each other. In contrast, many trivalent boranes do react rapidly with diazo compounds, and also give insertion products with loss of dinitrogen.[3]

To date, the single exception to this generalization is the reaction of **1a** with 5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione **4** (Figure 1b).[4] This pair reacts at room temperature and without catalyst to provide boryl hydrazone **5** in 61% isolated yield after purification by automated flash chromatography. This formal 1,1-hydroboration reaction is also a kind of B–H insertion reaction, but dinitrogen is not lost from the diazo compound. Instead, the insertion occurs on the terminal nitrogen, probably by hydride transfer and collapse of the resulting ion pair.

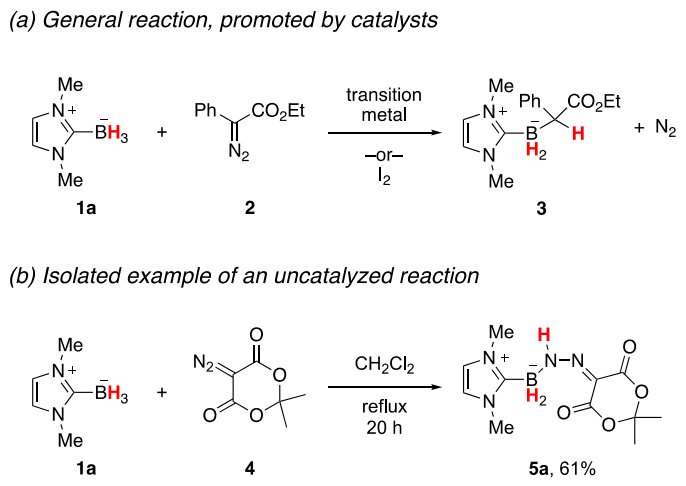
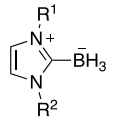
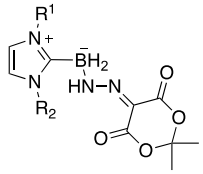
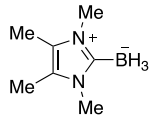
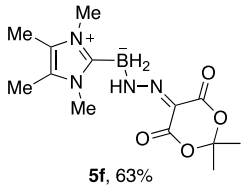
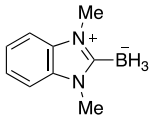
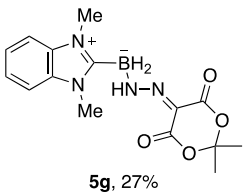


Figure 1. Reactions of NHC-boranes with diazo carbonyl compounds

Here we probe the generality of this B–H insertion reaction at nitrogen, and report that an assortment of other NHC-boranes also participate. We also report that the so formed NHC-boryl mono-hydrazones can be disproportionated to make NHC-boryl *bis*-hydrazones simply by treatment with diiodine (I_2). Members of both classes of products are typically yellow solids that are stable to air, water and chromatographic purification.

Table 1 summaries results of thermal reactions with seven different NHC-boranes with diazo compound **4**. In a typical experiment (entry a), **1a** (1 mmol) and **4** (1.2 mmol) were dissolved in dichloromethane (5 mL), then the resulting solution was warmed to 40 ˚C for 24 h. Cooling, solvent evaporation and automated flash chromatography provided boryl hydrazone **5a** in 57% yield. This is comparable the previously reported yield of 61%.[4]

Table 1. Isolated yields of mono-hydrazonyl boranes **5a**–**g**[a]

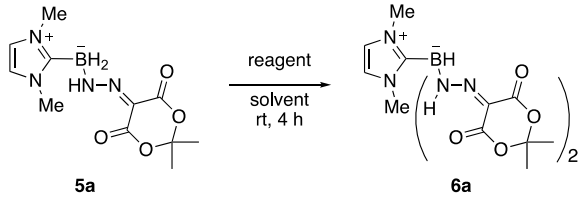
entry	NHC-borane	yield **5**[a,b]
		
a	**1a**, $R^1 = R^2 =$ Me	**5a**, 57%
b	**1b**, R^1 = iPr, R^2 = Me	**5b**, 54%
c	**1c**, $R^1 = R^2$ = iPr	**5c**, 59%
d	**1d**, R^1 = Bu, R^2 = Me	**5d**, 62%
e	**1e**, R^1 = Bn, R^2 = Me	**5e**, 55%
		
f	**1f**	**5f**, 63%
		
g	**1g**	**5g**, 27%

a) conditions: 1 mmol NHC-borane **1**, 1.2 mmol **4**, 5 mL CH_2Cl_2;
b) isolated yield after flash chromatography

1,3-Dialkylimidazol-2-ylidene boranes **1b**–**1e** with assorted alkyl groups (Me, iPr, Bu, Bn) provided stable boryl hydrazones **5b**–**e** in isolated yields ranging from 54–62% (entries b–e). Likewise, reaction of 1,3,4,5-tetramethylimidazol-2-ylidene borane **2f** with **4** gave **5f** in 63% yield (entry f). In contrast, the yield of **5g** in the reaction with benzimidazol-2-ylidene borane **1g** decreased to 27% (entry g). All of the new boryl hydrazones **5b**–**g** are stable yellow solids.

Rapid reaction with diiodine is one of the quintessential reactions of NHC-boranes.[5] When we reacted boryl hydrazone **5a** with diiodine, we did not observe an electrophlic iodination product (NHC-boryl iodide), but instead saw formation of a disproportionated bis-hydrazone **6a**. The results of several scouting experiments to improve the yield of **6a** are summarized in Table 2. Solid diiodine (40 mol%) was added in portions to a solution of **5a** (0.1 mmol) in dichloromethane (1.5 mL) at room temperature. After 5 h, the mixture was concentrated and residue was purified by automated flash chromatography to give bis-hydrazone **6a** in 66% yield (entry 1).

Table 2. Survey of reaction conditions to make **6a**



5a **6a**

entry	reagent	solvent	yield **6a**[a]
1	40% I_2	CH_2Cl_2	66%
2[b]	40% I_2	CH_2Cl_2	68%
3	30% I_2	CH_2Cl_2	52%
4	50% I_2	CH_2Cl_2	40%
5	40% I_2	toluene	–[c]
6	40% I_2	THF	–[c]
7	40% I_2	EtOAc	–[c]
8	40% I_2	CH_3OH	–[c]
9	40% Br_2	CH_2Cl_2	–[c]

a) isolated yield after flash chromatography;
b) reaction time = 6 h; c) little or no **6a** formed

About the same isolated yield of **6a** was obtained when the time of a reaction with 40% diiodine was extended from 4 h to 6 h (68%, entry 2). Modest decreases in isolated yield were observed at 4 h when the amount of diiodine was decreased to 30 mol% or increased to 50 mol% (52% and 40%, entries 3 and 4). Other solvents including toluene, THF, ethyl acetate and

methanol were not good media for the reaction (entries 5–8). Likewise, the combination of 40% dibromine in dichloromethane was ineffective (entry 9).

The structure of **6a** was clear from its ^{1}H and ^{13}C NMR spectra, which were generally similar to those of **5a** except that the hydrazone resonances were two times larger than the NHC-borane resonances. In the ^{11}B NMR spectrum, the resonance of **6a** (–8 ppm) is about 11 ppm downfield from **5a** (–19 ppm), but this resonance is too broad to discern a multiplicity or coupling constant. This broadening is normal for NHC-boranes with large substituents.[6] The bis-hydrazone **6a** also exhibited satisfactory HRMS data (*m/z* $[M + Na]^+$ calculated for $C_{17}H_{23}BN_6O_8Na$ 473.1568, found 473.1566).

Finally, the structure of **6a** was confirmed by X-ray crystallography, and Figure 2 shows the resulting ORTEP diagram. The boron atom in this structure is tetrahedral, with the B–H bond lying roughly in the plane of the NHC ring and the hydrazones above and below that plane. The hydrazones are also planar, and both of the N–N bonds are *anti*-configured.

Figure 2. ORTEP diagram of the X-ray crystal structure of **6a** (elipsoid contour plotted at 50% probability level)

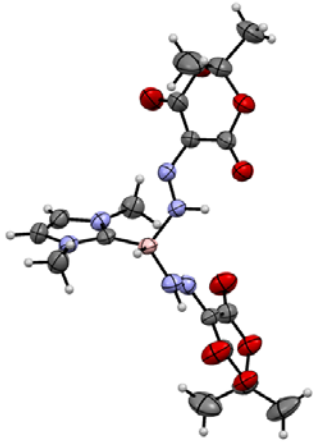
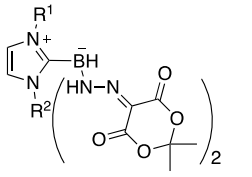
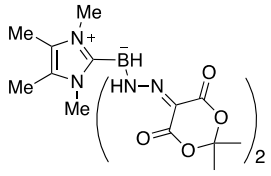


Figure 3 summarizes the preparative results of reactions of all the boryl hydrazones **5b**–**g** with diiodine under the preferred conditions of Table 2, entry 1 (40% I_2, CH_2Cl_2, 25 ˚C, 4 h). The isolated yields of **6a**–**g** are calculated based on the hydrazone component of precursors **5a**–**g**, and are rather consistent (60–76%). The bis-hydrazone **6b** (R^1 = Me, R^2 = iPr) is a yellow oil, while the rest of the products are yellow solids. Again, all of these compounds are stable and can be stored without special precautions.

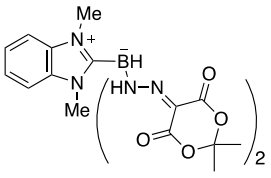
Figure 3. Isolated yields in reactions to form *bis*-hydrazones **6** from **5** (conditions: 0.1 mmol **5**, 0.04 mmol I_2, 1.5 mL CH_2Cl_2)



6b, R^1 = iPr, R^2 = CH_3 70%
6c, R^1 = R^2 = iPr, 72%
6d, R^1 = Bu, R^2 = CH_3, 76%
6e, R^1 = Bn, R^2 = CH_3, 76%



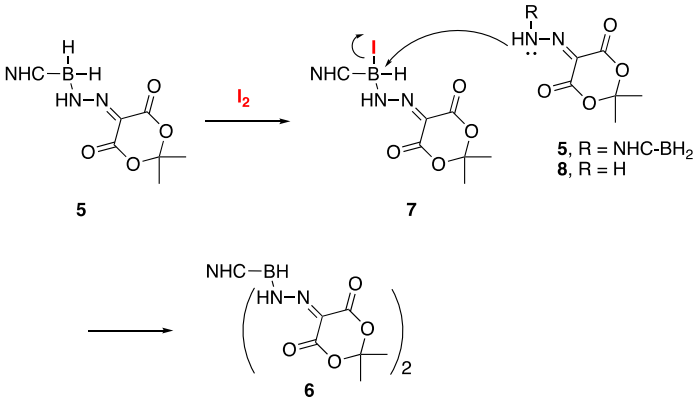
6f, 60%



6g, 60%

A possible mechanism for the iodine promoted disproportionation reaction is shown in Scheme 1. The reaction of **5** with I_2 is expected to provide two molecules of boryl iodide **7** and dihydrogen.[5] Nucleophilic substitution of **7** by starting boryl hydrazone **5** (R = NHC) may then occur to give the bis-hydrazone **6**. Alternatively, free hydrazone **8** (R = H) was isolated in small amounts from some experiments (see Supporting Information), so it may also be involved as a nucleophile.

Scheme 1. Possible mechanism for formation of **6**



In summary, NHC-boranes react with 5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione at 40 ˚C in dichloromethane to provide NHC-boryl hydrazone derivatives of 2,2-dimethyl-1,3-dioxane-4,6-dione. These *mono*-hydrazones disproportionate to *bis*-hydrazones on treatment with diiodine in dichloromethane at room temperature. The *mono*- and *bis*-hydrazones are yellow solids that are stable to chromatography and storage.

Experimental

General Experimental Information: All reactions were carried out under an inert argon atmosphere with dry solvents under anhydrous conditions unless otherwise stated. Dry dichloromethane (DCM) and toluene were obtained by passing the solvents through activated alumina. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under an argon atmosphere. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Thin layer chromatography (TLC) was performed on commercial silica gel plates and flash column chromatography was performed with 230–400 mesh silica gel cartridge. Visualization of TLC achieved using ultraviolet light (254 nm). Nuclear magnetic resonance spectra (NMR) were obtained on 400 MHz and 500 MHz

instruments. Chloroform (δ 7.26 ppm) was used as an internal standard for ^{1}H NMR spectra and $CDCl_3$ (δ 77.00 ppm) was used as an internal standard for ^{13}C NMR spectra. ^{11}B chemical shifts are relative to Et_2O-BF_3. Resonances of hydrogen or carbon atoms bonded to the boron atom are weak (sometimes absent) in both ^{1}H or ^{13}C NMR spectra. HRMS were obtained with a Q-Tof analyzer.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)dihydroborate (5a): (1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)trihydroborate **1a** (111.0 mg, 1.0 mmol) and diazo 2,2-dimethyl-1,3-dioxane-4,6-dione **4** (204.1 mg, 1.2 mmol) were dissolved in dry dichloromethane (5 mL). The reaction mixture was stirred at 40 ºC. After 24 h, the reaction mixture was concentrated under vacuum and purified by flash chromatography (hexane:ethyl acetate) to afford **5a** as a yellow solid (160 mg, 57%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.36 (s, 1H), 6.90 (s, 2H), 3.78 (s, 6H), 1.62 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 161.0, 121.5, 110.9, 103.8, 36.6, 27.0; ^{11}B NMR (160 MHz, $CDCl_3$) δ –18.7 (br t); HRMS (ESI) *m/z* $[M+H]^+$ calculated for $C_{11}H_{18}BN_4O_4$ 281.1423, found 281.1426.

(2-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)(3-isopropyl-1-methyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5b): Reaction of ((3-isopropyl-1-methyl-1*H*-imidazol-3-ium-2-yl)trihydroborate **1b** (138.0 mg, 1.0 mmol) and diazo 2,2-dimethyl-1,3-dioxane-4,6-dione **4** (204.1 mg, 1.2 mmol) according to the same procedure for synthesizing **5a** afforded **5b** as a yellow solid (166.4 mg, 54%), mp 186–189 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.39 (s, 1H), 6.99 (d, J = 2.0 Hz, 1H), 6.92 (d, J = 2.0 Hz, 1H), 4.98 (hept, J = 6.8 Hz, 1H), 3.78 (s, 3H), 1.62 (s, 6H), 1.37 (d, J = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 161.1, 122.1, 116.1, 111.0, 103.8, 50.7, 36.4, 27.0, 23.120; ^{11}B NMR (160 MHz, $CDCl_3$) δ –18.7 (br t); HRMS (ESI) *m/z* $[M+H]^+$ calculated for $C_{13}H_{22}BN_4O_4$ 309.1737, found 309.1744.

(1,3-Diisopropyl-1*H*-imidazol-3-ium-2-yl)(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)dihydroborate (5c): Reaction of (1,3-diisopropyl-1*H*-imidazol-3-ium-2-yl)trihydroborate **1c** (166.0 mg, 1.0 mmol) and diazo 2,2-dimethyl-1,3-dioxane-4,6-dione **4** (204.1 mg, 1.2 mmol) according to the same procedure for synthesizing **5a** afforded **5c** as a yellow solid (199.0 mg, 59%), mp 148–151 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.41 (s, 1H), 7.01 (s, 2H), 5.03 (hept, *J* = 6.7 Hz, 2H), 1.61 (s, 6H), 1.37 (d, *J* = 6.7 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 161.2, 116.6, 111.0, 103.7, 50.3, 26.9, 23.2; ^{11}B NMR (160 MHz, $CDCl_3$) δ –18.8 (s); HRMS (ESI) *m/z* $[M+Na]^+$ calculated for $C_{15}H_{25}BN_4O_4Na$ 359.1869, found 359.1878.

(3-Butyl-1-methyl-1*H*-imidazol-3-ium-2-yl)(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)dihydroborate (5d): Reaction of (3-butyl-1-methyl-1*H*-imidazol-3-ium-2-yl)trihydroborate **1d** (152.0 mg, 1.0 mmol) and diazo 2,2-dimethyl-1,3-dioxane-4,6-dione **4** (204.1 mg, 1.2 mmol) according to the same procedure for synthesizing **5a** afforded **5d** as a yellow solid (200.0 mg, 62%), mp 103–105 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.43 (s, 1H), 6.99 (d, *J* = 2.4 Hz, 2H), 4.16 (t, *J* = 7.5 Hz, 2H), 3.84 (s, 3H), 1.78–1.70 (m, 2H), 1.68 (s, 6H), 1.32 (sext, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 161.0, 121.8, 120.1, 110.9, 103.8, 49.1, 36.4, 32.7, 26.9, 19.6, 13.5; ^{11}B NMR (160 MHz, $CDCl_3$) δ –18.7 (s); HRMS (ESI) *m/z* $[M+H]^+$ calculated for $C_{14}H_{24}BN_4O_4$ 323.1893, found 323.1901.

(3-Benzyl-1-methyl-1*H*-imidazol-3-ium-2-yl)(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)dihydroborate (5e): Reaction of (3-benzyl-1-methyl-1*H*-imidazol-3-ium-2-yl)trihydroborate **1e** (186.1 mg, 1.0 mmol) and diazo 2,2-dimethyl-1,3-dioxane-4,6-dione **4** (204.1 mg, 1.2 mmol) according to the same procedure for synthesizing **5a** afforded **5e** as a

yellow solid (196.0 mg, 55%), mp 134–136 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.41 (s, 1H), 7.38–7.30 (m, 3H), 7.25–7.21 (m, 2H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 5.38 (s, 2H), 3.86 (s, 3H), 1.67 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 161.0, 135.0, 129.1, 128.5, 128.1, 122.2, 120.3, 111.0, 103.8, 52.6, 36.5, 27.0; ^{11}B NMR (160 MHz, $CDCl_3$) δ –18.6 (s); HRMS (ESI) *m/z* $[M+H]^+$ calculated for $C_{17}H_{22}BN_4O_4$ 357.1737, found 357.1742.

(2-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)(1,3,4,5 tetramethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (5f): Reaction of (1,3,4,5-tetramethyl-1*H*-imidazol-3-ium-2-yl)trihydroborate **1f** (138.0 mg, 1.0 mmol) and diazo 2,2-dimethyl-1,3-dioxane-4,6-dione **4** (204.1 mg, 1.2 mmol) according to the same procedure for synthesizing **5a** afforded **5f** as a yellow solid (194.2 mg, 63%), mp 170–172 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.48 (s, 1H), 3.71 (s, 6H), 2.19 (s, 6H), 1.71 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9, 161.1, 124.8, 110.8, 103.7, 33.0, 26.9, 14.2, 8.4; ^{11}B NMR (160 MHz, $CDCl_3$) δ –18.4 (s); HRMS (ESI) *m/z* $[M+H]^+$ calculated for $C_{13}H_{22}BN_4O_4$ 309.1737, found 309.1744.

(1,3-Dimethyl-1*H*-benzo[d]imidazol-3-ium-2-yl)(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl) (5g): Reaction of (1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium-2-yl)trihydroborate **1g** (160.0 mg, 1.0 mmol) and diazo 2,2-dimethyl-1,3-dioxane-4,6-dione **4** (204.1 mg, 1.2 mmol) according to the same procedure for synthesizing **5a** afforded **5g** as a yellow solid (89.0 mg, 27%), mp 173–176 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.42 (s, 1H), 7.52–7.46 (m, 2H), 7.43 (m, 2H), 3.99 (s, 6H), 1.62 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 160.0, 132.1, 124.2, 110.6, 110.3, 104.5, 102.9, 31.9, 26.5, 26.0; ^{11}B NMR (160 MHz, $CDCl_3$) δ –18.4 (s); HRMS (ESI) *m/z* $[M+Na]^+$ calculated for $C_{15}H_{19}BN_4O_4Na$ 353.1400, found 353.1405.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)bis(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)hydroborate (6a): Iodine (I_2, 10.0 mg, 0.04 mmol) was added in portions to a solution of **5a** (28.0 mg, 0.1 mmol) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at room temperature for 4 h, then concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane:ethyl acetate) to afford **6a** as yellow solid (15.0 mg, 66%), mp 186–189 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.20 (s, 2H), 7.02 (s, 2H), 3.94 (s, 6H), 1.75 (s, 6H), 1.73 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 160.4, 122.9, 113.6, 104.7, 37.6, 27.3, 27.3; ^{11}B NMR (160 MHz, $CDCl_3$) δ –8.2; HRMS (ESI) *m/z* $[M+Na]^+$ calculated for $C_{17}H_{23}BN_6O_8Na$ 473.1568, found 473.1566.

Bis(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)(3-isopropyl-1-methyl-1*H*-imidazol-3-ium-2-yl)hydroborate (6b): Iodine (I_2, 10.0 mg, 0.04 mmol) was added in portions to a solution of **5b** (31.0 mg, 0.1 mmol) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at room temperature for 4 h, then concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane:ethyl acetate) to afford **6b** as yellow oil (16.8 mg, 70%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.27 (s, 2H), 7.14 (d, *J* = 1.65 Hz, 2H), 7.05 (d, *J* = 1.45 Hz, 2H), 4.99 (hept, J = 6.7 Hz, 1H), 3.92 (s, 3H), 1.74 (s, 6H), 1.73 (s, 6H), 1.45 (d, *J* = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 160.5, 123.7, 117.1, 113.6, 104.6, 51.4, 37.5, 27.3, 27.2, 23.3; ^{11}B NMR (160 MHz, $CDCl_3$) δ –8.6; HRMS (ESI) *m/z* $[M-H]^+$ calculated for $C_{19}H_{26}BN_6O_8$ 477.1909, found 477.1920.

(1,3-Diisopropyl-1*H*-imidazol-3-ium-2-yl)bis(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)hydroborate (6c): Iodine (I_2, 10.0 mg, 0.04 mmol) was added in portions to a solution of **5c** (33.6 mg, 0.1 mmol) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at room temperature for 4 h, then concentrated under reduced pressure. The crude residue was

purified by flash chromatography (hexane:ethyl acetate) to afford **6c** as yellow solid (18.2 mg, 72%), mp 178–181 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.31 (s, 2H), 7.18 (s, 2H), 4.99 (hept, *J* = 6.6 Hz, 2H), 1.74 (s, 6H), 1.73 (s, 6H), 1.45 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 160.6, 117.8, 113.6, 104.5, 51.2, 27.3, 27.2, 23.4; ^{11}B NMR (160 MHz, $CDCl_3$) δ –8.0; HRMS (ESI) *m/z* $[M-H]^+$ calculated for $C_{21}H_{30}BN_6O_8$ 505.2218, found 505.2244.

(3-Butyl-1-methyl-1*H*-imidazol-3-ium-2-yl)bis(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)hydroborate (6d): Iodine (I_2, 10.0 mg, 0.04 mmol) was added in portions to a solution of **5d** (32.2 mg, 0.1 mmol) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at room temperature for 4 h, then concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane:ethyl acetate) to afford **6d** as yellow solid (18.7 mg, 76%), mp 160–163 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.22 (s, 2H), 7.04 (d, *J* = 1.55 Hz, 2H), 4.21 (t, *J* = 7.5 Hz, 2H), 3.95 (s, 3H), 1.74 (s, 6H), 1.72 (s, 6H), 1.32 (sext, *J* = 7.5 Hz, 2H), 0.92 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 160.5, 123.3, 121.1, 113.5, 104.6, 49.8, 37.7, 32.9, 27.3, 27.2, 19.6, 13.5; ^{11}B NMR (160 MHz, $CDCl_3$) δ –8.0; HRMS (ESI) *m/z* $[M+H]^+$ calculated for $C_{20}H_{30}BN_6O_8$ 493.2222, found 493.2245.

(3-Benzyl-1-methyl-1*H*-imidazol-3-ium-2-yl)bis(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)hydroborate (6e): Iodine (I_2, 10.0 mg, 0.04 mmol) was added in portions to a solution of **5e** (35.6 mg, 0.1 mmol) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at room temperature for 4 h, then concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane:ethyl acetate) to afford **6e** as yellow solid (20.0 mg, 76%), mp 181–183 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.16 (s, 2H), 7.34 (m, 3H), 7.20 (d, *J* = 7.1, 2H), 7.02 (s, 1H), 6.90 (s, 1H), 5.45 (s, 2H), 3.97 (s, 3H), 1.72 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 160.4, 134.2, 129.2, 128.8, 128.3, 128.0, 123.3, 121.5, 113.6, 104.6, 53.3,

37.6, 27.30, 27.25; ^{11}B NMR (160 MHz, $CDCl_3$) δ –8.0; HRMS (ESI) *m/z* $[M+H]^+$ calculated for $C_{23}H_{28}BN_6O_8$ 527.2066, found 527.2081.

Bis(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)(1,3,4,5-tetramethyl-1*H*-imidazol-3-ium-2-yl)hydroborate (6f): Iodine (I_2, 10.0 mg, 0.04 mmol) was added in portions to a solution of **5f** (30.8 mg, 0.1 mmol) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at room temperature for 4 h., then concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane:ethyl acetate) to afford **6f** as yellow solid (14.4 mg, 60%), mp 126–129 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.25 (s, 2H), 3.74 (s, 6H), 2.20 (s, 6H), 1.74 (s, 6H), 1.72 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 160.5, 126.3, 113.3, 104.6, 33.8, 27.3, 27.2; ^{11}B NMR (160 MHz, $CDCl_3$) δ –8.0; IR (film) HRMS 3140, 2985, 2415, 1732, 1672, 1504, 1373, 1263, 1194, 1062, 869, 728, 635 cm^{-1}; (ESI) *m/z* $[M-H]^+$ calculated for $C_{19}H_{26}BN_6O_8$ 477.1909, found 477.1916.

(1,3-Dimethyl-1*H*-benzo[*d*]imidazol-3-ium-2-yl)bis(2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)hydroborate (6g): Iodine (I_2, 10.0 mg, 0.04 mmol) was added in portions to a solution of **5g** (33.0 mg, 0.1 mmol) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at room temperature for 4 h, then concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane:ethyl acetate) to afford **6g** as yellow solid (15.0 mg, 60%), mp 196–189 ˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.29 (s, 2H), 7.60 (m, 2H), 7.57 (m, 2H), 4.14 (s, 6H), 1.75 (s, 6H), 1.72 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 133.2, 126.0, 113.9, 112.1, 104.7, 33.7, 27.34, 27.27; ^{11}B NMR (160 MHz, $CDCl_3$) δ –7.9; HRMS (ESI) *m/z* $[M+H]^+$ calculated for $C_{21}H_{26}BN_6O_8$ 501.1909, found 501.1929.

Isolation of 5-Hydrazono-2,2-dimethyl-1,3-dioxane-4,6-dione (8): Iodine (I_2, 10.0 mg, 0.04 mmol) was added in portions to a solution of **5a** (28.0 mg, 0.1 mmol) in CH_2Cl_2 (1.5 mL).

The reaction mixture was stirred at room temperature for 4 h. The mixture was concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane:ethyl acetate) to afford **8** as white solid (3.2 mg, 18%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.64 (d, J = 16.7 Hz, 1H), 9.34 (d, J = 15.2 Hz, 1H), 1.79 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 159.7, 114.1, 105.8, 27.55; HRMS (ESI) *m/z* $[M+H]^+$ calculated for $C_6H_9N_2O_4$ 173.0562, found 173.0554.

ASSOCIATED CONTENT

Supporting Information

Contains copies of NMR spectra of all reaction products. The Supporting Information is available free of charge on the ACS Publications website.

Copies of spectra (PDF)

Cif file of crystal structure of **6a**

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