Energetic Materials

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$[BH_3C(NO_2)_3]^-$: The First Room-Temperature Stable (Trinitromethyl)borate**

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Ever since the first report on the trinitromethanide, or "nitroformate" anion, $[C(NO_2)_3]^-$,[1] trinitromethyl derivatives have been a subject of significant interest.[2,3] The usefulness of the nitroformate anion and of the parent molecule, nitroform ($HC(NO_2)_3$), as reagents[4] and the high oxygen balance of the trinitromethyl moiety make these types of compounds attractive candidates for environmentally friendly high-energy density material (HEDM) applications. A major challenge in trinitromethyl chemistry is the limited thermal stability of many of the compounds.[2d,5–7]

In view of the relatively high average bond energy of B–C bonds (ca. 89 kcal mol^{-1}),[8] (trinitromethyl)borates can be expected to be stable compounds. In addition, the low atomic weight of boron, the low toxicity, and the high formation enthalpy of $B_2O_{3(g)}$ (−200 kcal mol^{-1})[9] would make (trinitromethyl)borates interesting prospects for green HEDMs.[10] The goal of this study was to explore methods for the stabilization of trinitromethyl substituted boron compounds.

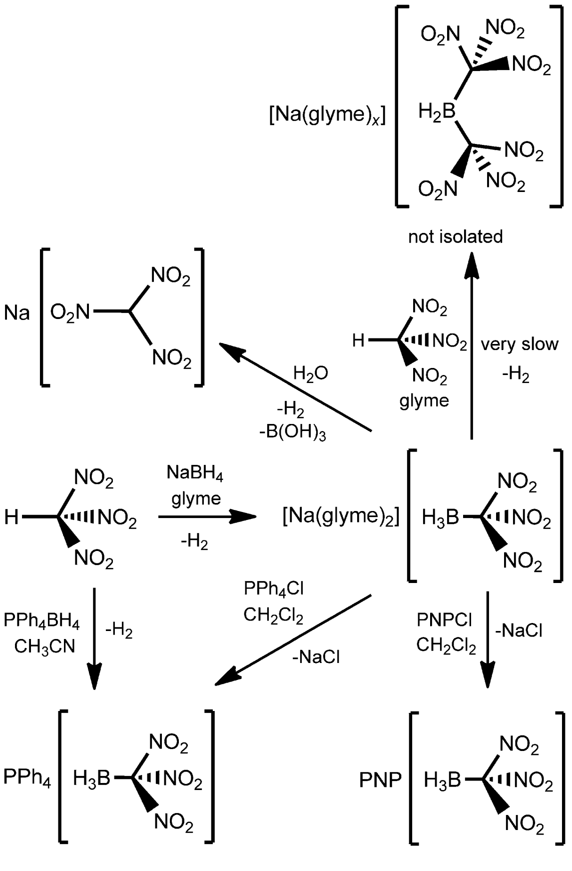
Surprisingly, only one previous report was found on the synthesis of group 13-trinitromethyl compounds. Titova et al. studied the reaction of BCl_3 with $[NR_4][C(NO_2)_3]$ salts and $[NR_4][BCl_4]$ salts with $Ag[C(NO_2)_3]$. They characterized salts of the postulated $[BCl_3C(NO_2)_3]^-$ ion and observed its decomposition at −20 °C to BCl_3 and $[C(NO_2)_3]^-$ and at 20 °C, to BCl_4^- and N_2O_4. At lower temperatures, a marginally stable solid was obtained and studied by IR spectroscopy.[6]

Since highly Lewis acidic fragments, such as BCl_3, are known to induce the decomposition of oxygen rich ligands,[10a,11] it was interesting to study whether the use of less Lewis acidic groups,[12] such as BH_3,[10a,c,d] might provide kinetically more stable (trinitromethyl)borates. Herein, we report the synthesis and structural characterization of $[BH_3C(NO_2)_3]^-$, the first stable (trinitromethyl)borate anion, and the detection of $[BH_2\{C(NO_2)_3\}_2]^-$ in solution.

In solution, the $[BH_3C(NO_2)_3]^-$ ion is formed by the elimination of H_2 from the reaction between the acidic proton of nitroform ($pK_a = 0.17$ at 20 °C in water)[13] and a hydrido ligand of BH_4^- [Eq. (1)]

$$[BH_4]^- + HC(NO_2)_3 \rightarrow [BH_3C(NO_2)_3]^- + H_2 \qquad (1)$$

Scheme 1 summarizes the reaction conditions for the formation of the various (trinitromethyl)borate salts and hydrolysis products. The best conditions for the synthesis of the (trinitromethyl)borate anion were the use glyme (1,2-dimethoxyethane) as solvent and of a 10 mol % excess of nitroform. The multinuclear NMR spectra[14] of the $[BH_3C(NO_2)_3]^-$ anion are given in Figure 1 and in the Supporting Information.



Scheme 1. Synthesis of $[BH_3C(NO_2)_3]^-$ salts (PNP = $[Ph_3P{=}N{=}PPh_3]^+$).

Although the monosubstituted ion, $[BH_3C(NO_2)_3]^-$, was the main product, even when a fourfold excess of nitroform

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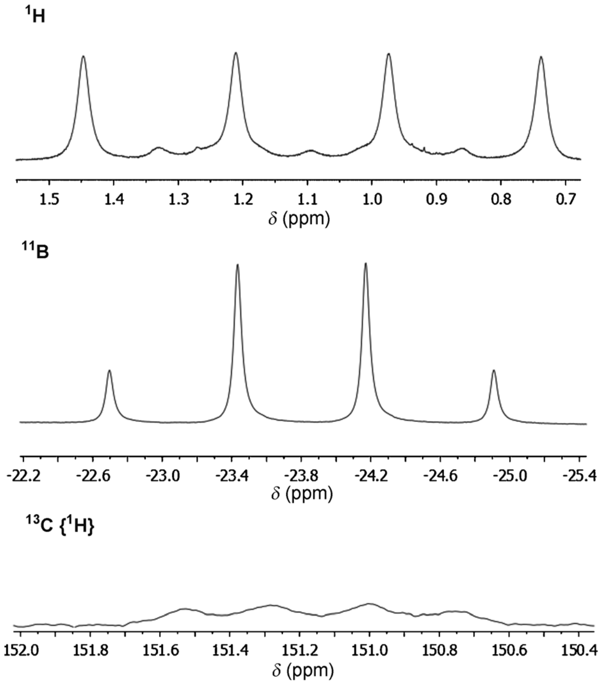


Figure 1. Multinuclear NMR spectra of $[BH_3C(NO_2)_3]^-$ measured in CD_3CN for ^{1}H and ^{11}B and in glyme for ^{13}C.

was used in the reaction, small amounts of the disubstituted anion, $[BH_2\{C(NO_2)_3\}_2]^-$, were also detected by ^{11}B and ^{14}N NMR spectroscopy[15] after one to two days. The formation of $[BH_2\{C(NO_2)_3\}_2]^-$ can be suppressed by extraction of the excess nitroform shortly after $[BH_3C(NO_2)_3]^-$ has been formed. The slower formation of $[BH_2\{C(NO_2)_3\}_2]^-$ indicates that the strong electron-withdrawing effect of the nitroformate ligand decreases the hydridic character and reactivity of the remaining H-substituents in $[BH_3C(NO_2)_3]^-$. However, these H-substituents still possess hydridic character, as demonstrated by the formation of $[C(NO_2)_3]^-$ and boric acid upon exposure of $[BH_3C(NO_2)_3]^-$ to water (Scheme 1).

The sodium salt of $[BH_3C(NO_2)_3]^-$, obtained as a green-yellow powder, contained two glyme molecules per sodium atom, which could only be removed under a dynamic vacuum at room temperature. The removal of glyme from $[Na(glyme)_2][BH_3C(NO_2)_3]$ favored the dissociation of the BH_3-nitroformate adduct and generated significant amounts of sodium nitroformate.

Since no crystals of the sodium salt of $[BH_3C(NO_2)_3]^-$ could be obtained, the PPh_4^+ and PNP^+ (bis(triphenylphosphoranylidene)ammonium) salts of $[BH_3C(NO_2)_3]^-$ were prepared by a metathetical reaction of glyme/dichloromethane solutions of $Na[BH_3C(NO_2)_3]$ with PPh_4Cl and PNPCl, respectively (Scheme 1). The compounds were obtained as neat, pale yellow and orange-yellow solids, respectively, by pumping off the solvent for 12 to 48 h between −40 and 0 °C. Crystalline materials were obtained from dichloromethane/pentane solutions, but only the PNP salt yielded X-ray quality crystals. All solids were characterized by IR and Raman spectroscopy, as well as by solution NMR spectroscopy. The observed spectra agree well with those predicted by DFT calculations (see Supporting Information).

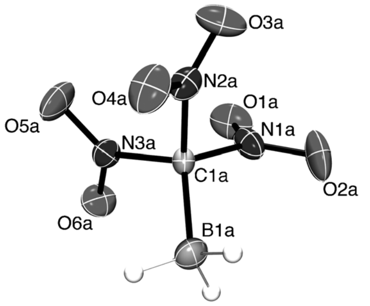


Figure 2. ORTEP plot for one of the two symmetry-independent anions in the asymmetric unit of $PNP[BH_3C(NO_2)_3]$. Thermal ellipsoids are set at 50% probability (hydrogen atom positions are idealized). Selected structural parameters with M06-2X/aug-cc-pVTZ calculated values in parentheses: Bond lengths [Å] and angles [°]: B1a–C1a 1.629(3) (B–C 1.645), C1a–N3a 1.513(2), C1a–N1a 1.517(2), C1a–N2a 1.527(2) (C–N 1.523), N1a–O1a 1.215(3), N1a–O2a 1.220(3), N2a–O3a 1.223(2), N2a–O4a 1.211(2), N3a–O5a 1.225(2), N3a–O6a 1.215(2) (N–O 1.201; 1.210); O1a-N1a-O2a 125.1(2), O6a-N3a-O5a 125.82(18), O4a-N2a-O3a 124.98(19) (O-N-O 125.75).

$PNP[BH_3C(NO_2)_3]$ crystallizes in the monoclinic space group $P2_1/n$ with two symmetry-independent formula units in the unit cell. One of the two $[BH_3C(NO_2)_3]^-$ ions is shown in Figure 2. The anions display a pseudo-tetrahedral arrangement of a $-BH_3$ and three nitro groups around the carbon atom. The nitro groups are arranged in a propeller-like fashion, as has been observed for trinitroethanol[16] and nitroform.[17] The observed geometries and conformations of the NO_2 groups in $[BH_3C(NO_2)_3]^-$ are in excellent agreement with those predicted by M06-2X/aug-cc-pVTZ calculations (Figure 2, also see Supporting Information). Only B-C connectivity is observed in $[BH_3C(NO_2)_3]^-$, in contrast to some organic nitroformates where both $-C(NO_2)_3$ and $-O-N(O)-C(NO_2)_2$ linkages have been observed.[18]

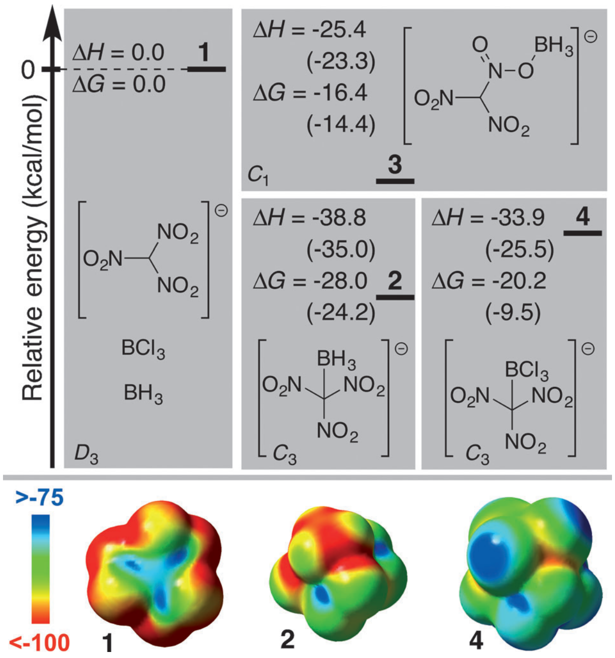
None of the salts, $PPh_4[BH_3C(NO_2)_3]$, $PNP[BH_3C(NO_2)_3]$, or $[Na(glyme)_2][BH_3C(NO_2)_3]$ could be detonated by hitting them with a hammer or by vigorously scraping them with a metal spatula, while exposure to the flame of a Bunsen burner resulted in deflagrations.

In an inert atmosphere, salts of $[BH_3C(NO_2)_3]^-$ can be stored for months without any decomposition when kept at −20 °C, both in the solid state and in solution. At room temperature, however, a slow decomposition to the nitroformate anion was observed for the solid PNP^+ and PPh_4^+ salts. However, this decomposition was so slow that, even after several months, $[BH_3C(NO_2)_3]^-$ was still the major species. The solid $[Na(glyme)_2][BH_3C(NO_2)_3]$ salt was much less stable and completely decomposed within a week at room temperature. Its instability at ambient temperature might be due to an inherent loss of glyme resulting in the formation of the naked sodium $[BH_3C(NO_2)_3]^-$ salt which, by analogy with naked sodium nitroformate, might possess only marginal stability at room temperature.[5] The lower stability of alkali-metal salts compared to salts containing bulky cations, such as PPh_4^+ and PNP^+, is common and has been observed by us for many polyazido salts.[19]

The very slow decomposition of solid $PPh_4[BH_3C(NO_2)_3]$ and $PNP[BH_3C(NO_2)_3]$ at room temperature contrasts with the differential thermal analysis (DTA) results, which show that the compounds seem to be thermally stable up to approximately 120 °C. This apparent difference might be due to the very fast heating rates typically used for DTA measurements and/or to potential photolytic instability of the complex anion, which exhibits absorptions between 200 and 400 nm in the UV/Vis spectrum.[20]

The successful synthesis of $[BH_3C(NO_2)_3]^-$ as room temperature stable $PPh_4[BH_3C(NO_2)_3]$ and $PNP[BH_3C(NO_2)_3]$ salts contrasts with the reported instability of $[NR_4][BCl_3C(NO_2)_3]$.[6] Consequently, we have carried out quantum mechanical (QM) calculations using basis set extrapolated CCSD(T) and M06-2X DFT methods to explore the relative strengths of the C–BH_3 and C–BCl_3 bonds and analyze possible decomposition pathways.

Our theoretical predictions agree with the observed significantly higher stability of $[BH_3C(NO_2)_3]^-$ relative to that of $[BCl_3C(NO_2)_3]^-$ with respect to dissociation (Scheme 2).



Scheme 2. Top: Relative energies of $C(NO_2)_3^-$, $[BH_3C(NO_2)_3]^-$, $[H_3BO\text{-}N(O)\text{-}C(NO_2)_2]^-$, and $[BCl_3C(NO_2)_3]^-$ in the gas phase and in acetonitrile solution (1 M, in parenthesis) shown in kcal mol^{-1}. Bottom: Electrostatic surface potentials (ESPs) plotted on constant 0.001 e/bohr^3 electron density isosurfaces, derived from M06-2X/aug-cc-pVTZ wave functions in vacuum.

The adiabatic enthalpies of dissociation in acetonitrile solution of $[BCl_3C(NO_2)_3]^-$ (25.5 kcal mol^{-1}) and $[BH_3C(NO_2)_3]^-$ (35.0 kcal mol^{-1}) differ by 10 kcal mol^{-1}. Assuming these values to represent the decomposition barriers and assuming first-order decomposition kinetics, a difference of 10 kcal mol^{-1} corresponds to a 9 million-fold rate difference at ambient conditions. This is in good agreement with the experimental observations, which show significant dissociation of $[BCl_3C(NO_2)_3]^-$ already at −20 °C[6] while, based on our DTA results, $[BH_3C(NO_2)_3]^-$ is stable up to about 120 °C.

The energy of the $[H_3BO\text{-}N(O)\text{-}C(NO_2)_2]^-$ isomer (**3**) is predicted to be roughly 10 kcal mol^{-1} higher than that of $[BH_3C(NO_2)_3]^-$ (Scheme 2). This explains why, contrary to some organic derivatives of nitroformates,[18] no mixture of isomers is observed.

The relatively low adiabatic dissociation enthalpy of 25.5 kcal mol^{-1} of $[BCl_3C(NO_2)_3]^-$ explains its dissociation even at low temperature. It should be understood that this value does not imply that the B–C bond strength in this anion has such a low value, because B–C bonds generally have considerably larger than 20 to 30 kcal mol^{-1}.[8] The reason for this low value is the fact that adiabatic dissociation energies can contain very large contributions from reorganization energies of the products. Reorganization energies have negative signs[21] and, therefore, decrease the value of the dissociation energy. In the case of the dissociation of the $[BX_3C(NO_2)_3]^-$ ions, the structures of the two fragments, BX_3 and $[C(NO_2)_3]^-$, are reorganized from tetrahedral to planar.

A second interesting aspect is the fact that the B–C bond dissociation energy in $[BCl_3C(NO_2)_3]^-$ is about 10 kcal mol^{-1} lower than that in $[BH_3C(NO_2)_3]^-$. This is surprising because $[BX_3C(NO_2)_3]^-$ can be considered as a Lewis acid/Lewis base adduct between the Lewis acid BX_3 and the Lewis base $[C(NO_2)_3]^-$. Therefore, based on Lewis acidity considerations alone, the stronger Lewis acid BCl_3 should form a stronger adduct with the $[C(NO_2)_3]^-$ anion than BH_3.[12] The reversal of this stability order can be partially attributed to the difference in the reorganization energies of BCl_3 and BH_3 and to steric factors. With a bulky ligand, such as $[C(NO_2)_3]^-$, the bulkier BCl_3 group will experience considerably more ligand/ligand repulsion than the much smaller BH_3 group.

$[BCl_3C(NO_2)_3]^-$ was also reported to decompose to BCl_4^- and N_2O_4 at 20 °C,[6] implying that dissociation alone might not fully account for the instability of that compound. An additional possible decomposition pathway involves a rapid ligand exchange reaction in $[BCl_3C(NO_2)_3]^-$ to form BCl_4^- and the less stable $[B\{C(NO_2)_3\}_4]^-$ ion [Eq. (2), where M =

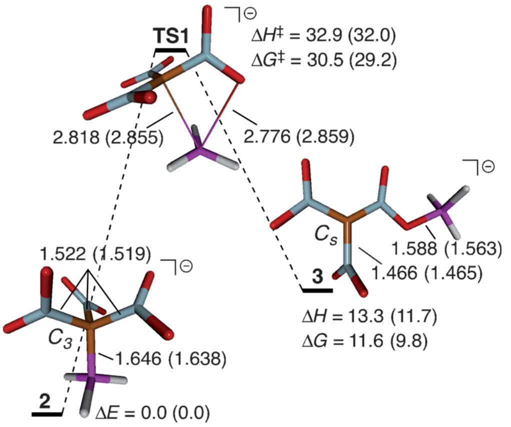
$$4\,M[BXCl_3] \rightarrow 3\,M[BCl_4] + M[BX_4] \qquad (2)$$

NMe_4^+, NEt_4^+].[6,11a] Preliminary results obtained by Titova et al. indicate that the subsequent decomposition of $[B\{C(NO_2)_3\}_4]^-$ is almost instantaneous at −30 °C.[6]

Following that reasoning, the higher adiabatic B–C bond dissociation energy in $[BH_3C(NO_2)_3]^-$ might make the cleavage of the B–C bonds more difficult and render the formation and subsequent decomposition of $[B\{C(NO_2)_3\}_4]^-$ less likely. This would also explain why we have not observed any N_2O_4 evolution nor any other sign of decomposition of the trinitromethyl group in the PNP^+ and PPh_4^+ salts of $[BH_3C(NO_2)_3]^-$.

The variation of the electrostatic potential over the molecular surface (ESP) relates to intermolecular interactions and is known to correlate with several macroscopic properties, such as lattice enthalpy, heat of sublimation, and boiling point.[22] Because the BH_3 and BCl_3 moieties in $[BH_3C(NO_2)_3]^-$ (**2**) and $[BCl_3C(NO_2)_3]^-$ (**4**) have markedly different electrostatic features (Scheme 2), they will affect overall macroscopic properties and influence the stability of the bulk material differently. For instance, visual inspection of the ESP of $[BCl_3C(NO_2)_3]^-$ shows less variation and less negative potentials, compared to those of $[BH_3C(NO_2)_3]^-$ and $[C(NO_2)_3]^-$. In the solid state, this should decrease the heat of sublimation of $[BCl_3C(NO_2)_3]^-$, relative to $BH_3C(NO_2)_3]^-$ and $[C(NO_2)_3]^-$,[23] and as a consequence lower the relative stability of the $[BCl_3C(NO_2)_3]^-$ salt.

Our search for potential decomposition pathways indicated that the most likely route is the heterolytic B−C bond dissociation (see Supporting Information). Because the largest part of the entropic gain associated with such a process can be realized only after the barrier is passed, the relative enthalpy of the infinitely separated fragments represents an upper boundary to the free energy barrier (ca. 35 kcal mol^{-1} in the case of $[BH_3C(NO_2)_3]^-$). The only process found with a lower barrier than the direct dissociative pathway is **TS1**, which corresponds to the isomerization of $[BH_3C(NO_2)_3]^-$ to $[H_3BO\text{-}N(O)\text{-}C(NO_2)_2]^-$ with a free energy barrier of 29.2 kcal mol^{-1} (Scheme 3). In **TS1**, the BH_3 group is almost completely separated from the nitroformate group with a C–B distance of over 2.8 Å. This barrier could possibly be further reduced if the leaving BH_3 molecule experienced specific interactions with a surrounding environment. Such interactions are not treated in the implicit solvation model employed in this study.



Scheme 3. The intramolecular isomerization of $[BH_3C(NO_2)_3]^-$ to $[H_3BO\text{-}N(O)\text{-}C(NO_2)_2]^-$ offers an approximate free energy estimate of the dissociation barrier toward BH_3 elimination. Relative energies [kcal mol]$^{-1}$ and bond lengths [Å]. Values for the process in acetonitrile solution (implicitly treated) are shown in parentheses. Gray N, red O, brown C, purple B.

Our experimental results support a dissociation-like decomposition pathway. Subjecting $[Na(glyme)_2][BH_3C(NO_2)_3]$ to a dynamic vacuum for a day at room temperature allowed the detection of B_2H_6 and nitroformate as decomposition products.

DTA measurements indicate that no significant decomposition occurs below 120 °C for PNP^+ and PPh_4^+ $[BH_3C(NO_2)_3]^-$ salts (see Supporting Information). This is in agreement with a barrier of about 29 kcal mol^{-1}, which, assuming first-order kinetics, would suggest a half-life of several years at room temperature but only of a few minutes at 120 °C.

In conclusion, the BH_3 group in $[BH_3C(NO_2)_3]^-$ provides a significant increase in stability compared to the previously studied BCl_3 analogue.[6] The $[Na(glyme)_2]^+$, PNP^+, and PPh_4^+ salts of $[BH_3C(NO_2)_3]^-$ were successfully isolated and characterized by NMR and vibrational spectroscopy. The PNP^+ salt was structurally characterized, confirming the theoretically predicted B–C connectivity. In addition, evidence was obtained for the slower formation of the disubstituted $[BH_2\{C(NO_2)_3\}_2]^-$ anion. While the dissociation barrier of $[BH_3C(NO_2)_3]^-$ is too low for practical applications, we demonstrated for the first time, both experimentally and theoretically, that kinetically stable boron trinitromethyl compounds can exist at room temperature. The most remarkable feature of the $[BH_3C(NO_2)_3]^-$ salts is the coexistence of a strongly oxidizing trinitromethyl and a strongly reducing BH_3 moiety in a single complex ion, a marriage between fire and water.

Experimental Section

Caution! The materials used and synthesized in this study are energetic. They should be handled in quantities not exceeding the milimolar scale. Manipulations should be carried out behind blast shields and with adequate personal safety gear (face shield, heavy leather jacket and gloves, ear protection). Ignoring safety precautions can lead to serious injuries!

All operations were performed using standard drybox, Schlenk, and vacuum-line techniques.

$[Na(glyme)_2][BH_3C(NO_2)_3]$: In a typical synthesis, a solution of nitroform (414 mg; 2.74 mmol) in glyme (5 mL) was rapidly added to a suspension of $NaBH_4$ (94.3 mg; 2.49 mmol) in glyme (5 mL), resulting in effervescence and a yellow solution. $Na[BH_3C(NO_2)_3]$ was formed quantitatively with respect to $NaBH_4$ according to ^{11}B NMR spectroscopy. The excess nitroform was removed by three extractions with pentane (<5 mL). Dichloromethane (10 mL) was added to the resulting bright yellow liquid and the solution was filtered into a FEP reactor. The solvent was removed under vacuum between −40 and −8 °C over the course of several days, yielding a green-yellow solid, which was characterized by NMR, Raman and IR spectroscopy. Metathesis with PPh_4Cl and PNPCl in dichloromethane yielded $PPh_4[BH_3C(NO_2)_3]$ and $PNP[BH_3C(NO_2)_3]$, respectively.

The multi-component complete basis set (CBS-QB3)[24] method was used for obtaining the energetics in the gas phase using the Gaussian 09 program.[25] To account for possibly significant solvation-induced structural rearrangements, accurate solvation energies (ΔH_{solv} and ΔG_{solv}) were obtained from separate vacuum and solution phase optimizations at the M06-2X/cc-pVTZ level of theory[26] using the SMD-PCM[27] method and $\varepsilon = 35.69$ (acetonitrile). The Hessian matrix was evaluated both for the gas-phase and SMD-PCM wave functions. This approach has been shown particularly important for intramolecular NO_2- transfer transition states, which can switch between NO_2-radical transfer in the gas-phase towards NO_2-cation character in polar solvents.[28] Nuclear magnetic shielding tensors were calculated in acetonitrile at the GIAO-PCM-B3LYP/6–311+(2d,p) level. Raman spectra were calculated at the B3LYP/aug-cc-pVTZ level, and scaled by 0.977 for best fit with the experimental results. Further method description and details on the numerous decomposition pathways considered as well as the complete characterization data and synthetic details can be found in the supporting information.

CCDC 936635 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[14] NMR data for $[BH_3C(NO_2)_3]^-$ in CD_3CN at 400 MHz unless otherwise stated : ^1H NMR (ref. to CHD_2CN) $\delta = 1.09$ ppm (1:1:1:1 quart., ^1J (^1H,^{11}B) = 94 Hz); ^{11}B NMR (ref. to $BF_3{\cdot}Et_2O$) $\delta = -23.8$ ppm (quart., ^1J (^{11}B,^1H) = 94 Hz); ^{13}C NMR (500 MHz, glyme, ref. to TMS) $\delta = 151.1$ ppm (quart., ^1J (^{11}B,^{13}C) = 32 Hz and ^{14}N NMR (500 MHz, ref. to CH_3NO_2): $\delta = -7.2$ ppm (s, $\Delta\upsilon_{1/2} = 14$ Hz) (predicted $\delta = -6$ ppm).

[15] NMR data for $[BH_2\{C(NO_2)_3\}_2]^-$ in glyme at 500 MHz: ^{11}B NMR:($\delta = -17.6$ ppm (t, ^1J (^{11}B,^1H) = 104 Hz); ^{14}N NMR: $\delta = -15.0$ ppm (s).

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