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1,3-Dipolar Cycloaddition of Nitrones to a Nitrile Functionality in *closo*-Decaborate Clusters: A Novel Reactivity Mode for the Borylated C≡N Group

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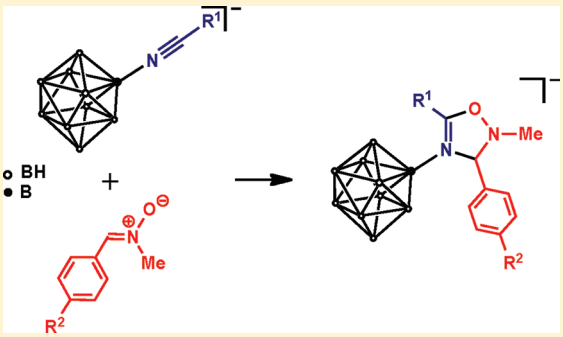
Supporting Information

ABSTRACT: The *Z*-configured nitrones $^{-}O^{+}N(Me)=C(H)C_6H_4R^2$-*p* ($R^2$ = OMe (**2a**), Me (**2b**), NO_2 (**2c**)) react with the nitrile functionality of the *closo*-decaborate clusters $[Bu^n_4N][B_{10}H_9(NCR^1)]$ (R^1 = Me (**1a**), Et (**1b**), Bu^t (**1c**), Ph (**1d**)) in $CHCl_3$ solution under mild conditions (20−25 °C, 16−18 h) to afford the products of cycloaddition: viz., the borylated 2,3-dihydro-1,2,4-oxadiazoles $[Bu^n_4N][B_{10}H_9\{N^a{=}CR^1ON(Me)C^bH(C_6H_4R^2\text{-}p)\}]^{(a-b)}$ (**3a−l**). This reaction represents the first example of boron-mediated 1,3-dipolar cycloaddition of allyl anion type dipoles, i.e. nitrones, to the nitrile group. Alteration of the lipophilic $[Bu^n_4N]^+$ counterion with the hydrophilic Na^+ via the metathetical reaction with $NaBPh_4$ in **3a,b,e,f** allows the modification of their hydrophilic−lipophilic properties and, consequently, solubility. Compounds **3a−j** and **5a−d** were characterized by high-resolution ESI-MS, IR, and ^1H, $^{13}C\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectroscopy. The structures of **3a,e,f** were determined by single-crystal X-ray diffraction.



In general, nitriles—although they represent attractive starting materials for generation of various nitrogen heterocycles—exhibit moderate dipolarophilicity, and this hampers the application of RCN species in cycloaddition (CA) reactions. The reactivity of the nitrile functionality can be enhanced either by an electron-withdrawing substituent at the C atom or by affecting the nitrile group through the N atom (i.e., protonation, alkylation, or coordination to the metal). The group of methods associated with the N atom includes alkylation (followed by cycloaddition to thus generated nitrilium salts) and coordination to a transition-metal center (and cycloaddition to these ligated nitrile substrates); these two approaches were considered in our reviews on the subject.[1−3]

1,3-Dipolar cycloaddition (DCA) to highly reactive nitrilium salts $[RN{\equiv}CR']^+$ has been studied for such dipoles as azides,[4−8] nitrile oxides,[9] and heterocyclic nitrones.[10] In recent years, growing attention has been paid to metal-mediated DCA to RCN,[3] and these works are greatly associated with the nitrile−azide interactions accomplishing tetrazole heterocycles[11−20] and, to a lesser degree, with the DCA of nitrones[21−23] and relevant allyl anion type dipoles (e.g., oxazoline *N*-oxides,[24] imidazoline *N*-oxides,[25] and nitronates[26]) and also nitrile oxides[27,28] that, as is the case for azides, represent dipoles of the propargyl−allenyl anion type.

In view of our general interest in reactions of substrates activated by binding to a Lewis acid and, in particular, those with the C≡N bond (for reviews see refs 1−3, and for recent works see refs 29−34), we decided to attempt DCA of the most common representatives of allyl anion type dipoles, i.e. nitrones, to borylated nitrilium derivatives having a relatively strong B−N bond, i.e. nitrilium hydroborates. The latter category of species has been scarcely investigated, although data for various nitrilium-substituted boron clusters gradually emerged in the literature indicating a high reactivity of the C≡N group. These examples include facile addition of H_2O (*a*

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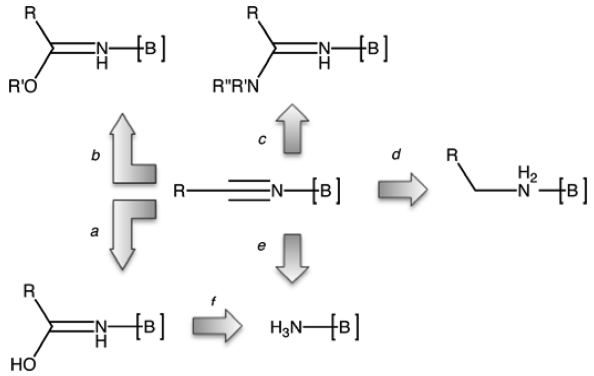
and *f*, Scheme 1),[35−37] R′OH (*b*),[38−40] and amines (*c*)[38,39,41] to nitrilium derivatives of borohydride[35,38,40] and carborane-(ate)[36,39] clusters as well as the hydrogenation of cobalt nitrilium bis(1,2-dicarbollide) with $Me_2S{\cdot}BH_3$ (*d*) and the reaction with hydrazine (*e*) in EtOH.[39]

Scheme 1. Reactivity Modes of the Nitrilium-Substituted Cage Boron Compounds



In the context of the current work, it is important to stress that no single example of the cycloaddition to the CN group bound to the B atom at any of the boron clusters has been reported to date, although BF_3-catalyzed DCAs are rather common in organic chemistry (see, e.g., refs 42−48).

The main goals of this work were at least 2-fold. First, we anticipated to determine the possibility of DCA of nitrones to the nitrile functionality in nitrilium *closo*-decaborates and to compare the reactivity of these C≡N dipolarophiles with that of uncomplexed and metal-bound RCN species. Second, we intended to synthesize various anionic *closo*-decaborate clusters featuring 2,3-dihydro-1,2,4-oxadiazoles and to obtain, via alteration of the counterion, their water-soluble forms for further biological investigations. We now report on an extension of the DCA reaction of nitrones to completely different dipolarophiles bearing the C≡N group, i.e., nitrilium borates, that allow the generation of a novel family of 2,3-dihydro-1,2,4-oxadiazoles linked via the N−B bond to *closo*-decaborate clusters.

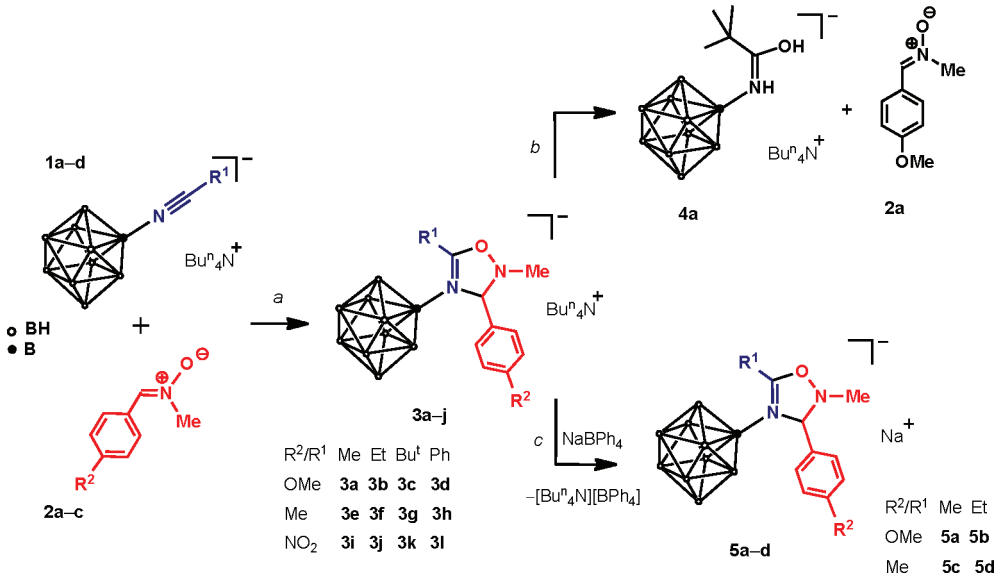
RESULTS AND DISCUSSION

1,3-Dipolar Cycloaddition. For this study we addressed the four *closo*-decaborates $[Bu^n_4N][B_{10}H_9(NCR^1)]$ (R^1 = Me (**1a**), Et (**1b**), Bu^t (**1c**), Ph (**1d**)) and three acyclic nitrones in the *Z* form, i.e., $^-O^+N(Me)=C(H)C_6H_4R^2$-*p* (R^2 = OMe (**2a**), Me (**2b**), NO_2 (**2c**)). The reaction between the nitrilium substituents in the clusters $[Bu^n_4N][B_{10}H_9(NCR^1)]$ and the nitrones (in all possible combinations) proceeds in $CHCl_3$ solution under mild conditions (20−25 °C, 16−18 h) to afford cycloaddition products **3a**−**l** (ca. 100% NMR yield; 39−69% isolated yield after column chromatography; the products slowly decompose on SiO_2 and the chromatography should be performed rapidly) (Scheme 2, route *a*).

Our experiments suggest that the C≡N group in the boron clusters is strongly activated toward DCA of nitrones as compared to the C≡N group in the conventional alkyl- and arylnitriles[49] and even in $(RCN)Pt^{II}$ moieties.[21] Under similar experimental conditions, no reaction was observed (by ^1H NMR) between the relevant free nitriles RCN and the nitrones, indicating that CA is boron-mediated. Moreover, no CA reaction of the most reactive nitrone **2a** was observed under similar reaction conditions (20−25 °C, $CDCl_3$) at prolonged times (24 h), even in the case of nitriles bearing strong acceptor substituents: viz., $CHCl_2CN$, EtO_2CCH_2CN, $MeC(O)CN$, *m*-$NO_2C_6H_4CN$, and *o*-BrC_6H_4CN. As noticed previously,[49] CA of acyclic nitrones to free alkylnitriles does not occur even at elevated temperatures and only the rather electron-deficient PhCN reacts with the acyclic nitrone (*Z*)-$^-O^+N(Me)=C(H)$Ar under harsh conditions (10 days at 110 °C) to give 2-methyl-3,5-diphenyl-2,3-dihydro-1,2,4-oxadiazole in moderate (57%) yield.[49]

The character of the substituent R^2 has a moderate effect on CA rate in spite of the considerable difference in electronic effects of the OMe, Me, and NO_2 substituents (σ_{para}(OMe) = −0.27, σ_{para}(Me) = −0.17, $\sigma_{para}(NO_2)$ = 0.78[50]) in the nitrones. Thus, competitive DCA of nitrones **2a**/**2b** and **2b**/**2c** to the nitrilium group of **1a** in a molar ratio 1:1:0.3 by means of ^1H

Scheme 2. Generation and Transformations of the Borylated 2,3-Dihydro-1,2,4-oxadiazoles



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NMR monitoring demonstrates the following relative reaction rate constants: $k_{1a}:k_{1b}:k_{1c} \approx 23:13:1$. This dependence indicates negative ρ values, and it supports attribution of this reaction to type I (normal electron demand) of CA in the Sustmann classification,[51] where $HOMO_{nitrone}$–$LUMO_{nitrile}$ interactions determine the occurrence of the reaction.

It is worth mentioning that the character of the substituent R^1 plays a dramatic role in the stability of **3a–j**. Thus, the *closo*-decaborate cluster ions with R^1 = Me, Et (**3a,b,e,f,i,j**) are stable in the solid state and in chloroform or methanol solutions, whereas the species with R^1 = Ph (**3d,h**) and especially with Bu^t (**3c,g**) (probably due to steric repulsion of the bulky Bu^t group) decompose at room temperature. Thus, the appearance of foreign signals in the ^{1}H NMR spectra was found upon keeping **3c,d,g,h** in the solid state for 3 days or after 12 h in an undried $CDCl_3$ solution. Compounds **3k,l** were detected by ^{1}H NMR and IR spectroscopy and HRESI$^-$-MS but not isolated as pure solids because of their instability. In the case of **3c**, an equimolar mixture of nitrone **2a** and amide **4a** (amides similar to **4a** are known and the X-ray data indicate the double bond between the N=C atoms[35]) was detected by both ^{1}H NMR and HRESI$^\pm$-MS; **2a** and **4a** are formed upon the hydrolytic cleavage of the heterocyclic moiety (Scheme, 2, route *b*). We also found that **3a–j** are unstable toward hydrolysis under both acidic (1 M AcOH/$CDCl_3$) and alkaline (1 M NaOH/CD_3OD) conditions: i.e., they decompose for 2 h, giving a broad mixture of as yet unidentified products (at least five new spots on TLC were detected along with the disappearance of the starting species). The instability most probably relates to the oxadiazole ring, insofar as we did not observe any changes in the *closo*-borate cluster at room temperature for 2–6 h, which is in agreement with literature data on the stability of these clusters.[35,40]

Cation Metathesis. Compounds **5a–d** were obtained in the metathetical reaction between **3a,b,e,f** and $NaBPh_4$ in methanol/acetonitrile solution (Scheme 2, route *c*). Sodium salts **5a–d** were isolated as pale yellow solids after separation of the solid $[Bu^n_4N]BPh_4$ followed by evaporation of the solvent and crystallization of the resulted oily residues in a desiccator (70% yields after crystallization). These species exhibit rather good solubility in water (>20 mg per 1 mL).

Characterization of the *closo*-Decaborate Clusters Featuring 2,3-Dihydro-1,2,4-oxadiazoles. All isolated species were characterized by HRESI$^\pm$ mass spectrometry, ICP-MS (% B for the six most stable species **3a,b,e,f,i,j**), IR and ^{1}H and ^{13}C{^{1}H} NMR (**3a–j**, **5a–d**), and ^{11}B{^{1}H} NMR (**3a–j**) spectroscopy and also by X-ray diffraction (for **3a,e,f**). All physicochemical data are in agreement with the proposed formulas.

In the ESI$^-$ mass spectra of **3a–j**, the most intense signals are due to $[A]^-$ (where A^- is the anionic borylated heterocycle) or, in some instances, $[2A + Bu^n_4N]^-$, while the ESI$^+$ mass spectra exhibit signals from $[Bu^n_4N]^+$ or $[2Bu^n_4N + A]^+$. In the ESI$^-$ mass spectra of **5a–d**, only signals of $[A]^-$ were detected and no signals from $[Bu^n_4N]^+$ were observed in ESI$^+$-MS. In the IR spectra of **3a–j** and **5a–d**, strong bands due to ν(B–H) and ν(C=N) stretching vibrations were found in the ranges of 2450–2510 and 1590–1650 cm^{-1}, respectively. No ν(C≡N) bands at ca. 2300 cm^{-1}, specific for the starting materials,[35] were detected. The IR spectra of **3a–j** exhibit strong bands for ν(C–H) in the range 2870–2970 cm^{-1}, in contrast to the spectra of **5a–d**, where only weak signals were observed in this region.

The specific feature of the ^{1}H NMR spectra of **3a–j** and **5a–d** is the presence of a singlet at 5.53–5.89 ppm from the N–C(5)H–N group. The most characteristic signal in the ^{13}C{^{1}H} NMR of **3a–j** and **5a–d** is the C(1)=N resonance that falls in the interval 166.4–177.4 ppm. The ^{11}B{^{1}H} NMR confirmed the *closo*-decaborate structure of **3a–j**. Two singlets assigned to apical boron atoms were observed in the range from +1.12 to −2.56 ppm, a weak singlet of the substituted boron atom appeared from −11.22 to −13.31 ppm, and multiple signals were observed corresponding to other equatorial atoms between −23.13 and −28.28 ppm.[35,40] ^{11}B NMR spectra demonstrate that the borate cluster has only one substituted B^2 atom; therefore, DCA does not lead to alterations of the borate unit.

The single-crystal X-ray diffraction study conducted for **3a,e** (Figures S1 and S2 in the Supporting Information) and **3f** (Figure 1) indicates the presence of two independent ionic

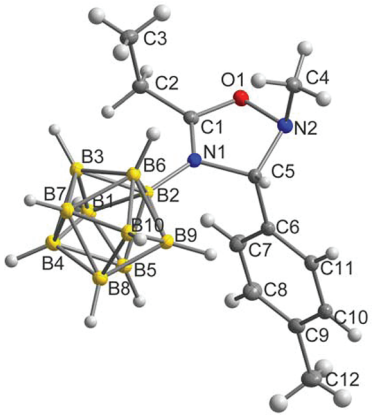

Figure 1. ORTEP view of **3f** with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level; the cation is omitted for clarity.

parts. In the cation, the alkyl chains of $[Bu^n_4N]^+$ are always in anti or gauche conformations and all bond lengths are close to those reported in the literature.[52] The anionic parts of **3a,e,f** consist of a substituted 2,3-dihydro-1,2,4-oxadiazole ring bound to a boron cluster via the N(1) atom. In the clusters, the B–B bond distances and angles are typical for 2-substituted nonahydro-*closo*-decaborate clusters.[35,53] The bond lengths N(1)–B(2) are equal, within 3σ, to those in the starting nitrilium *closo*-decaborate.[53] The geometrical parameters of the 2,3-dihydro-1,2,4-oxadiazole rings in **3a,e,f** are the same, within 3σ, as those in the previously described (2,3-dihydro-1,2,4-oxadiazole)Pt complexes[21,22] and also those in the known examples of structurally characterized uncomplexed 2,3-dihydro-1,2,4-oxadiazoles.[54–56] All other bonds and angles had normal values (Table 1).

Final Remarks. The results from this work could be considered from at least three perspectives. First, we observed that the nitrilium group bound to a *closo*-decaborate moiety exhibits dipolarophilicity so significant that DCA of rather inactive acyclic nitrones in the *Z* form proceeds efficiently under mild conditions. The competitive reactivity study indicates that the observed reaction belongs to type I (normal electron demand) of CA in the Sustmann classification,[51] where $HOMO_{nitrone}$–$LUMO_{nitrile}$ interactions determine the occurrence of DCA. However, on the basis of previous theoretical calculations conducted for boron-mediated CA to nitriles[57] and

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3a,e,f

	3a	3e	3f
O(1)−C(1)	1.336(2)	1.338(2)	1.3368(16)
O(1)−N(2)	1.503(2)	1.492(2)	1.4934(15)
N(1)−C(1)	1.284(2)	1.289(2)	1.2907(17)
N(1)−C(5)	1.493(2)	1.482(2)	1.4861(16)
N(1)−B(2)	1.546(3)	1.545(2)	1.5438(18)
N(2)−C(4)	1.470(2)	1.471(3)	1.471(3)
N(2)−C(5)	1.486(2)	1.485(2)	1.4852(17)
C(1)−C(2)	1.484(3)	1.473(3)	1.4805(19)
C(2)−C(3)			1.532(2)
C(1)−O(1)−N(2)	106.38(14)	106.91(13)	106.52(10)
C(1)−N(1)−C(5)	108.09(16)	108.25(15)	107.74(11)
C(1)−N(1)−B(2)	129.09(16)	128.83(16)	129.01(11)
C(5)−N(1)−B(2)	122.70(15)	122.79(14)	123.22(10)
C(4)−N(2)−C(5)	110.77(15)	110.86(15)	110.42(11)
C(4)−N(2)−O(1)	103.59(14)	103.74(14)	103.40(10)
C(5)−N(2)−O(1)	102.02(13)	102.34(13)	101.89(9)
N(1)−C(1)−O(1)	114.97(17)	114.57(17)	114.73(12)
N(1)−C(1)−C(2)	128.68(18)	128.97(18)	128.76(13)
O(1)−C(1)−C(2)	116.34(17)	116.46(16)	116.41(12)

also considering the coherent theoretical data on metal-mediated DCAs,[58] it is anticipated that the cycloaddition could exhibit an asynchronous character.

Second, the observed reaction represents the first example of boron-mediated DCA of *allyl anion type dipoles*, i.e. nitrones, to the nitrile functionality. Note that several boron-catalyzed DCAs to nitrile species were reported and all these examples (viz., F_3B-catalyzed CAs of N_3^-, organic azides, or nitrile oxides to RCN species[59−66]) are restricted exclusively to CA of *propargyl−allenyl type dipoles*.

In this context, it is of interest to compare the reaction conditions for various boron-mediated DCAs. Thus, in the case of the propargyl−allenyl type dipoles, CA of sodium azide or organic azides to substituted arylacetonitriles[64,65] and to perfluoro- or perchloroalkylnitriles[65] takes place only with prolonged heating at 100−150 °C. Furthermore, CAs of the nitrile oxides ArC≡N$^+$O$^-$ to RCN were conducted under reflux conditions for 0.5−2 h in the case R = alkyl,[59,60] aryl[60,61] or at room temperature for much more reactive malononitrile derivatives.[59,62,63] In contrast to all these examples, the nitrile functionality in the *closo*-decaborate clusters exhibits enhanced reactivity in the DCA of nitrones (CAs were completed over 16−18 h at 20−25 °C) similar to that found earlier for CA of nitrones to nitrile ligands bound to such exceptionally powerful activators as Pt^{IV} centers.[66] Moreover, in DCA with nitrones, the reactivity of the borylated CN group is quite comparable to that observed for the DCA of nitrones to highly reactive *N*-alkyl nitrilium salts.[22]

Third, the products originating from DCA, viz., *closo*-decaborate clusters featuring 2,3-dihydro-1,2,4-oxadiazoles **3a−j**, have a dual interest. On one hand, 2,3-dihydro-1,2,4-oxadiazoles represent a class of little explored heterocycles whose chemistry was elaborated only in the past decade upon developing the metal-mediated synthetic approaches to these species.[3] It is worth mentioning that—other than two reports on the antitumor activity of (2,3-dihydro-1,2,4-oxadiazole)Pt^{II} complexes[67,68]—the biological/medicinal properties of these heterocycles have not been unexplored. We believe that the *closo*-decaborate cluster unit behaves as a sufficiently stable, small, and hydrophilic functional group that imparts an aqueous solubility to the heterocycles. Consequently, water-soluble sodium salts (e.g., **5a−d**) seem to be logical candidates for biological tests and work in this direction is underway in our group. On the other hand, boron-containing species and, in particular, various polyhedral boranes have attracted special attention as potential agents in boron neutron capture cancer therapy.[69] The growing role of polyhedral boron hydrides in radionuclide diagnostics and drug design, including anti-AIDS agents, should also be noted.[69]

EXPERIMENTAL SECTION

Instrumentation and Materials. *N*-Methylhydroxylamine hydrochloride (Aldrich), *p*-R^{2}C$_6$H$_4$CHO (R^2 = Me, NO$_2$, Aldrich; R^2 = OMe, Lancaster), and solvents were obtained from commercial sources and used as received. *closo*-Decaborate clusters **1a**[70] and **1d**[37] were prepared in accord with the published methods, while the syntheses and characterization of **1b,c** are described later in this section. Nitrones **2a−c** were synthesized by condensation of the corresponding aldehyde and *N*-methylhydroxylamine via the known protocols.[10]

Elemental analysis for boron was performed by the FSUE IREA Center (Moscow) on a iCAP 6300 Duo ICP spectrometer using In as an internal standard. Infrared spectra were recorded on a Shimadzu FTIR 8400S instrument in KBr pellets. ^{1}H, ^{13}C{^{1}H}, and ^{11}B{^{1}H} NMR spectra were measured on a Bruker-DPX 300 spectrometer at ambient temperature (BF_3·Et_2O was used as the external standard for ^{11}B{^{1}H} NMR). Electrospray ionization mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with an electrospray ionization (ESI) source, and MeOH was used as the solvent. The instrument was operated both at positive and negative ion modes using a m/z range of 50−3000. The capillary voltage of the ion source was set at −4500 V (ESI$^+$-MS) or 3500 V (ESI$^-$-MS) and the capillary exit at ±30 V. In the isotopic pattern, the most abundant peak is reported. Melting points were determined in a capillary on a Büchi 530 melting point apparatus. TLC was carried out on Al plates precoated with a layer of silica gel Merck 60 F_{254}. For column chromatography silica gel 60 F_{254}, 0.063−0.200 mm (Merck), was used.

X-ray Crystal Structure Determinations. Crystals of **3a,e,f** were obtained by a slow evaporation of the solvent from methanol solution of **3a** or acetonitrile solutions of **3e,f**. Single-crystal X-ray diffraction experiments were carried out with a Bruker Kappa Apex II Duo diffractometer[71] (for **3a**) and a Bruker SMART 1000 CCD diffractometer[72] (for **3e,f**) using Mo Kα radiation (λ = 0.710 73 Å). A multiscan absorption correction based on equivalent reflections (SADABS)[73] was applied to the data. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with anisotropic temperature factors for all non-hydrogen atoms using the SHELXTL program package.[74] In **3e,f**, the hydrogen atoms of the boron cage were located from difference Fourier maps and involved in refinement in isotropic approximation. The rest of the hydrogen atoms in **3e,f**, as well as all hydrogen atoms in **3a**, were positioned geometrically and constrained to ride on their parent atoms, with C−H = 0.95−1.00 Å, B−H = 1.12 Å, and U_{iso} = 1.2−1.5[U_{eq}(parent atom)]. The crystallographic details are summarized in Table S1 (Supporting Information).

Competitive Reactivity Study. Compound **1a** (0.17 mmol) was added to a solution of nitrones **2a** (0.51 mmol) and **2b** (0.50 mmol) (or **2b** (0.54 mmol) and **2c** (0.45 mmol)) in $CDCl_3$ (0.5 mL) in an NMR tube. After 1 h at 25 °C no signals of compound **1a** were observed in the ^{1}H NMR spectra. The k_1/k_2 value was evaluated using integral intensities of the reaction products according to the formula

$$\frac{k_1}{k_2} = \frac{S(1)}{S(2)} \cdot a$$

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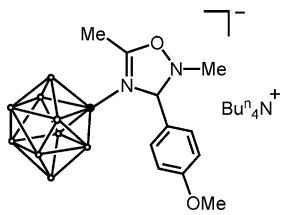
where $S(1)$ and $S(2)$ are integral intensities of signals of $C_6H_4OCH_3$ and $C_6H_4CH_3$-*p* groups in **3a,e**, correspondingly, or NC*H*N signals in **3e,i** and *a* is the initial ratio (**2a**:**2b** and **2b**:**2c**) of the starting nitrones.

Synthetic Work. *Synthesis of 1b,c.* Nitrilium borates were prepared by a modified literature method.[70] $[Bu^n_4N][B_{10}H_{11}]$ (5.00 g, 0.014 mol) was dissolved in RCN (30 mL; R = Et (**1b**), Bu^t (**1c**)), and the solution was heated to 75 °C for 1.5 h. Then the solvent was evaporated under vacuum at 40 °C to furnish a solid residue that was crystallized under CH_3CN and dried at 60 °C/10^{-2} mm Hg on a Kugelrohr apparatus.

1b: yield 5.37 g (93%). IR spectrum in Nujol, selected bands, cm^{-1}: 2482 s ν(B−H), 2331 s ν(C≡N). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 2.82 (q, 2H, NCH_2CH_3), 1.12 (t, 3H, NCH_2CH_3), 3.13 (t, 8H), 1.60−1.47 (m, 8H), 1.46−1.30 (m, 8H), 0.95 (t, 12H) (NBu^n_4). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 117.4, 58.4, 24.3, 23.0, 19.3, 14.3, 12.8. $^{11}B\{^1H\}$ NMR (96.32 MHz, $CDCl_3$): 1.0 (B^{10}), −1.9 (B^1), −20.5 (B^2), −25.4 (B^3, B^5, B^6, B^9), −28.1 (B^4, B^7, B^8). High-resolution ESI^--MS: *m*/*z* 172.2625 $[A]^-$ (172.2604 calcd), 586.9877 [2A + NBu^n_4]$^-$ (586.9852 calcd).

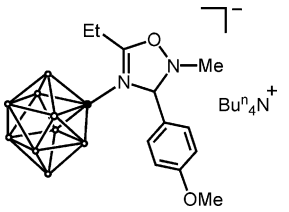
1c: yield 5.16 g (84%). IR spectrum in Nujol, selected bands, cm^{-1}: 2533 s, 2471 s ν(B−H), 2348 s ν(C≡N). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.37 (s, 9H, $NCC(CH_3)_3$), 3.13 (t, 8H), 1.60−1.47 (m, 8H), 1.46−1.30 (m, 8H), 0.95 (t, 12H) (NBu^n_4). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 115.4, 58.0, 30.6, 28.6, 23.0, 19.3, 12.6. $^{11}B\{^1H\}$ NMR (96.32 MHz, $CDCl_3$): 1.1 (B^{10}), −1.9 (B^1), −20.4 (B^2), −25.3 (B^3, B^5, B^6, B^9), −27.4 (B^4, B^7, B^8). High-resolution ESI^--MS: *m*/*z* 200.2656 $[A]^-$ (200.3136 calcd), 643.0985 [2A + NBu^n_4]$^-$ (643.0917 calcd).

Boron-Mediated Cycloaddition of the Nitrones. The reaction between each of the nitrones (**2a−c**; 0.14 mmol) and each of the nitrilium derivatives (**1a−d**; 0.14 mmol) was performed in a chloroform (3 mL) solution at room temperature, and its completeness was monitored by TLC. After 16−18 h the product of the cycloaddition was separated from the reaction mixture by column chromatography on silica gel (eluent is 10/1 v/v chloroform/acetone). Evaporation of the solvent (at 20−25 °C) from the first fraction gave an oily product that was crystallized under a layer of diethyl ether at room temperature to furnish solid **3a−j**.

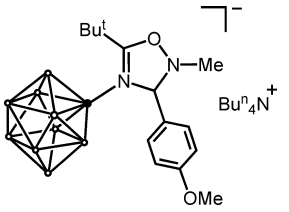


3a: yield 51 mg (64%). Anal. Found: B, 18.75. Calcd for $C_{27}H_{59}N_3B_{10}O_2$: B, 19.10. IR spectrum in KBr, selected bands, cm^{-1}: 2505 s, 2463 s ν(B−H), 1647 s ν(C═N). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.26 (d, 2H, *J* = 9 Hz, meta to MeO), 6.83 (d, 2H, *J* = 9 Hz, ortho to MeO), 5.53 (s, 1H, NC*H*N), 3.77 (s, 3H, OCH_3), 2.79 (s, 3H, NCH_3), 2.63 (s, 3H, CCH_3), 3.13 (t, 8H), 1.60−1.47 (m, 8H), 1.46−1.30 (m, 8H), 0.95 (t, *J* = 7 Hz, 12H) (NBu^n_4). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 169.7 (C═N), 160.6 (ipso to MeO), 129.0 (meta to MeO), 127.8 (para to MeO), 114.1 (ortho to MeO), 91.8 (NCN), 58.9 (NCH_2Pr), 55.7 (OCH_3), 47.2 (NCH_3), 24.4 (NCH_2CH_2Et), 20.1 ($N(CH_2)_2CH_2Me$), 14.2 ($N(CH_2)_3CH_3$), 13.1 (CCH_3). $^{11}B\{^1H\}$ NMR (96.32 MHz, $CDCl_3$): 0.69 (B^1), −2.35 (B^{10}), −13.03 (B^2), −24.12 (B^4, B^7, B^8), −28.13 (B^3, B^5, B^6, B^9). High-resolution ESI^+-MS: *m*/*z* 242.2846 $[Bu^n_4N]^+$ (242.2843 calcd). High-resolution ESI^--MS: *m*/*z* 325.2728 $[A]^-$ (325.2690 calcd), 892.8264 [2A + Bu^n_4N]$^+$ (892.8228 calcd). Mp: 125−128 °C dec.

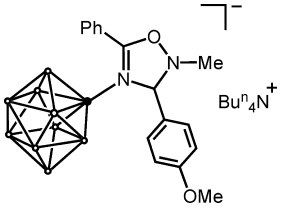
3b: yield 56 mg (69%). Anal. Found: B, 18.32. Calcd for $C_{28}H_{61}N_3B_{10}O_2$: B, 18.64. IR spectrum in KBr, selected bands, cm^{-1}: 2508 s, 2466 s, 2442 s ν(B−H), 1641 s ν(C═N). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.25 (d, 2H, *J* = 9 Hz, meta to MeO), 6.84 (d, 2H, *J* = 9 Hz, ortho to MeO), 5.54 (s, 1H, NC*H*N), 3.77 (s, 3H, OCH_3), 3.26−3.05 (m, 10H, NCH_2Pr and CCH_2CH_3), 2.77 (s, 3H,



NCH_3), 1.27 (t, 3H, *J* = 7 Hz, CCH_2CH_3), 1.61−1.48 (m, 8H), 1.47−1.33 (m, 8H), 0.96 (t, *J* = 7 Hz, 12H) (NBu^n_4). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 173.0 (C═N), 160.6 (ipso to MeO), 128.9 (meta to MeO), 128.0 (para to MeO), 114.1 (ortho to MeO), 91.6 (NCN), 59.0 (NCH_2Pr), 55.7 (OCH_3), 47.1 (NCH_3), 24.5 (NCH_2CH_2Et), 20.1 ($N(CH_2)_2CH_2Me$), 20.0 (CCH_2CH_3), 14.2 ($N(CH_2)_3CH_3$), 9.9 (CCH_2CH_3). $^{11}B\{^1H\}$ NMR (96.32 MHz, $CDCl_3$): 0.60 (B^1), −2.07 (B^{10}), −13.09 (B^2), −24.36 (B^4, B^7, B^8), −28.28 (B^3, B^5, B^6, B^9). High-resolution ESI^+-MS: *m*/*z* 823.8813 $[A + 2Bu^n_4N]^+$ (823.8542 calcd), 242.2927 $[Bu^n_4N]^+$ (242.2843 calcd). High-resolution ESI^--MS: *m*/*z* 339.2875 $[A]^-$ (339.2846 calcd), 920.8578 [2A + Bu^n_4N]$^-$ (920.8541 calcd). Mp: 123−125 °C dec.



3c: yield 51 mg (60%). IR spectrum in KBr, selected bands, cm^{-1}: 2505 s, 2463 s ν(B−H), 1610 s ν(C═N). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.17 (d, 2H, *J* = 9 Hz, meta to MeO), 6.87 (d, 2H, *J* = 9 Hz, ortho to MeO), 5.88 (s, 1H, NC*H*N), 3.81 (s, 3H, OCH_3), 2.81 (s, 3H, NCH_3), 1.71−1.50 (m, 17H, NCH_2CH_2Et and $C(CH_3)_3$), 3.16 (t, 8H), 1.49−1.36 (m, 8H), 0.99 (t, *J* = 7 Hz, 12H) (NBu^n_4). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 177.4 (C═N), 160.3 (ipso to MeO), 128.9 (meta to MeO), 128.2 (para to MeO), 114.1 (ortho to MeO), 93.1 (NCN), 59.0 (NCH_2Pr), 55.7 (OCH_3), 46.0 (NCH_3), 35.4 ($C(CH_3)_3$), 27.7 ($C(CH_3)_3$), 24.4 (NCH_2CH_2Et), 20.1 ($N(CH_2)_2CH_2Me$), 14.2 ($N(CH_2)_3CH_3$). $^{11}B\{^1H\}$ NMR (96.32 MHz, $CDCl_3$): 0.40 (B^1), −0.97 (B^{10}), −11.27 (B^2), −24.93 (B^4, B^7, B^8), −27.94 (B^3, B^5, B^6, B^9). High-resolution ESI^+-MS: *m*/*z* 851.9152 [A + $2Bu^n_4N$]$^+$ (851.8855 calcd), 242.2948 $[Bu^n_4N]^+$ (242.2843 calcd). High-resolution ESI^--MS: *m*/*z* 367.3124 $[A]^-$ (367.3159 calcd). Mp: 85−87 °C, dec.



3d: yield 57 mg (65%). IR spectrum in KBr, selected bands, cm^{-1}: 2505 s, 2463 s ν(B−H), 1647 s ν(C═N). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7 Hz, 2H, ortho in Ph), 7.60 (t, 1H, *J* = 7 Hz, para in Ph), 7.50−7.37 (m, 4H, meta to MeO and meta in Ph), 6.91 (d, 2H, *J* = 9 Hz, ortho to MeO), 5.83 (s, 1H, NC*H*N), 3.82 (s, 3H, OCH_3), 2.92 (s, 3H, NCH_3), 3.11 (t, 8H), 1.60−1.47 (m, 8H), 1.46−1.30 (m, 8H), 0.94 (t, *J* = 7 Hz, 12H) (NBu^n_4). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 167.0 (C═N), 160.7 (ipso to MeO), 135.1, 132.5, 129.0 128.5, 128.8, 127.6, 114.1 (Ar), 92.4 (NCN), 59.0 (NCH_2Pr), 55.7 (OCH_3), 46.8 (NCH_3), 24.4 (NCH_2CH_2Et), 20.1 ($N(CH_2)_2CH_2Me$), 14.2 ($N(CH_2)_3CH_3$). $^{11}B\{^1H\}$ NMR (96.32 MHz, $CDCl_3$): 0.38 (B^1), −1.88 (B^{10}), −11.52 (B^2), −23.75 (B^4, B^7, B^8), −27.89 (B^3, B^5, B^6, B^9). High-resolution ESI^+-MS: *m*/*z* 871.8863 [A + $2Bu^n_4N$]$^+$ (871.8541 calcd), 242.2991 $[Bu^n_4N]^+$ (242.2843 calcd).

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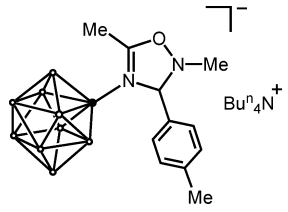
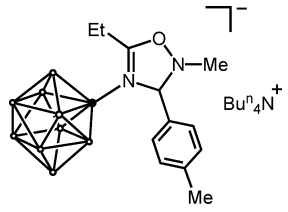
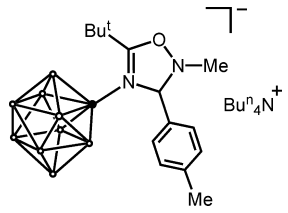
High-resolution ESI⁻-MS: *m*/*z* 387.2891 [A]⁻ (387.2846 calcd). Mp: 73−75 °C dec.



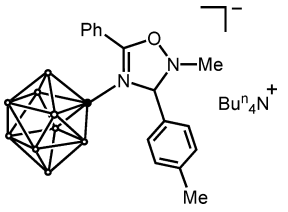
3e: yield 51 mg (66%). Anal. Found: B, 19.71. Calcd for $C_{27}H_{59}N_3B_{10}O$: B, 19.66. IR spectrum in KBr, selected bands, cm^{-1}: 2506 s, 2463 s ν(B−H), 1647 s ν(C═N). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.23 (d, 2H, J = 8 Hz, meta to Me), 7.13 (d, 2H, J = 8 Hz, ortho to Me) 5.56 (s, 1H, NC*H*N), 2.80 (s, 3H, NCH_3), 2.65 (s, 3H, CCH_3), 2.31 (s, 3H, CH_3C$_6$H$_4$), 3.15 (t, 8H), 1.68−1.51 (m, 8H), 1.50−1.30 (m, 8H), 0.97 (t, J = 7 Hz, 12H) (NBu$^n_4$). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$): δ 169.9 (C═N), 139.4, 132.8, 129.4, 127.4 (Ar), 91.1 (NCN), 59.0 (NCH_2Pr), 47.3 (NCH_3), 24.5 (NCH$_2$CH_2Et), 21.7 (C$_6$H$_4$CH_3), 20.1 (N(CH$_2$)$_2$CH_2Me), 14.2 (N(CH$_2$)$_3$CH_3), 13.1 (CCH_3). ^{11}B{^{1}H} NMR (96.32 MHz, $CDCl_3$): 1.12 (B^1), −2.56 (B^{10}), −13.26 (B^2), −23.90, −25.38 (B^4, B^7, B^8), −28.14 (B^3, B^5, B^6, B^9). High-resolution ESI⁻-MS: *m*/*z* 309.2767 [A]⁻ (309.2741 calcd). Mp: 119−120 °C dec.



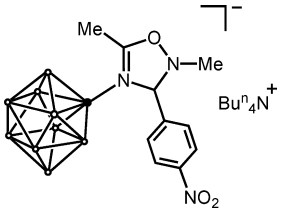
3f: yield 44 mg (64%). Anal. Found: B, 19.07. Calcd for $C_{28}H_{61}N_3B_{10}O$: B, 19.17. IR spectrum in KBr, selected bands, cm^{-1}: 2508 s, 2466 s ν(B−H), 1643 s ν(C═N). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.19 (d, 2H, J = 8 Hz, meta to Me), 7.10 (d, 2H, J = 8 Hz, ortho to Me) 5.54 (s, 1H, NC*H*N), 3.16−3.08 (m, 10H, NCH_2Pr and CCH_2CH$_3$), 2.77 (s, 3H, NCH_3), 2.29 (s, 3H, CH_3C$_6$H$_4$), 1.27 (t, 3H, J = 7 Hz, CCH$_2$CH_3), 1.60−1.42 (m, 8H), 1.42−1.33 (m, 8H), 0.99 (t, J = 7 Hz, 12H) (NBu$^n_4$). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$): δ 172.9 (C═N), 139.1, 133.0, 129.1, 127.0 (Ar), 91.5 (NCN), 58.7 (NCH$_2$Pr), 46.9 (NCH$_3$), 24.2 (NCH$_2$CH$_2$Et), 21.4 (C$_6$H$_4$CH$_3$), 19.8 (N(CH$_2$)$_3$CH$_3$), 19.7 (CCH$_2$CH$_3$), 13.9 N(CH$_2$)$_3$CH$_3$), 9.6 (CCH$_2$CH$_3$). ^{11}B{^{1}H} NMR (96.32 MHz, $CDCl_3$): 1.00 (B^1), −2.36 (B^{10}), −13.31 (B^2), −24.01, −25.44 (B^4, B^7, B^8), −28.14 (B^3, B^5, B^6, B^9). High-resolution ESI⁻-MS: *m*/*z* 323.2933 [A]⁻ (323.2897 calcd). Mp: 124−125 °C dec.



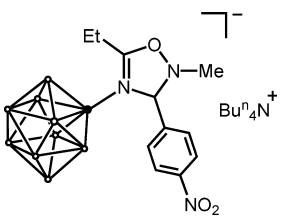
3g: yield 27 mg (39%). IR spectrum in KBr, selected bands, cm^{-1}: 2525 s, 2477 s ν(B−H), 1597 s ν(C═N). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.12 (d, 2H, J = 8 Hz, meta to Me), 7.08 (d, 2H, J = 8 Hz, ortho to Me) 5.89 (s, 1H, NC*H*N), 2.82 (s, 3H, NCH_3), 2.34 (s, 3H, CH_3C$_6$H$_4$), 1.63−1.44 (m, 17H, NCH$_2$CH_2Et and C(CH_3)$_3$), 3.17 (t, 8H), 1.43−1.30 (m, 8H), 0.94 (t, J = 7 Hz, 12H) (NBu$^n_4$). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$): δ 177.2 (C═N), 138.7, 133.5, 129.2, 126.5 (Ar), 93.0 (NCN), 58.8 (NCH$_2$Pr), 45.8 (NCH$_3$), 35.1 (C(CH$_3$)$_3$), 27.4 (C(CH$_3$)$_3$), 24.2 (NCH$_2$CH$_2$Et), 21.3 (C$_6$H$_4$CH$_3$), 19.8 (N(CH$_2$)$_2$CH$_2$Me), 13.9 (N(CH$_2$)$_3$CH$_3$). ^{11}B{^{1}H} NMR (96.32 MHz, $CDCl_3$): 1.10 (B^1), −0.84 (B^{10}), −11.22 (B^2), −23.13, −24.81 (B^4, B^7, B^8), −27.87 (B^3, B^5, B^6, B^9). High-resolution ESI⁻-MS: *m*/*z* 351.3259 [A]⁻ (351.3210 calcd). Mp: 118−120 °C dec.



3h: yield 35 mg (52%). IR spectrum in KBr, selected bands, cm^{-1}: 2472 s ν(B−H), 1622 s ν(C═N). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 8.09 (d, 2H, J = 7 Hz, ortho in Ph), 7.63−7.42 (m, 5H, meta and para in Ph and meta to Me), 7.21 (d, 2H, J = 8 Hz, ortho to Me) 5.88 (s, 1H, NC*H*N), 2.95 (s, 3H, NCH_3), 2.37 (s, 3H, CH_3C$_6$H$_4$), 3.12 (t, 8H), 1.68−1.48 (m, 8H), 1.47−1.35 (m, 8H), 0.97 (t, J = 7 Hz, 12H) (NBu$^n_4$). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$): δ 166.4 (C═N), 141.7, 135.0, 133.5, 131.4, 129.7, 128.3, 127.5, 126.2 (Ar), 92.5 (NCN), 59.0 (NCH$_2$Pr), 47.7 (NCH$_3$), 24.5 (NCH$_2$CH$_2$Et), 21.8 (C$_6$H$_4$CH$_3$), 20.1 (N(CH$_2$)$_2$CH$_2$Me), 14.2 (N(CH$_2$)$_3$CH$_3$). ^{11}B{^{1}H} NMR (96.32 MHz, $CDCl_3$): 1.00 (B^1), −1.64 (B^{10}), −11.42 (B^2), −23.35, −24.38 (B^4, B^7, B^8), −27.87 (B^3, B^5, B^6, B^9). High-resolution ESI⁻-MS: *m*/*z* 371.2937 [A]⁻ (371.2897 calcd). Mp: 69−70 °C dec.



3i: yield 55 mg (68%). Anal. Found: B, 18.48. Calcd for $C_{27}H_{59}N_3B_{10}O_2$: B, 18.61. IR spectrum in KBr, selected bands, cm^{-1}: 2501 s, 2464 s, ν(B−H), 1644 s ν(C═N), 1521, 1346 ν(NO$_2$). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 8.18 (d, 2H, J = 9 Hz, ortho to NO$_2$), 7.63 (d, 2H, J = 9 Hz, meta to NO$_2$), 5.69 (s, 1H, NC*H*N), 2.87 (s, 3H, NCH_3), 2.68 (s, 3H, CCH_3), 3.14 (t, 8H), 1.63−1.50 (m, 8H), 1.48−1.35 (m, 8H), 0.96 (t, J = 7 Hz, 12H) (NBu$^n_4$). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$): δ 170.9 (C═N), 148.7, 142.5 (ipso and para to NO$_2$), 129.1 (meta to NO$_2$), 123.8 (ortho to NO$_2$), 90.1 (NCN), 59.1 (NCH$_2$Pr), 47.5 (NCH$_3$), 24.4 (NCH$_2$CH$_2$Et), 20.1 (N-(CH$_2$)$_2$CH$_2$Me), 14.1 (N(CH$_2$)$_3$CH$_3$), 13.1 (CCH$_3$). ^{11}B{^{1}H} NMR (96.32 MHz, $CDCl_3$): 0.69 (B^1), −2.35 (B^{10}), −13.03 (B^2), −24.12 (B^4, B^7, B^8), −28.13 (B^3, B^5, B^6, B^9). High-resolution ESI$^+$-MS: *m*/*z* 242.2888 [Bu$^n_4$N]$^+$ (242.2843 calcd). High-resolution ESI⁻-MS: *m*/*z* 340.2466 [A]⁻ (340.2435 calcd). Mp: 85−90 °C dec.



3j: yield 45 mg (55%). Anal. Found: B, 18.01. Calcd for $C_{27}H_{59}N_3B_{10}O_2$: B, 18.17. IR spectrum in KBr, selected bands, cm^{-1}: 2473 s, ν(B−H), 1647 s ν(C═N), 1521, 1346 ν(NO$_2$). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 8.18 (d, 2H, J = 9 Hz, ortho to NO$_2$), 7.61 (d, 2H, J = 9 Hz, meta to NO$_2$), 5.70 (s, 1H, NC*H*N), 3.35−3.05 (m, 10H, NCH_2Pr and CCH_2CH$_3$), 2.86 (s, 3H, NCH_3), 1.29 (t, 3H, J = 8 Hz, CCH$_2$CH_3), 1.66−1.51 (m, 8H), 1.49−1.35 (m, 8H), 0.97 (t, J = 7 Hz, 12H) (NBu$^n_4$). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$): δ 174.2 (C═N), 148.6, 142.3 (ipso and para to NO$_2$), 129.0 (meta to NO$_2$), 123.8 (ortho to NO$_2$), 90.8 (NCN), 59.1 (NCH$_2$Pr), 47.3 (NCH$_3$), 24.4 (NCH$_2$CH$_2$Et), 20.0 (N(CH$_2$)$_2$CH$_2$Me and (CCH$_2$CH$_3$)), 14.1 (N(CH$_2$)$_3$CH$_3$), 9.8 (CCH$_2$CH$_3$). ^{11}B{^{1}H}

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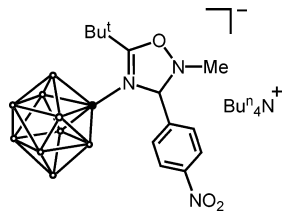
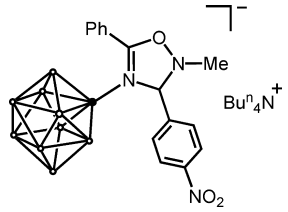
NMR (96.32 MHz, $CDCl_3$): 0.60 (B^1), −2.07 (B^{10}), −13.09 (B^2), −24.36 (B^4, B^7, B^8), −28.28 (B^3, B^5, B^6, B^9). High-resolution ESI^+-MS: m/z 242.2945 $[Bu^n_4N]^+$ (242.2843 calcd). High-resolution ESI^--MS: m/z 354.2650 $[A]^-$ (354.2591 calcd) Mp: 68−70 °C dec.

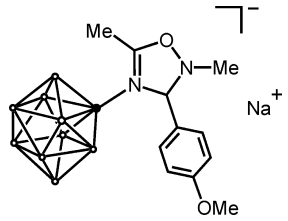


3k was not isolated as a pure solid because of its instability. IR spectrum in KBr, selected bands, cm^{-1}: 1647 ν(C═N). ^1H NMR (300.13 MHz, $CDCl_3$, selected signals): δ 6.01 (s, NC*H*N). High-resolution ESI^--MS: m/z 382.2936 $[A]^-$ (382.2905 calcd).

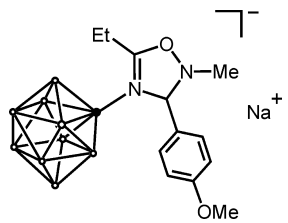


3l was not isolated as a pure solid because of its instability. IR spectrum in KBr, selected bands, cm^{-1}: 1644 ν(C═N). ^1H NMR (300.13 MHz, $CDCl_3$, selected signals): δ 5.98 (s, NC*H*N). High-resolution ESI^--MS: m/z 402.2613 $[A]^-$ (402.2592 calcd).

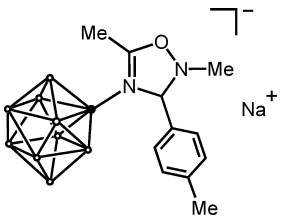
Preparation of Water-Soluble Compounds ***5a–d.*** A solution of each of **3a,b,e,f** (0.28 mmol) in a methanol/acetonitrile mixture (1.5 mL/0.5 mL) was added to a solution of sodium tetraphenylborate (0.28 mmol) in methanol (2 mL), whereupon the colorless precipitate of $[Bu^n_4N]BPh_4$ that formed was filtered off. The volume of the filtrate was reduced to 1 mL at room temperature, and water (0.5 mL) was added. The solid was separated by filtration, and the resulted solution was dried under vacuum until the formation of a yellow oily residue that was dried and crystallized in a desiccator over silica gel (in the presence of a moisture indicator) as a light yellow solid.



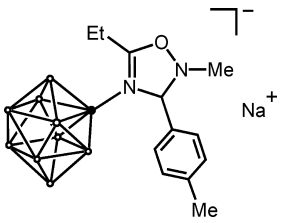
5a: yield 20 mg (70%). IR spectrum in KBr, selected bands, cm^{-1}: 2508 s, 2478 s, 2471 s, 2459 s ν(B−H), 1638 s ν(C═N). ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.24 (d, 2H, J = 9 Hz, meta to MeO), 6.90 (d, 2H, J = 9 Hz, ortho to MeO), 5.59 (s, 1H, NC*H*N), 3.81 (s, 3H, OCH_3), 2.81 (s, 3H, NCH_3), 2.62 (s, 3H, CCH_3). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 170.5 (C═N), 160.8 (ipso to MeO), 128.7 (meta to MeO), 128.0 (para to MeO), 113.6 (ortho to MeO), 91.7 (NCN), 54.8 (OCH_3), 46.0 (NCH_3), 11.6 (CCH_3). High-resolution ESI^--MS: m/z 325.2662 $[A]^-$ (325.2690 calcd).



5b: yield 21 mg (72%). IR spectrum in KBr, selected bands, cm^{-1}: 2508 s, 2478 s, 2471 s, 2459 s ν(B−H), 1638 s ν(C═N). ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.23 (d, 2H, J = 9 Hz, meta to MeO), 6.89 (d, 2H, J = 9 Hz, ortho to MeO), 5.59 (s, 1H, NC*H*N), 3.81 (s, 3H, OCH_3), 3.27−2.98 (m, 2H, CH_2CH_3) 2.80 (s, 3H, NCH_3), 1.29 (t, 3H, J = 8 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 173.5 (C═N), 160.8 (ipso to MeO), 128.7 (meta to MeO), 128.1 (para to MeO), 113.6 (ortho to MeO), 91.5 (NCN), 54.7 (OCH_3), 45.9 (NCH_3), 19.3 (CCH_2CH_3), 9.0 (CCH_2CH_3). High-resolution ESI^--MS: m/z 339.2902 $[A]^-$ (339.2846 calcd).



5c: yield 18 mg (68%). IR spectrum in KBr, selected bands, cm^{-1}: 2508 s, 2478 s, 2471 s, 2459 s ν(B−H), 1638 s ν(C═N). ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.22−7.13 (2d, 4H, C_6H_4), 5.61 (s, 1H, NC*H*N), 2.81 (s, 3H, NCH_3), 2.63 (s, 3H, CCH_3), 2.35 (s, 3H, $C_6H_4CH_3$). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 170.8 (C═N), 139.2, 133.1, 128.8, 127.2 (Ar), 91.8 (NCN), 46.1 (NCH_3), 20.3 ($C_6H_4CH_3$), 11.6 (CCH_3). High-resolution ESI^--MS: m/z 309.2751 $[A]^-$ (309.2741 calcd).



5d: yield 21 mg (76%). IR spectrum in KBr, selected bands, cm^{-1}: 2508 s, 2478 s, 2471 s, 2459 s ν(B−H), 1638 s ν(C═N). ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.22−7.13 (2d, 4H, C_6H_4), 5.61 (s, 1H, NC*H*N), 3.29−2.99 (m, 2H, CH_2CH_3), 2.80 (s, 3H, NCH_3), 2.34 (s, 3H, $C_6H_4CH_3$), 1.30 (t, 3H, J = 8 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 173.7 (C═N), 139.2, 133.1, 128.8, 127.2, 113.6 (Ar), 91.7 (NCN), 46.0 (NCH_3), 20.3 ($C_6H_4CH_3$), 19.3 (CCH_2CH_3), 8.9 (CCH_2CH_3). High-resolution ESI^--MS: m/z 323.2921 $[A]^-$ (323.2897 calcd).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, Figures S1 and S2, and a table giving crystallographic data, molecular structures, and details of the refinement for **3a,f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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